

Determination of Arsenic in Sinus Wash and Tap Water by Inductively Coupled Plasma–Mass Spectrometry

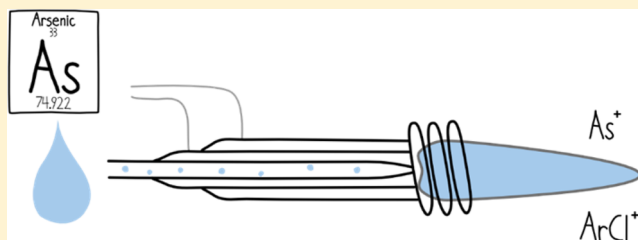
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S Supporting Information

ABSTRACT: Arsenic is a toxic element to which humans are primarily exposed through food and water; it occurs as a result of human activities and naturally from the earth's crust. An experiment was developed for a senior level analytical laboratory utilizing an Inductively Coupled Plasma–Mass Spectrometer (ICP–MS) for the analysis of arsenic in household sinus wash and tap water. This powerful instrumental technique can be used to elucidate the elemental composition of a complex sample while offering the benefits of high-precision quantitative analysis. The chosen matrices further provided the opportunity to demonstrate two important analytical concepts. First, the sinus wash samples displayed signal suppression, illustrating the necessity for employment of the internal standard calibration technique. Second, the high chloride matrix of the sinus wash led to the formation of the ArCl^+ polyatomic ion in the argon plasma, which overlapped with arsenic's single isotope at $m/z = 75$. Analysis was performed in no gas mode and also with the collision cell in helium mode, allowing the students to observe firsthand the false positive results for arsenic by comparing 75 m/z results in the two modes. In addition, in a third objective, students were able to compare the sinus wash and tap water to current federal drinking water regulations. This laboratory exercise provided a novel and engaging application of ICP–MS and allowed the students to use modern instrumentation and analytical techniques to investigate the current and relevant issue of arsenic in our environment.

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Inorganic Chemistry, Laboratory Instruction, Inquiry-Based/Discovery Learning, Atomic Spectroscopy, Quantitative Analysis



INTRODUCTION

Arsenic is of concern due to its toxic and carcinogenic properties. The toxicity of arsenic is related directly to its binding form, as inorganic forms are more toxic than organic forms.¹ Arsenic exists in nature in a variety of oxidation states: +5 (arsenate), +3 (arsenite), 0 (arsenic), and –3 (arsine). In aqueous environments, which are the focus of this experiment, arsenic is often in the +5 and +3 states as well as arsenous acid (As(III)), arsenic acid (As(V)), and their corresponding salts. Chronic arsenic exposure can lead to poisoning with symptoms including weakness, loss of reflexes, fatigue, gastritis, colitis, anorexia, weight loss, and hair loss.¹ Further, there is a well-established link between arsenic and skin, lung, and bladder cancer.² At a molecular level, As(III) can bond to the sulfur atom in biological proteins containing cysteine residues, disrupting tertiary structure and function.³ The U.S. Environmental Protection Agency (EPA) has established a maximum contaminant level of 10 ppb in drinking water to protect the public from long-term exposure of arsenic.⁴

Illustration of spectroscopic techniques is fundamental to the undergraduate instrumental analysis course. Atomic spectroscopy is used for elemental analysis in a host of industries including food, energy, environmental, agricultural, and pharmaceutical.^{5–12} Several instruments are employed including the Atomic Absorption Spectrometer (AAS) and the

Inductively Coupled Plasma–Optical Emission Spectrometer (ICP–OES). Laboratory experiments utilizing each have been published in *J. Chem. Educ.* (AAS,^{13–15} ICP–OES^{16–20}) and collectively demonstrate individual strengths and limitations. A third instrument used for elemental analysis, the Inductively Coupled Plasma–Mass Spectrometer (ICP–MS), has become an academic, industry, and government workhorse for the rapid and nearly simultaneous analysis of most elements in the periodic table at part per trillion (ppt) detection limits or lower.^{5–12} The experiment described in this work teaches students several important aspects of actual use of this instrument in the laboratory.

The principles of ICP–MS have been previously reviewed¹⁹ and the present laboratory experiment emphasizes the fact that ICP–MS is a powerful tool for rapid, sensitive, multielement analysis over a wide concentration range. In addition, three specific objectives were established for this laboratory experiment. The first objective was to introduce the use of internal standard calibration. Harvey reported on the importance of student understanding of matrix effects and options for calibration methods to improve accuracy of analytical results.²⁰

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The sinus wash samples show a decreased signal response for the analyte of interest, arsenic, and associated internal standard, germanium, as compared to tap water. Students were asked to use their data to describe how the matrix might affect the choice of calibration method.

