

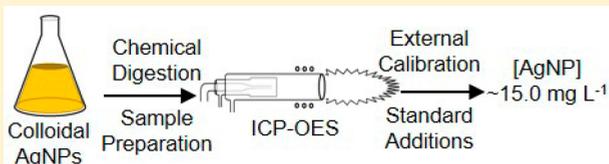
Measuring the Silver Composition of Nanocolloids by Inductively Coupled Plasma–Optical Emission Spectroscopy: A Laboratory Experiment for Chemistry and Engineering Students

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Supporting Information

ABSTRACT: The increased worldwide exploitation of nanomaterials has reinforced the importance of introducing nanoscale aspects into the undergraduate and graduate curriculum. To meet this need, a novel nano-laboratory module was developed and successfully performed by science and engineering students. The main goal of the experiment was to accurately quantify the total silver composition of a nanocolloid with modern inductively coupled plasma–optical emission spectroscopy (ICP-OES) instrumentation in conjunction with two well-established methods that are heavily employed in both research and industrial settings. Specifically, undergraduate and graduate students estimated the total silver composition of Creighton colloidal nanoparticles via the external calibration method ($16.3 \pm 4.7 \text{ mg L}^{-1}$) and the standard addition method ($14.9 \pm 4.2 \text{ mg L}^{-1}$) at two emission wavelengths (328.068 and 338.898 nm). The assessment of basic laboratory skills and the class assignments showed that the students successfully mastered the various aspects of sample/standard preparation, the operation of the ICP-OES instrument, and the data analysis. Students' interest and experience in this laboratory were highly rated in the anonymous student evaluations.



KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Laboratory Instruction, Interdisciplinary/Multidisciplinary, Hands-On Learning/Manipulatives, Nanotechnology, Colloids, Instrumental Methods

INTRODUCTION

In the last two decades, the nanoscience and nanotechnology sectors have exponentially proliferated across the world.¹ It is expected that by 2020, approximately 6 million people will be employed in nanofields.¹ In response to this workforce demand, many universities have now established curricula, in particular at the graduate level, to introduce students to the themes originating within the nanoareas.² Furthermore, current National Science Foundation (NSF) solicitations for proposals³ encourage the introduction of nanoscale science, engineering and technology into the undergraduate education.

Many of the unique properties of nanomaterials derive from their size, shape, and surface charge,^{4,5} but elemental composition is one of the most important characteristics because it directly relates to the controlled, safe, and efficient use of nanomaterials as well as to their toxicity.^{6,7} Inductively coupled plasma–optical emission spectrometry (ICP-OES), also commonly referred to as ICP–atomic emission spectroscopy (ICP-AES), is a well-established analytical technique that offers both qualitative and quantitative forms of elemental analysis.⁸ In addition, ICP-OES can detect up to 70 elements⁹ and exhibits better detection limits (down to the ppb level⁹) than other traditional techniques such as flame atomic absorption/emission spectroscopy (FAAS or FAES) and ultraviolet–visible (UV–vis) absorption spectroscopy. Thus, ICP-OES offers suitable quantification of a wide range of

elements in a relatively fast, single analysis and without the expense of a more costly mass spectrometer (ICP-MS).^{9,10}

This new laboratory module aimed to familiarize students enrolled in upper level *Instrumental Analysis* and *Experimental Nanomaterials and Nanoscience* laboratory courses (3 credit hours each course) with two well-established calibration methods, namely, the external calibration method and the standard addition method, for the accurate quantification of the total silver composition of nanocolloids. In this context, both science and engineering students were introduced to the theoretical and experimental aspects of ICP-OES, including sample/standard preparation, the operation of modern ICP-OES instrumentation, and data analysis. The proposed experiment module takes at least two 3 h lab periods and possibly a third one may also be necessary if students fabricate their own colloidal nanoparticles. Additional organizational details and suggestions for various laboratory time periods are provided in Supporting Information. The two calibration methods were compared for a widely used Creighton colloid of silver nanoparticles (AgNPs) by relating the actual yield to the theoretical yield of the reaction. The external calibration approach was selected to demonstrate the rapid analysis of a large set of colloidal samples, while the standard addition method was recommended for the analysis of complex,

