High Sensitivity Arsenic Analyzer Based on Liquid-reagent-free Hydride Generation and Chemiluminescence Detection for On-site Water Analysis

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In this work, a portable and reliable instrument based on manual hydride generation and subsequent ozone induced chemiluminescence analysis was developed and optimized for measurement of aqueous arsenic in drinking water. The aim was to develop a system for use in the field in villages in developing countries where water treatment systems have been installed. Consequently, it is beneficial that the system could be operated without reagent solutions or purified water. Arsenic trihydride (arsine) was generated by reaction with solid acid and solid borohydride, and then introduced to a chemiluminescence cell where the arsine was mixed with ozone to generate chemiluminescence. The measurement could be repeated with the throughput of 60 times h^{-1}, and the limit of detection was 0.4 µg L^{-1}. The measurable arsenic concentration was up to 1 mg L^{-1} for 2 mL samples. The system was evaluated for analysis of natural water samples, and the obtained data agreed well with those from ICP-MS and sequential hydride generation flow analysis. We expect this small and inexpensive instrument will be used in developing countries.

Introduction

One of the authors has contributed to development of a water treatment system, Yamaha Total Ecological Purification System,[1] to provide safe drinking water to small villages in developing countries, especially in Southeast Asia. Before installing a water system in a new area, the quality of the source water needs to be determined by the installers. To ensure water safety, it is preferable that the village people monitor the water quality after installation. The largest contamination concern is for arsenic contained in the water. Arsenite binds to sulfhydryl (–SH) groups and has broad toxicity,[2] which impairs the function of many proteins.[3] Chronic ingestion of inorganic arsenic causes cancer of the skin, bladder, and lungs, as well as neurological and cardiovascular problems.[4] The presence of arsenic in water and its toxic effect on humans through drinking and agricultural practices is a serious global environmental problem.

Many analytical methods have been developed to measure arsenic in water samples, including electrospray ionization mass spectrometry,[5] ion chromatography–hydride generation–atomic fluorescence spectrometry,[6] and automated hydride generation interfaced to ICP-MS.[7] Although these methods are highly sensitive, they unfortunately cannot be used in villages because they are time consuming and expensive. As simpler methods, flow analysis and sequential analysis were applied to determine trace arsenic with arsine vapor generation and applied to field analysis,[8,9] investigation of arsenic removal,[10] and leaching from contaminated sediments.[11] Generated arsine vapor can also be analyzed by chemiluminescence (CL) detection.[12,13] Arsine vapor has been generated electrochemically, which eliminates the need for a chemical reducing agent.[14] For on-site analysis of arsenic, several approaches have been reported such as electrochemical micro determinations,[15,16] colorimetric assay using nanoparticle formation,[17] and selective coprecipitation with $BaSO_4$.[18] A popular conventional field analysis kit is based on separation of arsenic from possible interferences by generation of volatile arsine by reduction using metallic zinc or sodium borohydride ($NaBH_4$) in an acidic medium. The arsine gas is passed through a mercuric bromide impregnated paper strip, which changes color to yellow if arsenic is present in the sample. Generally, users compare the color with a reference color chart to quantify the level of arsenic present in the tested sample. Color sensitivity of the human eye, color degradation in sunlight, and arsine generation with zinc sometimes produce false results with this method.[19] Another weakness of this approach is the use of highly concentrated hydrochloric acid to acidify the sample. Transportation and handling of inorganic acids for field measurements is difficult and dangerous for users without any formal chemistry training. In addition, in arsenic-affected areas it can be difficult to obtain pure water to prepare the required reagents.

In this work, a small and inexpensive instrument was developed for measurement of arsenic in drinking water based on manual hydride generation and chemiluminescence detection (HG-CL).

