

Voltammetric measurement of arsenic in natural waters

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Abstract

There are several U.S. EPA approved methodologies for the determination of arsenic in ground water. Such technologies are lab-based, time intensive and can lead to a large capital cost for multi-sample analysis. In light of the number of sites found to contain arsenic at levels higher than the maximum contaminant level (MCL), on-site screening and monitoring systems are an attractive alternative. This review article summarizes several examples in the recent literature to illustrate the breadth of work in voltammetric analysis of arsenic in environmental samples. Also, included are recent voltammetric results, obtained with a microfabricated gold array and a field portable potentiostat, at an arsenic contaminated site in southern New Jersey. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Arsenic is increasingly being found in drinking water in many parts of the world such as Bangladesh, India, England, and Thailand, and within the U.S. in California, Oregon, Massachusetts, Maine, and New Hampshire [1–5]. The recent increase in the number of reports in the literature can be directly attributed to the calamity in Bangladesh, where more than 44 districts have reported arsenic contamination and it has been estimated that up to 57 million people may be drinking water that contains harmful concentrations of arsenic [2]. The Bangladesh situation has been categorized as one of the largest

outbreaks of poisoning this century. This has also poignantly shown the necessity for developing rapid on-site measurement systems for such contaminants. Even though accurate and rapid field screening techniques for several other heavy metals, such as lead and copper, have been demonstrated using a field portable equipment, [6–8] there are no commercially available portable instruments that can be routinely used for rapid field screening of arsenic.

To this end, this paper presents an overview of the voltammetric methods that have been used to measure arsenic and concludes with a report on the field analysis of arsenic at a contaminated site in southern New Jersey using microfabricated gold arrays (AuUMEA). These arrays offer several benefits, such as uniform ultramicroelectrode (UME) geometries, sensitivity, cost efficiency, and applicability for use in field portable or in situ

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instrumentation. In addition, the electron beam evaporated gold surface of these UMEAs appears to offer unique characteristics for the formation of monolayer metallic films. Use of single UMEs for arsenic determinations has been very limited [9–11]. However, UMEAs possess inherent advantages for arsenic determinations, such as low noise level, amplification of the signal while keeping UME behavior, background current rejection, and potential incorporation into field portable instrumentation. Moreover, it has been previously demonstrated that microfabricated arrays are readily amendable for field measurements [8,12–14].

2. Experimental

Fabrication details of the gold ultramicroelectrode arrays (AuUMEAs) have previously been documented [15]. For the analyses in ground water, a Nafion coated AuUMEA was used to protect the gold surface. The Nafion was applied via microsyringe using a 5% Nafion 117 solution (Fluka) and was allowed to dry for 1 h. The array was then placed in a 120 °C oven for a few minutes to cure the Nafion film. Experiments performed on-site demonstrated that As^{3+} did not accumulate in the Nafion. Prior to all experiments, the AuUMEAs were conditioned by cycling the potential 10 times between 0 and 1.5 V at 100 mV s^{-1} in 0.1 M H_2SO_4 . Unless otherwise stated, a frequency (f) of 150 Hz, pulse amplitude (E_{sw}) of 25 mV, step height (ΔE_s) of 2 mV, and deposition potential (E_i) and time (t_d) of -0.4 V for 80 s were chosen as the square wave anodic stripping voltammetry (SWASV) parameters. A conditioning potential and time (30 s at 0.55 V) was added to renew the gold surface.

On-site analysis was carried out using a portable CS-3000 potentiostat/galvanostat system (Cypress Systems, Lawrence, KS) connected to a laptop computer. Bailers were used to obtain water samples from the ground water monitoring wells across the site. Split samples were taken and preserved for comparative analysis with ICP using U.S. EPA method 200.7.