The second objective was to demonstrate the presence of specific interferences in analytical techniques. In the present case, use of an ICP–MS necessitates the consideration of polyatomic ions formed in the plasma. In a high chloride matrix, the ArCl^+ ion may be produced in the plasma, overlapping the analyte's only isotope at $m/z = 75$. Sinus wash has a high saline content and therefore illustrates the inflated high arsenic level that may be inaccurately reported in a high chloride matrix. A collision cell is employed in this experiment to eliminate the interfering ArCl^+ ion, and students are able to view results without the collision cell in no gas mode and with the collision cell using helium. It should be noted that standard addition does not compensate for the error caused by the ArCl^+ ion, thus connecting the two objectives.

The third objective was to relate the experimental results to EPA regulations for arsenic in drinking water. Arsenic was partially chosen as the analyte of interest due to its relation with human health and the environment. Students were required to research the EPA's regulation for arsenic in drinking water either on a computer in the lab or outside of class and comment on their results with respect to the regulation. Many students discussed the health effects of arsenic poisoning and the need to correctly analyze the concentration of arsenic to maintain public safety. Connecting the EPA regulation with their experimental results provided students with relevant context, encouraging student engagement within course.

■ EXPERIMENTAL SECTION

This experiment was employed in an undergraduate Instrumental Analysis Laboratory class at The University of Cincinnati. The course is populated largely by senior chemistry and chemical engineering students. Students worked in groups of three in class sections of 24 students. This experiment was one of eight that each group performed under a weekly rotation schedule. Lab periods were scheduled on 2 days each week and for a period of 3.5 h each day. Due to the rapid sample analysis of the ICP–MS and the design of the laboratory experiment, students were generally able to complete this laboratory within the first laboratory period.

An Agilent 7700 Inductively Coupled Plasma–Mass Spectrometer equipped with an Octopole Reaction System, as the collision cell, was used in this experiment, although it could be adapted to any ICP–MS system with collision cell capability. Helium was used as the collision gas, and the 7700 Series MassHunter software was employed for data manipulation. Specific instrument conditions are detailed in the [Supporting Information](#).

Procedurally, students were asked to prepare an eight point calibration curve for arsenic including a blank. The range extended from 0 to 25 ppb and the working solution was a 100 ppb arsenic solution previously prepared by the graduate student Teaching Assistants (TAs). Within each calibration point, the students were required to add germanium at a final concentration of 1 ppb and the germanium working solution supplied was at a concentration of 40 ppb and was also previously prepared by the TAs. Finally, students were asked to ensure that their final calibration standards contained nitric acid at a concentration of 20 mL of concentrated (70%) nitric acid

per liter. All calculations for standard preparation were required to be complete by the start of the lab.

Two sample types were investigated for the presence of arsenic and these included commercially purchased sinus wash and local tap water. The students were asked to collect a tap water sample prior to their laboratory period and this exercise sparked their curiosity. Student groups collected water from a variety of sources (home, the lab, the water fountain, and filtered tap water), further connecting the experiment to the greater world. Students were asked to prepare each sample type in quadruplicate and discuss the importance of replicates and outliers in the lab reports.

■ HAZARDS

Caution and care must be exercised when working with nitric acid; it is a strong, corrosive acid and appropriate Personal Protective Equipment (PPE) and safety precautions must be employed. Students were required to wear goggles, gloves, and work in a fume hood. Care was taken when preparing solutions, as arsenic is toxic and carcinogenic. Arsenic and germanium standards were 1000 ppm commercially purchased stock solutions. These stock solutions were diluted by the TAs prior to the actual lab to concentrations of 100 ppb (arsenic) and 40 ppb (germanium) for use by the students. All waste should be disposed of in a proper manner according to institutional waste policy protocol.

■ DISCUSSION

This laboratory experiment was performed for the first time during the 2015 spring semester course 3030L, Instrumental Analysis Laboratory, at the University of Cincinnati. A total of 120 chemistry and chemical engineering seniors participated in this course and performed this laboratory experiment working in small groups to promote collaborative learning.

During the laboratory period, the TA discussed hazards and precautions regarding nitric acid, checked the student group's dilution calculations, and turned on the instrument with the students. After the student group prepared all standards and samples, the TA showed the students how to tune the instrument. Additionally, the TA discussed principles of operation as detailed in the [Supporting Information](#) as well as individual instrumental components and functions (peristaltic pump, nebulizer, spray chamber, torch, etc.). The students then set up a sequence to analyze their blank, calibration standards, and samples in both no gas mode and He mode. Student generated calibration curves are shown in [Figure 1](#); R^2 values were exceptional and generally at 0.9997 or higher, demonstrating that the students accurately prepared their calibration standards. Students were able to view the m/z 75 signal in both collision cell modes, promoting an initial conversation regarding the difference in signal for a given sample.

