

Differential pulse cathodic stripping voltammetric speciation of trace level inorganic arsenic compounds in natural water samples

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Abstract

A simple, fast and sensitive speciation method is described for inorganic arsenic in water at the $\mu\text{g/l}$ level, applicable in the laboratory and in the field, based on differential pulse cathodic stripping voltammetry (DPCSV). Only As(III) is deposited on a Hg electrode in the presence of Cu and Se in HCl medium. Determination of total As is performed by reducing As(V) to As(III) using sodium *meta*-bisulfite/sodium thiosulfate reagent stabilized with ascorbic acid. As(V) is quantified by difference. The detection limit ($S/N > 3$) was $0.5 \mu\text{g/l}$ with a linear range from 4.5 to $180 \mu\text{g/l}$. The relative standard deviation ($n = 6$) was 2.4, 2.5, 4.2% for As(III) and 8.0, 6.8, 9.0% for As(V) at levels of 45, 10, and $5 \mu\text{g/l}$, respectively. Analysis of the NIST 1640 natural water standard yielded total arsenic concentration $26.5 \pm 3.4 \mu\text{g/l}$ ($n = 3$) compared to the certified value of $26.7 \mu\text{g/l}$. Results obtained on several natural water samples analyzed both in the laboratory and on-site compared well with those obtained by HR ICP-MS, GFAAS and IC-AFS. Ions (phosphate, iron, manganese) commonly found in groundwater containing arsenic were found to have negligible interference.

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1. Introduction

Arsenic is a common trace element with toxic properties that have been known for centuries. The principal route of human environmental exposure to arsenic is through drinking water. Groundwaters with elevated arsenic levels have been found in many countries such as India, Bangladesh, Taiwan and Argentina, resulting in virulent arsenic-related epidemics in these countries [1]. In the USA, many areas have been identified as having a groundwater arsenic problem; the most affected areas are southwestern states and the less affected are eastern and central states [2,3]. About half of the drinking water supply in the US comes from ground-

water; 2.5 million people are supplied with water containing more than $25 \mu\text{g/l}$ arsenic [2,4]. Diseases resulting from chronic As exposure include skin lesions, various cancers, and cardiovascular diseases [5]. Because of increasing concern over the health impacts of arsenic at low levels, the US Environmental Protection Agency (EPA) recently proposed a much more stringent arsenic standard for drinking water under the Safe Drinking Water Amendments (SDWA), reducing the maximum contaminant level (MCL) from 50 to $10 \mu\text{g/l}$ [2]. Drinking water systems must comply the new standard by January 2006 [6].

Arsenic occurs naturally in several chemical forms, and the toxicity of these various species varies widely [7]. In general, inorganic arsenic compounds are much more hazardous than organic arsenic compounds. Inorganic As(III) and As(V) are recognized as the dominant species in natural waters with concentrations ranging from 0.02 to over

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4000 $\mu\text{g/l}$, but the much less toxic methylated forms are also found [8]. The distribution of inorganic arsenic species in water varies with the geochemical conditions, especially the redox condition of the water. As(III) predominates in reducing groundwater [9].

Development of sensitive on-site speciation methods is of great importance because exposure of groundwater samples to the atmosphere during transport and storage allows oxidation of As(III) to As(V), even with addition of preservatives such as EDTA [10]. Currently these two inorganic As species are separated in the field using an anion exchange resin with subsequent laboratory determination [11,12]; however, immediate results cannot be obtained by these methods. Well-established methods such as ion chromatography (IC) coupled with inductively coupled plasma mass spectrometry (ICP-MS), hydride generation atomic absorption spectrometry (HGAAS), and atomic fluorescence spectrometry (AFS) can provide extensive speciation information on both inorganic and organic arsenic [13–16]. They are not, however, suitable for use in the field.

On-site arsenic detection techniques generally provide only total inorganic arsenic data. The results using commercially available arsenic testing kits are far from satisfactory. For example, referring to the widely used Merck test kit, Erickson [17] stated “most experts agree that the kit works well for samples containing arsenic levels <10 or >100 $\mu\text{g/l}$, but not in between.” In addition, there are health concerns about the arsine gas generated by the kit. Electrochemical [18], colorimetric [17,19,20] and photometric methods [21] have been applied on-site. The electrochemical methods are relatively simple and inexpensive with superb sensitivity, and possess capability for speciation [18].

