A Gas-Phase Chemiluminescence-Based Analyzer for Waterborne Arsenic

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We show a practical sequential injection/zone fluidics-based analyzer that measures waterborne arsenic. The approach is capable of differentiating between inorganic As(III) and As(V). The principle is based on generating AsH$_3$ from the sample in a confined chamber by borohydride reduction at controlled pH, sparging the chamber to drive the AsH$_3$ to a small reflective cell located atop a photomultiplier tube, allowing it to react with ozone generated from ambient air, and measuring the intense chemiluminescence that results. Arsine generation and removal from solution results in isolation from the sample matrix, avoiding the pitfalls encountered in some solution-based analysis techniques. The differential determination of As(III) and As(V) is based on the different pH dependence of the reducibility of these species to AsH$_3$. At pH ≤ 1, both As(III) and As(V) are quantitatively converted to arsine in the presence of NaBH$_4$. At a pH of 4−5, only As(III) is converted to arsine. In the present form, the limit of detection (S/N = 3) is 0.05 μg/L As at pH ≤ 1 and 0.09 μg/L As(III) at pH $\sim$4−5 for a 3-mL sample. The analyzer is intrinsically automated and requires 4 min per determination. It is also possible to determine As-(III) first at pH 4.5 and then determine the remaining As in a sequential manner; this requires 6 min. There are no significant practical interferences. A new borohydride solution formulation permits month-long reagent stability.

Arsenic in drinking water has created a calamitous situation in some parts of the world.[1] In Bangladesh, where perhaps the problem is best characterized, the situation has apparently not improved.[2] Within the past few years, two special journal issues

have appeared on arsenic and provide much more detail.[3,4] The interest in areas related to the toxicology of arsenic, remediation of polluted sites, and field-usable means of detecting trace levels of arsenic are therefore very much alive.

In natural waters, arsenic exists as arsenite, arsenate, methylarsonic acid (also called monomethylarsonic acid, MMA), dimethylarsinic acid (DMA), etc. The inorganic forms are the more common and also the more toxic forms of arsenic,[5] especially arsenite.[6] Arsenic toxicity is believed to be mechanistically related to binding by certain proteins.[7] Acute toxicity decreases with the increase in degree of methylation,[8] although the tetramethylarsonium ion is an exception. Arsenic is classified as a group A known human carcinogen by the International Agency for Research on Cancer, the United States Environmental Protection Agency (USEPA), and the World Health Organization.[9] Chronic exposure to arsenic causes skin, bladder, lung, and prostate cancer; it has also been linked with reproductive, developmental, immunological, and neurological effects.[10]

Arsenic is the 20th most abundant element in the terrestrial crust;[11] toxic levels in groundwater have been documented in over 26 countries;[12] affordable and reliable field instruments will probably markedly increase this number. The United States Geological Survey (USGS) has conducted extensive groundwater surveys across the United States; high levels of As exist in many areas.[13,14] USEPA/USGS assessments show that ∼32 million in

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the U.S. drink water bearing 2−50 μg/L As. As of January 23, 2006, the USEPA has reduced the maximum permissible level of As in drinking water from 50 to 10 μg/L As.[15]

Analytical Methods for Waterborne Arsenic. There are several reviews that focus primarily on the speciation of arsenic in environmental and biological samples; this is beyond the scope of the present paper. Other recent reviews on arsenic measurement techniques[16,17] focus on (a) spectrophotometric methods (e.g., direct solution-phase measurement based on the arsenomolybdate chemistry, or arsine formation and its detection by some colorimetric approach), (b) electrochemical methods (mostly based on stripping voltammetry), and (c) atomic spectrometric methods. Present USEPA-approved methods are all based on atomic spectrometry.[18] Atomic spectrometry can readily provide detection limits in the submicrogram per liter range, but instruments are bulky, expensive, and require large amounts of pure gas in addition to the high cost of consumables. Of these, hydride generation atomic fluorescence spectrometry has been advocated as the best value in terms of the cost/performance ratio.[19] Regardless, field use is difficult, and although sample preservation methods have improved,[20] subsequent As oxidation-state speciation in the laboratory is often questioned.[21,22]

A robust field-usable technique capable of oxidation-state speciation is thus particularly desirable. Currently available field assays are typically based on the Gutzeit method, developed over 100 years ago.[23] How well these kits work has been passionately discussed.[24−26] Significant concentrations of arsine are produced and ∼50% of this can escape the device, thus posing a health hazard.[27] Hydrochloric acid and zinc dust are used to reduce all As species to arsine. Alternatively, $NaBH_4$ is used instead of zinc. To avoid interference from any H_2S produced, the liberated gases first pass through a lead acetate-soaked filter. The AsH_3 passes on to an $HgBr_2$-impregnated filter, turning it yellow to brown, depending on the amount of arsenic present. Commonly, comparison with a color chart is used; color degradation in sunlight and operator judgment can be factors.[28] In part, this can be avoided by a light-emitting diode-based photometer.[29] Still, the use of large sample volumes and a corresponding amount of acid, generation

of lead and mercury waste, etc., all constitute unresolved issues. In addition, the reproducibility of all arsine generation-based methods must depend on how effectively the arsine is sparged from the generation solution. From the available data on the solubility of arsine in water,[30] one can calculate a Henry's law constant of 10^{-2} M/atm. Consequently, even *if* equilibrium is reached between an equal volume of air and solution, some ∼20% of the arsine will remain in the solution.

The affordability, sensitivity, and ease of fabrication of electrochemistry-based field-deployable instruments are noteworthy; much work has been done in this area. There is at least one commercial instrument (www.tracedetect.com); an evaluation report is available from the EPA.[31] The effort to develop a fieldable and affordable arsenic analyzer is nearly a decade old in the senior author's laboratory, at least in part because of his umbilical connections to Bangladesh and West Bengal. A stripping voltammetry-based analyzer was indeed our first choice.[32] Continued experience in the field both with samples containing surfactants and with mine drainage waters led us to the conclusion that the method is not as robust as we had hoped. We came reluctantly to the same conclusion that others[28] articulated later: "...*it is unlikely that such methods could ever be made robust enough... Electrodes are notoriously fickle...*".

Among direct spectrophotometric methods, molybdenum blue or silver diethyldithiocarbamate chemistries are the most prominent; the latter has the highest consumable cost per sample among nonatomic spectrometric techniques, comparable to that of graphite furnace atomic absorption spectrometry (GFAAS).[33] The arsenomolybdate chemistry is highly sensitive, but the basic chemistry is sensitive to silicate and more importantly, phosphate. Because only As(V) and not As(III) responds to this chemistry, As can be determined by a difference method where the reaction is run with and without prereduction of As(V) to As(III); P(V) is not reduced under such conditions. In a sample where As(III) and As(V) both exist, it is possible in principle to run the sample (a) as such, (b) with preoxidation, and (c) with prereduction. These respectively measure P(V) + As(V), P(V) + As(V) + As(III), and only P(V), from which all three can be calculated. The limitation of obtaining a small number from the difference of two large numbers of course remains. This general approach has evolved over decades,[34−39] culminating in the recent elegant work of Dhar et al.[40] in which good comparability with a reference method was established for real samples. We ourselves also tried to use the arsenomolybdate chemistry in a different manner to

