

**Investigation of arsenic behavior in aqueous solution
by means of hydride generation from arsenite and arsenate**

A Dissertation

by

Md. Abul Hashem

Submitted to Graduate School
of Science and Technology, Kumamoto University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

September, 2011

Kumamoto, Japan

**Investigation of arsenic behavior in aqueous solution
by means of hydride generation from arsenite and arsenate**

A Dissertation

by

Md. Abul Hashem

Submitted to the Graduate School of
Science and Technology, Kumamoto University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Approved as to style and content by:

Kei Toda, Professor
(Chair of Committee)

Hiroshi Nishino, Professor
(Member)

Haruhiko Nakata, Professor
(Member)

Shinya Hayami, Professor
(Member)

Shin-Ichi Ohira, Asst. Professor
(Member)

**Dedicated
to
my parents**

Investigation of arsenic behavior in aqueous solution by means of hydride generation from arsenite and arsenate

ABSTRACT

Worldwide arsenic occurrence to groundwater and its toxic effect on human health is a serious environmental problem. It is released into the environment from a variety of natural and anthropogenic sources. Chemically, there are two types of arsenic compounds: inorganic and organic. Inorganic arsenic is more toxic than organic arsenic. Arsenite is considered 60 times more toxic than arsenate and binds to sulphhydryl (-SH) group which impairs function of many proteins. Chronic ingestion of inorganic arsenic causes cancer of the skin, bladder, and lung, as well as neurological and cardiovascular problems. The most severely groundwater contaminated countries including Bangladesh, West Bengal (India), Taiwan, Vietnam, Cambodia. It has become a challenge to researchers, reasons of arsenic leaching to groundwater and simpler removal technique obtaining safe drinking water. In the present research, I have investigated the behavior of hydride generation from arsenite and arsenate applied to monitoring arsenic removal, to investigate arsenic leaching from sediments, and development field instrument based on liquid-reagent-free hydride generation-chemiluminescence detection for water analysis.

Arsenic removal

To obtain safe drinking water removal of arsenic is very important. Metal base adsorbents, including aluminum, iron, titanium, zirconium, and manganese, have been extensively studied to remove arsenic from water. Many oxidants like ozone, chlorine, hydrogen peroxide use to oxidize As(III) to As(V) and finally arsenic is removed by adsorption process. To monitoring arsenic concentration of water treatment technologies many laboratory base analytical methods used to measure total arsenic. Speciation measurement is very important because arsenite is much more toxic than arsenate. An automated arsenic measurement system developed based on complete vaporization of arsenite and arsenate at pH 0 and vaporization of arsenite at pH 7 by a sequential procedure and collection/preconcentration of the vaporized arsine, which was

subsequently measured by a flow analysis. Interference from the heavy metals was less because arsine was generated more effectively by mild and long vaporization. The method was applied to monitoring As(III) and As(V) concentrations for arsenic removal in batch wise. Arsenic removal was effective by coprecipitation when hypochlorite (oxidant) was added at a tap water to oxidize As(III) to As(V). A small amount of steel wool is very effective in arsenic removal, adsorbing As quantitatively within 2 h.

Leaching of arsenic from sediments

Leaching of arsenic poses a potential risk to groundwater quality. Various industrial and mining wastes remained left in the nearby area after manufacturing which contained extremely high concentration of arsenic from where soil is polluted, possible mobilization and subsequent leaching into groundwater or surface water or enter the human food chain through various chemical and biological reactions. Sequential hydride generation flow analysis (SHGFA) was applied to water analysis and leaching investigation from the contaminated sediments near an arsenic mine river. The SHGFA system showed the excellent performance for leaching behavior of arsenic analysis by discriminating As(III) and As(V). It was observed that rate of As(III) leaching was faster than As(V) while As(V) leached more in amount compared to As(III).

Arsenate is a phosphate analog and both have the similar electron configuration and form triprotic acids with similar dissociation constants. Phosphate plays an important role to groundwater arsenic contamination leaching from soil/sediments. Application of phosphate fertilizer in agricultural activities to soil surfaces, released arsenic ions sorbed to aquifer minerals by competitive ion exchange with phosphate ion that migrates into aquifer. Simultaneously monitoring arsenite and arsenate by SHGFA was applied to investigate arsenic leaching from contaminated sediment by the effect of phosphate ion. Leaching of arsenate was significantly evaluated by the phosphate ion, as phosphate ion has more charge density than arsenate resulting replaced from sediment minerals surface.

Field Instrument Development

A manually hydride generation chemiluminescence instrument developed for on-site arsenic measurement in the aqueous sample. A hydride generation method based on

liquid-reagent-free by avoiding concentrated inorganic acid because transportation and handling of inorganic acids for field measurements is difficult and dangerous for the users without any formal chemistry training. In addition, in the arsenic affected areas it can be difficult to obtain pure water for reagents preparation. The optimized system was evaluated for analysis of natural water samples, and obtained data agreed well with those from ICP-MS and SHGFA. The sample throughput was 60 times h^{-1} and the limit of detection was $0.4 \mu\text{g L}^{-1}$. The measurable arsenic concentration was up to 1mg L^{-1} for 2 mL samples. The instrument is small and light with low power consumption, and could measure $\mu\text{g L}^{-1}$ concentrations of arsenic in a short time.