Polarography, cyclic voltammetry, and anodic and cathodic stripping voltammetry, have long been applied to the determination of arsenic [22–30]. Stripping analysis using hanging mercury drop electrodes (HMDE) utilizes a pre-electrolysis step to concentrate arsenic from solution onto the mercury electrode in the presence of Cu(II) or Se(IV), followed by a rest period to allow a more uniform distribution of the arsenic intermetallic compound within the amalgam. The compound is then stripped from the electrode upon application of potential [24,31,32]. This method is especially suitable for trace analysis due to the enrichment of analytes by pre-concentration, resulting in a detection limit usually at the sub- $\mu\text{g/l}$ level. HMDE effectively avoids memory problems because a new mercury drop is generated for each determination [22–24,30,33]. Usually arsenic is pre-concentrated on the HMDE by forming a copper–arsenic [23], or less often a selenium–arsenic [24] intermetallic compound during the deposition procedure, followed by cathodic stripping. Alternatively, ligands such as pyrrolidine dithiocarbamate can be used to complex arsenite, which is adsorptively deposited on the HMDE [22].

The objective of this work was to develop a simple, fast and sensitive DPCSV method that is applicable to on-site analysis. To improve the peak shape and the method sen-

sitivity, Cu(II) and Se(IV) were used together to form an intermetallic arsenic compound, $\text{Cu}_x\text{Se}_y\text{As}_z$, on the HMDE during the deposition procedure. A reducing reagent system for As(V) determination was also investigated and improved, featuring good stability which is essential to field work. The DPCSV deposition potential and time, amount of Cu(II) and Se(IV) added, and the amount of reducing reagent used and reduction time were optimized. Furthermore, the effect of organic arsenic (monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA)) on the electrode response, and the potential interference of ions (phosphate, iron, and manganese) commonly found in groundwater containing arsenic, were investigated. The accuracy of the method was demonstrated by analyzing the NIST natural water standard, spiked drinking water, and groundwater samples. The on-site analysis capability was demonstrated by analyses of groundwater performed at an EPA superfund site. The results compare favorably with those obtained by high resolution ICP-MS, graphite furnace AAS and IC-AFS.

2. Experimental section

2.1. Reagents and materials

2.1.1. As(III) and As(V) standard solutions

As(V) stock solution containing 1000 mg/l As was prepared by dissolving sodium arsenate (Na_2HAsO_4) (Sigma, St. Louis, MO, ACS reagent) in 1% (v/v) HCl solution, diluted from 12 M HCl (Fisher, Pittsburgh, PA, Optima). As(III) stock solution containing 1000 mg/l As was prepared by dissolving sodium *m*-arsenite (NaAsO_2) (Sigma, 96.7% purity) in 1% (v/v) HCl solution containing 1 mg/ml ascorbic acid [34]. Ascorbic acid served as an anti-oxidant to prevent As(III) from being oxidized to As(V) when refrigerated at 4 °C, for up to 3 months. Working solutions of As(III) and As(V) were freshly prepared daily by dilution with 18 M Ω water (Barnstead Infinity Nanopure system, referred to below as nanopure water).

2.1.2. Reducing agent

The reducing agent was adopted from Johnson and Pilson [35] with an important modification: ascorbic acid was added to stabilize the reagent for up to 100 h, compared to 6 h in the absence of ascorbic acid. 1.4 g sodium *meta*-bisulfite (Fisher, Certified ACS) and 0.14 g of sodium thiosulfate (Fisher, Certified ACS) were each dissolved in 10 ml of nanopure water. The reducing agent was prepared by slowly adding 5 ml of 10% (v/v) H_2SO_4 to the sodium *meta*-bisulfite solution, with vigorous shaking, followed by the addition of the 10 ml sodium thiosulfate solution and 0.2 g solid L-ascorbic acid (Fisher, Certified ACS).