3. Results

3.1. Voltammetric determinations of arsenic

Voltammetric stripping techniques are readily amendable for on-site analysis, providing accurate measurements of low concentrations with rapid analysis times and low cost/weight instruments. These methods provide an efficient and reliable way to analyze for As^{3+} at the ppb levels found in natural waters. In general, the methods for determining As^{3+} electrochemically have involved cathodic or anodic stripping voltammetry using a pulsed wave form [16–27]. Several recent papers describe analysis of As^{3+} at low ppb levels using mercury electrodes [19–22,28] and that include the addition of copper or selenium [24]. Macro-sized gold film electrodes [17,18,25] and solid gold electrode substrates [9,23,26] have also been used.

Sun et al. [17] addressed the need for a reproducible working electrode surface and reported on a new method of gold film preparation for the stripping voltammetric determination of As^{3+} and As^{5+} in seawater. The procedure called for a rotating glassy carbon electrode with a gold film deposited from a gold plating solution. For optimum reproducibility, the electrode was re-plated between each measurement and the electrode was washed with the sample before each measurement. Other factors likely to affect the stability of electrode response and method sensitivity, including: acidity, deposition time and potential, rotation rate, scan rate, electrode reaction and the reduction step of As^{5+} to As^{3+} , were also investigated. The limit of detection (LOD) was calculated to be 0.19 ppb for As^{3+} . The relative standard deviation of multiple measurements was 8% using a 1 nM arsenic solution. The new gold film procedure was implemented in the detection of arsenic in a sea water sample.

Li and Smart [19] reported on sub-nanomolar concentration of As^{3+} in natural waters by cathodic stripping voltammetry (CSV) for the purpose of developing a rapid and sensitive method for measuring arsenic in natural water. Square

wave CSV (SWCSV) at a HMDE was used to avoid problems caused by 'memory effects' at solid electrodes, which lead to poor precision and the interference with copper. The Cu_xAs_y complex concentration, deposition potential and time, and the hydrochloric acid and copper concentrations on the stripping signal, were all optimized. The calculated LOD was 0.9 nM with for a deposition time of 1 min. This methodology was employed in the analysis for arsenic in river and sea water samples.

Eguiarte et al. [29] proposed a method for the determination of total arsenic in soils using differential pulse CSV at a HMDE in the presence of copper after acid digestion of the sample in a microwave digester. KI was found to be the optimum reductant and HCl with NaHCO_3 provided the best stripping medium. The LOD was calculated to be 80 pg ml^{-1} . This technique has advantages over spectroscopic techniques due to the absence of interferences from transition metals such as Ni^{2+} , Co^{2+} , and other hydride-forming metals. The reproducibility in terms of relative standard deviation was between 3.8 and 4.5% using 2.6 ng ml^{-1} arsenic.

Most recently, Huang and Dasgupta [16] reported on a portable device for the measurement of As^{3+} and As^{5+} in water. The instrument operated with low power consumption and had a flow cell, which operated with the aid of gravity for simplicity. A gold film deposited on a platinum wire served as the working electrode. Measurement of arsenate involved complete oxidation using KMnO_4 or bromine-water, followed by electrolysis at -1.6 V . Plots of the first derivative of the stripping current were used for the quantification. In this way, measuring the amplitude from the maximum positive to the maximum negative excursion provided a means to minimize interferences from metals with close redox potentials to arsenic. Parameters and conditions were optimized and arsenic was successfully measured in the presence of mercury, copper, and bismuth. The LOD was calculated to be $0.5 \text{ } \mu\text{g l}^{-1}$. Reproducibility was also demonstrated with a relative standard deviation of 2.2% for several measurements in $10\text{--}60 \text{ } \mu\text{g l}^{-1}$ solutions or As^{3+} .

3.2. Microfabricated arrays for arsenic measurements

In recent years, the electroanalytical use of microlithographically fabricated arrays has dramatically increased. Photolithographic techniques, widely used in the microelectronics industry, have been utilized to construct electromechanical sensors since the late 1970s [30]. However, this technology can be employed to effectively fabricate thin film electrode materials such as gold, iridium, platinum, and carbon on silicon wafers, with well-defined and reproducible geometries of micron dimensions. In theory, such micromachining technologies allow for the mass production of individual chip-based sensors that possess identical physical and chemical performance characteristics, important criteria for widespread commercialization and use of any sensor technology. In practice however, variations are sometimes observed and further studies are necessary to overcome this limitation. However, microfabricated arrays are typically rugged, relatively inexpensive to mass produce, and provide measurable current at low parts-per-billion to parts-per-trillion levels.

