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Laboratory Experiment

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Quantifying Gold Nanoparticle Concentration in a Dietary Supplement Using Smartphone Colorimetry and Google Applications

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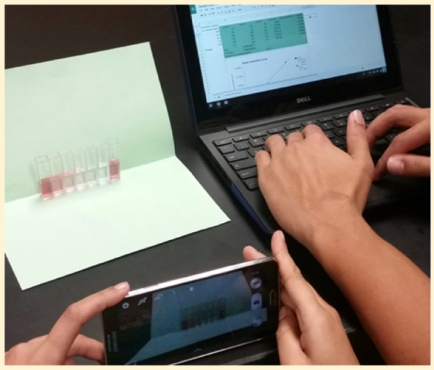
Supporting Information

ABSTRACT: Spectrophotometry and colorimetry experiments are common in high school and college chemistry courses, and nanotechnology is increasingly common in every day products and new devices. Previous work has demonstrated that handheld camera devices can be used to quantify the concentration of a colored analyte in solution in place of traditional spectrophotometric or colorimetric equipment. This paper extends this approach to quantifying the concentration of gold nanoparticles in a colloidal gold "dietary supplement". With the addition of free Google applications, the investigation provides a feasible, sophisticated lab experience and introduction to nanotechnology.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Analytical Chemistry, Laboratory Instruction, Physical Chemistry, Nanotechnology, Hands-On Learning/Manipulatives, Internet/Web-Based Learning, UV-Vis Spectroscopy*

A fundamental concept covered in both high school and college chemistry is the quantification of concentration by measuring the absorption of visible light by a colored analyte in solution. Typically, spectrophotometers and colorimeters are used to quantify absorbance, but these instruments can be cost prohibitive, particularly for many high schools. Digital cameras, including those installed in smartphones and tablets, can be used to perform quantitative colorimetric analysis.[1]

Recent teaching and learning models, such as Technological Pedagogical and Content Knowledge (TPACK), suggest that using technology combined with sound pedagogy and content knowledge improves student learning.[2] The addition of the International Society for Technology in Education (ISTE) technology standards for teachers and students has generated a need for lab experiments that use technology.[3] Furthermore, technology-enhanced, inquiry-based lab activities not only support learning but also meet state and national science education standards.

Recently, Kehoe and Penn published a method describing quantitative colorimetry using a camera capable device, such as a smartphone, in place of spectrophotometric or colorimetric equipment.[1] The use of smartphones coupled with data collection and analysis via Google applications can make sophisticated lab experiments more feasible, especially for teachers with limited budgets.[4,5]

Here, we describe an inquiry-based investigation of the concentration of gold nanoparticles in MesoGold, a dietary supplement made by Purest Colloids. The manufacturer claims their supplement improves motor skills for better sports performance.[6] Colloidal solutions of gold nanoparticles of less than 100 nm are ruby red in solution.[7] This ruby red color is accompanied by a large nanoparticle-based extinction coefficient, which makes gold nanoparticle suspensions ideal for quantitative colorimetric analysis. Furthermore, this choice of sample provides an interesting and timely platform for introducing nanotechnology[8] in the high school chemistry classroom, with the added benefit of students gaining first-hand experience with the unexpected red color of gold nanoparticles as compared to bulk gold.

■ EXPERIMENTAL OVERVIEW

Preparation of Chemicals for Standard Gold Nanoparticle Suspensions

Gold(III) chloride trihydrate (Sigma-Aldrich) and sodium citrate dihydrate (Sigma-Aldrich) were purchased and used as received. A 1.0 mM gold(III) chloride solution was prepared by dissolving 0.197 g in enough deionized water to produce 0.500 L of solution using a volumetric flask. A 38.8 mM sodium citrate solution was prepared by dissolving 2.853 g in enough deionized water to produce 250. mL of solution using a

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volumetric flask. The MesoGold (Purest Colloids) supplement was used as received.