ACKNOWLEDGEMENTS

Alhamdulillah. It is an immense pleasure to document here my sincere gratitude and the deepest indebtedness to my supervisor, Professor Dr. Kei Toda for the invaluable guidance, suggestion and enormous time, inspiration as well as criticism that I received from him during the years of my study. I would like to express my heartfelt thanks to my advisory committee members, Professor Dr. Hiroshi Nishino, Professor Dr. Haruhiko Nakata, Professor Dr. Shinya Hayami and Dr. Shin-Ichi Ohira, for devoting their valuable time and efforts in guiding me during this task.

Sincere thanks to Akira Tanaka for their cooperation during my study. Special thanks to all laboratory members during my study for their enthusiastic cooperation which will be last long into my memory.

I am deeply grateful to my parents and family members for their support and encouragement from Bangladesh, far away from Japan. I am especially indebted to my wife Nonju Ara and my beloved daughter, Nafisa Anzum.

I have got an opportunity to find accompany of many friends from my adored country Bangladesh as well as from different parts of the world. I would like to appreciate the friendly accompany, suggestions, unparalleled sacrifice and assistance bound me with debt which I can never repay. I owe my accomplishment to their love and encouragement for which I shall remain grateful to them for ever.

Finally, I am pleased to acknowledge the financial support of the Ministry of Education, Science, Sports and Culture of Japan (Monbukagakusho Scholarship) during my study in Japan.

TABLE OF CONTENTS

CHAPTER ONE. Introduction	Page
1.1. Chemistry of arsenic	1
1.2. Origin of arsenic in the environment	3
1.2.1. Natural sources	4
1.2.2. Anthropogenic sources	4
1.3. Mechanism of arsenic mobilization into groundwater	4
1.4. Conclusions	6
CHAPTER TWO. Measurement of arsenic by sequential hydride generation flow analysis	
2.1. Introduction	9
2.2. Experimental	10
2.2.1. Sequential hydride generation flow analysis	10
2.2.2. Measuring procedure	11
2.2.3. Diffusion scrubber	12
2.3. Results and discussion	12
2.3.1. Arsine generation at selective pH	12
2.3.2. Collection of AsH ₃ by absorbing solution	13
2.3.3. Measurement of collected arsine by MB chemistry	14
2.3.4. Effect of EDTA to retain oxidation state of arsenite and arsenate	14
2.3.5. Interferences	17
2.4. Conclusions	18
CHAPTER THREE. Investigation of leaching of arsenite and arsenate from contaminated sediments	
3.1. Introduction	20
3.2. Experimental	22
3.2.1. Sediment samples collection	22
3.2.2. Leaching examinations	23

3.2.3. Comparative measurement	24
3.2.4. Leaching test with phosphate ions	24
3.2.5. Leaching test with stepwise ions addition	25
3.2.6. Leaching test with synthetic As-containing ferric oxide	25
3.3. Results and discussion	25
3.3.1. Leaching test with SHGFA	25
3.3.2. Comparative measurement	28
3.3.3. Kinetic consideration of the leaching	28
3.3.4. Leaching characteristics with different sediments and different conditions	30
3.3.5. Arsenic leached by the effect of phosphate ions	32
3.3.6. Arsenic leached by the stepwise ions addition	36
3.3.7. Arsenic leached from As-containing ferric oxide	37
3.4. Conclusions	38

CHAPTER FOUR. Investigation of arsenic removal in batch wise water treatments

4.1. Introduction	43
4.2. Methodology	44
4.2.1. Reactor	44
4.2.2. Arsenic monitoring	44
4.2.3. Batch test	45
4.3. Results and discussion	45
4.3.1. Sequential measurement of As(III) and As(V)	45
4.3.2. Trends of arsenic removal from anaerobic water samples	47
4.3.3. Arsenic removal profile with aeration	50
4.3.4. Addition of oxidizing agent	51
4.3.5. Arsenic removal with zero valent	53
4.4. Conclusions	54

CHAPTER FIVE. High sensitivity arsenic analyzer based on liquid-reagent-free hydride generation and chemiluminescence detection for on-site water analysis

5.1. Introduction	59
5.2. Experimental	61
5.2.1. Reagents	61
5.2.2. Instrumental system	62
5.2.3. Measurement procedure	64
5.2.4. Comparative sample measurements	64
5.3. Results and discussion	65
5.3.1. Optimization of reagents	65
5.3.2. Investigation of CL cell	68
5.3.3. Effect of check valve on signal intensity	71
5.3.4. Ozone generation and optimization of ozone air flow	72
5.3.5. Performance of the HG-CL system	73
5.3.6. Interferences from the diverse ions	74
5.3.7. Analysis of natural water samples	76
5.4. Conclusions	78
CHAPTER SIX. Suggestion for future work as on research	83
Appendix	84

CHAPTER ONE

Introduction

1.1. Chemistry of arsenic

Arsenic is a ubiquitous and naturally occurring element widely distributed in the atmosphere, rocks, soils, natural waters and all living organisms. Average concentration of arsenic in the earth's crust reported range from 1.5 to 5 mg kg⁻¹ [1]. It releases into the environment from a variety of natural and anthropogenic sources and mainly associated with sulfide minerals. The presence of arsenic into groundwater poses a serious health concern to the population where groundwater is the main source for drinking and irrigation. Many countries of the world including Bangladesh, Nepal, West Bengal (India), Vietnam, Cambodia, Taiwan, groundwater is highly contaminated with arsenic.