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Experimental

Reagents

Standard stock solutions of 100 mg L^{-1} As(III) and As(V) were prepared using sodium meta-arsenite (Wako Pure Chemical Industries, Osaka, Japan) and disodium hydrogen arsenate heptahydrate (Nacalai Tesque, Kyoto, Japan), respectively, along with 0.18 mol L^{-1} H_2SO_4. For arsenic measurements, the acid and reductant were introduced in solid form. For one analysis, a pellet of tartaric acid (0.3 g) mixed with ethylenediamine tetra-acetate disodium salt (EDTA2Na) (10 mg) prepared by compression was used; EDTA2Na was for elimination of interference from heavy metal ions. Sodium borohydride ($NaBH_4$, 25 mg) powder was wrapped in a sheet of oblate (BOC oblate, Takikawa Oblate Co., Shinshiro, Japan), which is a starch-based wrapping usually used for powdered medicines. The pellet and oblate-covered reductant were stored in plastic film canisters with a silica gel pack. To prepare arsenic free samples in the field, the following two types of material were tested: a cerium hydroxide based arsenic removal agent (READ-As, Nihonkaisui, Tokyo, Japan) and a porous ceramic-rare earth compound (ADCERA, Nippon Sheet Glass, Tokyo, Japan).

Instrumental system

The HG-CL system is illustrated in Fig. 1. The system included an arsine generator and a gas phase CL detector. The arsine generator was made of a 50-mL plastic sample tube. The cap of the sample tube was connected to a CL cell *via* a stopcock (AP13SCL2XFCL, Ark-Plas Products®, Flippin, AR), a diaphragm check valve (CV3030VP, AsOne, Tokyo, Japan) and a 1/16" tee connector (P727, UpChurch Scientific, Oak Habor, WA), which had the holes enlarged to 2 mm using a drill bit. The stopcock and check valve were connected by 1/16" polytetrafluoroethylene (PTFE) tube (1/16" o.d. × 0.33 mm i.d. × 30 cm). The CL cell was made in our laboratory from a cylindrical glass tube (22 mm i.d. × 202 mm). The outside of the glass tube was coated with chromium film by RF sputtering to make the cell inside mirror-like, and then covered with black spray paint to protect the metal layer and make the cell opaque. During the metal-film and paint preparation, an 11 × 11 mm area on the flat bottom of the glass tube was masked with tape to make an optical window on which a small photomultiplier tube (PMT) module (H5784, Hamamatsu Photonics, Hamamatsu, Japan) was placed. High performance photodiodes OPT301 (Texas Instruments, Dallas, TX) and S9270 (Hamamatsu Photonics) were also tested for miniaturizing the detection device. Ozone gas was introduced *via* the 1/16" plastic tee connector, and arsine gas and O_3 were introduced into the cell *via* the tube-in-tube insert. The formed arsine gas and introduced O_3 were mixed 80 mm in front of the optical window. A small airpump (CM-15-12, Enomoto Micro Pump, Tokyo, Japan) was used to supply air at 100 mL min^{-1} for O_3 formation. After the air passed through a silica gel column (ϕ15 × 110 mm) and flow restriction tube (PTFE, 0.3 mm i.d. × 460 mm), O_3 was formed by an O_3 generator that used a corona discharge-cylindrical tube (Cylindrical A, 1000BT-12 (300 mg h^{-1}), Enaly, Shanghai, China). Other O_3 generators tested were Cylindrical B (OZX-300AT (200 mg h^{-1}), Enaly), Cylindrical C (OZX-300U (200 – 300 mg h^{-1}), Enaly), Cylindrical D (OZS-0230, Nomura Electronics, Osaka, Japan), a planar discharge electrode (1100N/LHV09K-12, Logy Electric, Tokyo, Japan) and a UV-lamp (SP-5-2H/PE-5D, Sen Lights, Toyonaka, Japan) placed in a stainless-steel tube air flow line. Waste from the CL cell was treated with
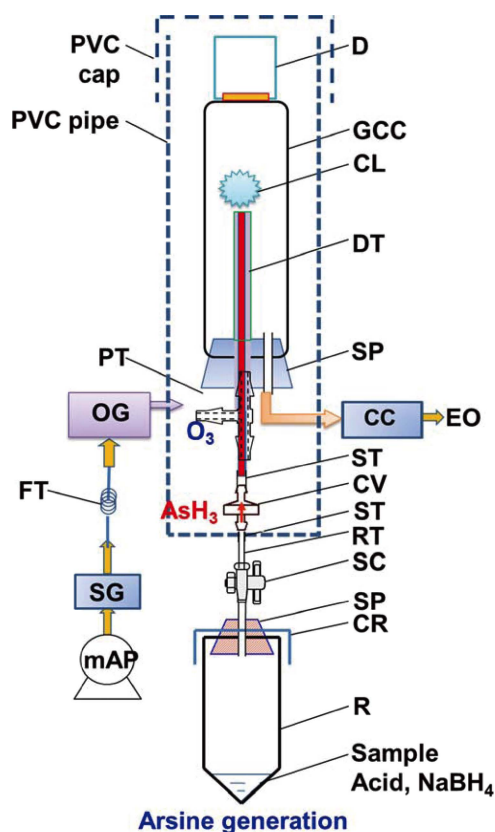