Experimental Overview

Students were given a small volume of the MesoGold supplement for analysis. Purest Colloids claims this supplement has a concentration of 20 ppm gold. Students were asked to determine the concentration of gold as well as the monetary value of gold in a 250 mL bottle of the supplement.

Each student group synthesized a gold nanoparticle solution with a concentration of 100 ppm gold and prepared 50 to 6.25 ppm gold calibration standards by serial dilution. A stock 100 ppm gold nanoparticle solution could be prepared for an entire class to minimize consumption of the gold salt. Students designed their own procedures to collect color intensity data to determine the absorbance of the gold nanoparticles in the standard solutions and the MesoGold sample as described by Kehoe and Penn.[1] They prepared a Beer's law plot of the absorbance versus the known concentration of the standards. To determine the concentration of gold nanoparticles in the sample, students used their measured absorbance of the sample and applied Beer's law (eq 1) where ε is the molar absorptivity coefficient, b is the path length of light, and c is the molar concentration of the solution. The product of ε and b is the slope of their Beer's law plot.

$$\text{Absorbance} = \varepsilon bc \qquad (1)$$

Preparation of 100 ppm Standard Gold Nanoparticle Suspension

A suspension of gold nanoparticles was prepared using the well-established method of MacFarland et al.[9] New glassware or glassware cleaned with aqua regia is preferred, and dirty glassware can result in a failed synthesis. A volume of 20.0 mL of 1.0 mM gold(III) chloride stock solution was transferred using a disposable 20 mL plastic pipet tip fitted with a rubber bulb to a 50 mL Erlenmeyer flask. The meniscus of the solution was marked on the outside of the flask using a permanent marker. The solution was heated to a gentle boil on a hot plate with stirring. When the solution began to boil, 2.0 mL of 38.8 mM sodium citrate stock solution was added using a disposable 10 mL plastic pipet tip fitted with rubber bulb. The solution was gently boiled for 10 min. Upon the addition of the sodium citrate solution, the pale yellow gold solution turns colorless, then a dark blue color, and then finally a ruby red color, as described by previous work.[9] The flask was removed from the hot plate and allowed to cool to room temperature. To account for evaporative loss, the solution volume was returned to 20. mL by adding deionized water until the meniscus of the gold nanoparticle suspension reached the level marked prior to heating, which brought the final gold nanoparticle loading to ~100 ppm. The procedure described was found to produce an average gold concentration of 97 (±4) ppm as determined by UV/vis spectroscopic analysis[10] (n = 15).

■ DATA COLLECTION

Each student group used smartphones to photograph polystyrene cuvettes containing their standards, a blank sample of distilled water, and a sample of MesoGold (Figure 1). The smartphone was held perpendicular to the lab bench with the camera lens planar and 12 in. away from the center of the cuvettes.[11] Students attempted to minimize shadows by adjusting lighting. The students used a free color picker application of their choice to collect three green intensity values for each sample in the image. The students used the green channel as it is the most complementary to the red of the colored suspensions and thus expected to yield the most quantitative results.[1]

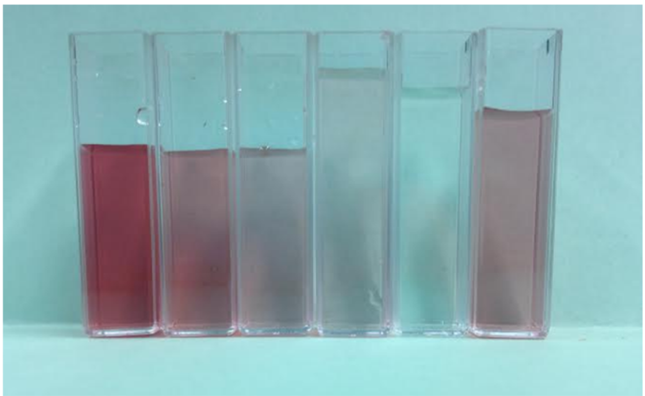

Figure 1. One student group's photograph of polystyrene cuvettes containing the 50, 25, 12.5, and 6.25 ppm gold nanoparticle standards, distilled water, and MesoGold sample, arranged from left to right against a blue background.

