Determination of Arsenic in Natural Waters

Using Surface Plasmon Resonance:

A Low-Cost Analytical Tool for Arsenic Screening

Carin P. King

Waterville, Maine

cpking@colby.edu

ABSTRACT

Arsenic is a known toxin found in water throughout the world. Arsenic contamination is a particular problem in some developing countries where drinking water is often drawn from shallow, unmonitored wells. An inexpensive and robust screening method for arsenic is needed for routine analysis of drinking water. Forzani et al. (2007) reported success in the detection of arsenic using differential surface plasmon resonance (SPR), which are expensive and not field portable. Forzani's arsenic binding chemistry was modified to work with a single-beam SPR instrument and allow arsenic detection limits of 20 ppb. This work is significant because single-beam SPR offers the potential for a low-cost, field-portable sensor for arsenic in drinking water.

1. INTRODUCTION

Arsenic is a well-known toxin, with a lethal dose of 10-180 mg for As_2O_3 and 70-210 mg for arsenide, H_3AsO_3. Arsenic binds and blocks the action of sulfur-containing enzymes. Symptoms of acute arsenic poisoning include nausea, vomiting, diarrhea, cyanosis, cardiac arrhythmia, confusion, and hallucinations (Lenntech 2008). Acute arsenic poisoning is rare; however, chronic arsenic poisoning has become a worldwide health crisis in both developed and developing countries. Chronic arsenic poisoning "causes cancer of the skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis)" and anemia (WHO 2001).

The World Health Organization (WHO) estimates that between 200,000 and 270,000 people will die in Bangladesh due to cancer caused by chronic arsenic exposure over 50 ppb. Skin pigment changes and hyperkeratosis are usually the first signs of chronic arsenic exposure. Cancer usually takes about 10 years to develop (WHO 2001). WHO and the U.S. Environmental Protection Agency have set drinking water standards for arsenic at 10 ppb as a result of its toxicity.

Arsenic enters groundwater through the dissolution of arsenic-containing minerals and the desorption of arsenic bound to iron oxides. Two geologic conditions promote high arsenic concentrations. Strongly reducing aquifers flowing slowly through young, alluvial sediments allows for the reductive dissolution of arsenic, releasing As (III) into groundwater. Alternatively, water flow through geologically young, inland or closed basins, can produce high pH conditions promoting desorption of As (V) from sediments (Smedley and Kinniburgh 2002). The red stars in Figure 1 show conditions in which arsenic will dissolve in groundwater. High arsenic concentrations are found all over the world, especially in the young deltaic sediments of Bangladesh (Figure 2). Closer to home,
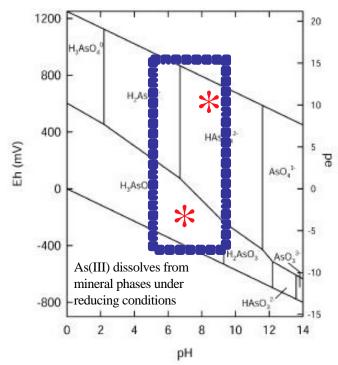

Figure 1. Eh-pH Diagram of Groundwater Arsenic. The blue box indicates the redox and pH range of natural ground waters.(Smedley and Kinniburgh 2002)

groundwater contamination by arsenic is also a real concern in the United States, with significant areas having arsenic concentrations greater than the 10 ppb U.S. drinking water standard (Figure 3). This is particularly true in Maine where over 25% of private drinking water wells exceed 10 ppb arsenic (Schmitt and Peckenham 2005).

The combination of toxicity and prevalence in groundwater makes arsenic detection a public health priority. In developed countries it is common to have access to lab facilities equipped to test for arsenic; however, some of the most severe arsenic contamination occurs in developing countries where lab access is limited.