Fig. 1 The HG-CL system. mAP, miniature airpump; SG, silica gel column; FT, flow restricting tube for O_3 air flow; OG, O_3 generator; PT, polyether ether ketone tee connector; R, reactor for AsH_3 generation; CR, cap for reactor; SP, silicone plug; SC, stopcock; RT, restrictor tube for AsH_3 introduction; ST, silicone tube; CV, check valve; DT, double tubes for AsH_3/O_3 introduction (tube-in-tube); GCC, glass chemiluminescence cell; CL, chemiluminescence; D, photo detector; CC, charcoal column; EO, exhaust outlet; PVC pipe and cap, pipe and cap made of polyvinyl chloride.

a small charcoal column to remove O_3. The PMT module and CL cell were placed in a polyvinyl chloride (PVC) tube (30.9 mm i.d. × 38.3 mm o.d. × 307 mm) to protect the cell and stabilize the signal. The control voltage for the PMT module was 0.6 V, and the signal was amplified one hundred times and recorded by a data logger (8421, Hioki, Ueda, Japan). The whole instrument comprised of a CL cell unit (ϕ38 × 307 mm, 0.4 kg), an arsine generator (50 mL sample tube) and an O_3 generator (200 × 210 × 110 mm, 2.6 kg, including the airpump, air dryer tube) was operated by 12 V dc or 100 V ac.

Measurement procedure

First, the instrument was turned on and O_3 was introduced to the CL cell continuously. The tartaric acid/EDTA2Na pellet (or powder mixture) was placed in the bottom of a 50-mL reactor tube and 2 mL of the water sample was introduced using a 2.5-mL disposable plastic syringe. After shaking well, 25 mg of oblate-wrapped $NaBH_4$ was added, and a silicone cap was placed on the tube immediately. The tube was shaken for 20 – 30 s to generate H_2 and AsH_3, and then the stopcock was opened to introduce AsH_3 into the CL cell. The AsH_3 reacted with O_3 in the cell and CL was detected with the photodetector. The response peak appeared in the CL signal within 1 min. After close of the stopcock, the sample tube containing acid and reductant was exchanged for the next measurement. To obtain a

blank signal in the field, 15 mL of water was shaken with 2.5 g of READ-As and 2.5 g of ADCERA in a 50-mL plastic sample tube for 5 min, and the upper clear layer was taken as the blank sample. If interference from reduced sulfur compounds was of concern, such as in cases where the water had an odor, air was bubbled though the acidified water sample before addition of $NaBH_4$.

Sample measurements

For comparison of data with other methods, fifteen river water samples were collected from a river near a closed mine, and five ground water samples were collected from fixed-point observation wells in Kumamoto city, Japan. The samples were preserved in a refrigerator until analysis. Before analysis, the samples were filtered with 0.45 μm cellulose acetate filters and then analyzed by ICP-MS, by the "Arsenator" commercial field kit (Digital Arsenic Test Kit, WAG-WEI0500, Wagtech, Tyne and Wear, UK),[20] by sequential hydride generation flow injection analysis (SHGFIA)[10] and by the HG-CL method developed in the present research.

In the ICP-MS analysis, arsenic was measured by high-resolution ICP-MS (Element, Thermo Fisher Scientific) at m/z 74.884 – 74.959 with 1300 W RF power, 16.7 L min^{-1} of total argon flow, and a resolution of 8000. Yttrium was added to be 1 μg L^{-1} in each sample as an internal standard. Sample and standard solutions were introduced into the nebulizer at 0.1 mL min^{-1}.