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measure As(III), by eluting unretained As(III) from the interstices of an anion-exchange resin column, oxidizing it, and carrying out the molybdate chemistry. Total As could be measured only after in-line prereduction of the sample,[41] making for an undeniably complex arrangement.
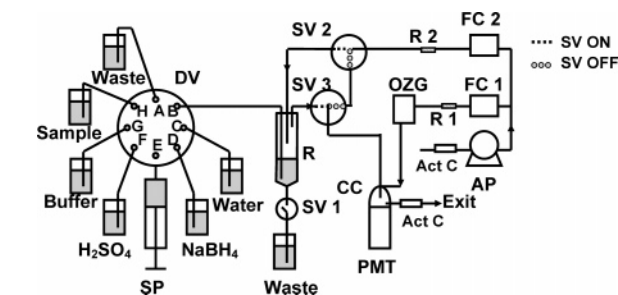
Another attractive photometric approach is to convert the As to AsH_3 and concentrating the AsH_3 thus liberated into a suitable oxidant receiver such as $KMnO_4$ or triiodide and determining it by direct colorimetry or after the molybdate reaction.[42−44] This approach can be attractive because borohydride-based reduction can exploit pH control to generate AsH_3 from all As species or from As(III) alone.[45−48]

Recently these two key concepts were exploited to make a sensitive, speciation-capable field instrument.[49] The issues of large sample volumes, difficulties in automating sample handling, etc., remained, however.

In the present paper, we describe a fully automated approach that is based on the gas-phase chemiluminescence (CL) reaction of arsine and ozone.[50−54] Last described in the literature more than a decade ago,[55] it has obviously slipped from the collective consciousness of researchers engaged in the current arsenic problem. We hope to show here that, in conjunction with sequential fluid handling[56]/zone fluidics[57] and the different pH dependence of the borohydride reducibility of As(III) and As(V) to AsH_3, this constitutes a very attractive and sensitive approach to measuring arsenic in water and possibly other matrixes.

EXPERIMENTAL SECTION

Reagents. Standard stock solutions of As(III) and As(V), 1000 mg/L As, were prepared using sodium arsenite and sodium arsenate heptahydrate (both from J. T. Baker), respectively. Working solutions were prepared by serial dilution with deionized water (18MΩ·cm) generally immediately before use. For hydride generation, 4% $NaBH_4$ (98%, Aldrich) was prepared in 0.5 M NaOH (Fisher) and 1 mM Na_2EDTA (Biochemical Corp., Cleveland, OH), except as stated. Sulfuric acid (1 M) was used for total As

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Figure 1. System schematic. SP, syringe pump, DV, 8-way distribution valve; R, reactor (30-mL disposable plastic syringe); SV1, two-way pinch valve; SV2,3, Three-way solenoid valve; PMT, photomultiplier tube; CC, chemiluminescence chamber; OZG, ozone generator; AP, air pump; FC1,2, optional mass flow controllers; R1,2, flow restrictors; Act C, activated carbon cartridge.
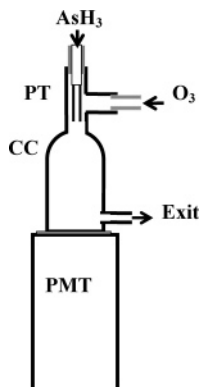
determination. For As(III) determination, 0.5 M potassium hydrogen phthalate (KHP) was initially used and later changed to 4 M NaH_2PO_4 (adjusted to pH 4.9 with 2 M NaOH). For sequential As(III) and As(V) measurement, the final choice of buffer was citrate; citric acid (1 M) was adjusted to pH 4.5 with solid NaOH pellets (fine adjustments with 2 M NaOH). In this approach, we first add a citrate buffer (1 mL) to the sample followed by the $NaBH_4$ reagent (0.5 mL). For the subsequent As(V) measurement, another aliquot of $NaBH_4$ is added, followed by 6.0 M H_2SO_4 (1 mL). Except as stated, the $NaBH_4$ reagent consisted of a solution of 4% w/v $NaBH_4$ (98%, Aldrich) in 0.5 M NaOH containing 1 mM Na_2EDTA. Other As test compounds included sodium monomethylarsonate (ChemService Standard, Westchester, PA), dimethylarsinic acid (98%, Aldrich), and tetraphenylarsonium chloride (Eastern Chemical, Pequannock, NJ).

Instrument Setup and Operation. The system is essentially set up as a sequential injection analyzer.[58] A 48 000-step syringe pump with rotary valve driver and control board, cooling fan, expanded memory, power supply, and communication cables (model V6, comprising P/N 54022, 24290, 50508, 23427, and 17734) equipped with a eight-position distribution valve (19323) and a 10-mL zero dead volume UHMW-PE tip glass syringe (P/N 24139), all from Kloehn Ltd. (Las Vegas, NV), forms the fluid distribution heart of the system. Once a program sequence, created on a PC by vendor-supplied KCOMM software, is loaded on to the resident memory of the pump, the pump can carry out the operations for the entire analytical cycle, without further need of the PC. In this work, we used an older Pentium III class laptop PC housing a 12-bit data acquisition card (PC-CARD-DAS16/12AO, Measurement Computing Inc., Middleboro, MA) to collect the instrument output using DAS Wizard, a vendor-supplied program that uses Microsoft Excel to record the data. The data were further processed, including moving average smoothing as needed, using MS Excel Data Analysis tools. Unless otherwise stated, results are based on peak height and reported as average ± sd ($n \geq 3$).

The instrument is schematically shown in Figure 1. The bidirectional syringe pump SP is connected to the common port of the eight-position distribution valve DV. The valve DV can addresses ports that are respectively connected to a sample container, a waste bottle, a reactor R, and reservoirs respectively containing solutions of $NaBH_4$, H_2SO_4, KHP, and water. One port (E) is dedicated to a standard (not shown) or can be left unused and vented to the atmosphere. All flow conduits were poly-

Figure 2. Details of chemiluminescence chamber gas entry and exit connections. CC, chemiluminescence chamber; PT, polypropylene tee.