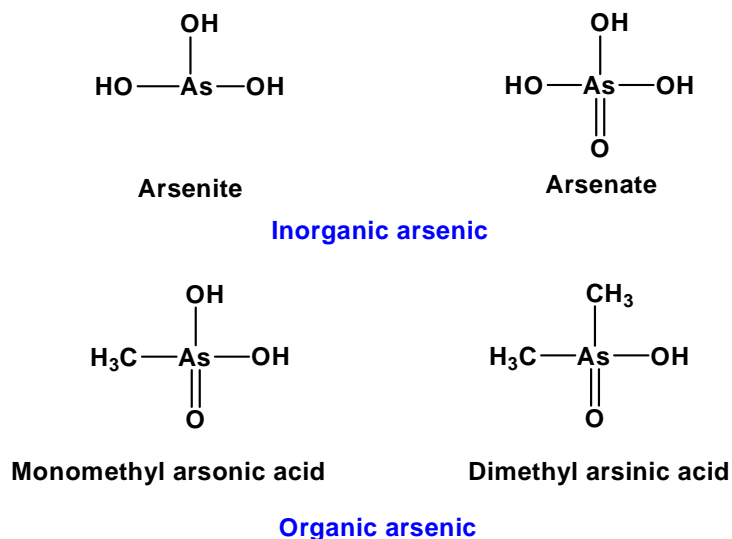


Fig. 1-1. Common inorganic and organic arsenic in the groundwater

Elementary arsenic is fairly insoluble whereas arsenic compounds may readily dissolve. Chemically, there are two types of arsenic compounds: inorganic and organic. In the environment, inorganic arsenic is typically present in either trivalent or pentavalent form. Trivalent arsenite is generally more toxic to humans and four to ten times more soluble in water than pentavalent arsenate [2-4]. The trivalent arsenite is 60 times more

toxic than pentavalent arsenate [5]. Organic arsenic species are abundant in seafood, and include such forms as monomethyl arsonic acid (MMAA), dimethyl arsinic acid (DMAA), and arseno-sugars. In the Fig. 1-1 shows some common inorganic and organic arsenic is found in the groundwater. Hydrogen atoms in both inorganic species dissociate leading to the formation of various anions.

Table 1-1. Dissociation constant for arsenate, arsenite and phosphate [6]

Anions	pK values			Dominating solutions species		
	pK _{a1}	pK _{a2}	pK _{a3}	pH 4	pH 7	pH 9
Arsenate	2.20	6.97	11.53	H ₂ AsO ₄ ⁻	H ₂ AsO ₄ ⁻ HAsO ₄ ²⁻	HAsO ₄ ²⁻
Arsenite	9.22	12.13	13.40	H ₃ AsO ₃ ⁰	H ₃ AsO ₃ ⁰	H ₃ AsO ₃ ⁰ H ₂ AsO ₃ ⁻
Phosphate	2.15	7.20	12.38	H ₂ PO ₄ ⁻	H ₂ PO ₄ ⁻ HPO ₄ ²⁻	HPO ₄ ²⁻

Arsenic perhaps unique among the heavy metalloids and oxyanion-forming elements (*e.g.* Se, Sb, Mo, V, Cr, U, Re) in its sensitivity to mobilization at the pH values typically found in the groundwater (pH 6.5 - 8.5) under oxidizing and reducing conditions [7]. The valency and species of inorganic arsenic are dependent on the redox conditions and the pH of the water. Generally, trivalent arsenite is formed in the reduced condition and normally found in the groundwater. On the other hand, pentavalent arsenate is formed in the oxidized condition and found in the surface water. This rule does not always hold true for groundwater.

Redox potential (Eh) and pH are the most important factors controlling the arsenic speciation is shown in Fig. 1-2. Under oxidizing condition, H₂AsO₄⁻ is dominant at low pH (less than 7) whilst at higher pH, HAsO₄²⁻ becomes dominant. The unchanged H₃AsO₄⁰ and AsO₄³⁻ may be present in extremely acidic and alkaline conditions, respectively. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H₃AsO₃⁰ will predominate [8]. The distributions of the species as a function of pH are shown in Fig. 1-3.