For analysis by the Arsenator kit, 50 mL of sample water was treated with two types of reagent and left to stand for 20 min to allow AsH_3 to vaporize. After 20 min of AsH_3 generation, the color formed on a paper strip placed above the AsH_3 generator was measured with an equipped digital meter to display the arsenic concentration in μg L^{-1}. The measurement range of the kit was from 2 to 100 μg L^{-1} with a resolution of 1 μg L^{-1}.

Analysis by SHGFIA was performed as described previously.[10] Detection is based on slow generation of AsH_3, collection of all the generated AsH_3, and subsequent flow based analysis with molybdenum blue chemistry. AsH_3 generation/collection and measurement was carried out automatically.

Results and Discussion

Optimization of reagents

The aim of this work was to develop an instrument that could be used in the field for arsenic analysis. In rural areas of developing countries, it is difficult to obtain pure water, which makes it difficult to prepare reagent solutions. Therefore, we initially tried to develop a procedure that did not require pure water or reagent solutions.

Solid organic acids were tested as well as liquid inorganic acids. Baghel *et al*. used oxalic acid with magnesium as the reductant and it took 10 min to obtain a limit of detection of 10 μg L^{-1}.[21] However, oxalic acid did not dissolve easily in the small volume samples used in the present study. The results for 100 μg L^{-1} As(III) and As(V) with the acids tested are summarized in Table 1. All acids were added at 3 eq L^{-1}. Some of the acids did not produce similar signal intensities for As(III) and As(V), especially citric acid, maleic acid, malonic acid, and ascorbic acid. Hydride generation from As(V) requires two step reductions (As(V) → As(III) → AsH_3) and under more severe conditions compared to those for As(III). The first reduction step, As(V) to As(III), proceeds smoothly from fully protonated form of arsenate (pK_{a1} = 2.3).[22] Citric, malonic, and ascorbic acids did not make pH low enough for arsenate protonation.

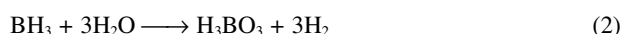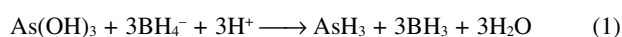Table 1   Response of the HG-CL method with various acids for 100 μg L^{-1} arsenic

| Acid | Concent-ration/M | pH[a] | Relative peak height[b] | | Ratio As(V)/As(III) |
			As(III)	As(V)	
Inorganic acid					
HCl	3.0	0.01	1.098 ± 0.015	1.089 ± 0.007	0.992
H_3PO_4	1.0	1.50	0.709 ± 0.002	0.526 ± 0.022	0.742
H_2SO_4	1.5	0.43	0.836 ± 0.012	0.753 ± 0.004	0.901
Organic acid					
Citric	1.0	1.85	0.982 ± 0.041	0.428 ± 0.002	0.436
Tartaric	1.5	1.43	1.000 ± 0.015	0.977 ± 0.021	0.977
Malic	1.5	1.90	0.913 ± 0.010	0.805 ± 0.001	0.882
Maleic	1.5	1.25	0.639 ± 0.004	0.536 ± 0.017	0.839
Malonic	1.5	1.98	0.668 ± 0.002	0.546 ± 0.003	0.817
Ascorbic	1.5	3.41	0.513 ± 0.020	0.087 ± 0.009	0.170
Tartaric acid	0.25	3.88	1.041 ± 0.014	0.887 ± 0.013	0.852
	0.5	2.56	1.030 ± 0.002	0.985 ± 0.002	0.956
	1.0	1.76	1.031 ± 0.005	1.032 ± 0.003	1.000
	1.5	1.46	1.000 ± 0.030	0.977 ± 0.021	0.977
	2.0	1.30	0.961 ± 0.047	0.942 ± 0.030	0.980
	2.5	1.17	1.024 ± 0.028	0.844 ± 0.019	0.824
	3.0	1.07	1.035 ± 0.020	0.759 ± 0.041	0.733

a. pH after AsH_3 generation,
b. Data are presented as the average ± standard deviation after normalization with 1.5 M tartaric acid data.