According to WHO, "accurate measurement of arsenic in drinking water at levels relevant to health requires … sophisticated and expensive techniques … not easily available or affordable in many parts of the world." (WHO 2001) WHO has determined that "simple, reliable, low-cost equipment for field measurements" is an urgent requirement (WHO 2001).
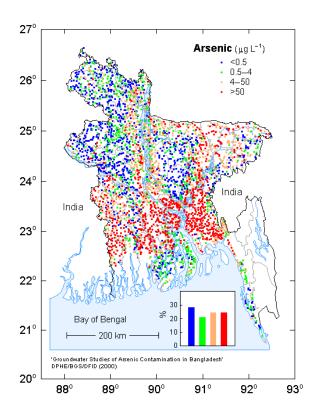
Figure 2. Arsenic Distribution in Bangladesh Groundwater Samples. Red sample points show areas of serious groundwater contamination. (Harvard 2004)
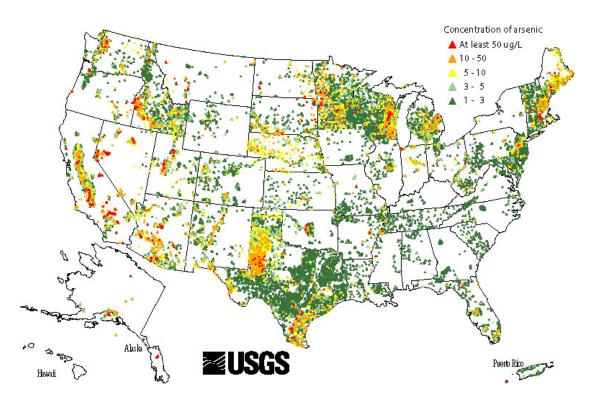
Figure 3. Arsenic Groundwater Concentrations in the United States. Orange and Red symbols indicate arsenic concentrations above the drinking water standard. (Ryker 2001)

Conventional methods for As detection include the generation of arsine gas (AsH_3) with colorimetric analysis, hydride generation of arsine gas with ICP-MS analysis, and colorimetric analysis of As-Mo complexes. As detailed in Table 1, all of these methods have analytical limitations for routine field analysis, being either too expensive or requiring a complicated set of reagents.

Recently, Forzani et al. (2007) reported success in the detection of arsenic using differential surface plasmon resonance (SPR). SPR uses the critical angle for surface plasmon formation to determine changes in the surface chemistry of a metal-solution interface caused by minute, but detectable, changes in the index of refraction (Figure 4). The advantage of SPR is that it is capable of
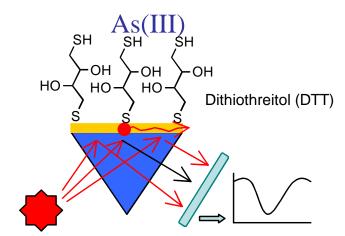

Figure 4. Schematic Diagram of a Single-Beam SPR Instrument. The gold surface is illuminated at different angles generating a surface plasmon at the critical angle. This angle is detected as a minimum in the diffracted light pattern.

detecting low levels of both As (III) and As (V) and only requires a small amount of one reagent for surface modification.

Table 1. Comparison of Common As Analysis Methods				
Method	**Detection Limit (ppb**	**Interference**	**Analytical Challenge**	**Reference**
Arsine Gas Production and Quantification	100	Sulfide	Toxicity of Arsine Gas, Poor Detection Limits	(Gutzeit 1891)
Molybdate	1	PO_4^{3-}	Requires Many Reagents	(Dhar et al. 2004)
ICP-MS	1	None	Cost	(Gomez-Ariza et al. 2000)
Double-Beam SPR	2	Metals	Cost	(Forzani et al. 2007)
Single-Beam SPR	20	Metals	Temperature Sensitivity	Author's Research

The disadvantage of SPR is that the instrument is expensive, costing between twenty and fifty thousand dollars. This project developed a method for detecting arsenic using a single beam, rather than a double-beam SPR because recent technological advancements have made single-beam instruments compact and cost effective. Figure 5 shows the Texas Instruments Spreeta single-beam SPR chip currently being adapted for a number of field-based SPR applications. This work sought to extend the Spreeta capabilities to the detection of arsenic in natural waters.

Figure 5. Spreeta SPR Chip Modula (Sensata 2008)

2. METHODS AND MATERIALS

A. Reagents

All solutions were prepared in 18 MΩ reagent-grade water (Millipore) from analytical-grade reagents. All solutions were degassed for 15 min. using a laboratory vacuum. Dithiothreitol (DTT) was 15 mM prepared

in pure water. Arsenic standards were prepared from a 1 part per thousand stock solution of arsenic (V) from arsenic acid. Working standards from zero to 100 ppm were prepared by diluting the arsenic stock into pH 7, 10 mM Tris buffer.

