

Implementation of Electrochemical Sensors in Arsenic-contaminated Areas of West Bengal in India toward Rapid and Point-of-Use Detection of Arsenic in Drinking Water

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Abstract— The difficulty of detecting small quantities of arsenic in water currently threatens the health of millions of people worldwide, as long-term exposure to arsenic has been associated with both cancerous and noncancerous health risks. Existing technologies make it possible to very accurately quantify arsenic levels in water; however the expense, extensive training, and off-site analysis required by these methods impede wide scale-use. Electrochemical detection offers many advantages, such as portability, minimal use of instrumentation, and ready integration with electronics. Toward a solution to water quality interventions, we have demonstrated an affordable and point-of-use platform capable of detecting trace amounts of arsenic in groundwater samples. Our electrochemical sensor utilizes a three-electrode system with carbon, silver, and silver/silver electrodes integrated with a handheld electrochemical analyzer. We employed our sensor to investigate arsenic concentration in drinking water on-site in the arsenic affected areas of the North 24 Parganas district in West Bengal, India. 38 samples were collected from shallow, midrange, and deep wells. A small water sample from each well was applied to the electrodes and the current response was quickly captured, returning quantitative results to the user, which alleviates the lag times and imprecise colorimetric assays that encumber current arsenic detection systems.

Keywords— *biosensors; electrochemical devices; arsenic; water contamination*

I. INTRODUCTION

Arsenic contamination of water supplies in Bangladesh, India, and parts of China is a serious international public health threat. Arsenic is naturally occurring at high levels in the groundwater of a number of countries and highly toxic in its inorganic form. The World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) both define the Maximum Contaminant Level (MCL) of arsenic in drinking water at 10 parts per billion (ppb), yet the arsenic concentration levels in many locations worldwide exceed 50 ppb [1]. Arsenic contaminated water is colorless,

odorless, and tasteless, and the adverse health effects of arsenic poisoning may not become apparent until long after initial consumption. As a result, an estimated 100 million people globally are at risk of long-term arsenic poisoning from the water they drink [2]. Long-term exposure to arsenic, mainly through drinking of contaminated water, eating of food prepared with this water and eating food irrigated with arsenic-rich water, has been associated with skin and lung cancers, as well as cancer of the urinary tract, kidney, and liver; other non-cancerous effects can include reproductive and child development health repercussions and skin diseases [3,4]. Therefore, the most important action in those affected communities is the prevention of further exposure to arsenic by providing a safe water supply, and testing of water sources/treated water supplies in high-risk regions is critical to protecting public health.

Current solutions for arsenic testing range from simple colorimetric assays to sophisticated laboratory tests. Colorimetric kits are simple and low-cost, yet these types of tests generally suffer from a lack of precision, have a higher limit of detection ($>10 \mu\text{g/L}$), and use toxic chemicals as test reagents [5]. Laboratory-based techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), atomic fluorescence spectroscopy (AFS), and HPLC-MS, are accurate but considerably more expensive, requiring off-site analysis of samples, impeding wide adoption of such techniques in those affected developing countries. The current technologies for on-site field detection has been review elsewhere, and there remains significant room for improvement [6,7]. Electrochemical devices combine the precision of analytical-grade equipment with a disposable test substrate, resulting in a product that is at once affordable, accurate, and portable. While traditional electrochemical tests are performed in a lab setting using bulk electrodes in a cell, printable ink electrodes have been shown to be effective replacements for their bulky counterparts. Therefore, we and others have developed electrochemical sensors consisting of printed electrodes from carbon, silver, and gold inks with complex geometries onto

disposable substrates at a fraction of the cost of bulk electrodes [8-10].

Motivated by these clear advantages, we propose a point-of-use (POU) electrochemical device that uses three-electrode configuration combined with a hand-held electrochemical analyzer for the detection of arsenic. Our electrochemical sensor is paired with the handheld electrochemical analyzer, capable of delivering quick and accurate readings at the test site (Fig. 1). The proposed device will seek to create an infrastructure in which water quality is analyzed and distributed in real-time. The establishment of a centralized database would allow public health agencies to more effectively manage contaminated sites and allocate the appropriate treatment solutions. Moreover, it will increase public awareness of the hazards associated with arsenic poisoning and act as a resource to help communities ensure their residents are drinking only safe and acceptably clean water.

