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Determination of Arsenic in Drinking Water by Graphite Furnace Atomic Absorption Spectroscopy. An Undergraduate Instrumental Analysis Laboratory

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Abstract: A laboratory exercise, the analysis of arsenic in drinking water by graphite furnace atomic absorption spectroscopy (GFAA), is presented for use in an undergraduate instrumental methods course. The purpose of this GFAA exercise is to expose students to a practical and commonly used application, to provide students with hands-on experience with the instrument, and to reinforce concepts taught in the classroom. Students safely analyze a real-world sample containing an analyte in the parts-per-billion concentration range.

Introduction

Inorganic arsenic finds its way into ground water through the natural degradation of rock, and thus it becomes a potential contaminant of drinking water [1]. Arsenic is undetectable in water based on sight and taste, which makes it difficult for a person to recognize during consumption of the water. People that regularly drink water containing high levels of inorganic arsenic become afflicted with arsenicosis, which is chronic arsenic poisoning. Arsenicosis has become a global health concern during the past two decades. For example, seventy million people in Bangladesh are potentially at risk to falling ill from arsenic poisoning due to the contamination of as many as one million wells [1]. Current projections estimate that efforts to end this large-scale poisoning could take 10 years and cost $200 million [2].

The level of arsenic in water that causes arsenicosis is currently under debate. In Bangladesh's water sources, arsenic levels as high as 1000 parts per billion (ppb) have been recorded. This far exceeds that country's guideline of 50 ppb [1, 2]. In response to the events in Bangladesh, the World Health Organization has recommended that governments allow no more than 10 ppb of arsenic in water supplies. In the United States, a standard of 50 ppb was established in 1942 and remains the present day standard despite congressional pressure on the Environmental Protection Agency (EPA) to lower the guideline [3]. Currently, the EPA is considering the issue and may lower the guideline to as low as 2 ppb. An adjustment to 10 ppb would affect 2,200 of the 56,000 public water supply systems in the United States costing taxpayers an estimated $1 billion to comply with the new regulations [4]. The geographic areas that would be most affected include Western, Midwestern, and New England states.

A recent local study of public water supplies in the state of Minnesota revealed that fourteen communities have arsenic levels above 20 ppb, with the highest level being 38 ppb in Buffalo Lake [3]. An analysis of Minnesota's private wells, which are not required to meet federal guidelines on arsenic, has found arsenic levels up to 150 ppb. The general trend, as shown in Figure 1, reveals that the highest arsenic levels run from the northern to the southern border throughout the western half of the state.

Considering the important implications of the studies presented above, our instrumental methods students analyzed drinking water for arsenic using a graphite furnace atomic absorption (GFAA) spectrometer. Arsenic analysis by GFAA is the method most widely used by EPA-approved laboratories [5]. GFAA is one of the most sensitive instruments found in many chemistry departments, however, very few structured laboratory exercises have been published for its use in undergraduate courses [6]. The purpose of this GFAA exercise is to expose students to a relevant and commonly used application, to provide students with hands-on experience with the instrument, and to reinforce concepts taught in the classroom. In addition, students are interested in experiments involving environmental issues.

GFAA is ideally suited for the analysis of arsenic in drinking water because it has high sensitivity, it requires low sample volumes, and it is subject to few interferences [7]. GFAA has a significantly lower detection limit (ppb versus ppm) than inductively coupled plasma (ICP) atomic emission spectroscopy, and this sensitivity is necessary to directly analyze for arsenic in drinking water. Moreover, there is no need to handle large volumes of highly concentrated toxic standards, because GFAA requires only microliters of sample. While ICP has replaced many analytical methods due to its availability and convenience, it is not a common method for arsenic analysis due to its lack of sensitivity. Lastly, arsenic is subject to minimal interferences via GFAA, especially in an uncomplicated sample matrix like drinking water. Most chemical interferences can be minimized or accounted for through the addition of copper nitrate or through standard addition [8].

