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Colorimetric-solid phase extraction method for trace level determination of arsenite in water

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ABSTRACT

This paper introduces a method for the determination of inorganic arsenite [As(III)] in water at low $\mu g\,L^{-1}$ by a sorption-photometric method known as colorimetric-solid phase extraction (C-SPE). The method relies on the selective extraction and concentration of an analyte on a reagent-impregnated SPE membrane, followed by direct detection of the extracted colored complex by a handheld diffuse reflectance spectrophotometer (DRS) operating in the visible spectral region. The well-established chemistry of the classic redox titrimetric method for molecular iodine (I_2) standardization by arsenious oxide (As_2O_3) serves as the basis for this analysis. I_2, which is added to the aqueous sample in an excess with respect to the analyte, serves as a colorimetric indicator. The arsenite–iodine reaction is rapid, allowing an exact volume of analyte solution to be immediately passed through an SPE membrane via a syringe after mixing with the indicator. An SPE membrane that is impregnated with the complexing agent poly(vinylpyrrolidone) (PVP) serves to complex and concentrate excess I_2 not consumed by the As(III) analyte. The amount of complexed I_2 is determined by a DRS reading directly on the membrane surface. The spectrophotometric measurement can be made in a few seconds, with a total sample workup and readout time of ~1–2 min. The limit of detection (LOD) for this determination is below $10\,\mu g\,L^{-1}$. The potential effectiveness of the method for the analysis of spiked tap water and surface water is examined, and results from preliminary interference studies are described. The work herein also shows that by applying the principles of negligible depletion (ND), the analytical procedure could be simplified by eliminating the need to pass an exact volume of a sample through the impregnated membrane as long as it exceeds the predetermined minimum volume.

1. Introduction

More than 100 million people worldwide are affected by environmental arsenic contamination caused by corrosion of natural deposits [1–3]. The situation is especially problematic in developing countries where arsenic levels in drinking and surface waters can far exceed those considered safe for consumption [4]. Arsenic in water and soil exists in both organic and inorganic forms, with the dominant oxidation states being arsenite [As(III)] and arsenate [As(V)] [2,5,6]. Arsenite is ~10 times more toxic than arsenate, and ~70 times that of its methylated forms [7]. The maximum allowable level of arsenic in drinking water, as specified by the World Health Organization (WHO), has been recently decreased from 50 to $10\,\mu g\,L^{-1}$ [1]. As such, there is an ongoing need for the development of low-cost, effective, and reliable platforms for the quantitative detection of arsenic in drinking water, particularly for its most toxic and prevalent inorganic forms. The work herein begins to address these needs.

There are a number of arsenic detection methods, including hydride generation (HG) and inductively coupled plasma (ICP), which are typically linked with atomic spectrometry, mass spectrometry, or electrochemical techniques [7,8], and cover a range of preparation, separation, and derivatization steps [9–28]. Of the methods that meet the needed detection level in drinking water, the associated costs and instrumentation often limit deployment beyond the formal laboratory setting [8]. Highly precise and accurate field kits are also available, but generally involve the generation of arsine gas [29].

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The oldest known methods for measuring arsenic in water use colorimetry, and reports of improvements or coupling with other analytical techniques regularly appear in the literature [30–37]. These approaches are frequently used in the design of kits for on-site measurements [38–40], but can be hard-pressed to meet the needed LOD and/or would clearly benefit from reductions in turn-around-time (TAT) and sample volume. Many of these kits are also limited in that the results are of a semi-quantitative as opposed to quantitative nature [41].

The C-SPE method concentrates and facilitates quantification of an analyte on a reagent-impregnated SPE membrane. The resulting colored complex is then measured directly on the membrane surface by a hand-held DRS. There are three main variations of C-SPE: (1) complexation and extraction; (2) extraction and exposure; and (3) immobilization and extraction. With complexation and extraction, an analyte and colorimetric reagent are combined in solution and the resulting soluble/insoluble complex is extracted by an SPE membrane. This variation has been used to measure a wide-range of metals [42–44]. Extraction and exposure entails the extraction of analytes on an SPE membrane, followed by exposure to a complexing reagent solution. Like the complexation/extraction methods, this approach has been used to measure a variety of metals [18,45–48], including As(V) [18] at trace levels (LOD of 4 $\mu g\,L^{-1}$). This method for As(V), however, is prone to interferences from alkali metal chlorides (e.g., KCl and NaCl) and various phosphates, requires a large sample volume (100 mL), and has a TAT of ~20 min. Immobilization and extraction relies on the impregnation of an SPE membrane with a colorimetric reagent that selectively extracts and concentrates the analyte from a sample. Several inorganic and organic analytes have been quantified by this strategy [49–56].