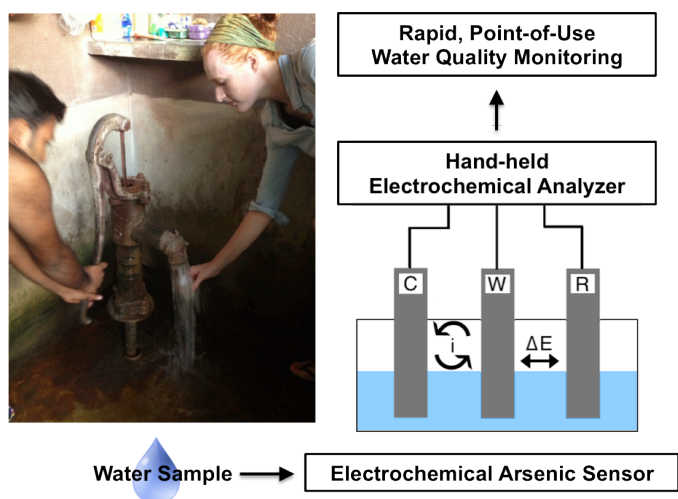


Fig. 1. Proposed system overview: (1) A water sample is applied to a sensing platform comprised of a three-electrode system (working, reference, and counter electrodes). (2) The handheld analyzer runs a voltammetric test on the sample to determine arsenic concentration.

II. CONTEXT OF OUR WORK

West Bengal irrespective of having a good monsoon every year is reeling under an environmental catastrophe known as arsenic poisoning in groundwater since 1983. Arsenic is a metalloid that is naturally occurring in the rocks and soils of the Gangetic delta. A high concentration of arsenic is found in the ground water of West Bengal in India and the two neighbouring countries of Bangladesh and Nepal. Although the mechanism and factors involved in release of arsenic into the groundwater are still an area of debate and study, it is generally thought that contamination results from natural geochemical soil leaching (reductive dissolution or desorption) brought about by excessive ground water withdrawal. Arsenic in water is colorless and odorless, making it impossible for the user to know whether water is contaminated or not. Chronic arsenic exposure can lead to skin effects (pigmentation, keratoses, lesions, and cancer); peripheral vascular disease; hypertension

and cardiovascular diseases; cancers of the bladder, kidney, and lung; diabetes mellitus; and possible neurological effects. By year 2000 it was discovered that the groundwater of nine districts out of the eighteen districts of West Bengal had tube wells contaminated with arsenic. A recent study showed that the number of affected villages has increased to 2600 in 74 blocks, and that the population at risk of exposure in the region was 42.7million. This study also found that 25% of the total (101,934) number of tube wells that have been analyzed contained arsenic concentrations more than 50 ppb (0.05 mg/L), while 52% contained above 10 ppb (0.01 mg/L), which is the Maximum Contamination Level (MCL) for the WHO [11].

Colorimetric reactions are the most common type of field test used to determine the presence of arsenic in water samples. These techniques rely upon a chemical color change to quantify the concentration of analyte present in a given sample. While a colorimetric test kit is cheaper than an electrochemical device, these types of tests suffer from lack of precision, typically have a higher limit of detection (LOD) at greater than 10 $\mu\text{g/L}$, and commonly use toxic chemicals as test reagents. A basic colorimetric assay is the Gutzeit reaction. In the Gutzeit reaction, arsine gas is generated using zinc and hydrochloric acid. The gas induces a color change on a paper substrate treated with a mercuric salt, and the level of color change is proportional to the amount of arsenic present [1]. There are several chemical hazards associated with this method. Arsine gas is highly toxic, and the hydrochloric acid and mercuric salt are both potentially damaging to the environment.

Colorimetric devices on the market today are based on arsine generation reactions similar to the Gutzeit method. For example, the commercially available Wagtech Visual Colour Arsenic Detection Kit uses strong acids as reagents and is only capable of measuring arsenic concentrations as low as 10 ppb [12]. The company's Arsenator Digital Arsenic Test Kit provides a slightly lower LOD by using a colorimeter to measure color change, but it is much more expensive and uses the same hazardous reagents and produces the same noxious byproducts. The health and environmental risks posed by these products are not suitable.

The sociological impacts generated by this underground poison is beyond measure. Reports reveal that the affected villages have been socially ostracised. In Haringhata, an arsenic affected village in Nadia district of West Bengal, many women remain spinsters for the pigmentation on their body due to arsenicosis blocked the wedlock, for very often people think the symptoms to be equal to leprosy. At least 28 people are believed to have died of arsenic-poisoning over the past decade and nearly 75 per cent of the total population of Nonaghata, Dasdiha and Uttarpara villages in the same district have reportedly been diagnosed with arsenic-induced ailments, suitable candidates for a prospective matrimonial alliance are even reluctant to visit these villages [13].

III. EXPERIMENTS

The sensor employs a three-electrode system (Fig. 1, right). The working electrode consists of silver, the counter electrode carbon, and the reference electrode silver/silver chloride. When

the device is connected to the potentiostat and a small volume of water sample deposited onto the detection zone, cyclic voltammetry or anodic stripping voltammetry can be applied to the electrode surface, producing a current peak for any reducible analytes through the range of the potential scanned [14].

