

Supporting information:

Analytical Sciences

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

Md. Abul HASHEM,* Takuma JODAI,* Shin-Ichi OHIRA,* Kazuo WAKUDA,** and Kei TODA*†

* *Department of Chemistry, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan*

** *Division for Aquatic Environment, Yamaha Motor Co., Ltd., Shingai 2500, Iwata 438-8501, Japan*

Ozone generation and optimization of ozone air flow

O₃ generation was examined. For the field CL detection, high O₃ concentration generated from air at low flow rate is required. In Fig. S1a, O₃ concentrations generated by different ozonators are shown as a function of airflow rate. The concentration was monitored with a commercial ozone monitor (Model 49i, Thermo) after appropriate dilution with purified air. Ozone concentration depended on ozone source air/oxygen and source flow rate. Dried air was used for the source of ozone generation because pure oxygen is not available in the field. With these particular ozonators at 0.1 L min⁻¹ of airflow, discharge ozone concentrations were 2000–3000 ppmv. In the case of UV-lamp, ozone concentration was only 70 ppmv at the same air flow rate though UV-lamp was small, light and low in power consumption. Concentration of ozone generated decreased with increasing the air flow rate.

In Fig. S1b, effect of ozonator airflow is shown with different CL cells and ozonators. It is obvious that lower the air flow rate through the ozonators shows the higher signal intensity. This was why the higher ozone concentration was suitable for the gas phase reaction of arsine and ozone. To have sufficient reaction time in the cell, lower ozone source air flow was favorable too. It was decided to use 0.1 L min⁻¹ airflow through the ozonator.

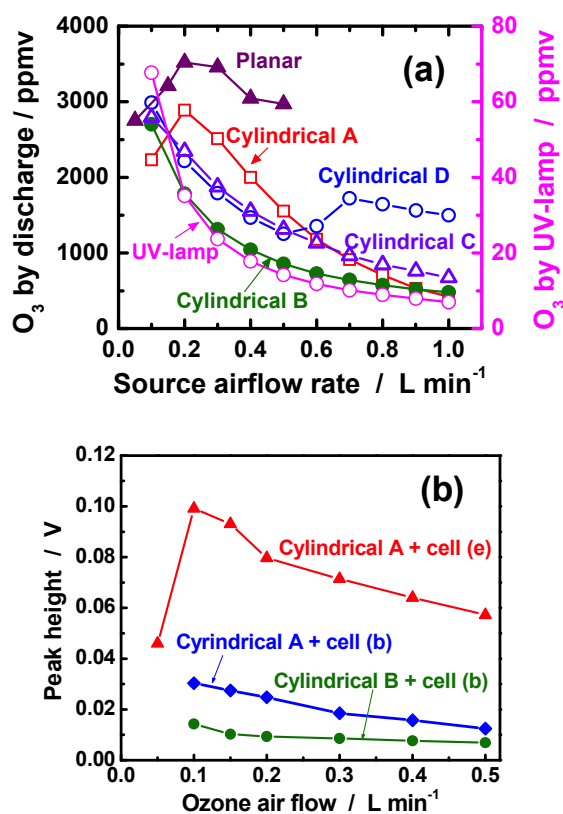


Fig. S1 Ozone concentration generated (a) and peak height for 50 µg/L As(III) (b) with different ozonators at different air flow rate.

Interferences from diverse ions:

Interferences from the diverse ions in this method were investigated. Results are summarized in the Table S1. There were no interferences from the common anions and cations such as phosphate, silicate, sulfate, Ca²⁺, Mg²⁺, and NH₄⁺. The divalent Cu²⁺ and Ni²⁺ made the As(V) signal smaller, and Fe²⁺ and Fe³⁺ made the recoveries for both As(III) and As(V) small. These problems were solved by addition of 10 mg of EDTA as mentioned in experimental section. Some volatile sulfur compounds (VSCs) gave response peaks even for As free samples. For examples, 10 mg L⁻¹ sulfide, 0.03 mg L⁻¹ CH₃SH and 0.03 mg L⁻¹ dimethyl sulfide (DMS) gave peaks corresponding to As concentrations 7.7, 4.6 and 3.4 µg L⁻¹. This was because these compounds react with O₃ to produce chemiluminescence. Chemiluminescence intensities increased 3~7 times when the acid and NaBH₄ were added not separately but simultaneously. Interferences from these VSCs were only when they exist in high concentrations and usually it is not concern. If the interference from the VSCs is a concern, it could be eliminated by 5 min bubbling performed after acid addition to remove the volatile sulfur compounds before arsenic reduction. As described above, the HG-CL method is useful for real water analysis with small concern of interference.

Table S1 Effect of interference from the diverse ions

Diverse ions		Recoveries (%) for 10 $\mu\text{g L}^{-1}$ As			
		Without EDTA		With EDTA	
Ions	mg L^{-1}	As(III)	As(V)	As(III)	As(V)
S^{2-}	2	100 \pm 2	100 \pm 2		
	4	115 \pm 2	113 \pm 2		
PO_4^{3-}	20	100 \pm 2	94 \pm 2		
SiO_3^{2-}	20	98 \pm 2	93 \pm 2		
CO_3^{2-}	200	98 \pm 2	104 \pm 2		
SO_4^{2-}	2000	102 \pm 2	105 \pm 2		
Mg^{2+}	2000	91 \pm 2	102 \pm 2		
Ca^{2+}	200	109 \pm 2	88 \pm 2		
CN^-	20	102 \pm 2	95 \pm 5		
NH_4^+	20	100 \pm 2	109 \pm 2		
SeO_4^{2-}	20	117 \pm 2	97 \pm 2		
ClO^-	2	104 \pm 2	85 \pm 6		
Cu^{2+}	2	102 \pm 2	84 \pm 2	104 \pm 4	98 \pm 1
Ni^{2+}	2	108 \pm 2	91 \pm 2	100 \pm 2	98 \pm 5
Fe^{2+}	10	63 \pm 2	79 \pm 2	104 \pm 4	108 \pm 1
	20	68 \pm 2	71 \pm 2	98 \pm 3	102 \pm 4
Fe^{3+}	10	57 \pm 2		105 \pm 3	103 \pm 0
	20	41 \pm 2		93 \pm 0	96 \pm 4