In research designed to meet a comparable set of objectives (e.g., low LOD, short TAT, small sample size, and deployability) to facilitate the exploration of space by humans, our laboratory has focused primarily on the immobilization and extraction version of C-SPE for determining biocide levels (i.e., total iodine and silver (I)) [57,58] and other trace level indicators [59–61] of water quality in spacecraft potable drinking water. C-SPE, which we have shown to function effectively in microgravity simulations [62], has recently undergone detailed performance testing on the International Space Station (ISS) [63]. Results of these tests have prompted NASA to designate C-SPE as operational hardware to be used aboard ISS in future endeavors. Importantly, C-SPE maintains the high concentration factors of SPE (~1000 or more) [64], which translate to, for example, an LOD of ~10 $\mu g\,L^{-1}$ for the measurement of molecular iodine (I_2) after metering a 10.0-mL water sample through a PVP-impregnated membrane [57]. It is also notable that our approach to C-SPE typically has a TAT of 1–2 min [57–61,65].

This paper describes the extension of C-SPE to the rapid measurement of trace levels of As(III) in water by adaptation of the redox titrimetric method used for the standardization of I_2 by As_2O_3 [66,67]. Our method relies on the addition of a known and excess amount of I_2 to a solution containing As(III). The ensuing redox reaction between the two species consumes a stoichiometric amount of I_2, and the unreacted I_2 is then complexed and concentrated on a PVP-impregnated membrane, which can be quantified by DRS. This approach therefore represents a variation of the immobilization and extraction format of C-SPE in that the unreacted level of a reagent in solution is captured and measured, rather than the amount of extracted analyte. The following details the development and interference testing of this new method, and a preliminary examination of its performance using spiked tap and surface water. Results from the adaptation of this technique for operation in a negligible depletion (ND) mode [68,69], which eliminates the need to pass an exact volume of sample through the impregnated membrane as long as it exceeds a predetermined minimum volume, are also described.

2. Methods

2.1. Reagents, chemicals and materials

All chemicals were analytical reagent grade and were used without further purification. Solutions were prepared in distilled deionized (DI) water (18.2 $M\Omega\,cm^{-1}$, Thermo Scientific, Waltham, MA). Nylon membranes (0.45-μm diameter pore, 0.2 mm thick) were products of Whatman, Inc. (Scarborough, ME); poly(styrenedivinylbenzene) membranes (0.8-nm diameter pore, 0.5 mm thick, Empore™ SDB-XC) were products of 3 M (St. Paul, MN).

2.2. Solution preparation

A 0.025 M Iodine solution was prepared by dissolving 1.6000 ± 0.0050 g of KI (Aldrich, Sheboygan Falls, WI) with as little water as possible in an amber, 50.00-mL volumetric flask, followed by addition of 0.3000 ± 0.0020 g of solid I_2 (Fisher, Fair Lawn, NJ). Lower concentration solutions of I_2 were prepared by diluting the stock solution with nitrogen-purged water, with the final concentrations of the diluted solutions determined spectrophotometrically.

Arsenic (III) oxide (As_2O_3) (Acros, NJ) was dried at 110 °C for 1 h, and then dissolved in a solution containing 15.00 mL of 1.00 M sodium hydroxide (Sigma–Aldrich, Milwaukee, WI), 18.00 mL of 0.50 M sulfuric acid (Fisher), 50.00 mL of 4% (w/v) sodium bicarbonate (Fisher), 25.00 mL of water, and 0.142 L of 0.200 M phosphate buffer (Fisher). This solution will be referred to hereafter as the "dissolution matrix". Standard samples were prepared by gravimetrically diluting the stock with this solution. Prior to extraction and read-out, 15 mL of a predetermined level of As(III) was weighed (15.00–15.05 g) and 0.100 mL of a given concentration of I_2 was added prior to extraction. The pH of the solution was 6.8–7.0.

As(III) solutions were spiked with a final concentration of 10 or 300 $\mu g\,L^{-1}$ of interferent. Pb(II), Ni(II), Cd(II), and Hg(II) used for solutions were purchased from Aldrich. Sodium arsenate was purchased from Sigma.

Solutions for impregnating the extraction membranes were prepared by dissolving 1.0, 1.5, 2.0, or 2.5 g of PVP (average M_W ~10,000, Aldrich) in 100.0 mL of 1:9 methanol:water for the Nylon membranes, or 3.0 g of PVP in 100.0 mL of 1:1 methanol:water for SDB-XC membranes.