A. Chemical Reagents/Sensor

Carbon, silver/silver chloride, and silver electrodes were purchased from CH Instruments, Inc (Austin, TX) for the counter, reference, and working electrodes, respectively. 1M HNO_3 was purchased from Sigma Aldrich (Saint Louis, MO).

B. Sensor Measurements

The sensor is connected to two different types of electrochemical analyzers: a bench-top CHI730D electrochemical analyzer (Austin, TX) for lab testing and a portable, open-source CheapStat electrochemical analyzer (Santa Barbara, CA) [15] for field testing. Electrochemical detection was carried out via either cyclic voltammetry (CV) or anodic stripping voltammetry (ASV). For cyclic voltammetry, current values were measured with a potential range of -0.5 to 0.6 V, a scan rate of 100 mV/s, and a sample interval of 1 mV. For anodic stripping voltammetry, the potential was held at -0.5 V for one minute followed by a potential sweep from -0.5 to 0.6 V, with a scan rate of 100 mV/s, and a sample interval of 1 mV. A control scan was conducted using 0.1 M HNO_3 . Immediately following, an As (III) contaminated sample in 0.1 M HNO_3 was deposited onto the sample zone and CV/ASV scans were obtained.

IV. RESULTS AND DISCUSSION

A. Detection of Arsenic from Arsenic Spiked Samples

First, to validate our sensing mechanism quantitatively, we performed anodic stripping voltammetry using the proposed three-electrode system with a bench-top electrochemical analyzer (CH Instruments, Inc., CHI730D). We employed a carbon counter electrode (CHI 104), a silver working electrode (CHI 103), and a silver/silver-chloride reference electrode (CHI 111) for the detection of arsenic. In absence of arsenic, no noticeable current peak was observed near stripping potential (Fig. 2, blue curve). Then, we spiked our sample with more arsenic and carried out ASV measurements (Fig. 2, green, red, cyan, and purple curves). Each spike contained ~ 100 μg of arsenic. As expected, in the presence of 100 μg of arsenic, we observed robust 2.2 μA in our signal (Fig. 2, green curve). As we increased the arsenic concentration with serial addition, we observed increasing currents as expected (Fig. 2, red, cyan, and purple curves), indicating that anodic stripping voltammetry is able to distinguish different concentrations of arsenic. This shows that the proposed electrode configuration (carbon, silver and silver/silver-chloride) is capable of detecting arsenic level

quantitatively.

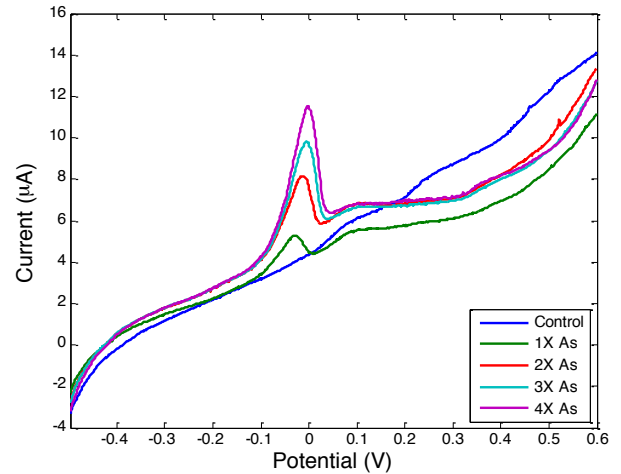


Fig. 2. Electrochemical detection of arsenic in water samples with spiked-in arsenic via a three-electrode system: the commercially available bulk-electrode system was interrogated via anodic stripping voltammetry. First, the baseline was established from the sample without any arsenic (blue curve), and measurements were taken after the serial addition of 100 μg (green, red, cyan, and purple curves), showing the current peak changes from baseline and increases with increasing arsenic concentrations.

B. Point-of-Use Detection of Arsenic from Water Samples in West Bengal, India

We employed our sensor to investigate arsenic concentration in drinking water on-site in the arsenic affected areas of the North 24 Parganas district in West Bengal, India. 38 samples were collected and tested from shallow, midrange, and deep wells over five blocks (Gaighata, Swarupnagar, Baduaria, Havra I, and Deganga). We performed both CV and ASV from the collected samples. CV measurements resulted in presented peaks in only three samples while ASV measurements resulted in presented peaks in 36 samples out of 38 samples. Therefore, we chose ASV as our detection method for further study.