(tetrafluoroethylene) (PTFE) tubes (0.86-mm i.d., 1.68-mm o.d., 20 SW; www.zeusinc.com), unless stated otherwise. Temporal operational sequence, aspiration/dispense volumes, and aspiration/dispense velocities are programmable. The reactor R consists of a 30-mL capacity disposable plastic syringe barrel (Becton-Dickinson) used in the inverted position with the Luer-lok tip at the bottom connected to a tube that drains to waste via a normally closed solenoid pinch valve SV1 (075P2NC24-02SQ, Biochem Valve Corp., Boonton, NJ). These and the two other solenoid valves in the system are energized in a temporally programmed manner through the digital output ports built in SP; the relevant schematic is given in Supporting Information (SI, Figure S1). The top of the reactor is plugged with a neoprene rubber stopper. Three fluid lines enter through the stopper; the stopper is secured in place with nylon ties. One of the tubes reaches nearly the bottom of the reactor and carries the liquid delivered by the SP. A second line reaches midway into the reactor (to a point that is just above the maximum fill volume of the reactor in operation such that the headspace can be swept) to form an air delivery line that comes from a three-way solenoid valve SV2 (075T3MP24-32; www.biochemvalve.com), through an optional mass flow controller FC 2 (Tylan FC 260; www.celerity.net) and a flow restriction tube R2 (PTFE, 0.25-mm i.d., 64 cm long), and serves to flush the reactor with air. The third fluid line entering the reactor is a gas exit line and terminates at the top. It goes to a solenoid valve SV 3, identical to SV 2. Restrictors R1 and R2 join at a tee T, which splits the output of a miniature air pump AP (5D1060-101-1073, Gast, Benton Harbor, MI). The other side of the T goes through an optional second flow controller FC 1 and restrictor tube R1 (PTFE, 0.25-mm i.d., 32 cm long), through a compact commercial ozone generator OZG (EOZ-300Y, http://www.ozone.enaly.com/EOZ-300Y.htm). The flow controllers were used for initial flow optimization. These optimized flows (60 mL/min through ozone generator, 30 mL/min headspace flush flow) were later achieved through the restrictors alone with the head pressure generated by air pump AP being ~4.5 psi. The output of the ozone generator and the output line of the reactor R from SV 3 are opaque black PTFE tubes (1.1-mm i.d.; www.zeusinc.com) that terminate in a polypropylene tee PT. As shown in Figure 2, the tee terminus is directly cemented with epoxy adhesive on the top of CC and the inner tube (0.38-mm i.d., 0.86-mm o.d.) is retracted 6 mm within the tee terminus. The chamber

CC itself is fabricated from the bottom ~1-cm portion of a 14-mm-i.d. glass test tube. It is silvered on the exterior with a commercial silvering solution (Lilly Industries, Woodbridge, CT) and then painted black repeatedly with black epoxy-based paint. Two holes are drilled into it, one at the top of the dome where the tee assembly is affixed and the other on the side toward the bottom where a black opaque tube is affixed as the gas exit. The bottom window of chamber CC is a 0.25-mm-thick, 12-mm square microscope cover glass that is centered at the bottom of the chamber and cemented in place with hot-melt adhesive. All exposed adhesive material reacts with ozone and contributes to the luminescence background. In our experience, the CL from polyethylene-type adhesives decreases to a low stable background value quicker than most others. Note that when the exit tube or the tee is cemented to CC, the adhesive is on the exterior and does not contact the ozone. The volume of the cell is ~1.5 cm³. To have tubes that could be directly affixed with threaded fittings, we machined a hemispherical Plexiglas cell of ~2-cm³ volume, also silvered on the outside. However, the sensitivity of this cell was 1.8× worse than the glass cell, presumably because of poorer window transparency. This was not further pursued.

The CC exit line proceeds through a small cartridge containing granular activated carbon, which serves to catalytically destroy any excess ozone in the exit stream. (CAUTION: An anonymous reviewer warns that high levels of ozone passage through activated carbon may pose a fire hazard. Catalytic destruction of ozone can also be accomplished by granular MnO_2 and better by activated manganese oxide catalysts such as Carulite 200; see ref 59.) A similar activated carbon cartridge is placed at the inlet of the air pump AP to remove organics that may produce CL when reacting with ozone.

The CL cell CC sits directly on the window of a metal packaged miniature photomultiplier tube (PMT; Hamamatsu photosensor module H5784). The cover glass window is exactly the same size as the square top surface of the PMT, and this makes it easy to affix it in place, first by electrician's black tape and then with aluminum adhesive tape. The PMT has an integrated, low-power consumption, high-voltage supply and a low-noise $i \rightarrow V$ converter, with an 8-mm window (spectral response 300−650 nm). The PMT was operated with a ±12 V external power supply, and the control voltage applied to it was 0.7 V, 70% of the maximum (note that the gain of the detector is an exponential function of the control voltage, such that this is 1/15th of the maximum gain[60]). The output signal from the PMT was further amplified using two serial sequential JFET-input low-noise operational amplifiers in one package (TL 072CN, Texas Instruments). The gain in the first stage is fixed at 50× and is 25× variable in the second stage. The variable gain setting depends on the range of analyte concentration that one is interested in. The final signal is displayed on a digital panel meter on the detector box and is simultaneously acquired by the PC-based data acquisition system. The relevant schematic is given in SI (Figure S2).

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(60) Hamamatsu Corp. Metal Package PMT. H5784 series. http://sales.hamamatsu.com/assets/pdf/parts_H/H5784_series.pdf.

Typical Operational Sequence. A typical operational sequence is as follows: (i) Turn to port H, aspirate 3 mL of sample (in shorthand notation we denote this as →H,3↓); this step could also involve aspirating 3 mL of a standard from port E or any volumetric combination of water (port C) and standard (E) to generate 3 mL of a sample of a desired concentration; (ii) dispense to reactor, →B,3↑; (iii) aspirate 1 mL of H_2SO_4, →F,1↓; (iv) dispense to reactor, →B,1↑; (v) wash syringe with water, →C,4↓; →A,4↑; (vi) repeat previous wash step; (vii) aspirate 0.5 mL of $NaBH_4$, →D,1↓; (viii) dispense to reactor, →B,0.5↑ (this dispensing of borohydride into an acidic sample immediately causes H_2 and AsH_3 to start to evolve); (ix) turn on SV2 and SV3 as soon as dispensing in the previous step is complete to purge the evolved gases to CC; (x) allow 60 s for arsine to be purged, react with ozone in CC, and be measured by the detector; (xi) turn on (open) SV1 to allow the liquid to drain to waste; (xii) close SV1, (xiii) aspirate and dispense 10 mL pf water to rinse reactor R, →C, 10↓, →B,10↑; (xiv) open SV1 to drain the liquid; (xv) close SV2 and SV3 and return to step i. The complete cycle takes ~4 min.

The above steps measure total As. To measure As(III), in step iii, 1 mL of buffer is aspirated, →G,1↓. The following are noteworthy. Liquid is held up in the tube connecting port B and the reactor. For this reason, this tube is made as small as possible (0.5-mm i.d., 15 cm long, total volume 30 μL). When making standards by mixing of water and small volume of a fixed concentration standard, this needs to be borne in mind. For liquid aspiration and delivery, an aspiration and delivery speed of 0.46 mL/s is used except when $NaBH_4$ is delivered; it is desirable for the liquid to mix quickly, and the liquid is delivered at a higher speed of 0.58 mL/s. The entire sequence of operations is fully automated and does not require operator intervention.

For sequential As(III) and As(V) measurement, the above protocol was modified in that in step iii, 1 mL of citrate buffer was aspirated; in step vii, 1 mL of the $NaBH_4$ was aspirated (of which 0.5 mL was delivered in step viii); and after step x, the subsequent steps were as follows: (xi) close SV2 and SV3; (xii) deliver remaining $NaBH_4$ in syringe to R, →B,0.5↑ (this increases the pH of the reaction mixture with excess borohydride solution; (xiii) wash syringe with water, →C,4↓, →A,4↑; (xiv) aspirate and dispense 1 mL of 6 M H_2SO_4, →F,1↓, →B,1↑; (xv) open SV2 and SV3 to purge the evolved gases to CC; (xvi) allow 60 s for arsine to be purged, react with ozone in CC, and be measured by the detector (this gives the second signal of the sequential determination); the subsequent steps involving washing of the reactor and getting it ready for the next determination are identical to steps xi−xv in the previous paragraph. The complete cycle takes ~6 min.