2.3. Membrane preparation

The 3.0% PVP solution was used to impregnate SDB-XC membranes, with the less concentrated solutions employed for Nylon membranes. Impregnation was accomplished by mounting a membrane on a Millipore 47-mm glass vacuum filter holder and passing 10.0 mL of PVP solution through the membrane by applying a vacuum. The membrane was subsequently vacuum-dried for ~30 s. Each membrane was then removed, air-dried for ~16 h in the dark, and cut into 13-mm disks. Each disk was placed in a Swinnex polypropylene cartridge (No. 09-753-10ASX00 0013 00, Fisher), which was sealed with a 13 mm O-ring. Assembled cartridges were stored in air-tight containers in the dark until use.

A CB-6834 Spectro Guide Sphere, $d/8°$ DRS (BYK-Gardner USA, Columbia, MD) was used to collect spectral data from unreacted I_2 captured to the disk. The small, lightweight, battery-operated spectrophotometer has a spectral range of 400–700 nm and a 10-nm spectral resolution. A single spectrum can be acquired in ~1–2 s. The unit incorporates a source, integrating sphere, and detector.

2.4. Tap and surface water

Tap water was provided by the City of Salt Lake. Surface water was obtained from runoff streams at Big Cottonwood Canyon, Utah, which feed into the Salt Lake City water supply. Runoff water was filtered prior to use (0.2-μm pore filter, Pall Corp, Ann Arbor, MI); water from each source was used in preparing the dissolution matrix, which was spiked with As(III).

2.5. UV–visible spectrophotometer

To determine the amount of I_2 extracted on SPE membranes, the effluent was analyzed using an Agilent 8453 diode array spectrophotometer and a 1.00-cm pathlength quartz cuvette (Agilent Technologies, Loveland, CO).

2.6. Extraction procedure and readout

A 10.0-mL glass syringe (SGE Inc., Austin, TX) was used to meter each liquid sample through the impregnated membranes by affixing a disk-containing cartridge to the syringe via a Luer Lock fitting, and manually ejecting the volume through the extraction cartridge. The SDB-XC disks were dried by forcing air through the cartridge with a 60-mL syringe; 30-mL was used for the Nylon disks. After extraction, the cartridge was disassembled, and the disk containing the complexed, unreacted I_2 was removed and placed at the sample port of the DRS for data acquisition. All LODs are reported as the intensity of a blank plus three times the standard deviation (S.D.).

2.7. Data analysis

The raw spectral data were downloaded to a desktop computer and analyzed using a Microsoft Excel® Spreadsheet. The fractional reflectance (R) is related to the concentration of reagent captured on the disk (C_f), which can be determined by converting the reflectance data to the Kubelka–Munk function, $F(R)$:

$$F(R) = \frac{(1-R)^2}{2R} = 2.303 C_f \frac{\varepsilon}{s} \quad (1)$$

where ε is absorptivity and s is the scattering coefficient. It is assumed that ε and s are constant over the concentration range of interest. As such, $F(R)$ is directly proportional to reagent concentration, which is determined from a standard calibration curve. For use in the field, calibration coefficients can be programmed into the unit to allow for readout in ppb or ppm.

3. Results and discussion

3.1. Principles of I_2 redox titrimetry and C-SPE

The reactions for standardizing iodine with arsenious oxide are given below [66,70,71]. Arsenious acid can be oxidized to arsenic acid by triiodide (I_3^-), which exists in aqueous solutions when I_2 is present in an excess of iodide (I^-). I^- increases the solubility of I_2 by the reaction in Eq. (2), which has an equilibrium constant (K) of 732 [72,73].

$$I_2 + I^- \rightleftharpoons I_3^- \quad (2)$$

If aqueous I_3^- is added to a solution of arsenious acid, the following pH-dependent, reaction takes place rapidly:

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 3I^- \quad (3)$$

The value of K for this reaction is small, 0.044 [74], but becomes much larger with an increase in pH. It is also essential to control the hydroxyl ion level because the following reactions of I_3^- become problematic in alkaline conditions, either through the formation of hypoiodous acid (Eq. (4)) or iodate (Eq. (5)) [66,67]:

$$OH^- + I_3^- \rightleftharpoons HOI + 2I^- \quad (4)$$

$$6OH^- + 3I_3^- \rightleftharpoons IO_3^- + 8I^- + 3H_2O \quad (5)$$

Thus, the ability to quantify As(III) by its redox reaction with I_2 dictates identifying a pH that favors the reaction in Eq. (3), but renders the processes in Eqs. (4) and (5) of negligible importance. In a classic example of combining the predictions of equilibrium modeling and determinations based on titrimetry [67], Washburn demonstrated that buffering at neutral pH represents the balance necessary for our purposes.