colloidal samples, where matrix effects are considerable.^{11–13} For further comparisons, two emission wavelengths were utilized in both calibrations (the main and secondary lines of Ag(I) ion at 328.068 and 338.898 nm, respectively). It is important to introduce students to the possibility of employing multiple emission wavelengths for the same elemental ion in order to avoid possible spectral overlaps, to interrogate different concentration ranges, or to confirm the results obtained by a specific wavelength. A more detailed explanation could elaborate upon the ionization energies associated with different ions. While the external calibration method in combination with quality control measurements is endorsed by the U.S. Environmental Protection Agency (EPA), the standard addition method is preferred for increased confidence.¹³ Thus, this laboratory experiment closely followed the U.S. EPA Method 200.7 with some minor modifications to fit the allotted time period (outlined in the Supporting Information). This approach effectively exposed students to the two methods frequently employed in research and industrial settings.

An ICP-OES-based laboratory experiment for the quantification of nanomaterial composition has been introduced before into the academic curricula, but it focused on the external calibration approach. For example, Metz et al. designed an ICP-OES experiment for non-STEM students to estimate AgNP accumulation in the Wisconsin Fast Plants, *Brassica rapa*.¹⁴ Numerous ICP-OES and FAAS laboratory modules encourage the utilization of both calibration methods, but these educational experiments are not relevant to nanomaterial characterization (e.g., experiments involving multivitamins, teeth, motor oil, and so on).^{15–17} The experiment reported here is unique in that it introduces students to more than one calibration method to accurately quantify the total silver composition of colloidal AgNPs using modern ICP-OES instrumentation.

MATERIALS AND METHODS

Chemicals

All chemicals in this laboratory experiment were purchased as high-grade analytical reagents from Fisher Scientific, and were used without further modification (Supporting Information). High quality (HQ) water (resistivity >18 M Ω cm) was the solvent in the AgNP synthesis, the quantitative dilutions of the digested samples, and the method blank. A SPEX CertiPrep ICP-OES grade Ag⁺ standard (1000 \pm 5 mg L⁻¹) and OPTIMA grade nitric acid (HNO₃) for trace metal analysis were employed for the standards preparation and chemical digestions.

Synthesis of Creighton Colloidal AgNPs

Colloidal AgNPs were synthesized in advance via a modified Creighton method^{18,19} through the titration reduction of Ag⁺ in silver nitrate (AgNO₃) with sodium borohydride (NaBH₄) at \sim 0 °C (Supporting Information). This nongreen synthesis was rigorously described by our group together with other green and nongreen bottom-up fabrication methods for silver and gold nanoparticles in a recently published, complementary nano-laboratory experiment.²⁰ Any of these nanocolloids could be utilized in the proposed ICP-OES-based laboratory experiment.

The Creighton colloid was wrapped in aluminum foil, stored at \sim 10 °C, and used within 1 week in order to avoid the potential release of Ag⁺ ions from AgNPs. This oxidation process may occur over time (6–125 days), in the presence of

dissolved O₂ and H⁺, and is temperature dependent (ion release rate increases with temperature, 0–37 °C).²¹

Chemical Digestion of AgNPs

Students digested 0.500 \pm 0.001 mL of colloidal AgNPs in 2.0 mL OPTIMA grade HNO₃. A “cold digestion” was employed first, where the solutions were allowed to sit for 15 min, followed by a “hot digestion” at \sim 180 °C. The samples were allowed to evaporate until a minimal amount of liquid remained (\sim 200 μ L), and the beakers were removed from the hot plate. The digested samples were then diluted to a total volume of 100.00 \pm 0.08 mL, and a final 2% HNO₃ matrix by volume was established. A method blank (MB) of HQ water was prepared in the same manner.

Blanks and Standards Preparation

External Calibration Method. External standards were prepared from the standard Ag⁺ solution that ranged from 0 to 150 μ g L⁻¹, in 25.0 μ g L⁻¹ increments. A matrix blank, consisting of HQ water and 2% HNO₃, was used as a calibration blank for 0.0 μ g L⁻¹.

Standard Addition Method. A standard addition calibration was performed by spiking five 5.0 mL samples of digested and diluted AgNPs with known volumes of a 10.0 μ g mL⁻¹ Ag⁺ standard in the following amounts: 0.0, 25.0, 50.0, 75.0, and 100.0 \pm 0.1 μ L, and then diluting to 10.0 mL.