As discussed above, voltammetric techniques are useful for measuring arsenic levels in the field with portable instrumentation. Moreover, unlike colorimetric field kits in use, voltammetric techniques can yield quantitative data when careful analytical methodologies are employed. For voltammetric measurements of arsenic, anodic stripping voltammetry or potentiometric stripping analysis are likely to find the most use. One major reason is that no mercury is needed. Both methodologies provide access to the more abundant arsenite and arsenate forms of the metal.

For all of the reasons presented above, Au-UMEs, used in conjunction with anodic stripping voltammetry, were investigated and were demonstrated to be a viable tool for arsenic field screening in ground water.

3.2.1. Characterization and use of a AuUMEA at an arsenic contaminated site

The AuUMEs have been previously demonstrated to be a good working electrode in the determination of As^{3+} in aqueous solutions using

SWASV after deposition of a partial As^0 monolayer [15]. The AuUMEA consists of an array of microfabricated gold UME disks created by electron beam evaporation. The linear dynamic range of the AuUMEA (0–500 ppb) and its response were characterized in 2 M HCl. Additionally, the other factors investigated included: (i) the influence of SW parameters on the stripping peaks; (ii) the long-term stability of the AuUMEA; (iii) the ability to measure both As^{3+} and As^{5+} ; and (iv) the affect of interfering metal ions on the arsenic stripping peak. The utility of the AuUMEA for arsenic was then demonstrated via on-site analysis of arsenic in ground water.

3.2.2. Influence of SWASV parameters on the arsenic stripping peak

According to the theory for SWASV at a thin mercury-film electrode [31], an increase in the pulse amplitude should cause a shift of the stripping peak to more negative values and an increase in the stripping net peak current (Δi_p), both a product of the increase in the reversibility of the system. In addition, for a thin film theory predicts that $\Delta i_p \propto f$, thus an increase in SW frequency should result in a linear increase in stripping peak height, and Δi_p should have a constant peak half-width $n(W_{1/2})$ of 100 mV. Even though only a monolayer of As^0 is deposited on the AuUMEA, the results when varying E_{sw} and f (Fig. 1) are

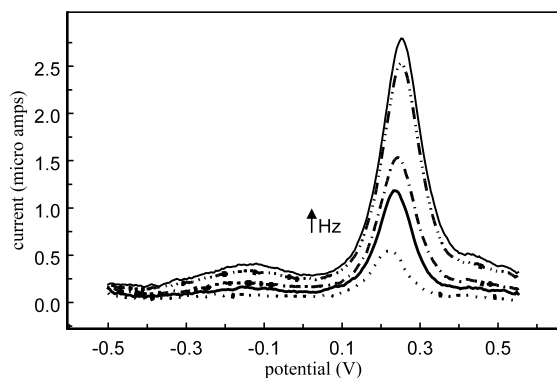


Fig. 1. Peak stripping current as a function of increasing square wave frequency, 35, 75, 105, 185, and 210 Hz. Parameters: $E_i = -0.375$ V, $E_f = 0.4$ V, $E_{sw} = 25$ mV, $\Delta E_s = 2$ mV, and $t_d = 80$ s. The solution consisted of 100 ppb As^{3+} in 2 M HCl.

surprisingly similar to those for the thin mercury-film case. The SWASV peak varies linearly with the frequency as indicated by a regression coefficient of 0.995 and a slope and intercept of 0.011 and 0.187, respectively. Varying the SW frequency from 35 to 210 Hz resulted in a sixfold linear increase of Δi_p ($R^2 = 0.997$, x, y intercept $\approx 0, 0$) as predicted by thin film theory. A frequency of 150 Hz was chosen for the analytical procedures because it provided a reasonable enhancement of the stripping peak with minimal noise. Current work in our laboratory on the theory of SWASV of a monolayer at solid electrodes suggests that these two cases do indeed result in similar responses.