■ DATA ANALYSIS

The green intensity values and gold nanoparticle concentrations of the standards and MesoGold sample were entered into Google Sheets shared among the members of the each student group. An average green intensity and corresponding absorbance was calculated using the spreadsheet tools and eq 2, where I is the average green intensity of each standard and I_0 is the average green intensity of the blank.

$$\text{Absorbance} = -\log(I/I_0) \qquad (2)$$

It is an approximation that the blank sample is equal to the incident intensity (I_0 is equal to I) when no light is absorbed as there are no absorbing species in the blank sample.

Students prepared a plot of absorbance versus gold concentration, and the equation for the line of best fit was used to determine the concentration of gold in the MesoGold sample (Figure 2).

Following spreadsheet analysis, students generated collaborative lab reports using Google Docs, while receiving instructor feedback through the commenting tool. Students shared their data and results with a broader audience of chemistry professionals and experts through Google Hangouts during a question and answer session.

■ HAZARDS

Gold(III) chloride may be harmful if swallowed or inhaled and can cause irritation to the skin, eyes and respiratory tract. Skin contact with sodium citrate should be avoided as it can cause irritation to the skin, eyes and respiratory tract. Nanoparticle solutions should be disposed of in accordance to local hazardous waste procedures. Safety glasses and gloves should be worn at all times. Clean up spills immediately and consult SDSs for complete safety information. Personal electronic devices, such as smartphones, may be placed inside clear plastic bags to prevent contamination of devices with chemicals.

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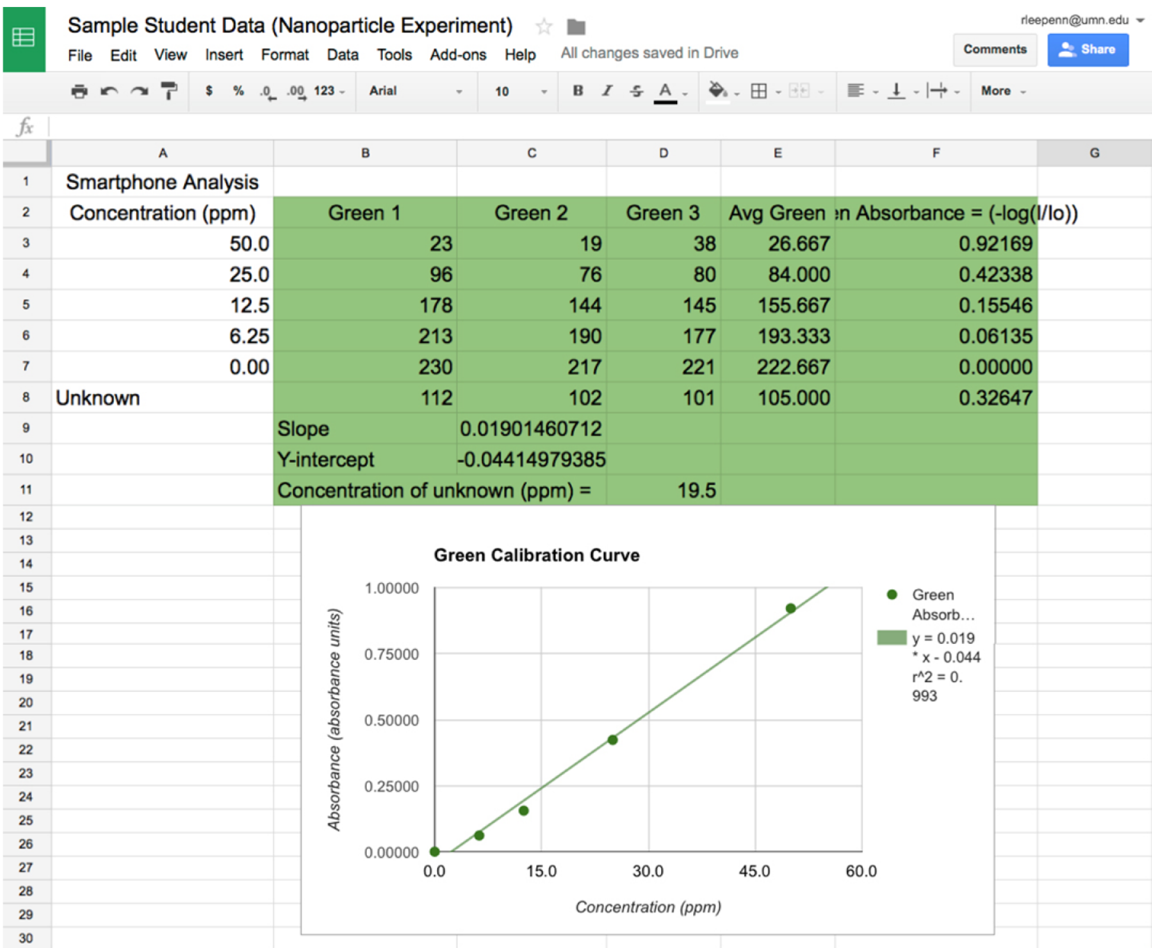