The internal standard method offers high accuracy because it alleviates errors introduced by sample introduction, matrix, and/or variations in detector response. Germanium was chosen as the internal standard due to its closeness in mass to arsenic on the periodic table as well as absence in the sample matrix. As demonstrated in [Figure 2](#), a graph of internal standard recovery, the students were able to see the depressed germanium signal in the sinus wash matrix, illustrating the importance of matrix consideration when choosing a calibration method. In the laboratory report, students were asked to comment on the

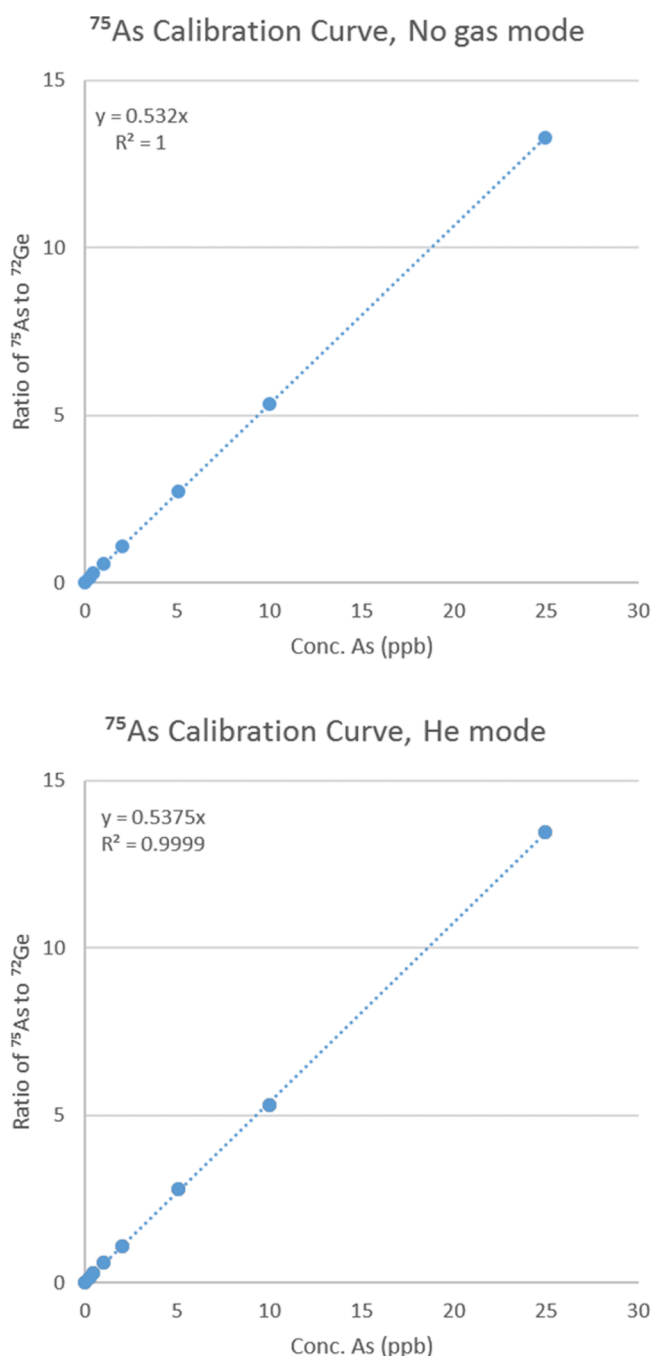


Figure 1. Example of student generated calibration curve for no gas mode and He mode.

advantages of internal standard calibration. Without using internal standard, the arsenic signal in sinus wash would be depressed and the incorrect concentration would be calculated. When using internal standard, the same amount of internal standard is added to each standard and sample. In this way, the ratio of internal standard to analyte is plotted and can be used to compensate for matrix effects. As shown in the calibration curve graphs in Figure 1, students were able to see a plot of the ratio to the concentration generated by the software.