RESULTS AND DISCUSSION

Arsine-Ozone Reaction. Some 25 years ago, Fujiwara et al.[61] first reported gas-phase CL when AsH_3 or SbH_3 was introduced in to an oxygen-rich hydrogen flame. Further studies showed that hydrides of As, Sb, Sn, and Se produced observable CL when reacted directly with ozone in front of a PMT.[50] The most intense CL was produced by the AsH_3−O_3 reaction. Fraser et al. described the CL emission as being a broad bluish continuum from 400 to 520 nm, with maximum at 460 nm.[51,52] They also provided evidence that the excimer $(AsO)_2$* is responsible for the long-lived CL emission.

Although these early pioneering studies were able to reach subnanogram limits of detection (LODs), the setup was neither automated nor simple. Fujiwara et al.[50] acidified a 20-mL water sample with HCl, removed dissolved air by He purging, added $NaBH_4$, and collected the AsH_3 in a liquid N_2 cryotrap after first removing water vapor. On warming the trap, AsH_3 was liberated as a sharp band and allowed to react with the highest concentration of ozone that could be generated (pure oxygen as feed gas to ozonizer). The resulting CL was measured with a state-of -the art photodetector. A decade later, the only time the technique was used to measure As in real samples, an identical approach was used.[54] Fraser and Stedman[53] reported that the emission consisted of two bands, one centered at ~325 nm and the other, much broader band, at ~460 nm. Visible CL detection is preferred because UV-sensitive PMTs are more expensive and also have lower quantum efficiency. This study also showed that, in the presence of significant amounts of oxygen, as would be the case in the presence of air, the intensity of the visible luminescence band decreased ~20×.

These accounts do not suggest a method for arsenic analysis that is obviously simple and affordable. In fact, Galbán et al.[55] last explored this approach a decade ago to make a practical laboratory method. They omitted the cryotrap and used a large benchtop top-of-the-line luminometer of the time (Perkin-Elmer LS-50), equipped with a high-end phototube. However, they reported only weak and irreproducible CL signals and obtained better results in the photoluminescence mode. They still used a water trap, very high ozone concentrations, and an inert purge gas (He/Ar/N_2) and applied the highest possible PMT voltage to the instrument, clearly stating that the lifetime of the PMT was compromised. They reported an LOD of 50 μg/L As for a 3-mL water sample.

Hydride Generation and Stability of Sodium Borohydride Solutions. It is well known that hydride generation provides a unique opportunity of selective volatilization of arsenic and its isolation from the matrix.[62] Quantitative conversion of specific arsenic species to arsine requires optimally controlled pH and $NaBH_4$ concentration.[63] Recent work shows that the As(III) is not reduced to AsH_3 by BH_4^- or "nascent hydrogen" but by hydroboron intermediates.[64] Relative to reduction by zinc and acid, $NaBH_4$ provides many advantages, including pH-based differentiation of As oxidation states. But $NaBH_4$ has two shortcomings. For use in developing countries, it is expensive. Second, for unattended automated use over any significant period, $NaBH_4$ solutions are too unstable. To reduce cost, we elected to use a lower purity (98%) grade of $NaBH_4$. However, we also found that the rate of its hydrolytic decomposition is higher than that of the higher purity material. When prepared in 0.01 M NaOH, such a solution must be prepared daily.[49] A solution of 2% $NaBH_4$ in 0.1 M NaOH was used in most of our early experiments (3 mL of sample + 1 mL of acid/buffer + 1 mL of $NaBH_4$). At laboratory temperature, this could be used no more than 5 days before a decrease in the signal was perceptible. At warmer temperatures in real field use,

(61) Fujiwara, K.; Bower, J. N.; Bradshaw, J. D.; Winefordner, J. D. *Anal. Chim. Acta* **1979**, *109*, 229−239.

(62) Tseng, C. M.; Amouroux, D.; Brindle, I. D.; Donard, O. F. X. *J. Environ. Monit.* **2000**, *2*, 603−613.

(63) Shraim, A.; Chiswell, B.; Olszowy, H. *Talanta* **1999**, *50*, 1109−1127.

(64) D'Ulivo, A.; Onor, M.; Pitzalis, E. *Anal. Chem.* **2004**, *76*, 6342−6352.
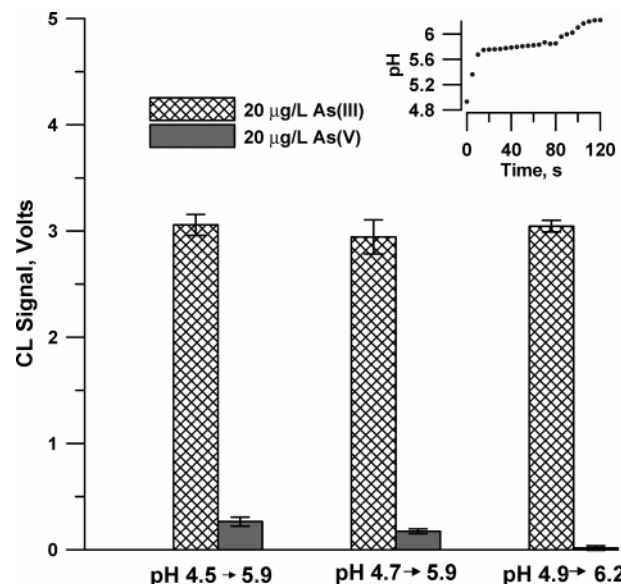
the longevity of such a preprepared reagent solution will obviously be limited and improvements are highly desirable.

The literature on the decomposition of $NaBH_4$ is extensive. Early work[65] suggested that the hydrolysis rate is first order each in the BH_4^- and H^+ concentrations, the product of the rate constant and the hydrogen ion concentration being (0.87, 1.5, and 2.4) $\times$ 10^7 min^{-1} at 15, 25, and 35 °C, respectively. Subsequent work[66] indicated that the rate of decay also contains a proton-independent path; quite possibly this can be related to metal impurities present in the system. The predicted half-lives at 25 °C in this later study was 1.5 orders of magnitude greater than the first work,[65] clearly indicating that impurities play a role. In recent years, the role of heterogeneous metal catalysis as well as metal ion catalysis of borohydride decomposition has been of much interest to generate H_2 for fuel cells.[67,68] We explored water-miscible organic solvents to see if the stability is increased. Solubility of $NaBH_4$ in acetonitrile was very poor. Glycol and amines led to elevated blank signals and generally poorer arsenic signals (probably due to enhanced arsine solubility) making this avenue unattractive.

Based on these results and the prior literature, we experimented with $NaBH_4$ formulations with higher NaOH concentration (1 M). This reagent could be used at the laboratory temperature for at least 25 days. Presumably this can be extended past 1 month by adding even more NaOH. But to get to the final intended pH, a large amount of acid or buffer will be needed. Selective measurement of As(III) at a buffered pH is especially difficult. A significant portion of the alkalinity is due to $NaBH_4$ itself, and the hydrolysis is not rapid at pH greater than ~6. The pH change upon adding $NaBH_4$ is thus not instantaneous. A reagent formulation that involves further increasing the alkali content of the $NaBH_4$ reagent is therefore not acceptable.