B. Instrumentation

Solution pH was measured using a Ross Sure-Flow pH electrode and Accumet meter calibrated using NBS buffers. Surface refraction angle was measured using a Reichert SR 7000, single-beam Surface Plasmon Resonance (SPR) instrument. The instrument was operated at 12.000^{o}C. A gold-coated chip was mounted in the instrument according to manufacturer's instructions and was connected to a sample valve with PEEK tubing. Solutions were pumped through the instrument and across the gold chip using a syringe pump operated at a flow rate of 6mL/h. The SPR chip was cleaned with reagent-grade water and ethanol. The gold surface was modified with DTT by repeated injections
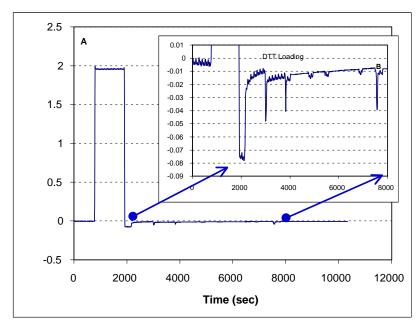

Figure 6. SPR Response to Ethanol Rinses. Panel A shows a large refractive index change. Panel B shows a blowup from time 2,000 to time 8,000, showing the binding of the DTT to the gold surface.

of DTT over a 2-hour period followed by a Tris buffer rinse. Figure 6 shows a typical index of refraction change associated with changes of solvents from water to ethanol and a much more subtle change when the DTT is bonded to the gold surface. The instrument is capable of measuring index of refraction changes less than 10^{-4} units. Samples were injected into the instrument in two modes. In mode one, samples were pumped continuously through the flow cell, while in mode two, samples were pumped for 2 min. and then flow was stopped for two minutes of data acquisition. These two modes were investigated due to the oscillation of our syringe pump. The type of oscillation experienced could be eliminated by using a better syringe pump, but is typical of what would be encountered for a field-based instrument.
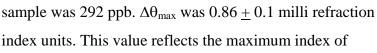
3. RESULTS

The DTT reagent immobilized on the SPR gold chip provided a highly reactive surface for the bonding of arsenic. The formation of an Arsenic-DTT bond changes the index of refraction of the gold-solution interface and thus the angle at which a surface plasmon forms. Figure 7 shows the change in index of refraction for different arsenic concentrations. The average index of refraction change for each As addition was fit to a Langmuir Isotherm of the form

$$\Delta\theta = \frac{\Delta\theta_{max}C}{K_d + C} \quad (1)$$

where;

$\Delta\theta_{max}$ is the change in angle of refraction when all DTT sites are saturated with arsenic, K_d is the equilibrium binding constant for the DTT-As (III) complex, and

C is the arsenic concentration in ppb. This equation describes the nonlinear behavior of arsenic binding to the gold chip, as shown in Figure 8. The data was fitted using the nonlinear curve fitting routine, Solver, in Microsoft Excel. The equilibrium binding constant (K_d) was 292 $\pm$ 225 ppb indicating that the chip was half saturated when the concentration of arsenic in the sample was 292 ppb. $\Delta\theta_{max}$ was 0.86 $\pm$ 0.1 milli refraction index units. This value reflects the maximum index of
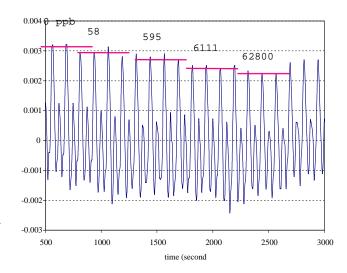

Figure 7. SPR Index of Refraction Change Due to the Addition of Increasing Arsenic (V) Concentrations. Oscillations in the signal are due to running the instrument in mode 1.
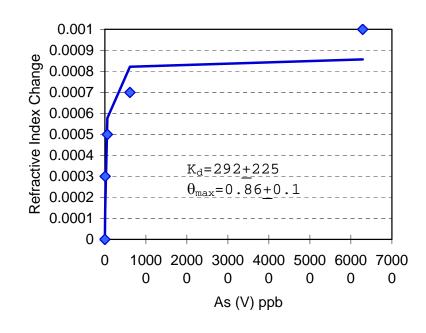

Figure 8. As (V) Additions Fit to a Langmuir Isotherm

refraction change expected at maximum arsenic concentrations. This number determines the required sensitivity of an SPR instrument for arsenic analysis. In other words, a successful SPR instrument for arsenic

must be able to detect changes of index of refraction better than one part in 10^{-4}. This will be important when evaluating potential field instruments.