Electrochemical analyzers, also known as potentiostats, are the cornerstone of electrochemical detection employed here. However, their high cost (even the least expensive commercially available ones sell for more than a thousand dollars) is an important factor preventing a wide adoption of electrochemical detection in resource poor environments despite various advantages of such detection mechanisms, as mentioned earlier. Therefore, we adopted an alternative electrochemical analyzer, CheapStat, which is open-source (software and hardware), inexpensive ($< \$80$), and hand-held (weighs only 115 grams), developed by Rowe *et al* [15]. While this analyzer cannot compete the abilities and quality of top-of-the-line commercial equipment, it does offer a number of potential waveforms sufficient for our application. In our previous work, we have compared electrochemical measurements from the bench-top analyzer (CHI730D) and CheapStat, and have shown that CheapStat analyzer combined with our sensor system can successfully detect arsenic concentration in arsenic spiked water samples [8].

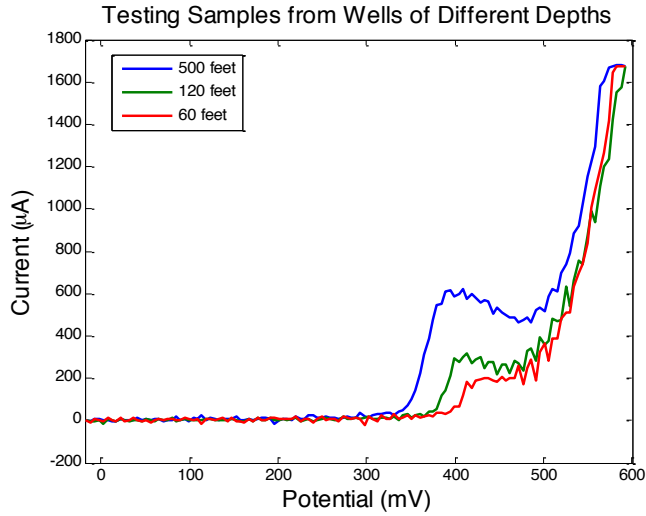


Fig. 3. Electrochemical detection of arsenic in water samples from West Bengal, India: the sensor was interrogated via anodic stripping voltammetry in samples from wells of different depth. As the depth of well increases, the current peak increases (red curve for 60 feet, green curve for 120 feet, and blue curve for 500 feet).

We carried out ASV using our system integrated with CheapStat analyzer from the collected samples. First, in absence of arsenic, a negligible current peak was observed from the working electrode and the counter electrode using CheapStat. As expected, from arsenic contaminated samples, we observed robust current values ranging from 156 to 651 μA in our signal from the working electrode vs. the counter electrode (Fig. 3). The current peak measurement data over different blocks are summarized in Table. 1. An increase in depth was shown to correspond with an increase in current peak heights, and therefore arsenic concentration, confirming the findings from previous studies [16].

Our electrochemical sensing mechanism is particularly suited for point-of-use applications because it enables real-time, continuous monitoring of arsenic with high sensitivity and specificity. One can define a threshold current and determine the concentration of arsenic from the measured current.

As future work, we plan to incorporate mobile interface that enables the device to be effectively used in these remote areas, where testing the water is really important, but the ability to do so is limited by the lack of access to trained personnel to analyze the data obtained by the sensor locally. We have previously adapted electrochemical sensors for bacterial pathogen detection to a mobile device to enable the instant interpretation of the data obtained and the mapping of the test results at different places, indicating safe vs. not-safe water sources [17], and we plan to further create a web-based application to coordinate the water prevention and control. For instance, our system can be employed to discriminate between high-arsenic and low-arsenic sources to reduce levels of arsenic in drinking water. Water samples could be tested and interpreted for arsenic levels, and water sources such as tube

wells or hand pumps could be painted with different colors depending on the contamination level. This can be an effective and low-cost means to rapidly reduce exposure to arsenic when accompanied by effective education [18]. One can also blend low arsenic water with higher arsenic water in order to achieve an acceptable arsenic concentration level.

Block	Average Peak Height (μA)		
	Shallow (30-60 ft)	Midrange (80-120 ft)	Deep (>120 ft)
Gaighata	183	N/A	581
Swarupnagar	200	N/A	621
Baduaria	186	233.5	N/A
Havra I	156	N/A	300
Deganga	192	325	651

Table 1. Average current peak measurements from samples over different blocks in North 24 Parganas district: an increase in depth was shown to correspond with an increase in current peak heights, and therefore arsenic concentration.

V. CONCLUSIONS

We demonstrated an affordable and point-of-use platform capable of detecting trace amounts of arsenic in groundwater samples. Our electrochemical sensor utilizes a three-electrode system with carbon, silver, and silver/silver electrodes integrated with a handheld electrochemical analyzer. We employed our sensor to investigate arsenic concentration in drinking water on-site in the arsenic affected areas of the North 24 Parganas district in West Bengal, India. 38 samples were collected from shallow, midrange, and deep wells. The proposed system is an inexpensive, portable unit, which alleviates the issues in imprecise colorimetric assays and provides an attractive platform in resource limited settings.

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