Tartaric acid (final pH 1.43), on the other hand, gave the same signal intensities for As(III) and As(V). Though the pH with maleic acid was low enough (pH 1.25), the signal intensities for As(III) and As(V) were not the same. Probably this was because proton addition reaction at the double bonds of maleic acid molecules might consume $NaBH_4$ to inhibit the reduction of arsenate. Among the acids tested, tartaric acid was the best so the effect of tartaric acid concentration was examined. More than 2 mol L^{-1} of the acid made the arsine generation worse especially from As(V) probably due to high ionic strength. When 0.5 to 2.0 tartaric acid was used, the response signals for As(III) and As(V) were almost constant and equivalent to each other. From these results, 1.0 mol L^{-1} tartaric acid (0.3 g) was used for each 2 mL sample for arsine generation without pre-reduction of As(V).

Tartaric acid was tested in powder and pellet forms: the form of the reagent did not affect the signal. Solid EDTA2Na was mixed with the solid acid to mask heavy metal ions, and both solid reagents dissolved in water quickly and were convenient for field use. $NaBH_4$ was added as a reducing agent. Immediately after $NaBH_4$ addition, H_2 gas formed, which may lead to leaking of the analyte AsH_3 from the reactor tube with H_2 before capping. To overcome this problem, we wrapped $NaBH_4$ in a sheet of oblate. This wrapping was beneficial for field use because the required mass of $NaBH_4$ could be weighed into a convenient pack for use in the field.   Furthermore, the wrapping delayed the start of reaction of $NaBH_4$ after its introduction into the reactor tube. The mass of $NaBH_4$ required for one analysis was only 25 mg, which was sufficient to convert the arsenic to arsine gas completely.[11] Too much $NaBH_4$ (*e.g.* 40 mg) caused headspace gas to leak from the generator. With 25 mg of $NaBH_4$, about 50 mL of H_2 was generated because of reactions 1 and 2 as follows:[23]
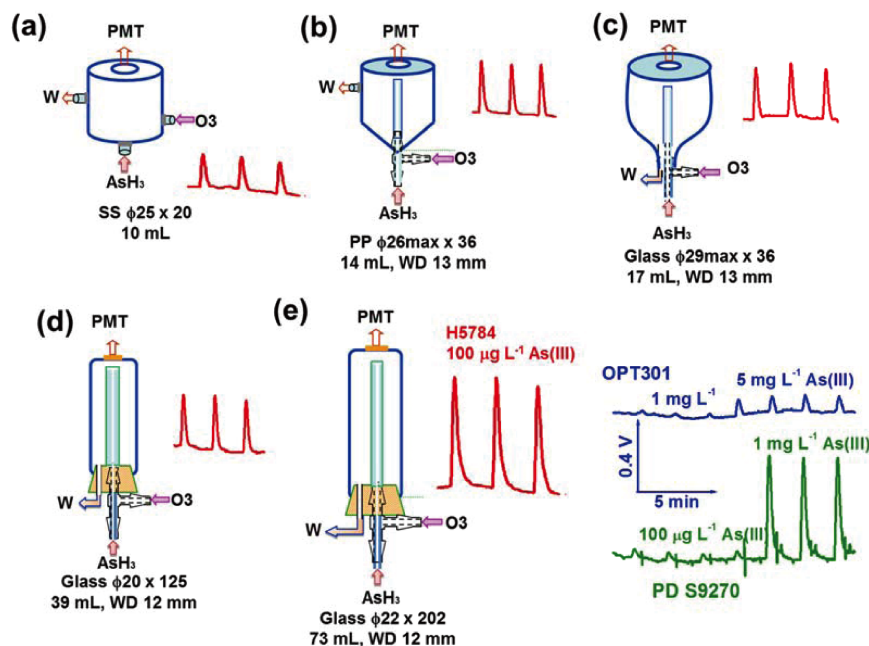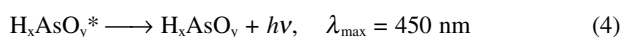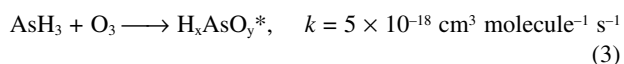
$$As(OH)_3 + 3BH_4^- + 3H^+ \longrightarrow AsH_3 + 3BH_3 + 3H_2O \qquad (1)$$

$$BH_3 + 3H_2O \longrightarrow H_3BO_3 + 3H_2 \qquad (2)$$

Fig. 2   Testing of CL cells and their performance.   Response signals shown were obtained for 100 µg L^{-1} As(III). AsH$_3$ gas was generated as reported previously.[10] The cell in (e) was tested with the following photodetectors: small PMT module H5784, miniature photodiode integrated with amplification circuit OPT301, and large sensitive area photodiode S9270. WD means the working distance between the end of the gas inlet tube and the optical window.