We sought instead to suppress trace metal-catalyzed decomposition of $NaBH_4$. Even low concentrations of EDTA were found to be very effective. A solution of 4% $NaBH_4$ in 0.5 M NaOH, 1 mM Na_2EDTA was stable for at least 30 days, even with the 98% pure $NaBH_4$ reagent, and was used henceforth.

Differentiation between As(III) and As(V). Present experiments showed that ~0.4% $NaBH_4$ in the final mixture was adequate to reduce both inorganic As(III) and As(V) to AsH_3 in strongly acidic solution at least up to 2 mg/L As. The differentiation of As(III) and As(V) by pH variation of the generation solution has been reported.[49] These data suggest that between pH 5 and 7, As(III) response is 78.0 $\pm$ 1.0% of that obtained in strongly acidic solution. Under the same conditions, As(V) responds 4.9 $\pm$ 4.8%. For As(III) determination, the desired buffer should have an initial pH of 4−5 and sufficient buffer capacity to prevent a pH much beyond ~7 upon $NaBH_4$ addition. Because the buffer must obviously be used at high concentrations, cost and low As content become important considerations. A KHP buffer was effectively used initially. However, better results were obtained with a 4 M NaH_2PO_4 buffer (pH 4.6). Further studies (Figure 3) with initial pH adjustment with varying amounts of NaOH added suggested we chose an initial pH of 4.9. The inset in Figure 3 shows the pH

(65) Pecsok, R. L. *J. Am. Chem. Soc.* **1953**, *44*, 2862−2864.
(66) Mesmer, R. E.; Jolly, W. L. *Inorg. Chem.* **1962**, *1*, 608−612.
(67) Marsh, S. A.; Parker, D. M.; Pintauro, P. N. PCT Int. Appl. WO 2005049485 A1 20050602, 2005.
(68) Tsang, Joseph W. Eur. Pat. Appl. EP 1369947 A2 20031210, 2003.

Figure 3. Response of As(III) and As(V) for a phosphate buffer of different initial pH. The pH transition indicated in the inset is the change in pH upon addition of the $NaBH_4$ reagent to the pH 4.9 citrate-buffered solution.

change as $NaBH_4$ is added; note that the hydrolysis of $NaBH_4$ requires finite time, especially as pH increases. As in previous work, it is possible to determine total As at pH ≤1 with strong acid and As(III) only at pH >4.9 with buffer. Note that this buffer is only used to measure As(III). Even though reagent grade NaH_2PO_4 may contain arsenic, it is present in the As(V) form. In our experience, most reagent grade $NaH_2PO_4 \cdot H_2O$ produces an acceptable blank for As(III) (≤1 μg/L; see supplementary note 3 in SI).

However, in the present setup, it is also uniquely possible to determine As(III) and As(V) *sequentially* in the same sample. In principle, one would first determine As(III) at a pH of 4−5, add more $NaBH_4$, and then add sufficient strong acid (1 mL 6 M H_2SO_4) to attain a pH of ≤1 and measure As(V). For this purpose, our finding is that the arsenate content of most reagent grade phosphates may be too high for measurement of As(V) at the ≤10 μg/L level. A buffer based on citric acid (citric acid adjusted to the desired pH with NaOH produced lower blanks than sodium citrate) produced superior results. A pH 4.5 citrate buffer produced As(III) signals comparable to that of pH 4.9 phosphate buffer. With further $NaBH_4$ addition and acidification with H_2SO_4 to pH ≤1, the As(V) blank was ~2× lower for the citrate buffer. The data that underlies the choice of the initial citrate buffer pH is given in SI Figure 3a.

Modes of Operation. Fluidically, the present analyzer can be operated in four separate readily configurable modes that affect both the signal intensity and reproducibility: (a) as described in the Experimental Section, SV2,3 are both turned on as soon as the $NaBH_4$ solution is delivered, causing the purge air from SV2 to sweep R headspace and deliver the arsine via SV3 to CC; (b) as in (a), except that the tip of the purge air tube reaches the base of the reactor and allows for sparging of the solution; (c) SV2,3 are kept off such that they are joined to each other and R is isolated; pressure due to evolved H_2 (and AsH_3) is allowed to build up until 10 s after $NaBH_4$ addition, and then SV3 is opened

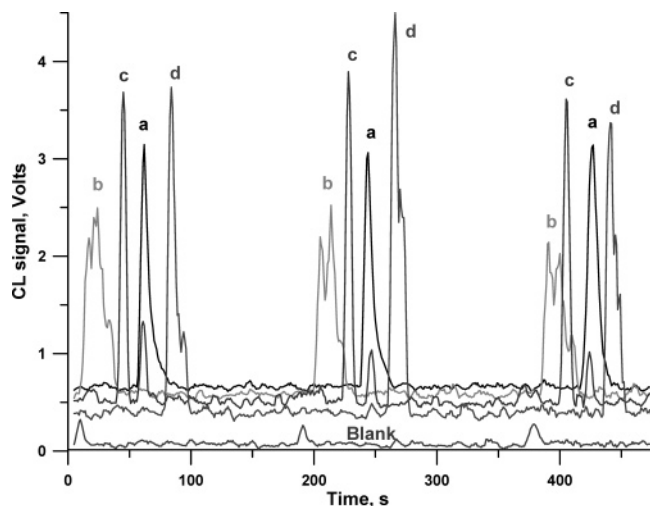**Figure 4.** Response from 20 μg/L As As(III) standards, pH ≤1, in the four different modes. The blank trace is also shown as the very bottom trace. Note that there is a small response associated with borohydride addition even in the absence of As. Some *X*- and *Y*-offsets have been applied to all signals for visual clarity.

for the gases to proceed to the CL reactor. (d) This mode is similar to (c), but SV2 is also opened when SV3 is opened, to allow air to purge the headspace.

Figure 4 shows typical As(III) signals in the four modes obtained in preliminary experiments. The peak intensities (±% rsd) were 2.46 (±2.8%), 1.81 (±10.3%), 3.95 (±1.4%), and 3.49 V (±16.5%) for modes a−d, respectively. The corresponding peak areas were 21.9 (±11.8%), 27.9 (±9.4%), 21.2 (±2.9%), and 30.1 (±16.8%) V·s. Note that mode c produces two peaks; the second smaller peak appears only when the residual solution in reactor R begins to drain through SV1. The above data includes the sum of both the peaks in mode c. While mode c produced the best height and area reproducibilities as well as the maximum signal height, presently we chose to optimize mode a for quantitation purposes. Although it showed slightly poorer reproducibility and lower signal, the ease of data interpretation from a single peak led us to adopt this mode. With better software for quantitation, mode c may be the one of choice in the future.

Parametric Optimization. Purge Air Flow. Approximately 50 mL (at room temperature and atmospheric pressure) of H_2 is evolved from the decomposition of the added $NaBH_4$. The solubility of H_2 in water is negligible; this volume of gas is sufficient to purge the reactor to a reasonable extent. Accordingly, while purging the reactor with additional air helps obtain better signal reproducibility, there is relatively little dependence of the signal on the precise value of the air flow rate. Excessive air flow merely serves to dilute the arsine generated further. An air flow rate of 30 mL/min was chosen.