2.1.3. Auxiliary solutions

Cu(II) and Se(IV) solutions used were the 1000 mg/l AAS reference standard solutions (Fisher). The working

solution of Se(IV) (1 mg/l) was prepared by dilution of the standard solution. Monosodium acid methane arsonate (MMA) (Chem Service, West Chester, PA, 99.0% purity) and dimethylarsonic acid (Sigma, 98% purity) stock solutions containing 1000 mg/l As were prepared in nanopure water. A 0.01 M Fe(II) stock solution was freshly prepared before use by dissolving $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Fisher) in nanopure water. The Mn solution was a 1000 mg/l AAS reference standard (Fisher). A 0.1 M phosphate stock solution was prepared by dissolving KH_2PO_4 (Fisher) in nanopure water. Samples with different levels of Fe(II), Mn and phosphate were prepared by spiking the desired amount of stock solution.

2.2. Instrumentation for DPCSV

An Eco Chemie μ Autolab voltammetric apparatus (Brinkmann Instruments, Westbury, NY) equipped with a Metrohm 663VA electrode stand and controlled by a notebook computer running Eco Chemie GPES 4.9 software was used. A HMDE working electrode, a Pt auxiliary electrode, and a Ag/AgCl/3 M KCl double-junction reference electrode were used. The electrode cell was equipped with a nitrogen purge tube to remove oxygen prior to sample analysis, as well as to remove gaseous sulfur compounds produced during the reduction step in the total arsenic measurement. A built-in motor-driven stirrer drives a PTFE stirring rod to stir the sample during purge and deposition. The unit is small and light enough to be portable, and sufficiently rugged to take on-site. An automobile battery (12 V, DC) is linked to a commercial UPS system (Back-Ups CS 350, APC, Kingston, RI) to provide 110 V AC power to the unit. The battery allowed a few days of analysis time before recharging was required.

2.3. Analytical procedure for DPCSV

An appropriate amount of standard or sample was added to the analysis vessel containing nanopure water, making the total volume 10.0 ml, followed by addition of 12 M HCl (Fisher Optima) to provide a 1 M HCl supporting electrolyte. Optimized volumes of the 1000 mg/l Cu(II) and 1 mg/l Se(IV) solutions, 50 and 40 μl , respectively, were also added to produce concentrations of 4.6 mg/l Cu(II) and 3.7 $\mu\text{g/l}$ Se(IV), respectively. Sample was purged for 300 s with N_2 . DPCSV was performed using a deposition potential of -0.44 V versus Ag/AgCl reference, applied for 60 s with stirring, during which time As(III) was deposited as $\text{Cu}_x\text{Se}_y\text{As}_z$ intermetallic compound on the Hg electrode. Stirring and purge were stopped. After a 15 s equilibration time, the stripping potential was scanned from -0.4 to -0.9 V versus Ag/AgCl reference electrode with a 10 mV step potential, 50 mV modulation amplitude, 33.3 ms pulse width, 16.7 ms measurement time, and 25 mV/s scan rate. The As(III) peak appeared at ~ -0.68 V. Since only As(III) is electroactive during the DPCSV procedure, optimization

procedures for all parameters were carried out using As(III) solution.

2.4. Quantification by standard addition

For samples containing both As(III) and As(V), two 10 ml sub-samples were used. As(III) in the presence of HCl, Cu(II) and Se(IV) was quantified by standard addition in first sub-sample. Total arsenic was determined in the second sub-sample by spiking with concentrations of 2 mg/ml of sodium *meta*-bisulfite and 0.2 mg/ml of sodium thiosulfate, and allowing reduction to proceed for 420 s with N_2 purge before DPCSV analysis. Total arsenic was then quantified by following the standard addition procedure for As(III). The As(V) concentration is the difference between total arsenic and As(III) concentrations. Groundwater samples or samples with high arsenic concentration were diluted with nanopure water to reduce matrix effects or to reduce arsenic concentrations to within the linear range.