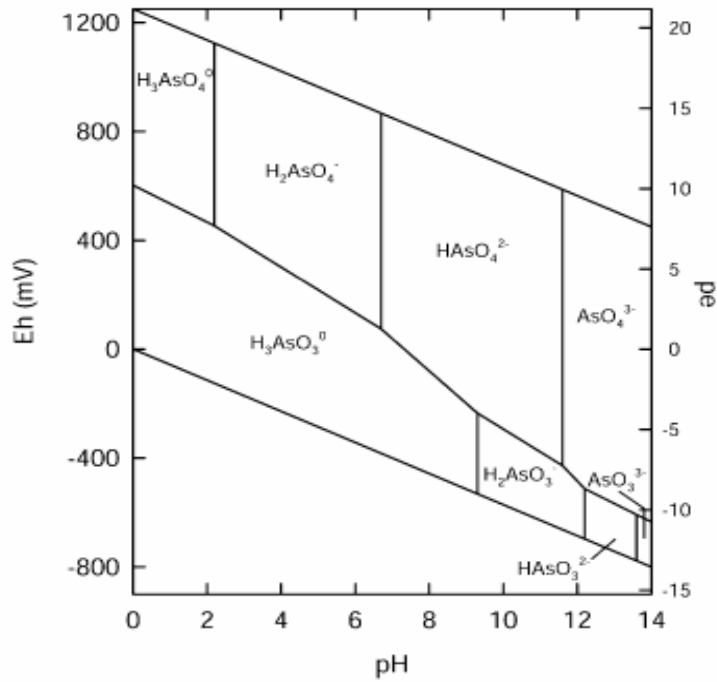


Fig. 1-2. Eh-pH diagram for aqueous arsenic (As) species in the system As-O₂-H₂O at 25°C and 1 bar total pressure [7].

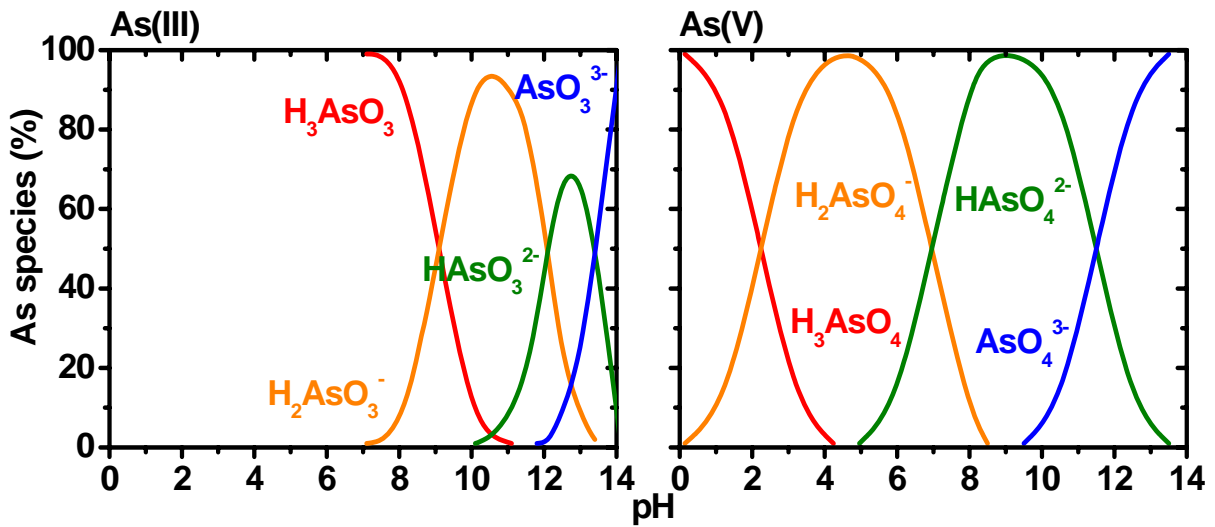


Fig. 1-3. Arsenite and arsenate species as a function of pH

1.2. Origin of arsenic in the environment

Arsenic is released into environment from a variety of natural and anthropogenic sources. It can be released into groundwater or surface water through erosion, dissolution

and weathering. Geothermal water and high evaporation rates also are associated with arsenic concentration into groundwater and surface water particularly in the Western United State [9]. Natural dominating processes are volcanic eruptions, weathering and may be transported over long distance as suspended particulates, through air and water. Emission of arsenic from the industrial activity also accounts for widespread contamination of soil and groundwater environment. Arsenic once introduced into the atmosphere it may circulate in the natural ecosystem for a long time depending on the prevailing geochemical environments [1].

1.2.1. Natural sources

Arsenic occurs naturally in all minerals and rocks, although its distribution within them varies widely. In the environment arsenic is mainly associated with sulfide minerals. The most important minerals are arsenopyrite (FeAsS), orpiment (As_2S_3), realgar (AsS), arsenian pyrite [$\text{Fe}(\text{S},\text{As})_2$] [9]. High concentration of arsenic are also found in many oxides minerals and hydrous metals oxides, either as a part of mineral structure or adsorbed to the surfaces.