Ozone Flow and Concentration. Changing the flow through the ozonizer has two opposing effects; increasing the flow results in a temporally sharper signal but reduces the ozone concentration. A flow of 60 mL/min provided optimum results. The ozone concentration from the ozonizer at this flow rate was measured iodometrically to be 0.3% v/v. Putting three ozonizers in series approximately doubled the ozone concentration but increased the signal by only 1.25×; such an effort did not therefore seem worthwhile. Light olefins such as ethene are not efficiently retained

by the activated carbon trap and can contribute to the background chemiluminescence. In the absence of the ozone flow, the background CL signal is essentially the dark current of the PMT. The primary PMT output with and without the ozonizer on is 4.02 and 3.98 mV, respectively. The difference is reproducible. The finite background signal that is observed in the actual experiments is believed to be due to the reaction of ozone with the chamber wall material and background gases. The reaction rates of light olefins with ozone are very fast, however. The reaction half-life for ethene from published rate data[69] is computed to be ~50 ms with 0.3% ozone. The length of the 1.1-mm-i.d. tube leading from the ozonizer to the CL cell was increased to 36 cm (t_R = 340 ms), to allow olefinic gases to react fully before the CL cell was reached. Note also that the AsH_3-O_3 chemiluminescence is not only very intense, the concentration of the gas-phase AsH_3 thus liberated is significant. For a 3-mL sample containing the regulatory limit of 10 μg of As/L (30 ng of As), the AsH_3 concentration released in 50 mL of H_2 will be ~200 ppbv, much higher than commonly occurring olefin concentrations in background air. It is for this reason that light olefins that have not been trapped by the pump inlet and are thus present in the sparging air have a minimal effect even without spectral filtering.

Prereaction. Previous studies of this reaction[51] has shown that the peak emission from the arsine−ozone CL reaction is not instantaneous but reaches a maximum a measurable time after the components are mixed. Retraction of the tube bearing the arsine to different depths within the outer tee (see Figure 2) allows facile variations in the prereaction time in the millisecond time scale before the mixture enters the CL chamber proper. The results of this experiment are shown in SI (Figure S4). In terms of both the signal intensity and the reproducibility, the best results are obtained with the arsine delivery tube retracted 6 mm inside the tee, which amounts to a prereaction time of 5−10 ms (depending on how rapidly the evolved H_2 comes out). This configuration was henceforth used. Considering that the residence time in the CL cell is clearly much larger, it is not clear if the benefits really accrue from a finite prereaction time or better mixing in the much smaller premix zone.

The effect of the cell volume on the signal was examined. An externally silvered 0.85-cm-i.d. glass test tube bottom, 1.5−7.5 cm in length, was used. The maximum cell volume is limited by the length of the test tube. For 1.5-, 2.5-, 5.0-, and 7.5-cm chamber heights (respective volumes 0.9, 1.4, 2.8, 4.3 cm³), the observed signals for a 2 μg/L As(III) standard were 0.199 ± 0.026, 0.511 ± 0.008, 0.512 ± 0.011, and 0.549 ± 0.014 V, respectively. A larger cell volume (longer t_R) allows a greater fraction of the CL to be detected, if, as noted in the prior literature, the CL from the AsH_3-O_3 reaction is relatively long-lasting. But the efficiency of light detection must also decrease as the chamber becomes taller. Obviously a fully optimized instrument should have a larger volume CL chamber along with a larger area photomultiplier tube. Of note is that we conducted the cell volume study after much of the other data reported in this paper were already collected with a 14 mm i.d., ~1.5-cm³ volume cell. For the 2 μg/L As(III) standard, the 0.85 × 25 mm, 1.4-cm³ volume cell actually produced a 1.5× better S/N compared to the cell we have used to generate the other data.

(69) Fatemi, M. H. *Anal. Chim. Acta* **2006**, *44*, 355−363.

System Response. Total Inorganic Arsenic. Under the recommended strongly acidic conditions, both As(III) and As(V) are rapidly and efficiently converted to AsH_3. The observed CL signals are linear with arsenic concentration at least up to a concentration of 1 mg/L. For the range of greatest interest (0−50 μg/L), the calibration equation was

$$\text{peak height,} \quad V = 0.1916(\pm0.0012) \text{ As(III),}$$
$$\mu\text{g/L} + 0.0942(\pm0.0233), \quad (n = 30), \quad r^2 = 0.9997 \quad (1)$$

Although the data above were for As(III), the response from As(V) was statistically indistinguishable, suggesting that either As(III) or As(V) standards can be used as calibrant for total As assays. Either the peak height or the peak area produce linear response; the linear r^2 value for the peak area data for the results corresponding to eq 1 above was 0.9995, for example.

Differential and Sequential Measurement. The response equation for As(III) (0−100 μg/L) with the pH 4.5 citrate buffer was

$$\text{peak height,} \quad V = 0.1797(\pm0.0036) \text{ As(III),}$$
$$\mu\text{g/L} + 0.2832(\pm0.2232), \quad r^2 = 0.9988 \quad (2)$$

The response for a pH 4.9 phosphate buffer was very similar. At this pH, As(V) did not significantly respond with either buffer; data below are for the citrate buffer:

$$\text{peak height,} \quad V = 0.0054(\pm0.0006) \text{ As(V),}$$
$$\mu\text{g/L} + 0.3373(\pm0.0342), \quad r^2 = 0.9692 \quad (3)$$

It would be apparent that at pH 4−5, As(III) is determined with a very high degree of selectivity. The concentrations of As(V) in a sample can be determined by the difference between total As measured at a low pH and As(III) determined at this buffered pH with the implicit assumption that there are negligible amounts of organic As present (this generally holds true for groundwater samples). The response of organic As is lower (vide infra).

As previously outlined, the alternative to making As(V) measurement by difference is to remeasure the same sample aliquot after it has been measured at pH 4−5. The advantages include lower overall analysis time, lower overall sample requirement, and better accuracy in As(V) measurements, especially at low As(V) levels because the first approach relies on the difference between two large numbers. There is very little response from As(V) in the first step ($\sim$30$\times$ lower than that of As(III)); however, not all the As(III) appears to be converted to AsH_3 in the first step in our conditions. The residual As(III) produces a signal in the second step that best fits a quadratic response:

$$\text{peak height,} \quad V = -0.00809(\text{As(III),} \mu\text{g/L}),$$
$$+ 0.00042(\text{As(III),} \mu\text{g/L})^2 + 0.1363, \quad r^2 = 0.9816 \quad (4)$$

It is not presently clear why the signal from the residual As(III), albeit small, exhibits a quadratic dependence on As(III) concentration, at least within the As(III) concentration range examined ($\leq$1 mg/L). The As(V) signal in the second step exhibits a linear response, however:

$$\text{peak height,} \quad V = 0.0822(\pm0.0019) \text{ As(V),}$$
$$\mu\text{g/L} + 0.0717(\pm0.1136), \quad r^2 = 0.9985 \quad (5)$$

The sequential analysis data above were generated with pure standards of each oxidation state. Samples containing mixtures of arsenic in both oxidation states were analyzed to test any interaction between species. The data shown in Table 1 were fit with a nonlinear least-squares fitting model using MS Excel Solver.[70] The first signal S_1 best fits a linear model that includes both As(III) and As(V):

$$\text{signal 1 } (S_1) \text{ height,} \quad V = 0.1793 \text{ As(III),}$$
$$\mu\text{g/L} + 5.909 \times 10^{-3} \text{ As(V), } \mu\text{g/L} + 0.3514 \quad (6)$$

This is very close to what would be expected from eqs 2 and 3 obtained with As(III) only and As(V) only, by far the dominant component in eq 6 is the As(III) term, and this is identical within experimental uncertainty to that given in eq 2. Similarly, a model that best fits the second signal S_2 involves a quadratic dependence on As(III) and a linear dependence on As(V), similar to eqs 4 and 5. Again, the dominant terms have coefficients essentially identical to those in eqs 4 and 5 (all concentrations are in μg/L):

$$\text{signal 2 } (S_2) \text{ height,} \quad V = -3.83 \times 10^{-3} \text{ (As(III))} +$$
$$3.89 \times 10^{-4} \text{ (As(III))}^2 + 0.0804 \text{ As(V)} + 0.055 \quad (7)$$

These results suggest that there is no significant interaction between As(III) and As(V) during this analysis.