3.2.3. Stability of the stripping peaks

Careful electrode conditioning was found to enhance the quality and reproducibility of the stripping peak. Both, cycling the potential and applying a conditioning potential were performed to estimate their effect on maintaining reproducibility of the stripping peak. It was determined that application of a conditioning potential was the best approach. However, in chloride containing solutions, the conditioning potential should not exceed 0.55 V, since at more positive potentials, chloride can adsorb or an oxide can form and alter the surface of the gold electrode. After the AuUMEA were subjected to potential cycling in a 0.1 M H_2SO_4 solution they displayed a substantial change in behavior when used to perform SWASV experiments (Fig. 2). Typically, before and after each day's experiments, a CV was collected to monitor the state of the AuUMEA. The arrays that functioned well generally exhibited the behavior seen in Fig. 2A. The arrays that began to perform badly, evidenced by lower stripping signals for arsenic, typically generated a voltammogram shown in Fig. 2B. The growth of an oxide layer on the gold represents a change in the electrode surface that hinders the deposition of arsenic. The oxide peak was irreversible, in that any pretreatments attempted did not alter this anodic peak. Such pretreatments included, using a conditioning potential, cycling from 0 to -1 V, and sonication. Immersion into ethanol alleviated the problem temporarily. However, it should be noted that multiple SWASV runs could be ob-

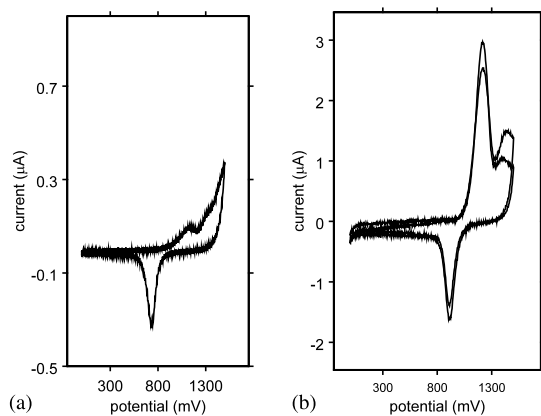


Fig. 2. CVs obtained with AuUMEA in 0.1 M H_2SO_4 before (A) and after multiple SWASV runs (B) in determination of As^{3+} . The potential was cycled between 0 at 1500 mV at a scan rate of 100 mV s^{-1} .

tained with the AuUMEA before this deleterious behavior became evident (Fig. 3).

The lifetime of the AuUMEA was evaluated via a long-term study. A single AuUMEA was used to measure a standard of 50 ppb As^{3+} over a period of 30 days. For each day, three runs were made and the average value with standard deviations is reported in Fig. 3. In general, the AuUMEA gave stable stripping peak currents over the 30 days of testing. The coefficient of variance

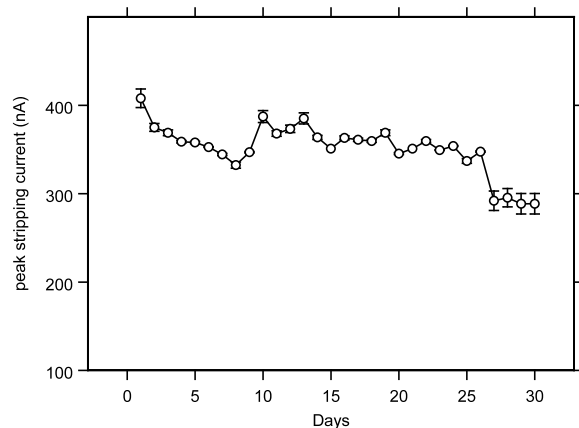


Fig. 3. Long-term reproducibility for the response of the AuUMEA to As^{3+} . All solutions contained 50 ppb As^{3+} in 2 M HCl. Conditions: $E_i = -0.375 \text{ V}$, $E_f = 0.4 \text{ V}$, $t_d = 60 \text{ s}$, $f = 150 \text{ Hz}$, $E_{sw} = 25 \text{ mV}$, $\Delta E_s = 2 \text{ mV}$.