All digested samples, blanks and standards were prepared with a final 2% HNO₃ matrix.

ICP-OES Measurements

A Varian 710-ES ICP-OES instrument having an axially positioned torch was employed for the elemental quantitation of total Ag within the digested, colloidal AgNP. Other ICP-OES instrument models such as Optima8x00 (PerkinElmer) and Ultima Expert (Horiba Scientific) may also be utilized for this experiment. Optimized acquisition parameters included a replicate read time of 15 s, an internal stabilization delay of 45 s, a sample uptake delay of 40 s, a peristaltic pump rate of 2 mL min⁻¹ (\sim 30 rpm) and a rinse time of 15 s. Each sample was measured in triplicate using the two emission lines for Ag employing an autosampler (Varian SPS 3) and a wide dynamic range CCD detector. Light intensities were transduced into electrical signals and a resultant spectrum was created by plotting the emitted intensities versus wavelength.

HAZARDS

The toxicity of AgNPs is still under investigation;^{6,7} thus, care should be exercised when working with any AgNPs. Aqueous solutions of corrosive NaBH₄ should be used in less than 1 week and stored in loosely fitted containers without agitation. Silver nitrate (AgNO₃) should be identified as a possibly toxic and corrosive chemical. Concentrated HNO₃ is extremely corrosive and should be handled carefully, especially during high-temperature digestions. All sample-related activities should be carried out in a chemical fume hood to avoid buildup of flammable gas (hydrogen gas evolved during AgNP synthesis) and toxic inhalations (oxides of nitrogen evolved during AgNP digestion). Operation of the ICP-OES should be performed under the supervision of trained personnel, and should closely follow a standard operating procedure (SOP). Personal protective equipment should be worn at all times during the experiment.

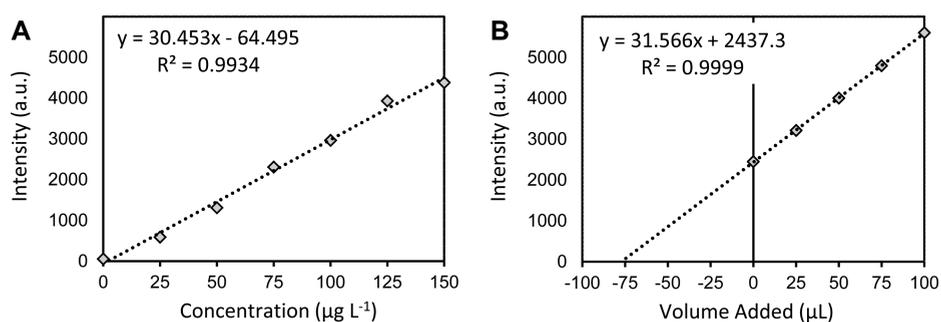


Figure 1. Sample external calibration curve (A) and standard addition curve (B), which were constructed by students for the main emission line of Ag at 328.068 nm.

RESULTS AND DISCUSSION

Student Results

The theoretical yield of the Creighton AgNPs was estimated through simple, stoichiometric calculations (sample calculation in Supporting Information). Briefly, 50.0 mL of 1 mM AgNO_3 was reduced with 300.0 mL of 2 mM NaBH_4 , yielding 350.0 mL of Creighton colloid. Given the atomic weight of Ag ($107.8682 \text{ g mol}^{-1}$), the total Ag amount present in the colloid was estimated to be 15.4 mg L^{-1} . Next, small aliquots of colloidal AgNPs and HQ water were chemically digested by each student group and quantitatively diluted to fit within the Ag concentration range of the calibration curves based off the estimated theoretical yield. Students then individually analyzed the external calibration and standard addition standards.

External Calibration Method. Students constructed the external calibration curve by plotting the instrument response (i.e., the emission intensity) as a function of the known Ag concentrations (i.e., the concentration of each external standard), and used a linear least-square analysis to fit the data. A sample curve is shown in Figure 1A for the main emission line of Ag at 328.068 nm. Unknown Ag composition in the colloidal samples of AgNPs was then interpolated according to their signal response from the calibration curve. For example, one student group obtained an intensity of 1626.2 a.u. for the Creighton sample. This emission value (y) was found to correspond to a total Ag amount of 11.1 mg L^{-1} (x) after solving the regression equation and considering the 200-fold dilution factor (sample calculation in Supporting Information). Standard deviations across the two courses are presented in Table 1.

