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A novel field deployable filter paper based amperometric gas sensor for the measurement of arsenic in water

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ABSTRACT

The presence of toxic levels of inorganic arsenic in drinking water is a worldwide problem. Measurement of millions of samples in the field for arsenic is an analytical challenge and the first step to solve the problem. Here, we developed a novel electrochemical arsine sensor and system based on the cell: $C(s)/I_3^- I_2$, $AsH_3(g/aq)//I_3^-$, I_2 $AgI(s)/Ag(s)$, where I_3^-/I_2 mediated $AsH_3(g/l)$ oxidation which occurred on the C(s) electrode. The sensor system requires 50 μL of 10 mM iodine solution and a small piece of filter paper placed inside a novel electrochemical cell. The cell exhibited highly efficient arsine mass transport with a limit of detection of 15 μg/L As(III) in water. A mathematical model of mass transfer of $AsH_3(g/aq)$ and following electrochemical reaction was developed and applied to explain the experimental data. Groundwater samples containing arsenic were measured to prove its utility in a field deployable instrument.

1. Introduction

Arsenic poisoning was called by the World Health Organization (WHO) the largest mass poisoning disaster in human history caused by the natural occurrences of inorganic arsenic in groundwater used for drinking and cooking [1]. There might be 200 million people drinking groundwater contaminated with arsenic in many countries of the world [2]. Accurate measurement of arsenic in drinking water in the field is the first step to solve the problem. For example, there are over 11 million hand tube-wells in Bangladesh alone, which need immediate examination at least once [3]. Therefore, the development and deployment of an inexpensive and accurate instrumental technique are challenging goals yet to be realized.

Presently, arsenic in water is measured by atomic spectroscopy (emission, absorption and fluorescence — AE, AA and AFS) often employing hydride generation (arsine, $AsH_3(g)$) to increase the sensitivity [4]. These instruments require fully equipped laboratory and are bulky and very expensive to operate and maintain. More economic solution could come from gas phase chemiluminescence of arsine–ozone reaction [5–9] which is still not portable and uses ozone, which is also toxic. Lastly, colorimetric detection of arsenic, based on the reaction between $AsH_3(g)$ with Ag(I) or Hg(II) salts to form red-orange complex (known as the Gutzeit method [10,11]) is semi-quantitative at best [12]. To remove human error in interpreting the color with naked eyes, electronics for measuring color intensity has been introduced. Reflectance of the developed color spot can be measured and signal can be digitized through an electronic transducer. The time required to develop color for a reliable measurement (30–40 min) is too high for rapid assay [13].

Here, we report the development of an electrochemical AsH_3 (g/aq) sensor while retaining the framework of the Gutzeit method. Electrochemical gas sensors based on direct oxidation of $AsH_3(g)$ on metal surface in acidic electrolyte are commercially available [14,15]. Such electrochemical gas sensors failed due to the production of high concentration of $H_2(g)$ during $AsH_3(g)$ generation. The oxidation signal from $H_2(g)$ to H^+ is overwhelmingly large, which renders commercial arsine sensors unusable [16]. We found that excessively large anodic current from $H_2(g)$ on Au-electrode in aqueous acidic electrolyte rendered the method unsuitable with no selectivity for $AsH_3(g)$ (supplementary materials, Fig. A.1). Unless the electrochemical system is approximately one million times more sensitive to $AsH_3(g)$ than to $H_2(g)$ it is not possible to detect $AsH_3(g)$ with commercial arsine gas sensors. The use of a gas chromatograph to separate $H_2(g)$ from $AsH_3(g)$ makes this development expensive and not field deployable [15].

To overcome the severe interference from $H_2(g)$, we employed the reaction of $AsH_3(g)$ and $I_3^-(aq)$ on a filter paper disk with minimal amount of $I_2/I_3^-(aq)$ solution and monitored the anodic current from $I_3^-(aq)$ amperometrically at 1.1 V vs. Ag/AgI(s). The electrochemical oxidation of iodide $I_3^-(aq)$ generated by $AsH_3(g)$ at constant potential is the analytical signal without any interference from excessive H_2 (g). It was suggested that electrocatalytic oxidation of iodide on a boron-doped diamond electrode might be useful

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in detecting As(III) in solution where the oxidation current was proportional to the amount of As(III) initially present in the aqueous sample [17]. However, these electrodes are expensive and need occasional cleaning and conditioning to retain precision and accuracy. The basis of our technique is a novel cell design where a filter paper impregnated with I_2 can be used as substrate for electrochemical reaction. The filter paper containing I_2 can be easily replaced while the electrodes remain intact. Here, we describe the complete system with cell design, electrochemical principles involving mass-transport coupled reaction kinetics, and the instrumentation to measure inorganic arsenic in groundwater field samples. The technique was validated with multielement high purity ICP standard mixture made from EPA Method 200.7 standard solution (High-Purity Standards, Cat. # ICP-200.7-6A, LOT # 0,912,519) and was tested for field portability.

2. Theory

The overall measurement instrument consists of two compartments. In the first compartment, $AsH_3(g)$ is generated by chemical reduction of inorganic arsenic species (As(III) and As(V)) by a reducing agent, and in the second compartment $AsH_3(g)$ is detected by the electrochemical cell. Hereafter, we designate the first compartment as 'generator' and the second one as 'cell'. These two compartments are connected by an inert tube (Fig. 1).