Table 1

Methods reported in the literature involving reduction of arsenate

Methods for the reduction of As^{5+} to As^{3+}

Directly reducing As^{5+} by applying a large negative potential in 4 M HCl [11,33]

Deposition at -1 V at a heated gold microelectrode ($22\text{--}60 \text{ }^\circ\text{C}$) [34]

Using constant current or Au^{3+} as a chemical oxidant in PSA [35]

Sulphur dioxide is bubbled through a heated solution ($80 \text{ }^\circ\text{C}$) for a few minutes [17,25]

over this period was 1.5%. After 30 days, the response of the AuUMEA dropped off significantly and a visual passivation layer was observed on the electrode surface under a microscope.

The LOD was also investigated for these UMEAs using a statistical and experimental approach. In either case, the LOD associated with this technique is at or near 0.1 ppb [15].

3.2.4. Speciation

We have also performed studies to determine the viability of measuring arsenate, a dominant, but electroinactive species. We have also explored the use of both chemical and electrochemical methods to reduce As^{5+} to As^{3+} in the attempt to establish a field applicable method to determining the total amount of arsenic in aqueous samples. There are only a few methodologies described in the literature for the reduction of arsenate (Table 1), most being either not field amendable or are not reproducible.

Electrochemical reduction of arsenate was attempted but yielded unsuccessful results. Excessive evolution of hydrogen gas at the working electrode surface prevented any reproducible data from being obtained. Various chemical reducing agents were also investigated, namely potassium iodide, ascorbic acid, hydrazinium dichloride and sodium sulfite. Sodium sulfite was the only one found that gave satisfactory analytical results. An example of the SWASV voltammograms obtained after addition of sodium sulfite and heat to a solution containing As^{5+} is shown in Fig. 4. Only, sodium sulfite was effective in reducing

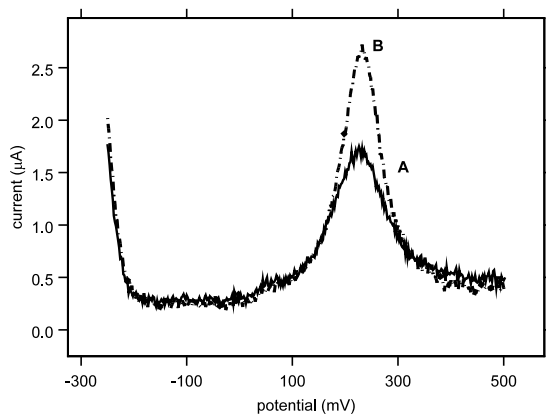


Fig. 4. SWASV of the chemical reduction of As^{5+} to As^{3+} with sodium sulfite in 2 M HCl. (A) 300 ppb As^{5+} and (B) addition of 300 ppb As^{3+} to the solution. SWASV parameters: $E_i = -0.375$ V, $E_f = 0.4$ V, $t_d = 80$ s, $f = 150$ Hz, $E_{sw} = 25$ mV, $\Delta E_s = 2$ mV.

arsenic and maintaining a stripping signal. The time required for the sodium sulfite to reduce the As^{5+} was determined by monitoring a test solution over a period of time. As shown in Fig. 5, the reduction of most of the As^{5+} has been completed after approximately 30 min. Therefore, sodium sulfite can be used for field work in determining a total concentration value for arsenic in ground water.

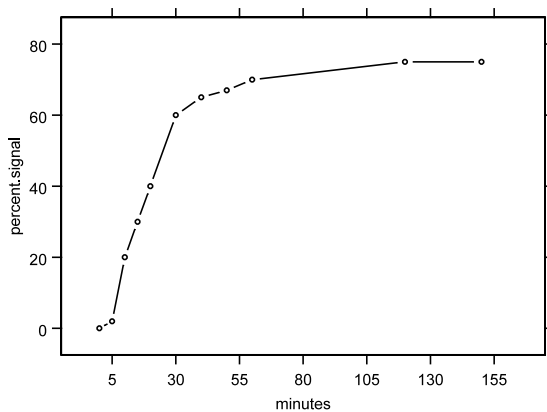


Fig. 5. Signal of As^{3+} monitored over time after the addition of sodium sulfite (0.1 g) to a solution of 100 ppb As^{5+} in 2 M HCl (15 ml). SWASV parameters: $E_i = -0.375$ V, $E_f = 0.4$ V, $t_d = 80$ s, $f = 150$ Hz, $E_{sw} = 25$ mV, $\Delta E_s = 2$ mV.