2.5. Quantification by HR ICP-MS, GFAAS and IC-AFS

Total dissolved arsenic, including both inorganic and organic arsenic in the samples were quantified by standard addition. An Axiom single collector high resolution (HR) ICP-MS (Thermo Elemental, Germany) at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University was used. Arsenic was quantified by standard addition calibration after drift correction using Ge as an internal standard at a high resolving power of 12,000 to eliminate ArCl interference. The detection limit for As is 0.1 $\mu\text{g/l}$. A Perkin-Elmer A Analyst 800 was used for graphite furnace AAS, following a standard GFAAS protocol using $\text{Pd}(\text{NO}_3)_2$ as matrix modifier. We also speciated the inorganic arsenic in our samples by IC-AFS using a Varian 9012 HPLC system with a Varian 9100 autosampler with a 250 μl injection loop. The separation column was PRP X-100 (Hamilton, 250 mm \times 4.1 mm i.d., 10 μm particle size). A guard column with same packing material was connected between the injector and the separation column. The mobile phase was 10 mM $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ adjusted to pH 6.25 at a flow rate of 0.8 ml/min. Arsenic species were detected by an atomic fluorescence spectrometer (PS Analytical, Kent, UK) after hydride generation. The carrier acid was 12.5% (v/v) HCl and the reductant was 1.4% (m/v) NaBH_4 (Fisher) in 0.1 M NaOH. Flow of HCl and reductant was set at 50% full pump rate.

3. Results and discussion

3.1. Optimization of deposition potential and time

DPCSV deposition potential and time were investigated. For 10 ml samples containing 45 $\mu\text{g/l}$ As(III), 4.6 mg/l Cu(II) and 3.7 $\mu\text{g/l}$ Se(IV), the deposition potential was varied

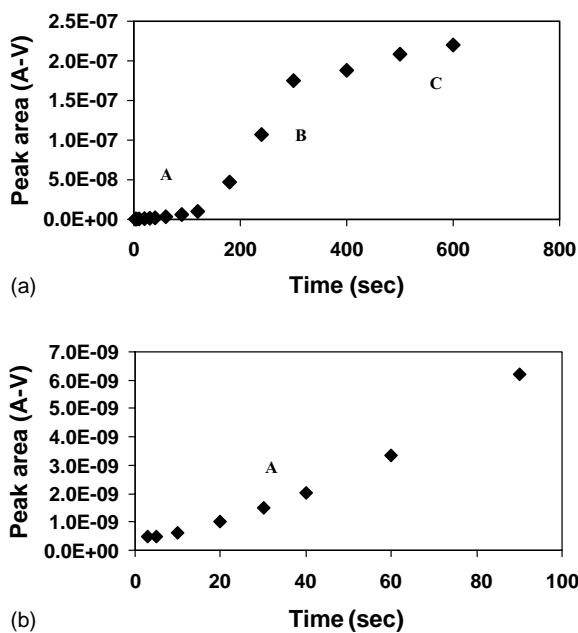


Fig. 1. Effect of deposition time on As(III) peak area: (a) for up to 600 s deposition time, which includes range A (<60 s), range B (from 60 to 300 s) and range C (>300 s) and (b) for up to 100 s deposition time. The scales of y-axis are different for panels (a) and (b). The experiments were performed by varying deposition time at deposition potential of -0.44 V using a solution containing $45 \mu\text{g/l}$ As(III), 4.6 mg/l Cu(II) and $3.7 \mu\text{g/l}$ Se(IV).

from -0.35 to -0.70 V versus reference electrode. Peak response increased initially and then decreased, maximizing at -0.44 V, the same potential found by Barra and Correia dos Santos [33]. The same peak maximum potential was observed for As(III) formed by reduction of As(V) in the analysis vessel. As(III) peak area increased with longer deposition time (Fig. 1a), however, two types of peaks were observed with the increasing deposition time. For deposition times up to 60 s (range A in Fig. 1a), the peak was sharp and symmetrical and the peak area increased linearly with time (Fig. 1b). For longer deposition times (>60 s, Fig. 1a), the peak became broader and lower, and the peak position gradually shifted from ~ -0.68 to ~ -0.80 V. The peak area increased with deposition time between 60 and 300 s (range B, Fig. 1a) but leveled off when deposition time was >300 s (range C, Fig. 1a). Both the peak shape change and peak potential shift with deposition time suggest formation of a succession of intermetallic compounds, $\text{Cu}_x\text{Se}_y\text{As}_z$, with different stoichiometric ratios. Based on peak shape and sensitivity, 60 s was chosen as the optimized deposition time. For extremely low concentrations, increased deposition time can be used to improve sensitivity, but requires a separate calibration.