In our method, a known amount and excess of I_2 is reacted with As(III) in solution and a precise volume of this reaction mixture is then metered through a PVP-impregnated SPE membrane disk. Upon passage through the disk, PVP complexes unreacted I_2 [72]. Next, the disk is dried allowing the reflectance spectrum of the complex to be acquired via DRS. By converting the reflectance data to F(R), a calibration plot can be constructed and the depletion of I_2 can be directly related to As(III) concentration.

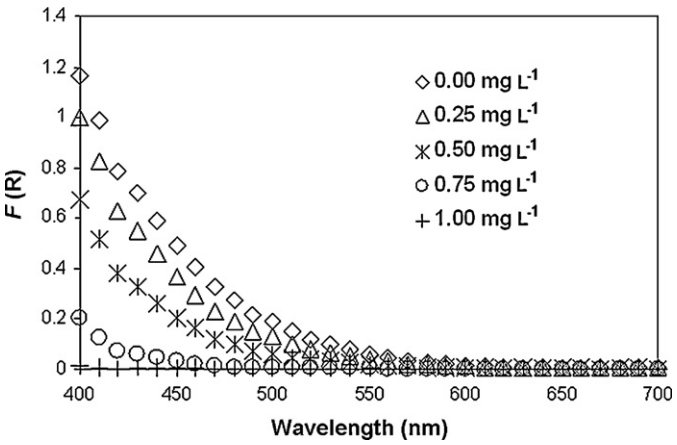

Fig. 1. Diffuse reflectance spectra for unreacted I_2 as a function of As(III) concentration, using SDB-XC membranes impregnated with 3% PVP solution. I_2 concentration was constant at 3.0 mg L^{-1}; sample volume was 10.0 mL.

3.2. C-SPE studies

Fig. 1 presents a set of DRS data representative of the depletion of I_2 by its reaction with different concentrations of As(III). Note that I_2 levels from 0.050 to 5.0 mg L^{-1} span the linear dynamic range for our C-SPE method for I_2 [57,75], prompting us to choose an I_2 concentration of 3.00 mg L^{-1} and a sample volume of 10.0 mL as starting points. The TAT, which includes the time to meter the sample through the impregnated membrane followed by disk readout by DRS, is ~1–2 min. As evident, the intensity of the spectra decreases with increasing As(III) concentration, consistent with a decrease in the formation of the yellow I_2–PVP complex, which has a maximum $F(R)$ just below 400 nm [69,72]. Moreover, the sample containing 1.00 mg L^{-1} As(III) has no observable features because the absolute amount of As(III) at this sample volume for this solution (3.00 mg L^{-1} I_2) depletes all of the available I_2. The change in signal (i.e. sensitivity of the measurement) is greatest at 400 nm [69] and the plot in Fig. 2 of F(R) against the concentration of As(III) decreases linearly. Between 0.0–0.10 mg L^{-1}, there is a large sample-to-sample variability and no clear correlation between As(III) concentration and F(R). As a consequence, this set of measurements has an LOD of 140 μg L^{-1}.

These results, while not at the target LOD of ~10 μg L^{-1}, demonstrate the potential merits of this method (i.e., a TAT of ~1–2 min

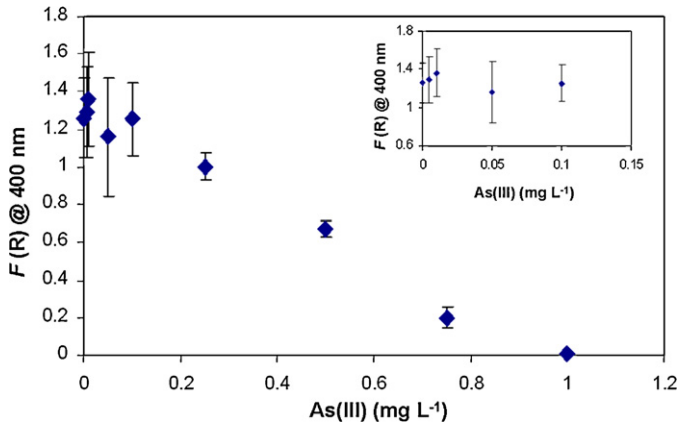

Fig. 2. Calibration plot for unreacted I_2 as a function of As(III) concentration ($n = 5$) using the spectral data from Fig. 1.