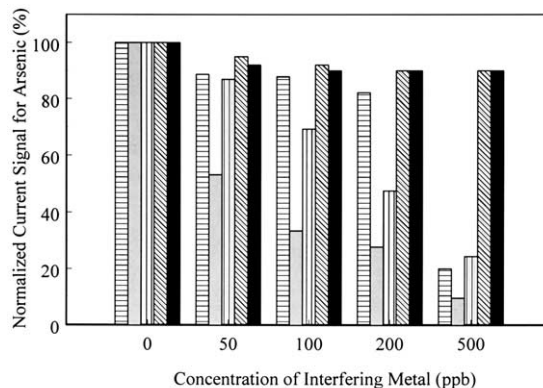


Fig. 6. Normalized current signals for a solution containing 100 ppb As^{3+} in 2 M HCl in the presence of increasing concentrations of Pb^{2+} (horizontal), Cu^{2+} (gray), Hg^{2+} (vertical), Fe^{2+} (cross-hatch), and Zn^{2+} (black).

3.2.5. Interference studies

Interference studies were performed in 2 M HCl to examine the effect other metal cations may have on the arsenic monolayer stripping peak. Lead, copper, zinc, iron and mercury were chosen. Lead and mercury compete for sites on the gold surface without forming intermetallic compounds. It has been shown in the literature that copper and arsenic form intermetallic compounds, which severely hinder determinations of arsenic. Lead, copper, and iron are commonly present in many water systems. The results for three different AuUMEAs, normalized for comparison and each value being the average of three runs, are shown in Fig. 6. The relative standard deviation for 15 runs with the solution containing only arsenic was 2.5%. The peak stripping current, Δi_p , decreased for all the interfering metals additions, but not to the same degree. Copper had the most deleterious affect on the arsenic stripping signal, even at low concentrations. However, the other metals, lead, mercury, iron, and zinc showed minimal suppression of the arsenic peak at concentrations ≤ 200 ppb.

3.2.6. On-site analysis

Our field portable device was used to perform on-site analysis at the Vineland Chemical Co. site in Vineland, NJ. The company was involved with the manufacture of arsenic based herbicides from

1950 to 1994. According to EPA site data, sub-surface soils and ground water have been contaminated with various levels of arsenic across the 54 acre site [32]. The water has been found to be anoxic with no other heavy metals present.

We found the ground water to be clear, with very little particulate matter, thus filtering was considered unnecessary. Samples were removed from three wells with bailers, acidified, and covered. The pH values for the water samples were 6.2, 6.5 and 6.3, respectively. A second batch of samples were extracted, acidified, deoxygenated with nitrogen, and capped for lab-based analysis. SWASV was performed with a Au/UMEAs protected with a thin Nafion coating. A Ag/AgCl reference and a counter electrode completed the electrochemical cell. In all acidified samples, a gaussian stripping peak for As^{3+} was obtained. No interferences were seen within this potential window. Standard additions were performed to quantify the amount of arsenic present. A typical series of the resulting voltammograms is shown in Fig. 7. After several runs, it was determined that

there was no accumulation of arsenic in the Nafion film.