1.2.2. Anthropogenic sources

Arsenic is introduced in the environment through the various anthropogenic sources. Apart from the mining activities and combustion of fossil fuels which involve redistribution of increasing arsenic in the environment through the manufacturing and uses of arsenical compounds such as pesticides, herbicides, crop desiccants and additives in the livestock feed particularly for poultry. Arsenic also released from other heavy industrial process including smelting, pulp and paper production, glass manufacturing, cement manufacturing and waste products. Also released from the agricultural and industrial activities; mining waste and leaching from the cattle dip sites, cemeteries [10].

1.3. Mechanism of arsenic mobilization into groundwater

Occurrences of dissolved arsenic in surface and ground waters and its adverse effects on human health have emphasized the need for better understanding of reactions that govern arsenic mobility in the environment [11]. The mobility of arsenic in the

groundwater governs by the geochemical and hydro-geological characteristics as well as the source of arsenic in the sediments depends on the geology of the source of terrain [12]. The retention or mobility of arsenic under varying redox condition depends on the interaction of the aqueous phase with mineral phases of the sediments. The mechanism of arsenic releases and mobilization into groundwater has been a subject of considerable controversy. There are three contrasting hypotheses for mobilization of arsenic in the groundwater [13-15].

- Oxidation of arsenopyrite
- Reductive dissolution of iron hydroxide
- Anion exchange of sorbed arsenic with phosphate from fertilizers.

According to the oxidation theory, arsenic is released from the sulfide minerals (arsenopyrite) in the shallow aquifer due to oxidation. The lowering of water table owing to over exploitation of groundwater for irrigation, as a results atmospheric oxygen enter into aquifers where it reacts with arsenopyrite which influenced to release the arsenic into groundwater. The extensive extraction of groundwater has caused quick diffusion of oxygen within the pore spaces of sediments as well as an increase to dissolve oxygen in the upper part of groundwater. The newly introduced oxygen oxidizes the arsenopyrite and forms hydrated mixture of arsenate and sulfate compound known as pitticite in presence of water. This mixture is very soft and water-soluble compound. The light pressures of tube-well water break the pitticite layer into fine particles and make it readily soluble in water.

Based on reductive dissolution theory, arsenic is derived by desorption from ferric hydroxide minerals under reducing conditions. In the presence of iron, inorganic arsenic species are predominantly retained in the solid phase under oxidizing conditions through interaction with iron oxy-hydroxide coatings on soil particles by different types of interactions *e.g.*, adsorption on amorphous iron hydroxide [16], adsorption on ferrihydrite [17], and co-precipitation [18] of As(III) and As(V) with iron hydroxides. In the reducing conditions the dissolution of iron-hydroxide coatings, resulting to release of iron(II), As(III) and As(V) present on such coatings. Of course, pH is strongly influenced for adsorption of As(V) and As(III) by iron-hydroxide. Higher the pH causing desorption of As(V) sometimes As(III) from iron oxy-hydroxide surface [19].

The application of fertilizers has caused mobilization of phosphate from the fertilizers down to shallow aquifers, which resulting the mobilization of arsenic due to anion exchange onto the reactive mineral surfaces. Since phosphate is bound strongly onto these surfaces, arsenate can be mobilized into groundwater [20].

1.4. Conclusions

There is a need for integrated research to understand the sources, mechanisms of arsenic leaching from sediments/soils into groundwater. Numerous factors which affect the mobility of arsenic into groundwater and it is not easy to predict how it will change under well defined conditions. Investigations have been carried out to have useful information for leaching of arsenic from the contaminated sediments under various conditions. Leachates arsenic was monitored as arsenite and arsenate by sequentially hydride generation flow analysis (SHGFA).

References

1. Cullen, W. R., Reimer, K. J. Arsenic speciation in the environment. *Chem. Rev.*, **1989**, *89*, 713-764.
2. US Environmental Protection Agency (USEPA). Treatment technology performance and cost data for remediation of wood preserving sites. **1997**, Washington, DC, USA.
3. US Occupational Safety and Health Administration (USOSHA). Occupational safety and health guidelines for arsenic, organic compounds (as As). **2001**, Washington, DC, USA. www.osha.gov/SLTC/healthguidelines/arsenic/recognition.html
4. Singh, A. K. Chemistry of arsenic in groundwater of Ganges-Brahmaputra river basin. *Curr. Sci.*, **2006**, *91*, 599-606.
5. Fazal, M. A., Kawachi, T., Ichion, E. Extent and Severity of Groundwater Arsenic Contamination in Bangladesh. *Water Int.*, **2001**, *26*, 370-379.
6. Jain, A., Loeppert, R. H. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. *J. Environ. Qual.*, **2000**, *29*, 1422-1430.
7. Smedley, P. L., Kinniburgh, D. G. A review of the sources, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.*, **2002**, *17*, 517-568.