3.2. Effect of Cu(II)

Arsenic cannot be electrolytically deposited directly onto a Hg electrode. As(III) reacts with Cu(II) to form an intermetallic compound Cu_xAs_y [23,32] that is deposited onto

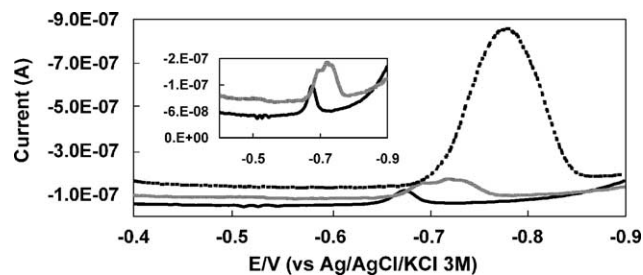


Fig. 2. Effect of Cu(II) concentration on As peak shape: The solid line, shaded line and dashed line refer to Cu(II) concentrations of 4.6, 10.1 and 18.4 mg/l, respectively. The insert enlarges the voltammograms of the two lower concentrations of Cu(II) addition at 4.6 and 10.1 mg/l, respectively. The unit of the axis in insert voltammogram is the same as the large one. As(III) concentration was $20 \mu\text{g/l}$. There was no Se(IV) in these samples.

the HMDE and is subsequently stripped cathodically. The amount of Cu(II) affects peak area and peak shape as shown in Fig. 2. For $5\text{--}45 \mu\text{g/l}$ As(III), the peak area increased for up to 4.6 mg/l Cu(II) added; however, Cu(II) concentrations between 4.6 and 10.1 mg/l produced peak splitting. Further increase in Cu(II) to 18.4 mg/l produced a broad and large single peak. Still higher Cu(II) concentrations led to decreasing peak area, and ultimately the peak disappeared. Increasing Cu(II) concentration also shifted the peak position from ~ -0.65 to ~ -0.77 V. This observation demonstrated the formation of an intermetallic compound with a different Cu:As ratio. On the basis of sufficient sensitivity and good peak shape over the range from 4.5 to $180 \mu\text{g/l}$ As(III), the entire linear range (see below), we chose the optimum Cu(II) concentration to be 4.6 mg/l . For an As(III) concentration of $45 \mu\text{g/l}$ and Cu(II) concentration of 4.6 mg/l , the peak of the Cu_xAs_y intermetallic compound was found to exhibit a shoulder, leading to some uncertainty in quantification. Similarly, a peak with shoulder was also observed by Barra and Correia dos Santos [33].

3.3. Effect of Se(IV)

Addition of $50 \mu\text{g/l}$ Se(IV) has been used for arsenic measurement in a H_2SO_4 -acidified sample [24]. Se(IV) presumably forms an intermetallic compound with arsenic, such as As_2Se_3 , during deposition [24]. In the presence of Cu(II), Se(IV) was reported [30] to interfere with the arsenic signal. However, we found a major improvement in As peak shape was achieved by addition of both Cu(II) and trace level Se(IV), as shown in Fig. 3. The peak shoulder gradually disappeared with increasing trace levels of Se(IV). At a Se(IV) concentration of $3.7 \mu\text{g/l}$ with 4.6 mg/l Cu(II), a sharp and symmetric As peak was obtained, and sensitivity was improved over the linear As(III) range of $4.5\text{--}180 \mu\text{g/l}$. Se(IV) and Cu(II) have not been applied previously together in arsenic measurement. Although further study is needed, we assume a different intermetallic compound, $\text{Cu}_x\text{As}_y\text{Se}_z$, forms during deposition, which leads to the improvement in peak response.