Algebraic transformation of eqs 6 and 7 produce eqs 8 and 9 that allow us to calculate the concentrations of As(III) and As(V):

$$\text{As(III),} \mu\text{g/L} =$$
$$3.137 \times 10^3 - 50.68(3.835 \times 10^3 - 13.6S_1 + S_2)^{0.5} \quad (8)$$

$$\text{As(V),} \mu\text{g/L} =$$
$$(S_1 - 0.351 - 0.179 \text{ As(III)})/5.9 \times 10^{-3} \quad (9)$$

The values so calculated are also listed in Table 1 and obviously are in good agreement with the actual concentrations.

Organic Arsenic. In freshwater bodies, organic As can sometimes occur in measurable concentrations. The two most common species are MMA and DMA, both of which contain As in the +5 oxidation state. Both compounds respond only in the pH $\leq$1 assay. On an equimolar basis, response from MMA and DMA are $\sim$65 and $\sim$15%, respectively, of that of inorganic As(V). We believe that the corresponding arsines are formed: the response trend is consistent with the relative volatilities of the respective arsine species; AsH_3, CH_3AsH_2, and $(CH_3)_2AsH$ have boiling points of −55, 2, and 36 °C, respectively. Tetraphenylarsonium chloride did not produce a measurable response.

Interference Studies. It is well known that ozone can produce CL with many volatile gases. However, relative to the CL from

(70) Walsh, S.; Diamond D. *Talanta* **1995**, *42*, 561−572.

Table 1. Sequential Analysis Data for As(III)−As(V) Mixtures

As III μg/L taken	As V μg/L taken	S1, V (mean ± sd)	S2, V (mean ± sd)	As(III) calcd from eq 8	As(V) calcd from eq 9
0	0	0.3514 ± 0.060	0.055 ± 0.049	−(0.00 ± 1.27)	0.00 ± 0.60
0	100	0.890 ± 0.058	8.1396 ± 0.150	−(0.31 ± 1.62)	100.58 ± 0.16
25	75	5.494 ± 0.232	6.044 ± 0.130	26.30 ± 1.67	72.43 ± 1.10
50	50	9.229 ± 0.255	5.124 ± 0.144	47.73 ± 0.69	54.32 ± 0.90
75	25	14.260 ± 0.686	3.792 ± 0.133	76.87 ± 0.57	21.55 ± 1.09
100	0	18.179 ± 0.127	3.605 ± 0.109	99.41 ± 1.07	1.83 ± 1.05

Table 2. Results from Interference Studies of Common Ions in Water Samples

potential interference (concn) in 10 μg/L As(III) solution	exptl results (μg/L)	
	total As	As III
sulfide (1 mg/L)	9.7 ± 0.2	9.8 ± 0.3
silicate (1 mg/L)	9.5 ± 0.2	9.3 ± 0.3
nitrate (10 mg/L)	9.6 ± 0.2	9.3 ± 0.3
phosphate (10 mg/L)	9.4 ± 0.2	9.6 ± 0.3
chloride (100 mg/L)	9.7 ± 0.2	9.8 ± 0.3
sulfate (100 mg/L)	10.2 ± 0.2	10.6 ± 0.3
bicarbonate (100 mg/L)	9.9 ± 0.2	9.8 ± 0.3

AsH_3, most of these produce weak luminescence. The intensity of the well-known CL reaction of NO with O_3 is very weak at ambient pressures. The available literature indicates that H_2S and its methylated analogues also produce CL with ozone at ambient pressures, but this luminescence is centered in the UV where the present PMT has minimal response. In so far as drinking water is concerned, the presence of reduced sulfur compounds in sufficient concentration to cause interference in As measurements is unlikely because of the associated odor. Among hydrides that will produce CL with ozone, neither PH_3 nor SiH_4 can be produced in aqueous media.[71] Spectral filtration was not presently practiced but, if needed, can be easily implemented to improve selectivity.

We separately determined the effect of 1−100 mg/L of common ions added to 10 μg/L As(III) and 10 μg/L As(V) in As-(III) and total As assays separately. These results, summarized in Table 2, show that the system produces no detectable response from phosphate (As(III) measurement carried out in citrate-buffered media) and silicate, both of which respond in the spectrophotometric molybdenum blue method. No significant interference was observed from bicarbonate, nitrate, sulfate, and most notably sulfide, under the conditions tested.

Antimony and tin are known to produce hydrides that produce CL with O_3, albeit this CL is much weaker than that with arsenic. In the pH ≤1 measurement regime, it required 600 and 1100 μg/L Sb and Sn, respectively, to produce a response comparable to 10 μg/L As. This is consistent with the findings of Fujiwara et al.[50] that the LODs they could obtain for Sb and Sn were respectively ~67 and ~230 times worse than for arsenic. For real drinking water samples, these metals are unlikely to present a problem.

Tap Water and Groundwater Samples. Instrument performance was initially tested with municipal tap water samples in Lubbock, TX. The values ranged from 1.1 to 3.1 μg/L As. No As-(III) was detected at any time, consistent with chlorination of the water that the city practices. Within the same period, the city reported an As concentration of 0.5−4.1 μg/L by GFAAS.

Table 3. As Content of Southern High Plains Groundwater Samples

sample	As(III)	As(V)
	μg/L	μg/L
A	2.73	1.97
B	10.45	0.79
C	16.45	3.60
D	7.39	0.26
E	11.83	2.81

Groundwater samples from the southern high plains are characterized by their high salinity and often represent an analytical challenge.[72] We measured the total As and As(III) content of several groundwater samples and obtained As(V) by the difference method; some typical results, shown in Table 3, indicated that the dominant form of As is As(III), especially when the total As content is high. The samples were then spiked with known amounts of As(III) and As(V) from 5 to 35 μg/L. Total As and As(III) determinations were then separately carried out, with quantitative recoveries as indicated below:

$$\text{As(III) recovered, } \mu\text{g/L} = 1.0050(\pm0.0421) \text{ As(III) spiked,}$$
$$\mu\text{g/L} + 0.1239(\pm0.4577), \quad r^2 = 0.9948 \quad (10)$$

$$\text{As}_{\text{Total}} \text{ recovered, } \mu\text{g/L} = 1.0055(\pm0.0113) \text{ As}_{\text{Total}} \text{ spiked,}$$
$$\mu\text{g/L} - 0.2702(\pm0.2111), \quad r^2 = 0.9992 \quad (11)$$

Method Intercomparison. In a collaborative experiment, the U.S. Geological Survey supplied 12 samples preserved with EDTA. These samples were previously analyzed for arsenite, arsenate, MMA, and DMA using LC−ICPMS. Analyses in our laboratory were conducted blind to these results. The amounts of sample supplied were generally insufficient to carry out triplicate analyses with 3-mL samples. One sample was <1 mL and was not analyzed. For the other 11, our method was therefore modified to analyze 1-mL sample aliquots (3 replicates). All other reagent volumes were proportionately decreased. The sensitivity was still sufficient for submicrogram per liter- As analysis.