8. Yan, X. -P., Kerrich, R., Hendry, M. J. Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochim. Cosmochim. Acta*, **2000**, *62*, 2637-2648.
9. Welch, A. H., Westjohn, D. B., Helsel, D. R., Wanty, R. B. Arsenic in groundwater in the United States: Occurrence and Geochemistry. *Groundwater*, **2000**, *38*, 589-604.
10. O'Shea, B., Jankowski, J., Sammut, J. The source of naturally occurring arsenic in a coastal sand aquifer of eastern Australia. *Sci. Total Environ.*, **2007**, *379*, 151-166.
11. Lee, Y. J., Stephens, P. W., Tang, Y., Li, W., Phillips, B. L., Parise, J. B., Reeder, R. J. Arsenate substitution in hydroxylapatite: structural characterization of the $\text{Ca}_5(\text{P}_x\text{As}_{1-x}\text{O}_4)_3\text{OH}$ solid solution. *Am. Mineral.*, **2009**, *94*, 666-675.
12. Juillot, F., Ildefonse, Ph., Morin, G., de Kersabiece, A. M., Benedetti, M. Remobilization of arsenic from buried wastes at an industrial site: mineralogical and geochemical control. *Appl. Geochem.*, **1999**, *14*, 1031-1048.
13. Nickson, R., McArthur, J. M., Ravenscroft, P., Burgess, W. G., Ahmed, K. M. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.*, **2000**, *15*, 403-413.
14. Acharyya, S. K., Chakraborty, P., Lahiri, S., Raymahashay, B. C., Guha, S., Bhowmik, A. Arsenic poisoning in the Ganges delta. *Nature*, **1999**, *401*, 545-546.
15. Das, D., Samanta, G., Mandal, B. K., Chowdhury, R. T., Chandra, C. R., Chowdhury, P. P., Basu, G. K., Chakraborti, D. Arsenic in groundwater in six districts of West Bengal, India. *Environ. Geochem. Health*, **1996**, *18*, 5-15.
16. Masue, Y., Loeppert, R. H., Kramer, T. A. Arsenate and Arsenite Adsorption and Desorption Behavior on Coprecipitated Aluminum: Iron Hydroxides. *Environ. Sci. Technol.*, **2007**, *41*, 837-842.
17. Raven, K. P., Jain, A., Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium and adsorption envelopes. *Environ. Sci. Technol.*, **1998**, *32*, 344-349.
18. Manning, B. A, Fendorf, S. E., Goldberg, S. Surfaces structures and stability of arsenic(III) goethite: spectroscopic evidence for inner-sphere complexes. *Environ. Sci. Technol.*, **1998**, *32*, 2383-2399.

19. Jain, A., Raven, K. P., Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH-release stoichiometry. *Environ. Sci. Technol.*, **1999**, 33, 1179-1184.
20. Acharyya, S. K., Lahiri, S., Ramahashay, B. C., Bhowmik, A. Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environ. Geol.*, **2000**, 39, 1127-1137.

CHAPTER TWO

Measurement of arsenic by sequential hydride generation flow analysis

2.1. Introduction

Groundwater and surface water contamination with arsenic is a serious environmental problem for human beings as well as for all living organisms. Worldwide in 20 countries groundwater is contaminated with arsenic [1] and the most severely affected countries including Bangladesh, West Bengal (India), Taiwan, Vietnam, Cambodia, Argentina. While WHO guideline value arsenic in drinking water $10 \mu\text{g L}^{-1}$ [2] but in those countries groundwater arsenic concentration beyond the permissible level and sometimes the level is several thousand $\mu\text{g L}^{-1}$. The sources of waterborne arsenic is largely natural and being derived from the oxidation of arsenopyrite and under reducing condition desorption from ferric hydroxide minerals in aquifer sediments [3]. In the natural water, arsenic is primarily present in inorganic forms and exists as arsenite and arsenate. Arsenite is 60 times more toxic than arsenate [4] and more difficult to remove from the water than arsenate. Speciation measurement of arsenite and arsenate is very important to know the arsenic concentration in the water sample as well as leaching of arsenic from the various environmental samples like contaminated sediments, soils, industrial wastage etc. In the conventional methods hydride generation-atomic adsorption spectrometry (HG-AAS) [5], hydride generation-inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) [6] and liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS) [5] can determine arsenic. But to generate hydride and subsequently measure with AAS and ICP-AES, As(V) has to be reduced to As(III) prior to the experiment and there is a large interferences from the heavy metals. On the other hand LC-ICP-MS can differentiate the arsenite and arsenate but very difficult for iron rich sample.

In our laboratory developed a novel method which can measure arsenic by discriminating arsenite and arsenate [7]. To investigate the mechanism of arsenic leaching from the sediments sequential hydride generation flow analysis (SHGFA) was applied. This is based on the perfect vaporization of both arsenite and arsenate at pH 0 and perfect vaporization of arsenite at pH 7, and subsequent analysis of arsenic with

molybdenum blue (MB) chemistry. Differences from the conventional arsenic analysis methods based on hydride generation, in this method, arsenic is completely vaporized so that interference from heavy metals is very little. In the next stage, hydride generation was automated with the sequential hydride generation flow analysis (SHGFA) and was applied to investigate the behavior of arsenite and arsenate in their removal processes [8]. Determination of arsenic with SHGFA by discriminating As(III) and As(V) offers many advantages including high sensitivity, large linear range, low detection limit, interferences from the heavy metals is very little, inexpensive and easy. On the other hand in the conventional methods require comparatively expensive equipments, require high degree of trained operators, high operating cost and finally they are not readily amenable to portable instrumentation.