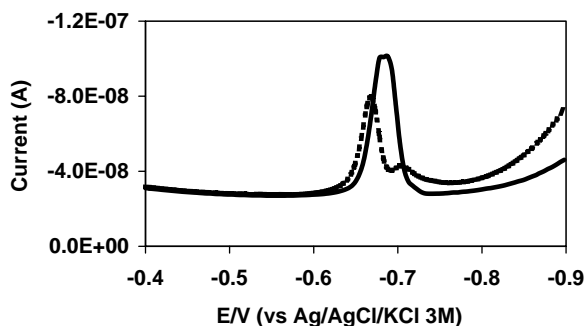
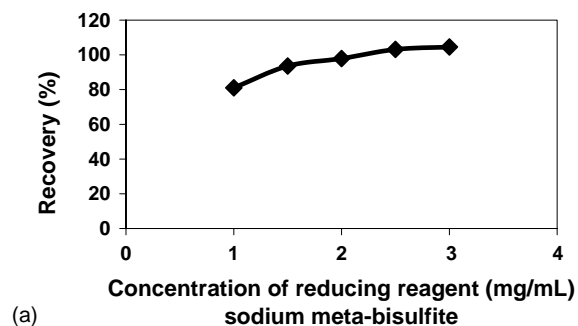


Fig. 3. Effect of Se(IV) on As peak shape. The dashed line and solid line represent the voltammograms without and with $3.7 \mu\text{g/l}$ Se(IV), respectively, in a solution containing $45 \mu\text{g/l}$ As(III) and 4.6 mg/l Cu(II).

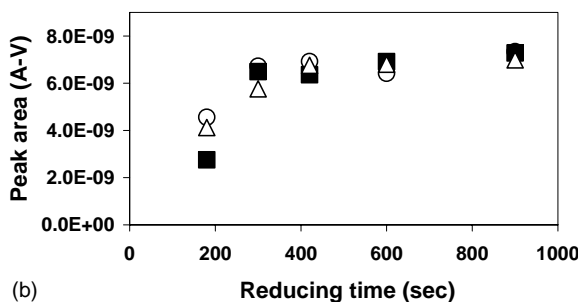
3.4. Effect of reducing agent

Because As(V) is generally electrochemically inactive, total inorganic arsenic determination requires chemical reduction of As(V) to As(III). The reduction procedures employed in reported electrochemical methods are time consuming and not straightforward. For example, Kotoucek et al. reported that As(V) was reduced by hydrobromic acid and solid $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ with heating for 45 min on a steam bath at $95\text{--}100^\circ\text{C}$ [28]. Sulfur dioxide was also used as a reducing reagent by passing the gas through a sample solution at 80°C [22,27]. Manipulations such as sample cooling and volume corrections due to evaporation had to be performed before determination of As(III). Less aggressive reduction methods, such as potassium iodide and ascorbic acid solution, often used in atomic absorption spectroscopic determinations with the hydride generation technique, was also applied to the voltammetric method [33], but Ferreira and Barros [30] and our own experience found these reagents ineffective in DPCSV. Instead, a reducing reagent with thiosulfate alone [30], or combined with *meta*-bisulfite were much more effective (see below). Direct As(V) deposition on an HMDE with mannitol serving as an activator was reported, but the determination of total arsenic was restricted because response to As(III) was higher than that to As(V). Thus chemical conversion to a single arsenic species by oxidation of As(III) to As(V) was necessary for accurate assessment [36].

We adopted as a reducing reagent the sodium *meta*-bisulfite/sodium thiosulfate in sulfuric acid reagent that was previously employed in a colorimetric method [20,35]. However, a major drawback of this reducing agent is that it was not stable in colorimetric applications [20] and deteriorates even faster in voltammetric applications ($<6\text{ h}$) because of the lower concentrations of reagents used. To overcome this limitation, which would otherwise make this method impossible to use for fieldwork, ascorbic acid was added as an anti-oxidant. The modified reducing agent is stable up to 100 h at room temperature.



(a)



(b)

Fig. 4. Optimization of reducing conditions. (a) Effect of the amount of reducing agent on recovery with a reducing time of 600 s. The concentration of sodium thiosulfate is always 10 times less than the concentration of sodium *meta*-bisulfite in the reducing reagent, which is indicated by the X-axis. (b) Effect of reduction time for conversion of As(V) to As(III) with addition of 2/0.2 mg/ml (open circles), 2.5/0.25 mg/ml (solid squares) and 3/0.3 mg/ml (open triangles) sodium *meta*-bisulfite/sodium thiosulfate. As(V) concentration in all cases was $180 \mu\text{g/l}$.