Standard Addition Method. In this calibration approach, students measured the instrument response for five samples spiked with various amounts of an Ag standard. The emission intensities (y) were then plotted as a function of the volume of

standard solution added (x). A sample curve is shown in Figure 1B for the main emission line of Ag at 328.068 nm. Subsequently, a linear regression was performed to determine the total Ag amount of the Creighton colloidal samples. For example, one student group estimated the amount of Ag in their colloidal sample as being 15.4 mg L^{-1} after solving for x when $y = 0$. The dilution factor and concentration of the standard added were also taken into consideration (sample calculation in Supporting Information).

Comparison of the External Calibration and Standard Addition Methods for the Determination of the Total Ag Composition of Nanocolloids

Both calibration methods were effective in quantifying the total Ag composition of the Creighton colloid. Average Ag amounts and standard deviations across the two courses are presented in Table 1, while percent errors are given in Table S2 (Supporting Information). The percent error were determined by comparing the class average values (i.e., the actual yield for both courses) to the theoretical yield for the Creighton reaction, which was estimated from stoichiometric calculations (15.4 mg L^{-1}). This value was assumed to correspond to an ideal 100% yield for simplicity. Overall, the standard addition method provided more accurate Ag estimates (by 1.3–8.4%) and exhibited smaller deviations (by 0.0–27.3%) than the external calibration method for the main excitation line of Ag at 328.068 nm (Table 1). The average Ag amount obtained via the standard addition method in the two courses was $14.9 \pm 4.2 \text{ mg L}^{-1}$ at 328.068 nm, which corresponds to a percent error of 3.3% (Supporting Information Table S2) for the Creighton reaction. It should be noted that students were also asked to calculate percent recoveries and percent error in order to compare both calibrations and both emission lines (Supporting Information). It was found that the improved precision for the standard addition method may be attributed to the consideration of matrix effects.

In considering both emission lines, the 328.068 nm wavelength performed better than the 338.898 nm wavelength for both calibration methods (Table 1). It should be noted that the external calibration method led to more accurate Ag amounts than the standard addition method for the 338.898 nm emission line (Supporting Information Table S4). The statistical weights of the states corresponding to the emission wavelengths could be quite different and lead to the greater intensity observed for the 328.068 nm line (from an increased population in this state). Given the proximity of the two states on an energy scale, even a subtle difference in statistical weights could explain the observed differences. Because the lower energy state electronic configuration is the same for both

Table 1. Class Average Values and Standard Deviations for the total Ag Composition of Creighton Colloids As Obtained by Students through ICP-OES^a

Course name	External Calibration		Standard Addition	
	328.068 nm	338.898 nm	328.068 nm	338.898 nm
Instrumental Analysis	14.6 ± 6.5	10.5 ± 4.0	14.8 ± 2.3	7.9 ± 4.9
Experimental Nanomaterials and Nanoscience	13.7 ± 2.9	13.6 ± 3.7	15.0 ± 2.9	11.5 ± 8.0

^aAll amounts are reported as mg L^{-1} (ppm). Error is reported as 1σ .

emission lines (namely, $[\text{Kr}]4d^{10}5s^1$), the ground state has the same energy and the same term symbol $^2S_{1/2}$. However, upon excitation, the electronic configuration changes to $[\text{Kr}]4d^{10}5p^1$. This upper state electronic configuration has two possible term symbols, namely $^2P_{3/2}$ for the 328.068 nm line and $^2P_{1/2}$ for the 338.898 nm line, due to LS coupling. Thus, recombination to this excited state configuration would be more favorable, and have a higher population of excited Ag atoms than that of the $^2P_{1/2}$ state (corresponding to emission at 338.898 nm).^{9,10}

Formative Assessment

The knowledge gained by the undergraduate and graduate students was assessed through pre- and post-laboratory assignments (Supporting Information), which showed that the proposed educational goals were successfully achieved in both courses. Briefly, before performing the proposed experiment, students were graded on their ability to correctly answer a set of pre-lab questions using relevant material, which was made available to them in advance. After the completion of the experiments, students prepared a full laboratory report and were graded with the help of a rubric including the topics that were interrogated in the pre-lab assignment. The achievement of the proposed educational goals was further substantiated by the excellent ratings of a set of laboratory skills (#S1–S6) that were performed by the instructor and were identified as vital for the successful completion of the experiment (Table 2).