For quantification, three standard additions, of the appropriate amount, were made to the electrochemical cell and linear concentration curves were obtained for the three well samples (Table 2). Again, the Au/UMEAs responded well under field conditions and linear results were obtained. The voltammetric results were compared with ICP analysis using EPA method 200.7 (Table 3) and show that our technique accurately quantified the arsenic levels in the water samples. Measurements after chemical reduction of any arsenate in the samples were attempted after returning to the lab. Both MW-6 and MW-21 showed an appreciable increase in the As^{3+} stripping signal. The 'total' arsenic concentrations were then calculated to be 760 and 57 ppb, which put the values to within 1.3 and 5% of the ICP values, respectively. Addition of the reducing agent to the sample from MW-41 did not result in an As^{3+} peak enhancement. In fact, the stripping peak became distorted. We have no hypothesis as to what caused

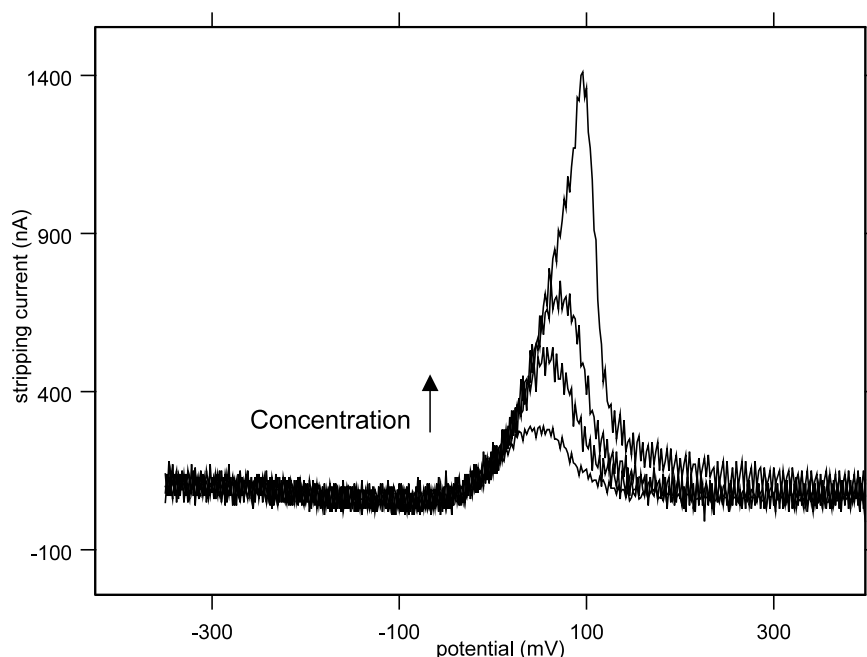


Fig. 7. On-site voltammograms for the standard additions performed on the Vineland Chemical Co. site with the battery-powered potentiostat and a Nafion coated Au/UMEAs. Parameters: $E_i = -0.375$ V, $E_f = 0.4$ V, $t_d = 80$ s, $f = 200$ Hz, $E_{sw} = 25$ mV, $\Delta E_s = 2$ mV. Sample from MW-21 was acidified to 2 M HCl.

Table 2

Linear results from the multiple standard additions to the water samples from the Vineland site

Well number	Regression coefficient R^2	Slope (nA ml ⁻¹)	y -Intercept (nA)
MW-6	0.995	1692 ± 84	187 ± 33
MW-21	0.999	1707 ± 25	138 ± 10
MW-41	0.996	884 ± 39	107 ± 16

Table 3

Comparisons of voltammetric and spectrometry data from the Vineland samples

Well number	AuUMEA (ppb)	ICP-AES (ppb)	% Difference
MW-6	730 ± 130	770 ± 20	5
MW-21	54 ± 4	60 ± 6	10
MW-41	81 ± 13	60 ± 10	-35

this distortion, but further investigation is required. Overall, we found it interesting that the water samples were composed mainly of arsenite. A possible reason for this may be that the water, being anoxic, stabilizes the As³⁺ form. Various wells across the site have been verified by EPA analysis to be mostly composed of arsenite. However, it should be noted that other wells on the site, contained primarily arsenate.

4. Conclusion

This work demonstrates the ability to obtain analytically relevant, on-site measurements for arsenic. After comparison to ICP-AES, the on-site data generated revealed accurate measures of arsenic in ground water samples. In this way, the voltammetric approach can meet the needs for rapid field screening tools and is an attractive alternative for real time, on-site measurements.

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