and sample volume of 10.0 mL). Because this is a depletion measurement, a greater signal change in I_2 concentration when reacted with As(III) is necessary in order to lower the LOD. This condition may be achieved by lowering the I_2 concentration while ensuring that the concentration of unreacted I_2 results in a reflectance signal between $0.2 < R < 0.7$. The latter is important because errors at larger and smaller reflectance increase rapidly (i.e., $F(R)$ underestimates high reflectance and enhances low reflectance [76]). Preliminary tests have indicated that lowering the I_2 concentration from 3.00 mg L^{-1} to 500 μg L^{-1} has the potential of achieving an LOD of ~20 μg L^{-1}.

One means of lowering the LOD further is by using SPE membranes made from other materials. In an earlier C-SPE study [69], we found that the LOD for I_2 was ~5× lower (10 μg L^{-1}) for Nylon membranes impregnated with 1.0% PVP solution as opposed to SDB-XC membranes doped with 3.0% PVP solution. To determine if there is an advantage to using Nylon for As(III) determination, experiments were carried out using both types of membranes at As(III) concentrations ranging from 0.0 to 50.0 μg L^{-1} and an I_2 concentration of 500 μg L^{-1}.

Fig. 3 presents the results of these experiments. The data in both plots show a linear decrease in $F(R)$ as the As(III) level increases, with the dependence of the response being almost twice that for Nylon membranes with respect to SDB-XC membranes. The results also demonstrate that the reproducibility of the measurements for

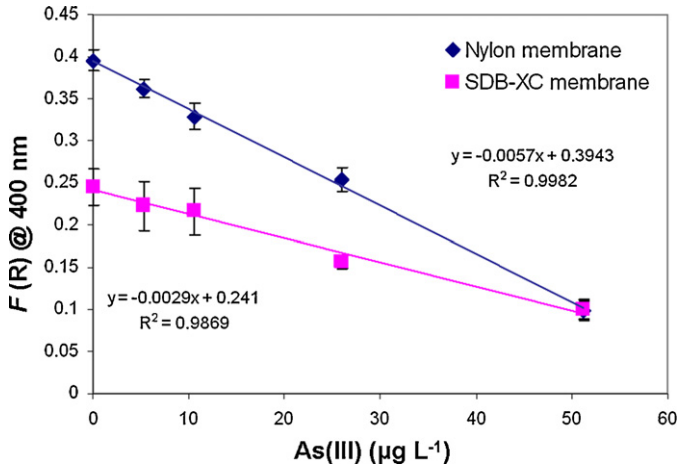

Fig. 3. Calibration plot from spectral data for unreacted I_2 as a function of As(III) concentration ($n = 5$). Nylon membranes (♦), 1% PVP; SDB-XC membranes (■), 3% PVP. I_2 concentration was constant at 500 μg L^{-1}; sample volume was 10.0 mL. LODs were 6 μg L^{-1} (Nylon) and 20 μg L^{-1} (SDB-XC).

Nylon membranes is generally better than that acquired with SDB-XC membranes. In combination, these two sets of parameters yield an LOD for As(III) determined with PVP-impregnated Nylon membranes of 6 μg L^{-1}, which is slightly better than that of the 20 μg L^{-1} found for PVP-impregnated SDB-XC membranes. Thus, the use of PVP-impregnated membranes enables the detection of As(III) at a level that is on par with the exposure limit in water. Furthermore, the analysis is rapid, typically requiring ~1–2 min per sample.

3.3. Origin(s) of performance difference

To identify factors that give rise to the difference in the effectiveness of the two types of membranes, two experiments were performed. By collecting the effluent after passage of 10.0 mL of an As(III) sample containing 5.00 mg L^{-1} I_2 and measuring the unreacted reagent solution level spectrophotometrically at 460 nm, the first experiment quantified the amount of I_2 extracted by the two types of impregnated membranes. The second experiment measured PVP uptake gravimetrically after allowing the impregnated membranes to dry. These results, which reflect the averages of 2–5 separate tests, yielded respective I_2 depletion and PVP uptake values in the 3% PVP-impregnated SDB-XC membranes of 5.58 (±0.14) × 10^{-9} mol mm^{-3} and 4.51 (±0.85) × 10^{-5} g mm^{-3}. The same set of tests gave values for the 1% PVP-impregnated Nylon membranes of 1.10 (±0.02) × 10^{-8} mol mm^{-3} of I_2 and 2.38 (±0.26) × 10^{-5} g mm^{-3} of PVP. Thus, the amount of PVP impregnated in the Nylon membranes is only ~50% of that in the doped SDB-XC membranes, but the amount of I_2 retained by Nylon membranes roughly doubles that of the SDB-XC membrane.