2.2. Experimental

2.2.1. Sequential hydride generation flow analysis (SHGFA)

Sequential hydride generation flow analysis is based on perfect vaporization of arsenite and arsenate at pH 0 and vaporization of arsenite at pH 7 by a sequential procedure. A flow diagram is shown in the [Fig. 2-1](#). All reagents solutions are derived by using a 10 mL syringe pump (Versa pump 6 48K, 54021 Kloehn) equipped with a 12-port selected valves (V6 rotary valve, 24105, Kloehn). Once the programme sequence created on PC, the pump can carry out the operations for the entire analytical cycle without further need of the PC. Each step of the program is summarized in [Table A-1](#).

The generated arsine (AsH_3) is introduced into an annular diffusion scrubber where the collected AsH_3 is trapped in the absorbing solution (15 mM KMnO_4 + 0.01 M NaOH) as arsenate. Arsenate reacts with ammonium molybdate to form hetero poly compound. Finally, the compound is reduced by the ascorbic acid and form blue color and absorbance measure at 870 nm with a flow through detector (UV-1570, Jasco) Absorbing solution of potassium permanganate and the molybdenum blue were pumped with peristaltic pump (Gilson Minipuls 3, France) at the flow rate of 0.2 mL min^{-1} . In the absorbing solution line, two three-way solenoid valves (EXAK-3 12V dc, Takasago Electric, Nagoya, Japan) were allowed; solution normally flow through the central porous membrane channel of the diffusion scrubber is shown in the [Fig. 2-2](#). During arsine

generation valves were turned on and absorbing solution by-passed so that absorbing solution contained in the diffusion scrubber unit remained stationary.

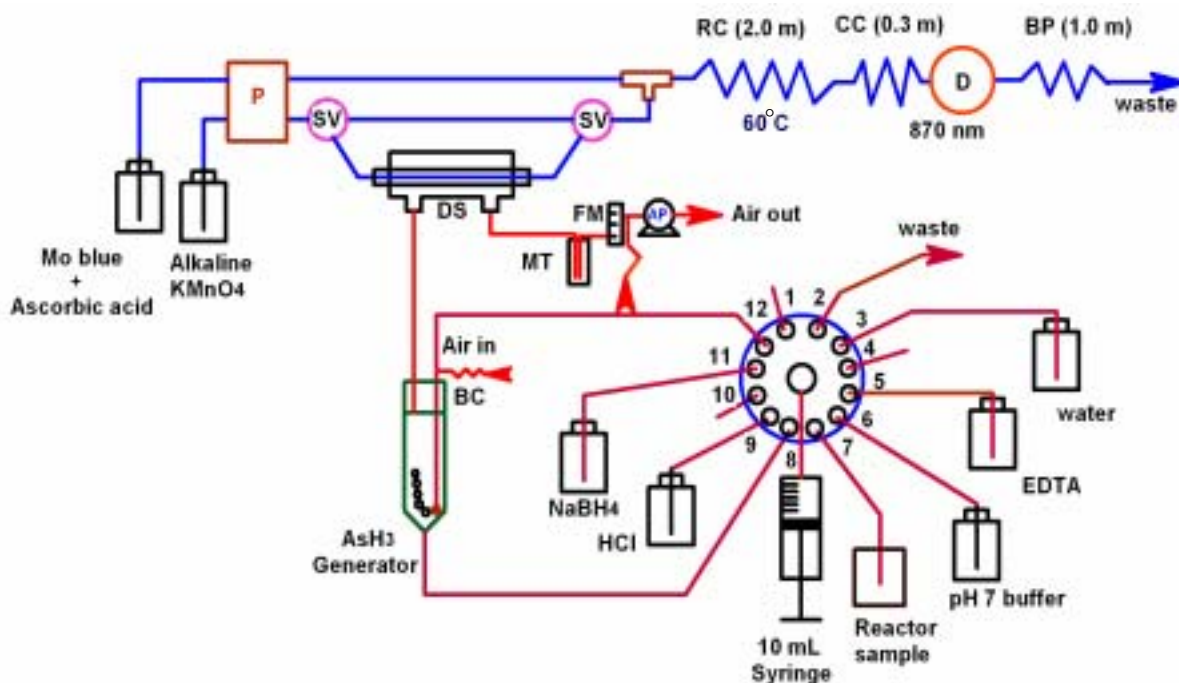


Fig. 2-1. Flow diagram for leaching analysis of arsenic. SV: three-way solenoid valves, DS: miniature diffusion scrubber, RC: reaction coil, CC: cooling coil, D: absorbance detector, BP: back pressure coil, MT: mist trap, FM: air flow meter, AP: miniature air pump

2.2.2. Measuring procedure

For determination of As(III), sample 2.0 mL was taken in 10 mL syringe, then added 0.5 mL of 0.05 M EDTA, 1.0 mL of 1 M phosphate buffer total 3.5 mL aspirate to the arsine generator from the bottom. Then gradually, 10 mL 0.33 M NaBH₄ (Nacalai) added to the arsine generator through the glass frit air inlet from the bottom for 8 min. Total arsenic was measured in the same way but AsH₃ was generated with 9 M HCl (Nacalai) for 4 min instead of the phosphate buffer for 8 min. Arsenate was determined by subtraction of the arsenite concentration from the total arsenic. Generation of AsH₃ from arsenite and total arsenic were repeated every 17 min automatically with the syringe pump, and measurement of collected arsenic was performed with the continuous flow system.