Figure 5 shows the comparison of the results (a colored version of this plot, easier to perceive, is given in SI as Figure S5). The bar graph (sample numbers on the bottom abscissa) shows the data for each sample, the left and right bars of each pair corresponding to the USGS, and the present instrument data, respectively, left ordinate pertaining to both. In a few of the samples, USGS reported measurable concentrations of MMA and/

(71) Matsumoto, K.; Fujiwara, K.; Fuwa, K. *Anal. Chem.* **1983**, *55*, 1665−1668.

(72) Tian, K.; Dasgupta, P. K.; Anderson, T. A. *Anal. Chem.* **2003**, *75*, 701−706.
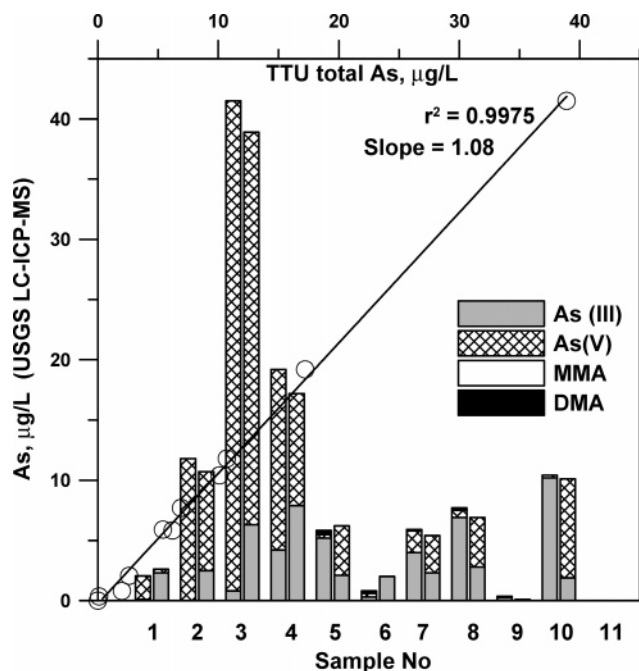
Figure 5. U.S. Geological Survey LC−ICPMS results vs data from present approach. See text for details.

or DMA; admittedly, the exact values will be difficult to decipher in this figure. Our technique cannot distinguish between As(V) and the two organoarsenic compounds. The open circles are the TTU total As values (upper abscissa) plotted against the USGS total As values. The overall correlation for total As is excellent, especially considering blind analysis, independent calibration standards, and the fact that although MMA and DMA respond in our system, their response is substantially smaller than those of the inorganic As species. Also notable are samples 9 and 11; the original analytical data supplied to us differed significantly from our results to prompt us to send back these two samples for reanalysis. In both cases, just as we found in our measurements, sample 11 contained no detectable As in the repeat analysis and sample 9 contained As near the LOD.

Relative to total As, the agreement on the oxidation-state speciated As values was clearly less ideal. In most cases, the present assay reported more As(V) than was reported in the USGS analysis. There was a large amount of iron in these samples, and the oxidation of As(III) to As(V) may not have been completely prevented. Although EDTA preservation is generally effective, Gallagher et al.[73] observed the conversion of up to $2-3$ μg/L As-(III) to As(V) for storage periods of $14-27$ days. The present samples were stored 60+ days between the two sets of analyses.

Analytical Figures of Merit. With a primary PMT gain control voltage of 0.7 V and 1000× secondary amplification, the output reaches near saturation (10 V) with 50 μg/L As. For trace analysis, 0.9 V is preferred as the primary PMT gain control voltage with adjustment of secondary amplification as needed. Figure 6 shows data traces for the otherwise optimized instrument (CC volume 1.5 cm³) for a total As ($0-40$ μg/L, pH ≤1) calibration series with each concentration run in triplicate. Inset a shows a magnified view of blank and a 1 μg/L standard under the same conditions.

(73) Gallagher, P. A.; Schwegel, C. A.; Wei, X.; Creed, J. T. *J. Environ. Monit.* **2001**, *3*, 371−376.
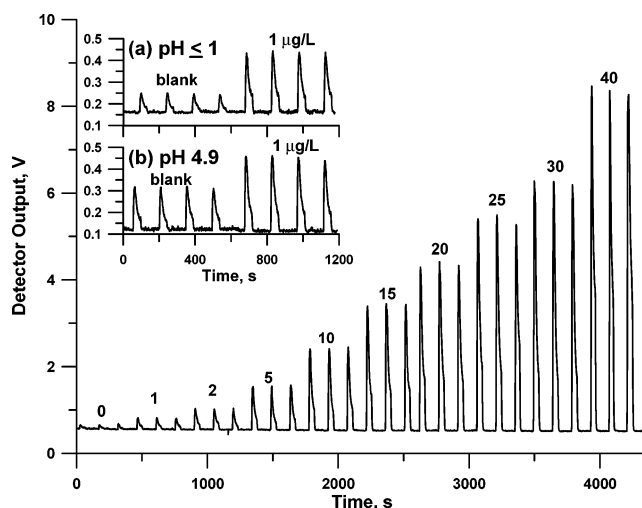
Figure 6. Typical system output for total As (As(III) standards were used here); concentrations (μg/L) are indicated on top of each triplicate set. Inset a shows magnified view of response of blank and 1 μg/L As standard. Inset b shows the response for blank (pH 4.5 citrate buffer) and 1 μg/L As(III) standard.

For a 3-mL sample as used here, the S/N = 3 LOD based on the standard deviation of the blank as shown in Figure 6a is estimated to be 0.05 μg/L. Inset b shows the response for As(III) in a pH 4.5 citrate buffer. In this case, the blank from the significant buffer present is discernibly higher and the net signal is also lower, resulting in a somewhat poorer LOD of 0.09 μg/L.

CONCLUSION AND FUTURE WORK

We have described here a fully automated sensitive instrument that can be assembled at modest cost and thus can potentially replace toxic mercuric bromide-based test kits. We have greatly improved the longevity of NaBH₄ solutions to permit facile field use. The approach offers a reasonably fast turnaround time with modest consumable cost. Ongoing exploration of the technique as a postcolumn detector to the speciation of both inorganic and organic As species appears very promising. Following other pioneering work in the literature, we have also succeeded in reducing the arsenic to arsine electrochemically rather than by chemical reduction. These developments will be reported soon. The need to develop better, more affordable, field-deployable instruments for speciated As analysis is not a matter of academic curiosity. It is a real societal issue in places that can least afford expensive instruments. To this end, we provide a complete parts list in Supporting Information (Table S6) and will provide reasonable advisory assistance to those interested in building such instruments for nonprofit purposes.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.