The measured uptakes of I_2 on the two sets of membranes qualitatively agree with the differences in the values of $F(R)$, ~2× (Fig. 3). However, the difference in levels of PVP-impregnation does not track with the difference in the amounts of extracted I_2. We had previously speculated that the higher level of I_2 retention with Nylon reflected more PVP loading, even though the solvents for the impregnation of the two types of membranes were different [69]. These two sets of uptake measurements, however, counter our earlier hypothesis. To understand the chemical/physical origins central to this difference (e.g., membrane hydrophobicity), we are presently designing experiments to determine if the effective binding ability of PVP when impregnated in the Nylon membranes, even though loaded at a lower absolute amount, is greater than that when incorporated into SDB-XC membranes.

3.4. Interference studies

Experiments were conducted to determine the effect of foreign ions (Table 1) on the quantification of As(III). First, a reference sample composed of 10 μg L^{-1} As(III) and 500 μg L^{-1} I_2 was analyzed at 400 nm. Second, a known amount (10 or 300 μg L^{-1}) of interferent that was spiked into a 10 μg L^{-1} As(III) sample and mixed with a solution of I_2 to achieve an I_2 concentration of 500 μg L^{-1}, was extracted and then analyzed by DRS at 400 nm. Interference was determined at 95% confidence by comparing F(R) of the reference to the values for each of the interferents studied (the interval of confidence in these studies, based on five repetitions of a 500 μg L^{-1} I_2 solution, is ±14%).

The results from analyzing the samples spiked with interferents are shown in Table 1. At a concentration of 10 μg L^{-1}, each interferent studied had no observable impact on the analysis; however, at 300 μg L^{-1}, both Hg(II) and As(V) interfere. The Hg(II) interference is likely a result of Hg(II) reacting with I^-, which leads to the production of mercury(II) iodide (HgI_2) [77]. By consuming I^-, the product in Eq. (3) is depleted, which causes an equilibrium shift, making the forward reaction more favorable. Thus, the depletion of I_2 in the presence of Hg(II) is reflected by the 34% decrease in $F(R)$ listed in

Table 1
C-SPE interference study of various foreign ions on a reference As(III) sample using Nylon membranes.[a]

Interferent	Concentration ($\mu g\,L^{-1}$)[b]	$F(R)$	Error (%)	Interference[c]
Blank	–	0.434	–	–
Hg(II)	10	0.420	−3	No
	300	0.286	−34	Yes
Pb(II)	10	0.422	−3	No
	300	0.449	+1	No
Cd(II)	10	0.469	+8	No
	300	0.445	+3	No
Ni(II)	10	0.403	−7	No
	300	0.386	−11	No
As(V)	10	0.406	−6	No
	300	0.497	+15	Yes

[a] Reference sample contained 10 $\mu g\,L^{-1}$ As(III) and 500 $\mu g\,L^{-1}$ I_2, membrane doping was 1% PVP, sample size was 10.0 mL, $n = 5$.
[b] Final interferent concentration.
[c] Considered interfering when %error >confidence interval (±14%).

Table 1. The addition of 300 $\mu g\,L^{-1}$ As(V) resulted in a 15% increase of $F(R)$ signal compared to the blank. Based on Le Chatelier's principle, the addition of As(V) would counter the equilibrium shift in Eq. (3), leading to the forward reaction being less favorable. The increase in $F(R)$ signal in the sample containing As(V) compared to the reference agrees with this assertion because less I_2 is depleted under these conditions. We note that the specificity of the method can potentially be improved by the use of complexing agents for interference masking. For example, ethylenediaminetetraacetate ($EDTA^{4-}$), which complexes with Hg(II) but not at a detectable level with As(III) [78], may prove of value in minimizing the effect of Hg(II) interference. Such experiments are being planned. The next section summarizes the results from a preliminary performance assessment using spiked tap and surface water.

3.5. Tap and surface water

To further examine the potential use of this method for determinations beyond the formal laboratory setting, tests were carried out on spiked (Salt Lake City) tap water, and surface water collected from Big Cottonwood Canyon, UT. From our initial studies, the utility of this method for tap water samples containing 20, 30 and 50 $\mu g\,L^{-1}$ As(III). The analyte concentration was calculated based on the calibration equation $[As(III)] = -(F(R) - 0.3943)/0.0057$, which was generated from DI water data. Positive readings (>10 $\mu g\,L^{-1}$ WHO guideline) were obtained for all tap water samples. Positive readings were obtained for >20 $\mu g\,L^{-1}$ As(III) in surface water.