Figure 9 shows the same data plotted on a logarithmic scale. From the propagation of the errors in the slope and intersect of this fit, it was possible to calculate the detection limit of 20 ppb for this technique. Similar results were obtained using the instrument operated in mode 2 (data not shown). It is notable that As (V) additions were being made, while DTT only binds to As (III). This is consistent with the work of Forzani et al. (2007) that demonstrated that DTT reduces As (V) to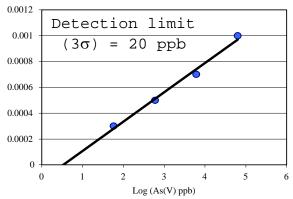 As (III) prior to binding. This means that DTT-based SPR can be used for the detection of both oxidation states of arsenic found in groundwater.

Figure 9. SPR Data Plotted as a Function of Log(As (V))Concentration

4. DISCUSSION

This work demonstrated that single-beam SPR has comparable detection limits to the double-beam method described by Forzani et al. (2007). At a detection limit of 20 ppb, single-beam SPR is a powerful analytical method for determining both As (III) and As (V) concentrations in water. This work was the first step in the development of a field-portable SPR arsenic screening method. This method could be used in developing countries where lab access is limited and arsenic screening of drinking water is an urgent need. Based on the 50 ppb guideline value set by WHO, this screening method could be used to differentiate between drinkable and undrinkable water sources, evaluate arsenic remediation techniques, and test agricultural irrigation water-analytical capabilities, which could save many lives.

The next step in this work should be to lower the detection limit to below the WHO provisional guideline of 10 ppb and to determine the longevity of the DTT coating on the gold surface. This work has shown that the surface lasts for tens to hundreds of samples, but the longevity of the surface needs to be investigated for hundreds to thousands of samples. A subsequent step is to evaluate fully this method with added metals and organic materials to test for potential

Figure 10. Spreeta Chip Mounted in a Field-Portable Readout Module. (Sensata 2008)

interferences. Finally, it would be desirable to obtain a Spreeta evaluation kit to determine the feasibility of building a field-portable SPR for arsenic detection, similar to that shown in Figure 10. Manufacturer's literature indicates that the Spreeta chip has an instrument resolution of 10^{-6} refractive index units, more than sufficient for As analysis. Important issues that will need to be overcome for a successful field instrument are temperature control of the SPR chip and susceptibility of the method to variations in sample flow rate.

5. CONCLUSIONS

1. A sensitive, robust, and field-portable sensor for As (III) and As (V) is a public health priority.

2. Current analytical methods for arsenic detection are either too costly, too dangerous, or require too many reagents to be practical for field analysis of arsenic.

3. SPR offers a new approach to arsenic measurement. This work shows that the lower-cost single-beam SPR instrumentation can detect arsenic concentrations in water as low as 20 ppb.

4. Ongoing research is evaluating single-beam SPR arsenic analysis in the presence of interferences and for analytical throughput.

5. This work provides a solid beginning and a clear development path toward a field-portable sensor for As analysis in natural waters.

6. ACKNOWLEDGMENTS

A. Credits

B. Author

I am the daughter of Jan and Whitney King. I am a senior at Waterville Senior High School where I have explored my interests in science and mathematics. I am a member of the Waterville Science Olympiad team, which won its 13th consecutive Maine state championship this April. In addition to my science

interests, I enjoy playing the cello and am a member of the Tri-M Music Honor Society. I have been running cross-country since my sophomore year, and have been swimming since the 5th grade. In my free time, I enjoy running, and spending time with my family and friends. This March, I was a co-winner of the High School juried poster competition at the Maine Water Conference. I was recently inducted into the National Honor Society, and also received the society of Women Engineers Award. This summer I attended the Women's Technology Program at the Massachusetts Institute of Technology, focusing on electrical engineering, computer science, and discrete mathematics. I am interested in pursuing a career in science, specifically neuroscience or biochemistry.

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