Experimental

A 50-mL arsenic standard (75 ppb), which was stored in a polypropylene bottle, was obtained from a local analytical laboratory (Legend Technical Services, St. Paul, MN). An alternative method is to dissolve an appropriate amount of anhydrous As_2O_3 in 0.1 M NaOH. The preparation of the standard MUST be done by the instructor! Five standards (0.5 mL) ranging from 0 to 75 ppb were

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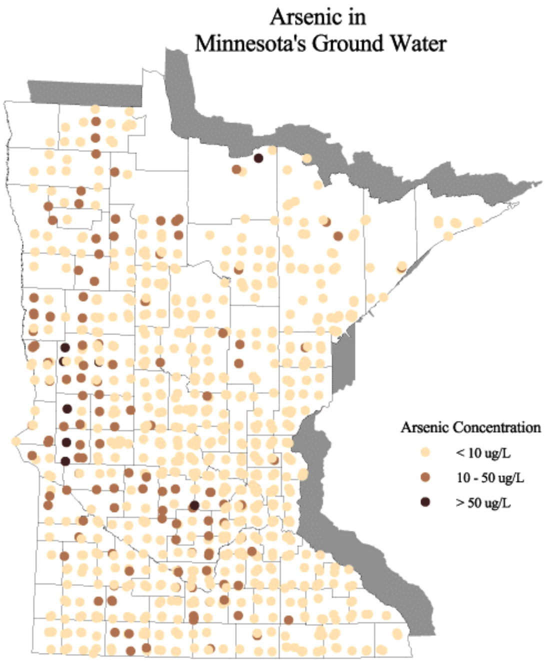

Figure 1. Arsenic levels in Minnesota groundwater displayed as 3 categories: <10 ppb, 10 to 50 ppb, and >50 ppb (Extracted with permission from Minnesota Pollution Control Agency, Dec. 23, 1998. http://www.pca.state.mn.us/water/groundwater/gwmap/gw-baseline.html#arsenic.

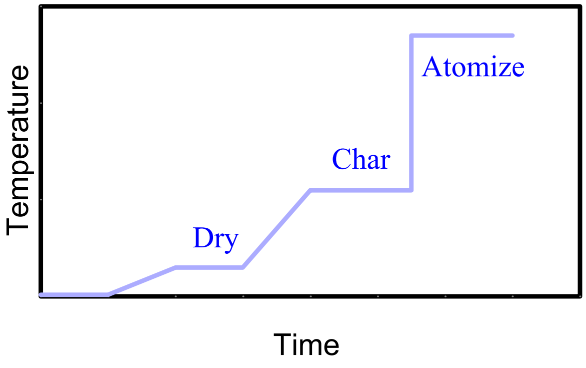

Figure 2. Schematic representation of a typical three-step temperature program typically used in graphite furnace atomic absorption spectroscopy.

made prior to analysis using a micropipetman. It was observed that standards gave inconsistent results if they were stored in borosilicate vials. Because the volumes and concentrations of arsenic were both small, no special precautions were necessary for handling or disposing of samples. Any excess reagents were disposed of properly. All hazardous waste from the department is disposed of through the Integrated Waste Management Facility at the University of Minnesota. Students collected various water samples from private wells, public water supplies, and bottled water from the Minnesota area.

The theory and applications of GFAA have been extensively discussed in the literature (e.g., [7]) and will not be discussed here. The purpose of this article is to provide instructors with a practical and relevant experiment that reinforces atomic absorption concepts traditionally taught in instrumental methods. Students receive verbal instructions on how the instrument works (lamp alignment, temperature programming, etc.).

A 50-mL aliquot was directly delivered via a pipetman into a Perkin-Elmer 4000 graphite furnace atomic absorption spectrometer fitted with an HGA 400 temperature programmer. The slit width was set at 0.7 nm, the optimal wavelength was 193.7 nm, and the potential applied to the hollow cathode lamp was 18 mV. The furnace assembly was purged with argon at flow rates from 50 to 200 mL/min. It was determined that the flow rate had little effect on observed absorbances, and a flow rate of 50 mL/min was used throughout the study.