Depending on the matrix or the specific isotopes, interferences may disrupt the analysis of particular elements and employment of a collision cell is useful for their removal. Arsenic is one such element, as it is monoisotopic (75 amu),

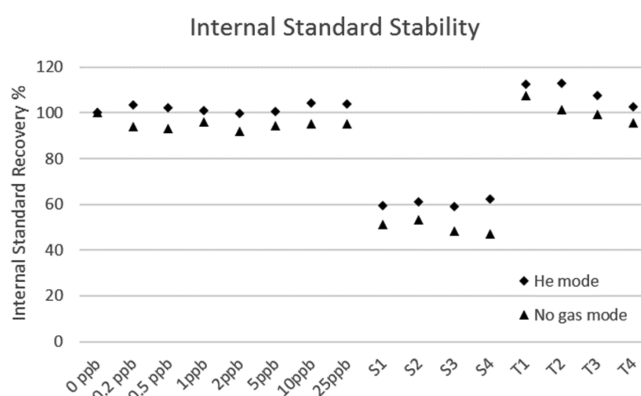


Figure 2. Example of internal standard recovery plot. S1–S4 refer to Sinus Wash replicates. T1–T4 refer to Tap Water replicates.

and in a high chloride matrix (such as some drinking waters), it is difficult to measure at low levels because of the formation of ArCl^+ in the plasma, a polyatomic with the same m/z . In this experiment, a collision cell was employed to facilitate the low level detection of this harmful element. Students were able to observe the results generated both with and without the use of the collision cell. The students were also asked to consider the sinus wash vs the tap water in both modes (no gas mode and He mode) in their laboratory report as part of a hypothesis and in the discussion. Table 1 illustrates the results of the quantification of arsenic in both sinus wash and tap water both with and without using the collision cell, allowing observation of the presence of the ArCl^+ interferant in the no gas mode analysis of the sinus wash.

Students were asked to prepare samples in quadruplicate (see Replicates 1–4 in Table 1) to allow them to calculate the precision in their results and comment on the sample preparation in the lab report. Overall, students were able to explain the advantage of preparing samples in quadruplicate over triplicate, given enough sample. A few students used the Grubbs test to determine if any of the replicates were outliers. This activity informed students on how measurement variability can be addressed in the development of an analytical method.

Before students analyzed their samples, many looked up the federal regulation for arsenic in drinking water and formed their hypothesis. Almost all students believed that the arsenic concentration in tap water and sinus wash would fall below the EPA's 10 ppb As regulation. At first, this seemed to be the obvious conclusion to students, but further research of arsenic led to concerns over environmental contamination and human health. Students were able to go beyond performing the laboratory experiment and discuss in their lab reports why such an analysis can benefit the wider community by monitoring arsenic and other toxic metals in drinking water and consumer products. This connection between the course and the greater world not only fosters student engagement, but also creates a lasting connection between the classroom experience and industrial applications.

SUMMARY

A laboratory experiment employing ICP–MS with collision cell to determine low part-per-billion levels of arsenic in sinus wash and tap water was successfully developed and implemented in an undergraduate instrumental analysis laboratory course. It is the hope that collectively, with this laboratory experiment and the other seven experimental procedures taught in this course,

Table 1. Example of Student Results

Sample	Sinus Wash		Tap water	
	No Gas	Helium	No Gas	Helium
Instrument Mode				
Replicate 1 (ppb As)	6.52	0.26	0.69	0.43
Replicate 2 (ppb As)	6.69	0.33	0.72	0.46
Replicate 3 (ppb As)	6.75	0.24	0.67	0.47
Replicate 4 (ppb As)	6.83	0.39	0.51	0.35
Average concentration of As (ppb As)	6.70	0.31	0.64	0.43
Standard Deviation (ppb As)	0.13	0.07	0.09	0.05
% Relative Standard Deviation (%)	1.95	22.62	14.33	12.59

students will be able to evaluate the limitations and capabilities of different analytical instrumentation as well as fully understand the application of these instruments based on the principles of operation. Specific to this experiment, ICP–MS is a standard tool in industry and it is critical that chemists and chemical engineers have an understanding of the principles of its operation as well as practical hands-on experience. During this experiment, students learned that sample matrix can significantly affect the results of a given analytical method. The use of the germanium internal standard in the sinus wash samples illustrated the necessity of matrix consideration when choosing the calibration method. Further, specific matrices may mask certain analytes, yielding biased analytical results. These interferences must be approached and considered with the utmost care to avoid the reporting of false positives, and the use of a collision cell in ICP–MS is one approach to address such problems. Finally, students were able to relate their results to current EPA regulations and discussed the importance of monitoring toxic metals, further connecting the classroom experience to the greater world.

■ ASSOCIATED CONTENT

● Supporting Information

and are available in this issue of *JCE Online*. The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00744.

Instructions for the students (PDF, DOC)

Notes for the instructor (PDF, DOC)

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Notes

The authors declare no competing financial interest.

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