Peak intensity as As concentration ($\mu\text{g L}^{-1}$) with different reagent treatments ^{a)}

VSC	mg L^{-1}	Simultaneous	Acid \rightarrow NaBH_4	Acid \rightarrow bubbling $\rightarrow \text{NaBH}_4$
S^{2-}	10	44.1	7.7	0.0
DMS	0.03	15.3	4.6	0.0
CH_3SH	0.03	21.9	3.4	0.0

a) Acid and NaBH_4 were added to the sample simultaneously, added separately in the order of acid and NaBH_4 or bubbling was performed between additions of acid and NaBH_4 .

Comparative measurements of natural water samples

To demonstrate the usefulness of this method, As contained in several water samples were analyzed by the presented HG-CL and other methods, namely ICP-MS, SHG-FIA, and commercial field instrument (Arsenator, purchased from Wagtech). The instruments had merits and demerits. HG-CL (12 V, 1.7 A) and Arsenator (9 V, 10 mA) were operated in the field with small power consumption. SHG-FIA previously presented to analyze arsenic removal process was tested together. Results are shown in [Table S2](#). Measurements were repeated three times each and averages and deviations are shown in [Table S2](#). Data by ICP-MS, SHGFIA and HG-CL agreed well with correlation efficiency 0.987 and 0.989 for ICP-MS and SHG-FIA with respect to HG-CL. Good correlation can be observed in [Fig. 5](#) in the manuscript as well. Thus the presented method HG-CL was reliable for contaminated river waters and well water analysis. Arsenator is well known instrument and used as fieldable instrument in the developing countries with recommendation by UNICEF ¹⁾ and WHO.²⁾ In our results, As in the samples No. 1, 2, 16 and 17 were not detected by the Arsenator. There were differences against the data by the other methods, and correlation efficiency with respect to HG-CL was 0.914 a little bit worse. The HG-CL instrument is fieldable as well as the Arsenator. Furthermore the measurement time in HG-CL was much shorter than the Arsenator (>20 min) with the throughput of 60 samples h⁻¹. The HG-CL presented higher sensitivity, higher reliability and better throughput.

¹ UNICEF, *Evaluation of Arsenic Mitigation in Four Countries of the Greater Mekong Region, Final Report*, 2008.

² WHO, *Development of Regional Policy and Guideline for Arsenic Testing, Report for an intercountry Workshop, Kolkata, 24-26 March, 2003*.

Table S2 Results of comparative measurement.

No.	Concentration ($\mu\text{g L}^{-1}$)			
	ICP-MS	SHGFIA	Arsenator	HG-CL
River water				
1	1.4 \pm 0.8	1.9 \pm 0.1	ND*	1.5 \pm 0.4
2	2.0 \pm 0.0	2.1 \pm 0.3	ND	1.5 \pm 0.0
3	64.7 \pm 2.5	66.9 \pm 0.4	64 \pm 2	64.5 \pm 0.5
4	66.5 \pm 3.0	65.0 \pm 0.1	57 \pm 2	66.9 \pm 0.3
5	70.5 \pm 4.5	73.6 \pm 0.6	69 \pm 2	70.4 \pm 0.6
6	69.4 \pm 1.3	71.7 \pm 0.3	67 \pm 1	63.0 \pm 0.5
7	87.8 \pm 1.9	90.6 \pm 0.0	86 \pm 2	87.0 \pm 0.2
8	58.0 \pm 3.9	58.8 \pm 0.2	45 \pm 2	57.0 \pm 0.2
9	60.6 \pm 1.8	60.4 \pm 0.7	63 \pm 3	59.2 \pm 0.7
10	43.9 \pm 1.3	42.2 \pm 1.0	49 \pm 2	41.1 \pm 0.8
11	29.1 \pm 0.3	39.4 \pm 0.2	48 \pm 1	39.6 \pm 0.9
12	29.3 \pm 1.8	29.2 \pm 0.3	36 \pm 2	32.1 \pm 0.3
13	29.6 \pm 2.4	30.8 \pm 0.7	33 \pm 3	32.0 \pm 0.5
14	46.1 \pm 1.3	43.8 \pm 0.1	53 \pm 2	46.3 \pm 0.4
15	32.8 \pm 1.3	36.6 \pm 0.2	45 \pm 2	35.3 \pm 0.7
Well water				
16	5.3 \pm 0.2		ND	5.6 \pm 0.5
17	4.6 \pm 0.1		ND	5.5 \pm 0.5
18	19.2 \pm 0.1		21 \pm 1	22.8 \pm 0.6
19	21.0 \pm 0.1		21 \pm 1	24.0 \pm 0.2
20	5.8 \pm 0.1		4 \pm 1	6.7 \pm 0.4
Values with respect to HG-CL				
Slope	1.033	1.049	0.946	
Intercept	-1.984	-1.215	3.398	
R^2	0.987	0.989	0.914	

*ND: Not detected