The estimated final pressure in the generator was 2 atm (0.2 MPa). Thus, after the stopcock was opened, half of the headspace gas was introduced to the CL cell.

   Preparation of arsenic-free water was investigated for the blank test. In the polluted field test areas, the available water might be contaminated and not suitable for use as a blank test. The following two arsenic adsorbents were tested for arsenic removal from the water samples: READ-As and ADCERA. READ-As and ADCERA acted as good adsorbents for As(III) and As(V), respectively. When 100 µg L^{-1} As(III) and As(V) solutions were passed separately through a column packed with 10 g of READ-As, the As(III) and As(V) concentrations in the eluent were 1.5 and 5.9 µg L^{-1}, respectively. When the column was packed with ADCERA, the As(III) and As(V) concentrations in the eluent were 14.8 and 0.5 µg L^{-1}, respectively. Consequently, a mixture of both adsorbents (1:1) was used in the developed method to remove both As(III) and As(V) effectively. Batch treatment is easier to perform than column treatment in the field. Therefore, a batch test was conducted with 5 g of the adsorbent mixture and 15 mL of arsenic-spiked water (100 µg L^{-1} As(III) + As(V)), which was shaken for >5 min and left to stand for 25 min. This resulted in a total arsenic removal rate of >99%.

Investigation of CL cell

   Arsine reacts with O$_3$ to produce CL[24] as follows:

$$AsH_3 + O_3 \longrightarrow H_xAsO_y^*, \quad k = 5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{3}$$

$$H_xAsO_y^* \longrightarrow H_xAsO_y + h\nu, \quad \lambda_{max} = 450 \text{ nm} \tag{4}$$

Several attempts to measure AsH$_3$/O$_3$ CL have been reported. However, there are few reports of CL cells for this reaction.

In the present study, several types of CL cell (Fig. 2) made of different materials were tested, including cells made of stainless-steel (Fig. 2(a)), polypropylene (Fig. 2(b)) and glass (Figs. 2(c) – 2(e)). The cell made of stainless-steel was the same as that used in our previous studies for sulfur gases[25,26] and isoprene.[27,28] AsH$_3$ and O$_3$ were introduced to the cell by different inlets. Although relatively good responses were obtained for the 100 µg L^{-1} arsenic solution, the intensities decreased gradually because of corrosion of the cell during AsH$_3$ detection. Consequently, other materials that were inexpensive and corrosion resistant were considered for the CL cell. The outside surfaces of polypropylene and glass cells were coated with a thin layer of wet deposited silver or sputtered chromium, respectively. This layer was used to reflect CL inside the cell and thus enhance the CL signal. AsH$_3$ and O$_3$ were introduced to the cells through PTFE tubes arranged in tube-in-tube configuration. The working distance, which is the distance between the end of the tubes and the optical window, and the O$_3$ flow rate were optimized for each cell. Among the cells tested, the glass cell in Fig. 2(e) gave the highest reflection and longest residence time. By comparison, the stainless-steel and plastic cells produced lower reflection. The response signals were strongly affected by the gas phase reaction time (residence time) of AsH$_3$ and O$_3$. The O$_3$-reaction rate of AsH$_3$, 5×10^{-18} cm^3 molecule^{-1} s^{-1},[29,30] is five orders of magnitude smaller than that of NO (2×10^{-13} cm^3 molecule^{-1} s^{-1}),[31] and even smaller than that of isoprene (1.4×10^{-17} cm^3 molecule^{-1} s^{-1}).[32] Consequently, a long residence time is required for the reaction and a large cell is better for this. The sample gas (50 mL, mostly H$_2$) was introduced in a short time, and if the cell was smaller than the sample gas volume it could not hold all the introduced AsH$_3$. For these reasons, the long glass cell (cell volume 73 mL) coated with chromium was adopted as the cell for subsequent experiments.
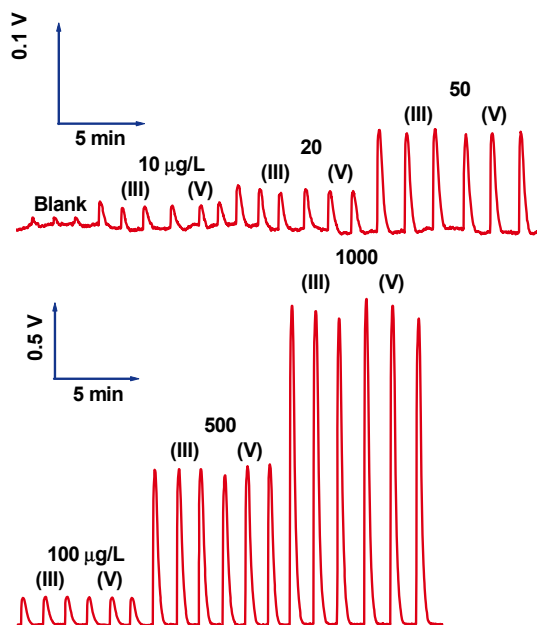
Fig. 3   Response signals obtained by HG-CL for 0, 10, 20, 50, 100, 500 and 1000 μg L^{-1} arsenic standard solutions of As(III) and As(V).