Figure 2. Sample screenshot of student data analysis from the colorimetric smartphone method using Google Sheets.

DISCUSSION

Twelve of the 15 participating student groups successfully completed both the experiment and analysis and obtained an average concentration of the MesoGold mineral supplement of 22 (±4) ppm, which compares well to the advertised 20 ppm gold concentration of MesoGold. Unsuccessful student groups had problems with dirty equipment, dilution errors, or poor image quality. As previously published,[1] images that yield the best results are collected using an appropriately colored background and sufficient, consistent lighting.

In Figure 2, a screenshot of Google Sheets containing sample student data is shown. Data analysis can be readily performed using any spreadsheet software or even a graphing calculator. However, Google Sheets offers collaborative features to facilitate group work involving the calculations. Teachers can offer immediate and ongoing feedback. Students access shared documents from their own accounts, regardless of whether they work synchronously or asynchronously. Teachers can review student participation through the document's revision history tool, which means ambiguity regarding individual contributions can be eliminated and student group participation assessment more accurate. The cloud based storage of the document eliminates concerns about document version control. In addition, students can work on separate aspects of the analysis and check their work against other group members.[4] Finally, multiple groups from different classes or even different schools can combine data into a single spreadsheet to achieve better statistical analysis. A current limitation of Google Sheets is that the *y*-intercept cannot be forced through zero. The data shown in Figure 2 were also plotted using a *y*-intercept forced through zero, and the resulting slope was 0.018, as compared to 0.019 via Google Sheets. This difference is small enough that the benefit of using Google Sheets outweighs this disadvantage, and future improvements in the software are anticipated. Teachers can use this as a learning opportunity through discussion of these differences.

A template spreadsheet was provided to students to introduce the tools offered in Google Sheets. This template is available in the Supporting Information, along with a student guide. While students performed the analysis with guidance from the template, they distributed their workload independently. The template and other lab materials were distributed in a streamlined approach via Google Classroom, which is available to educators via Google Apps for Education.[12]

CONCLUSION

A camera capable device can be used to quantify the concentration of gold in a sample of colloidal gold of unknown concentration. The combination of a camera capable device and free Google applications provides a unique and viable lab experience for high school and college chemistry students to explore fundamental chemistry concepts in the context of nanoscience while also practicing skills valued in technology education standards. The use of Google applications facilitates

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efficient instruction and feedback between the students and teachers for effective collaboration.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00385. A spreadsheet template for analysis can be copied from https://docs.google.com/spreadsheets/d/1U-cTyu8gKOtMQg1VASSAAzruSWAoApgAIIuWOk8IoIg/edit#gid=0.

Student guide containing a detailed introduction and procedure for the experiment (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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