These results demonstrate that there is potential for the use of C-SPE to detect low concentrations of As(III) in aqueous samples, but also indicates the need for refinement of the method in order for it to be used outside the laboratory setting. For example, it was noted that $F(R)$ values at 400 nm are generally higher in the tap and surface water compared to DI water. This may be due to interferents in both tap and surface water that could potentially disrupt the I_2–I^- and/or arsenic acid–arsenious acid equilibrium, or perhaps there are trace-levels of I_2 present. The difference between tap and surface water at 20 $\mu g\,L^{-1}$ spiked As(III) concentration may be due to a higher content of interferent found in surface water compared to tap water. Likely sources of interferents/contaminants can originate from erosion of natural land deposits, and discharge from eroding drainage pipes [79]. In order to improve the specificity of this method for real samples, a panel consisting of a large variety of water sources should be probed and independent verification of interfering species made. This approach will allow more effort to be placed on finding masking agents that can minimize the effects of a series of potential interferents.

At times, we have observed an increase in background intensity at 400 nm when evaluating analyte concentration in some types of aqueous media (e.g., ground water with visibly observable particulate matter). We plan to examine two approaches to deal with this situation and extend the applicability of our new method to more complex media: (1) run a calibration curve for each sample in a manner of the method of standard addition, and (2) account for increased background by monitoring spectral changes of the sample with respect to its corresponding blank. Both these avenues will be pursued in the near future.

3.6. ND studies

We have previously applied the principles of ND to eliminate the need for metering a precise volume of a sample through a C-SPE membrane [68,69]. The principle of ND states that beyond a predetermined volume (V_{ND}), the concentration of an analyte in a sample before and after its passage through the extraction disk is unchanged, and thus the value of V_{ND} can be determined from plots of $F(R)$ as a function of sample volume. When the value of $F(R)$ plateaus (i.e., becomes independent of volume), ND conditions are achieved and V_{ND} is then defined by the volume needed to reach the plateau.

Theory states that the concentration of analyte partitioned into the extraction phase, C_f, at equilibrium is:

$$C_f = C_o \left[\frac{K_D}{1 + (K_D(V_f/V_o))} \right] \tag{6}$$

where K_D is the partition coefficient, V_f is the volume of the extraction phase, C_o is the concentration of the analyte in the original sample, and V_o is the volume of the original sample. When $V_o \gg K_D V_f$, $K_D V_f / V_o \ll 1$, and Eq. (6) reduces to:

$$C_f = K_D\, C_o \tag{7}$$

In terms of the Kubelka–Munk function, Eq. (1) can now be rewritten as:

$$F(R) = 2.303\, K_D\, C_o \frac{\varepsilon}{s} \tag{8}$$

By recognizing that the number of moles of analyte partitioned into the extraction phase, i.e., n_f, is equal to $C_f\, V_f$, the amount of extracted analyte can be changed by altering the level of PVP doping, which in turn may change K_D, since:

$$K_D = \left(\frac{n_f}{C_o V_f} \right) \tag{9}$$

The results of our study to determine V_{ND} are given in Fig. 4. In an effort to alter K_D, two different PVP dopings, 1.0% and 2.5%, were used to see what effect this parameter may have on V_{ND}. As the plot shows, the signals for both dopings are comparable, and the $F(R)$ values level off between 5.0 and 9.0 mL. These data suggest that K_D is not significantly affected by changing the concentration of PVP solution from 1.0 to 2.5%, which we attribute to PVP being present in a considerable excess in comparison to I_2. By repeating the study with volumes of 5.0, 7.0, 9.0 and 10.0 mL (Fig. 4 inset), V_{ND} was determined to be 7.0 mL.

C-SPE data acquired by using a 7.0 mL sample volume is displayed as the plot in Fig. 5. Data show the low sample-to-sample variability that is routinely found when using Nylon membranes. Under V_{ND} conditions, the LOD was calculated to be 4 $\mu g\,L^{-1}$. Based on this study, the determination of As(III) by C-SPE in an ND mode can be performed in ~1 min by eliminating the need for metering an exact sample volume, so long as this volume exceeds 7.0 mL. Establishing the minimum sample size as 7.0 mL enables us to summarize the attributes of our C-SPE method for arsenite determination in water as shown in Table 2.