3.4.1. Amount of reducing agent

To study the effect of the concentration of reducing agent on the DPCSV response, amounts of reducing agent ranging from 1 mg/ml sodium *meta*-bisulfite/0.1 mg/ml sodium thiosulfate to 3 mg/ml sodium *meta*-bisulfite/0.3 mg/ml sodium thiosulfate, were added to 10 ml of solution containing $180 \mu\text{g/l}$ As(V). The solution was purged for 600 s during reduction. Purging was important because gaseous sulfur compounds formed from the reducing agent caused a high background and distorted the voltammogram. Generally, the longer the purging time, the better the voltammogram. It was found that for a $180 \mu\text{g/l}$ As(V) solution, 100% recovery, which was defined as the percentage of a signal obtained by As(III) reduced from As(V) compared with that where the same concentration of standard As(III) was used, was achieved if at least 2 mg/ml sodium *meta*-bisulfite/0.2 mg/ml sodium thiosulfate of reducing reagent was added, as shown in Fig. 4a.

3.4.2. Reduction time

To determine the time required to quantitatively reduce As(V) to As(III), the reduction time was varied from 180 to 900 s with addition of 2/0.2, 2.5/0.25, and 3/0.3 mg/ml sodium *meta*-bisulfite/sodium thiosulfate, respectively, to a sample containing $180 \mu\text{g/l}$ As(V). The minimum time required to eliminate background and obtain

a reasonable voltammogram with 3/0.3 mg/ml sodium *meta*-bisulfite/sodium thiosulfate was 180 s. For all three levels of added reducing agent, arsenic response was stable for reduction times greater than 420 s, as shown in Fig. 4b. Thus we chose addition of 2/0.2 mg/ml sodium *meta*-bisulfite/sodium thiosulfate to minimize background current, and 420 s reduction time to allow quantitative reduction of As(V) to As(III) in the 10 ml sample solution.

3.5. Effect of organic arsenic compounds

Low levels (<100 µg/l) of organoarsenic compounds such as MMA and DMA may be found in natural waters. Spiking MMA and DMA at levels up to 100 µg/l into a water sample containing inorganic arsenic produced no DPCSV response to either compound, and no obvious peak change for As(III) or As(V). We conclude organic arsenic compounds provide no interference.

3.6. Quantitative analysis

As(III) and As(V) were analyzed using the optimized conditions, i.e., in a 10 ml water sample, with addition of 4.6 mg/l of Cu (II) and 3.7 µg/l Se(IV). For the As(V) determination, 2/0.2 mg/ml sodium *meta*-bisulfite/sodium thiosulfate was also added and the reduction time with purging was 420 s. The range of linearity for As(III) was from 4.5 to 180 µg/l with slope of 2.71×10^{-11} µg/l/A-V and linear regression correlation coefficient (r^2) of 0.9963. For As(V), the linear range was the same, the slope of calibration curve was 3.66×10^{-11} µg/l/A-V with $r^2 = 0.9961$. The precision was evaluated from six replicate measurements of an arsenic

standard containing 45, 10, and 5 µg/l each of As(III) and As(V), yielding a peak area RSD of 2.4, 2.5, 4.2% for As(III) and 8.0, 6.8, 9.0% for As(V), respectively. The method detection limit, $S/N > 3$, was determined to be 0.5 µg/l for both As(III) and As(V). Noise is fluctuation of the baseline current for a blank solution.

3.7. Interferences

Interference caused by substances commonly present in groundwater, Fe(II), Mn and phosphate, were investigated. The DPCSV response to an aqueous solution containing 45 µg/l As(III or V) and different levels of Fe(II) up to 300 µM, and Mn up to 100 µM, was investigated. Presence of these ions was found to have negligible interference. Phosphate concentrations ranging from 5 to 100 µM had no effect on the analysis of a 45 µg/l As(III) solution. The response to As(V) in the presence of phosphate, however, was found to be slightly depressed, showing an average peak area decrease of 10%.