The temperature programming was composed of a drying, charring, and atomization steps as illustrated in Figure 2. The heating process is important because it removes unwanted matrix components, which can alter the measured absorbance of the sample, and it determines the residence time of the atomized sample in the light path. In the drying step, the solvent is removed from the sample matrix through vaporization, and the time and temperature is determined by the solvent. In this application, the sample was heated to 130 °C for 50 s under a stream of argon (50 mL/min). Rapid solvent boiling is to be avoided. Organic material was decomposed or vaporized during the charring step (1700 °C for 30 s) and removed under a stream of argon (50 mL/min). To reduce spattering, the temperature was ramped over a period of two seconds during these first two heating steps. The third and final step in the heating process (2700 °C for 10 s) atomizes the sample for analysis. Gas flow was slowed or stopped before the rapid increase in temperature to ensure the analyte remained in the graphite tube. In the atomization step, the element of interest was atomized to a gaseous state, and an absorbance reading was obtained. To ensure complete removal of the last sample, the graphite furnace was manually fired to 2700 °C for 5 s, and a blank was run to zero the instrument before running the next sample.

Results and Discussion

A standard calibration curve (not shown) was used to determine the concentration of arsenic in various samples of drinking water. Despite the fact that GFAA is known to suffer from poor reproducibility and accuracy, we experienced no significant problems reproducing our results (R^2 for the calibration curves was always >0.998), and this observation was likely due to the simplicity of the matrix. The highest levels of arsenic recorded for samples were from private wells (values ranged from 2 to 68 ppb), and the lowest concentrations were found in samples from public water systems (<1 ppb). The detection limit was determined to be 1 ppb. This limit was calculated by first determining the minimum distinguishable signal (S_m) as follows [7]:

$$S_m = \bar{S}_{blank} + 3S_{blank}$$

where $\bar{S}_{blank}$ is the average of the blank (n = 15) and S_{blank} is the standard deviation of the blank. The detection limit (C_m) is then calculated as follows:

$$C_m = \left(S_m - \bar{S}_{blank}\right)/m$$

where m is the slope of the calibration curve.

The results of the water samples analyzed confirmed that the public water systems were, in fact, complying with EPA regulations. Private wells are not required to meet EPA guidelines for arsenic levels, and indeed some wells were found to exceed these levels. The concentrations determined for private wells were consistent with values reported for Minnesota ground water (see Figure 1).

The experiment described above can easily be completed in one three-hour laboratory period. Unknown samples can be prepared by the instructor and supplied to the students in addition to the water samples collected by the students. While this laboratory exercise seems simple, it does provide students with the opportunity to safely work with a toxic substance, to carry out an EPA recommended and widely used protocol, and to gain hands-on experience with a spectrometer that is discussed in instrumental methods. Because of the growing number of instrumental methods to which students should be exposed, we do not spend more than one laboratory period on this instrument. If additional time is available, however, this laboratory exercise can be easily expanded to encompass more sophisticated exercises (e.g., accounting for interferences or optimizing temperature programming). Although drinking water is a relatively uncomplicated matrix, we found that some well-water samples were noticeably rust colored. A standard addition method can be used to analyze these samples to account for any interference due to the atomization of elements, such as iron, during the analysis.

The effect of temperature programming on the analysis of arsenic has been previously examined [9]. It has been shown that the drying step has little impact on the analysis as long as the solvent is not boiled rapidly (suggested range 100 to 130 °C for 50 s). Secondly, it was found that the charring step did have a significant impact on the measured absorbance (optimum conditions were 600 °C for 30 s [9]). We, however, obtained better results following the equipment manufacturer's guidelines for this step (1100 °C for 30 s). Lastly, it was found that complete atomization was attained at any temperature above 2300 °C [9]. The process of temperature optimization for a quantitative analysis laboratory utilizing a GFAA spectrometer has been previously described for copper [6], and the procedure is typically described in the operational manual of a specific GFAA instrument (e.g., ref. 8).

The GFAA laboratory exercise described above serves to reinforce concepts traditionally taught in instrumental methods. Students enjoy being able to collect their own samples, and they gain practical experience at measuring a sample in the ppb range. Because sample concentration and volume requirements are low, the amount of waste generated is minimal. Lastly, this experiment provides the opportunity to study a real-world problem that has recently generated a lot of student, public, and scientific interest.

References and Notes

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