Table 2
Attributes for C-SPE analysis of arsenite in water.[a]

TAT	Chemical reactants	Reaction products	Sample size	As(III) concentration range	Features	Restrictions
≤2 min; minimal skills needed	I_3^- (0.50–5.0 mg L^{-1}); neutral pH; PVP reagent impregnated at 2.4×10^{-5} g mm^{-3}	As(V); complexed I_2 (remains on membrane)	>7.0 mL (glass syringe)	4 μg L^{-1} (optimized)– > 3.8 mg L^{-1} (verified from I_2 studies up to 5.0 mg L^{-1} [57,75])	No elution step; deployable; can be multiplexed [59]; no arsine generated; no phosphate interference	0.2 < R < 0.7; SPE characteristics define optimum working range

[a] Optimization studies for complex matrices as well as As(V) determination are continuing.

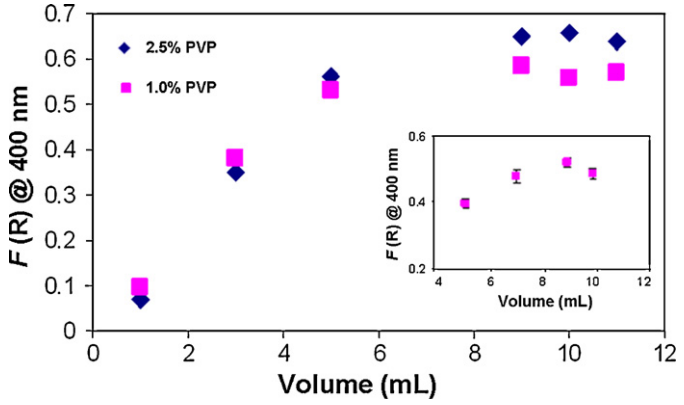

Fig. 4. Plot of spectral data from Negligible Depletion study showing the effect of sample volume on *F*(R). Nylon membranes with 1.0% (♦) and 2.5% (■) PVP. Final iodine concentration after addition to dissolution matrix (blank) was 500 μg L^{-1}. *F*(R) was shown to reach a plateau between 5.0–9.0 mL. Inset shows data from additional study with smaller increment volumes between 5.0 and 10.0 mL.

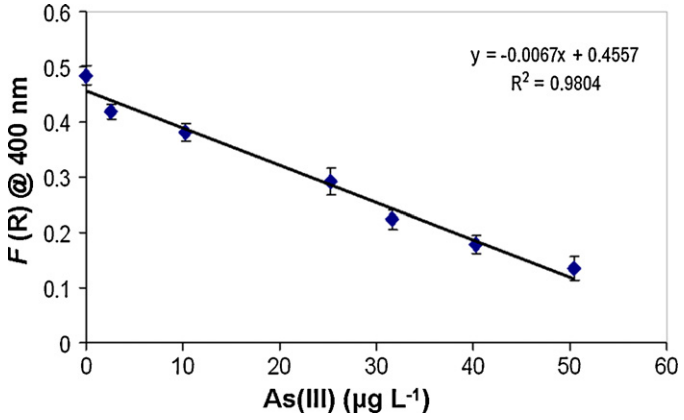

Fig. 5. Calibration plot from spectral data as a function of As(III) using V_{ND} = 7.0 mL (n = 3). Nylon membranes (1.0% PVP) were used; I_2 concentration was constant at 500 μg L^{-1}. LOD was 4 μg L^{-1}.

4. Conclusion

C-SPE has been extended to an easy-to-use, rapid (~1–2 min) approach for detecting As(III) in water samples. It was shown that concentrations as low as 4 μg L^{-1} can be detected, which is below the WHO guideline for the maximum allowable arsenic level in drinking water.

The analytical range can be easily extended to mg L^{-1} by increasing the I_2 reagent concentration. The hardware employed is lightweight, compact, and easy-to-use, which is attractive for the on-site analysis of drinking water in areas where As contamination poses a major health risk. The detection of As(III) at μg L^{-1} levels was preliminarily demonstrated in more complex matrices (tap and surface water), which makes this method a potential alternative to arsine-producing field kits and to more expensive methods currently available. Moreover, greater convenience was achieved by combining the principles of ND with C-SPE, which resulted in the elimination of metering an exact sample volume so long as this volume exceeds a certain predetermined minimum value (7.0 mL in this instance). Future work with the current method will focus on detection of As(V) and other arsenic species for total arsenic determination, and on approaches to handle more complex sample matrices (e.g., water with high turbidity). Efforts to examine the factors critical to C-SPE use in developing countries (e.g., cost) are also planned.

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