Table 2. Results of the Anonymous Evaluations of Several Laboratory Skills (S1–S6) Performed by the Instructors in the Experimental Nanomaterials and Nanoscience Course

Laboratory Skill	Instructor Ratings ^{a,b,c}	
	Fall 2012	Fall 2013
S1	2.7 (0.3)	2.3 (0.3)
S2	2.7 (0.4)	2.2 (0.4)
S3	3.0 (0.0)	2.0 (0.0)
S4	2.2 (0.3)	2.7 (0.3)
S5	3.0 (0.0)	2.0 (0.0)
S6	2.7 (0.3)	2.2 (0.3)

^aValues in parentheses represent standard deviations of 1σ . ^bEach section contained $N = 8$ groups of students. A total of 14 and 15 students completed the laboratory course in the Fall 2012 and Fall 2013 semester, respectively. ^cA rating of 3.0 indicates that student groups always met the laboratory goal, while ratings of 2.0 and 1.0 indicate that student groups sometimes and never met the laboratory goal, respectively.

Students were found capable of S1, correctly performing the cold and hot digestions; S2, performing the appropriate dilutions of the digested samples for ICP-OES analysis; S3, completing all necessary safety checks and operation of the ICP-OES equipment, noting any irregularities and reporting them as directed; S4, setting the instrument computer to the appropriate data collection parameters; S5, loading the autosampler with the appropriate number of blanks, standards, and samples in the correct order; and S6, taking into consideration the conditions/parameters that must be met to allow for accurate sample analysis. Furthermore, anonymous evaluations were administered to examine students' interest in the laboratory before (Q1) and after its completion (Q2) as well as the overall experience in the performed experiment (Q3). The high ratings in Table 3 and anonymous comments showed that students found the new laboratory experiment stimulating and enjoyable.

Table 3. Results of the Anonymous, Student Evaluations of Several Laboratory Aspects (Q1–Q3) in the Two Courses

Laboratory Aspect	Student Ratings ^{a,b,c}	
	Instrumental Analysis	Experimental Nanomaterials and Nanoscience
Q1: Prelab interest	2.7 (2.5)	8.4 (1.8)
Q2: Postlab interest	8.5 (2.3)	8.5 (2.1)
Q3: Overall lab experience	8.2 (2.4)	8.5 (2.4)

^aValues in parentheses represent standard deviation (1σ) of assessments and responses. ^b $N = 13$ students who volunteered to answer the questions for both courses. ^cOn a scale from 1 to 10, 1 corresponds to the lowest score assigned by students, while 10 is the highest score.

CONCLUSIONS

As nanoparticle research and applications continue to grow, young scientists and engineers must be exposed to the fundamentals of nanotechnology and nanoscience. This laboratory experiment successfully introduced a diverse population of science and engineering students to one of the most important aspects in the characterization of metallic NPs: the accurate quantification of the metal composition of nanocolloids by ICP-OES. It should be noted that over 50% of the students in the *Experimental Nanomaterials and Nanoscience* laboratory class were represented by female and other underrepresented groups. In this context, students were exposed to the convenience of the external calibration method and the importance of spiked samples in the standard addition method, at different emission wavelengths. Successful fulfillment of the laboratory experiment was verified through pre- and post-laboratory assignments and the assessment of a set of basic laboratory skills. Overall, students gained the scientific knowledge and the laboratory skills to confidently employ both ICP-OES calibration methods with metallic NPs-based samples. Additionally, anonymous evaluations indicated that the proposed ICP-OES based experiment was well received and highly rated by the students. This laboratory experiment could be implemented for the ICP-OES-based quantification of other metallic NPs in chemistry, environmental sciences or engineering undergraduate curricula.

ASSOCIATED CONTENT

Supporting Information

Additional material for instructors, students, a detailed description of the ICP-OES measurements, additional safety aspects and expected laboratory outcomes. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support through the NSF-Nanotechnology Undergraduate Education in Engineering Program, NSF-Environmental Health and Safety of Nanotechnology, and WSU start-up is gratefully acknowledged. The authors would also like to thank Garrett VanNess and Joseph Solch, laboratory

instrumentation specialists at Wright State University, for their technical support during both courses.

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