Fig. 4   Response signals for low concentration As solutions (a) and for 30 repeat analyses of 5 μg L^{-1} As(III) + 5 μg L^{-1} As(V) (b).

Different photodetectors were tested to obtain high sensitivity and better compactness of the detector with low cost. The tested photodetectors included a high performance photodiode with an integrated amplification circuit (OPT301, 2.29 × 2.29 mm optical area), which is used for fluorescence detection in micro gas analysis systems,[33] a large optical area photodiode (S9270, Hamamatsu, 10 × 10 mm), and a small PMT module (H5784, Hamamatsu, φ8 mm). The optical sensitivity specifications of OPT301, S9270 and H5784 were 0.10, 0.62 and 6 V nW^{-1}, respectively at 450 nm. The relative signal-to-noise ratios for a 100 μg L^{-1} arsenic solution with OPT301, S9270 and H5784 were 0.00050, 0.20, and 1.0, respectively. Unfortunately, neither of the photodiodes showed enough sensitivity (Fig. 2(e), right). Consequently, the small PMT module was adopted for subsequent use.

The ozone generation and ozone air flow were also optimized, and the details are presented in Fig. S1 (Supporting Information).

Performance of the HG-CL system

Under the optimum conditions, the responses of the HG-CL system to As(III) and As(V) were recorded (Fig. 3).   No differences were observed in the response intensities for As(III) and As(V), which indicates that the system is suitable for measurement of total As in water samples. The peak height increased linearly with the arsenic concentration up to 1000 μg L^{-1}. Calibration curves obtained for As(III) and As(V) were:

Peak height (mV) = 2.11As(III) (μg/L) − 5.65
$$R^2 = 0.9998 \qquad\qquad (5)$$

Peak height (mV) = 2.13As(V) (μg/L) − 7.28
$$R^2 = 0.9998 \qquad\qquad (6)$$

The slopes of the calibration curves were the same for As(III) and As(V). The limit of detection obtained from three times the standard deviation of the blank signal was 0.4 μg L^{-1}. Repeatability of the method was excellent even though it was
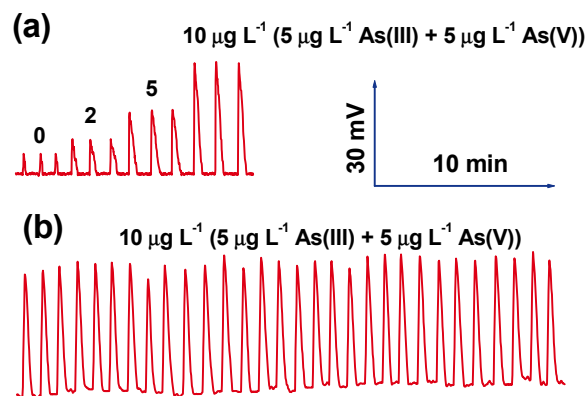
operated manually, and the relative standard deviation for a 10 μg L^{-1} arsenic solution was 3.0% over 30 measurements. Measurements were simple and easy, which would allow high throughput.   Low concentration measurements were performed for 2, 5, and 10 μg L^{-1} arsenic mixtures (As(III):As(V) = 1:1) and continuous measurements for As(III) + As(V) (total concentration 10 μg L^{-1}) 30 times in 30 min (Fig. 4), which is a throughput of 60 samples h^{-1}. The next sample was prepared in another sample tube with solid acid/EDTA2Na during the peak signal monitoring. After the signal returned to the baseline, oblate-covered borohydride was added to the next sample tube and then the used tube was exchanged with the next one. Thus the measurements could be repeated every minute. This system has sufficient sensitivity to measure total arsenic at concentrations below World Health Organization guidelines with good repeatability and high throughput.