3.8. Analysis of environmental samples and comparison with other techniques

Tap water from a laboratory at Queens College was collected in a polyethylene bottle and analyzed immediately. No arsenic species was detected in the sample. As(III) and As(V) standard solution were spiked into this tap water sample at a concentration of 20 µg/l for each analyte. Three replicate determinations using the standard addition method gave average results for As(III) of 20.4 ± 0.7 µg/l and for As(V), 21.7 ± 2.5 µg/l. The optimized method was applied to

Table 1
Summary of results from analysis of arsenic in water samples

Sample name	On-site DPCSV sample analysis (July 2003)			In-laboratory analysis			
	DPCSV(µg/l)			IC-AFS(µg/l) ^a			GFAAS(µg/l)
	As(III)	As(V)	As(III) + As(V)	As(III) + As(V)	MMA	DMA	Total As
GW-1	2.8 ± 0.4	904 ± 45	907 ± 45	923	<100	<100	1193 ± 23
GW-2	5.0 ± 1.2	1445 ± 136	1450 ± 135	1445	<100	<100	1563 ± 31
GW-3	ND ^b	2.5 ± 0.9	2.5 ± 0.9	3.7	<5	<5	<5
GW-4	1189 ± 94	130 ± 102	1319 ± 41	1440	216	<100	1872 ± 24
GW-5	97 ± 11	29 ± 14	127 ± 10	106	8.2	9.1	124 ± 3
	In-laboratory sample analysis						
	DPCSV(µg/l)			HRICP-MS(µg/l) ^c	GFAAS(µg/l)		
	As(III)	As(V)	As(III) + As(V)	Total As	Total As		
NIST 1640 ([As] = 26.7 g/l)	ND	26.5 ± 3.4	26.5 ± 3.4	26.3 ± 0.5	24 ± 6		
Spiked drinking water	ND	40.4 ± 3.2	40.4 ± 3.2	44 ± 0.1	45 ± 4		
Spiked LDEO groundwater	ND	323 ± 23	323 ± 23	320 ± 2	311 ± 9		

Triplicate analysis was performed for all in-laboratory samples except when noted. All DPCSV on-site analysis were average of two measurements.

^a Single analysis was performed. Detection limits of IC-AFS method used were 5 µg/l for MMA and DMA. However, GW-1, GW-2, GW-4 were subjected to 20 times dilution and therefore had a higher detection limit of 100 µg/l for MMA and DMA.

^b Non-detectable.

^c Values were based on average of 26 measurements over approx. 1 year.

various other water samples, including an NIST SRM 1640 natural water standard, spiked commercial bottled drinking water, and LDEO groundwater. These samples were chosen because they had been analyzed previously as internal laboratory standards repeatedly by HR ICP-MS at LDEO and GFAAS at Queens College. Because these samples had been stored for months, only As(V) was found (Table 1).

On-site analysis of inorganic arsenic by DPCSV was conducted at an EPA Superfund site in Vineland, New Jersey, in July 2003 to speciate groundwater extracted from five wells (Table 1). Because MMA and DMA were known to be present in the Vineland groundwater [37], the inorganic As speciation data obtained on site by DPCSV was later confirmed using IC-AFS analysis, and the total arsenic determination was confirmed using GFAAS in the laboratory. Because of the conversion of As(III) to As(V), the total inorganic arsenic concentration obtained by IC-AFS was used for comparison with the on-site DPCSV results. Due to time constraints in performing analysis in the field and the rapid change of oxidation state of reducing groundwater upon exposure to air which results in arsenic removal from the sample, each sample was analyzed only twice. Therefore, the concentration error for As(III) and As(III) + As(V) (Table 1) was estimated by error propagation from linear regression errors obtained by a least-square fit from both the slope and the intercept of the standard addition curve of each sample. As(V) concentration was based on the difference of As(III) and As(III) + As(V), the error was propagated from errors estimated for As(III) and As(III) + As(V) [38]. Results obtained by the different techniques agree well, demonstrating that DPCSV is not only a technique useful in the laboratory, but is also applicable to on-site inorganic arsenic determination and speciation.

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