Generally, inorganic arsenic species (H_3AsO_3 or $AsO(OH)_3$) in the generator vial is reduced by $NaBH_4$ (BH) to form AsH_3(g/aq), which escapes the aqueous phase to become $AsH_3(g)$ and finally $AsH_3(g)$ is redissolved in the cell for amperometric detection. In short, the following sequence of events is occurring:

$$H_3AsO_3(aq) \overset{k_1}{\rightarrow} AsH_3(aq) \overset{k_2}{\rightarrow} AsH_3(g) \rightarrow AsH_3(dmso). \quad (1)$$

In lieu of oxidizing $AsH_3(g)$ directly; we sought species that can be generated from chemical redox reaction with $AsH_3(g)$. It is known that I_2 is readily reducible above 600 mV vs. NHE by dissolved $AsH_3(aq)$ as follows [18,19].

$$AsH_3(aq) + 12I_2(aq) + 4H_2O \rightarrow AsO(OH)_3(aq) + 8H^+ + 8I_3^- \quad (2)$$

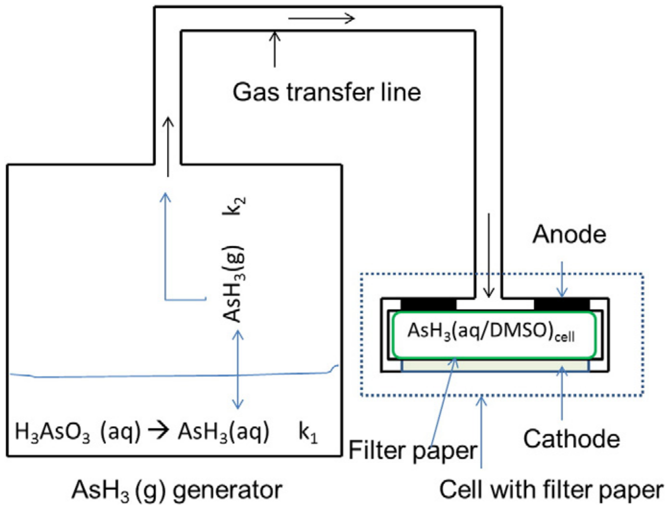

Fig. 1. Schematic diagram of $AsH_3(g)$ generator and the electrochemical cell for the measurement of As(III) in water. The details of formation and detection of $AsH_3(g)$ and its gas–liquid equilibrium $AsH_3(g/aq)$ are discussed in the theoretical section.

Based on Eq. (2), we can obtain the amperometric signal (oxidation current) from I_3^-, chemically generated by reaction with $AsH_3(aq)$. The electrochemical cell is as follows:

$$C(s)/I_2(aq), I_3^-(aq), AsH_3(g/aq), H_3AsO_3(aq), AsO(OH)_3(aq)//I_2(aq), I_3^-(aq), AgI(s)/Ag(s) \quad (3)$$

where, C(s) is the carbon (fiber or clothe) and used as working electrode. Here, the filter paper (//) acts as the separator and substrate for the electrochemical reaction between the working and reference electrodes ($I^-(aq)$, AgI(s)/Ag(s)). To increase the solubility of iodine, we used dimethylsulfoxide (dmso) as the solvent.

Here, we will introduce a brief description of chemical kinetics of arsine generation with BH and its effect on the baseline current. The measured current is the sum of three components:

$$i = i_{AsH_3} + i_{nonfaradaic} + i_{cathode} \quad (4)$$

where, i_{AsH_3} is the I_2 mediated $AsH_3(aq)$ oxidation current, $i_{nonfaradaic}$ is the capacitance current of the cell, and $i_{cathode}$ is the diffusion current due to a constant gradient of triiodide, I_3^-, formed in the thin layer cell. Regardless of whether $AsH_3(g)$ is arriving in the cell or not, this current is always present as a constant background. The amperometric signal of I_3^- is the diffusion current, which reflects the change in $[AsH_3]_{cell}$ in the following equation:

$$\frac{i_{AsH_3}}{FA} = D_1\frac{[I_3^-]}{d_1} = 8D_2\frac{[AsH_3(dmso)]_{cell}}{d_2}. \quad (5)$$

Here, d_1 and d_2 are the diffusion layer thickness and D_1 and D_2 are the diffusion coefficients of I_3^- and AsH_3(dmso), respectively. By knowing time dependence of $[AsH_3(dmso)]_{cell}$, the transient i_{AsH_3} can be calculated. As $AsH_3(g)$ is generated by BH in the generator, the time dependence of $[AsH_3(dmso)]_{cell}$ in the cell can be derived from the kinetics of $AsH_3(g)$ generation reaction. It has been found that the mass transfer of $AsH_3(g)$ from the generator vial was dictated by the kinetics of chemical reaction of H_3AsO_3 with BH [20].

$$BH_4^-(aq) + H^+(aq) + 3H_2O \rightarrow B(OH)_3 + 4H_2(g) \quad (6)$$

$$H_3AsO_3 + 3H_2(g) \rightarrow AsH_3(g) + 2H_2O \quad (7)$$

The solution of two coupled first order differential equations is necessary to obtain the transient concentration of $AsH_3(aq)$ in the generator as follows:

$$-\frac{d[H_3AsO_3]}{dt} = \frac{d[AsH_3]_{aq}}{dt} = k_1[H_3AsO_3] \quad (8)$$

$$\frac{d[AsH_3(aq)]}{dt} = k_1[H_3AsO_3(aq)] - k_2[AsH_3(aq)]. \quad (9)$$

Here, k_1 is the first order rate constant for arsine generation, and k_2 is the first order depletion (or removal) rate constant of arsine from the aqueous solution in the generator. By performing *Laplace* transformation on both Eqs. (8) and (9), we obtained the following solution (details are shown in the supplementary materials, Section B):

$$[AsH_3(aq)] = \left(\frac{k_1}{k_2 - k_1}\right)C_0\{\exp(-k_1t) - \exp(-k_2t)\}, \quad (10)$$

where, C_0 is the analytical concentration of As(III), $[H_3AsO_3]_0$ in the generator. In the generator, the total AsH_3 produced from the sample