The effect of a number of ions on the arsenic measurement by HG-CL was investigated. Interferences from Cu^{2+}, Ni^{2+}, Fe^{2+}, and Fe^{3+} were found but were masked by EDTA2Na. Serious interference was not observed in the optimized condition. These results are detailed in Table S1 (Supporting Information).

Analysis of natural water samples

To demonstrate the usefulness of this method, we analyzed several water samples for arsenic by the HG-CL method and other methods, including ICP-MS, SHGFIA, and the Arsenator kit (Wagtech). These instruments have various advantages and disadvantages, but the HG-CL (12 V) and the Arsenator kit (9 V) can be operated in the field with a battery. The results are shown in Fig. 5 and Table S2 (Supporting Information). Measurements were repeated in triplicate. The HG-CL data agreed with that from ICP-MS and SHGFIA with correlation coefficients of 0.987 and 0.989, respectively. This agreement showed that the developed HG-CL method was reliable for analysis of contaminated river water and well water.   The Arsenator is a well-known test kit that is used in the field in developing countries, and is recommended by the United Nations Children's Fund and World Health Organization. In this study, arsenic was not detected in samples 1, 2, 16 and 17 (Table S2, Supporting Information) by the Arsenator kit, while arsenic was detected by all the other methods. There were some differences between the Arsenator kit data and that from the other methods, and the correlation coefficient of Arsenator kit data to the HG-CL data was lower (0.9149) than the other correlation coefficients. The HG-CL method developed in this
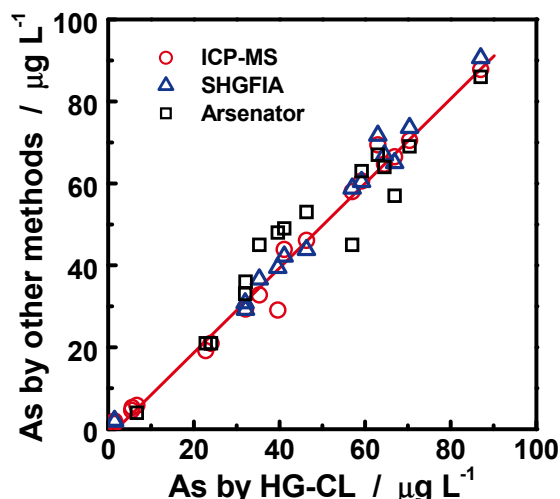
Fig. 5 Comparison of arsenic results obtained with HG-CL, ICP-MS, SHGFIA and the Arsenator test kit. Data from the other methods are plotted against the values obtained by HG-CL. The red line is a fitted linear line for the ICP-MS data plotted against the HG-CL data.

study can be used in the field. Furthermore, it has a shorter measurement time (1 min) compared to the Arsenator kit (>20 min), and gives a high throughput of 60 samples h^{-1}. In comparison to the Arsenator kit, the HG-CL method is more sensitive and reliable with higher throughput.

Conclusions

A HG-CL instrument was developed for measurement of aqueous arsenic. This instrument is small and light with low power consumption, and could measure µg L^{-1} concentrations of arsenic in a short time. Results could be obtained almost instantly in the field, and effective monitoring of water quality could be achieved with this instrument. After integration with a data processor, the HG-CL instrument could be applied to drinking water safety monitoring and surveys of water quality for drinking water treatment systems in the future, especially in developing countries.

Acknowledgements

Supporting Information

Supporting Information: ozone generation and optimization of ozone air flow, interferences from diverse ions, and comparative measurements of natural water samples. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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