2.2.3. Diffusion scrubber

The diffusion scrubber unit is composed of 50-cm long porous polypropylene (pPP) membrane tubes (0.5 mm i.d., 0.9 mm o.d., 0.2 μm pore size, Accurel PP, Membrana, Wuppertal, Germany). A 10 cm length AWG30 teflon tube about 1 cm is passed through the membrane from one side and sealed with seal tape. Opposite side of the tube also installed the same way. After that, pPP membrane tube inserted in a 3.0 mm i.d. polytetrafluoroethylene (PTFE) jacket tube and set the tee both sides of the jacket tube. The teflon tubes of AWG14, AWG18 and AWG22 were piled up in that tee; as a result the teflon tube AWG30 was fasten up inside the tee and was air tightness. The pPP membrane tube diffusion scrubber has the effective absorption liquid volume is 100 μL .

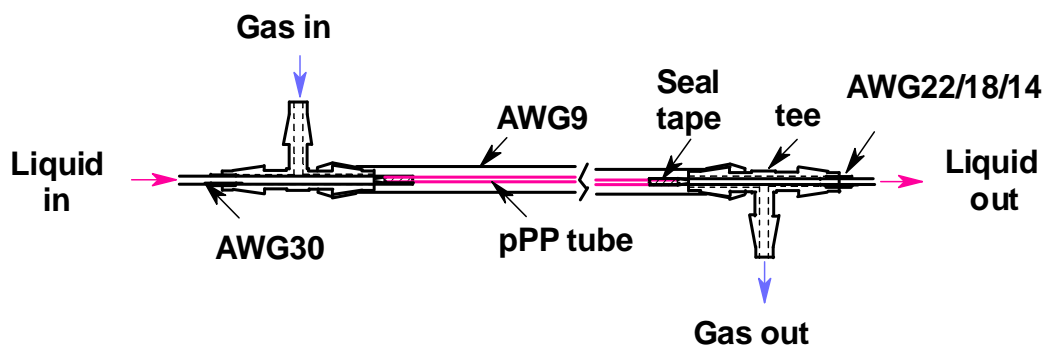


Fig. 2-2. Miniature diffusion scrubber

2.3. Results and discussion

2.3.1. Arsine generation at selective pH

In Fig. 2-3 shows the behavior of the arsenite and arsenate at the present system to generate arsine as a function of solution pH. At pH 7 only arsenite vaporize to arsine completely and at pH 0 arsenite and arsenate vaporize to arsine. If generation time is allowed for a long time all As(III) converted to arsine at pH 7. After 8 min all As(III) converted to arsine but at pH 0 after 4 min all As(V) converted to arsine. Addition of NaBH_4 is very important factor to generate arsine. If the NaBH_4 is added at once as the conventional hydride generation, AsH_3 (and H_2) generation rate is initially high. But the efficiency of AsH_3 collection by diffusion scrubber (DS) depends on the flow rate pass through the DS unit and decreases with increasing the gas flow rate as the Gormley-Kennedy's equation [9]. At the present system, the NaBH_4 is introduced directly on the

top through glass frit of the air bubbler and is distributed immediately by the aspirated air, resulting in rapid mixing throughout the solution.

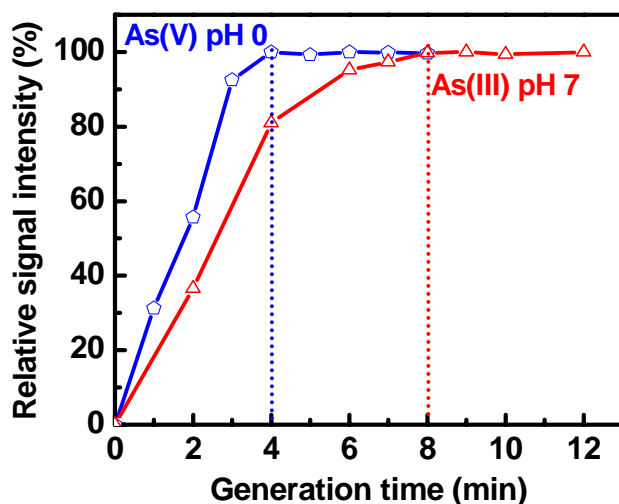


Fig. 2-3. Generation of arsine from As(III) $50 \mu\text{g L}^{-1}$ at pH 7 and As(V) $50 \mu\text{g L}^{-1}$ at pH 0.

2.3.2. Collection of AsH₃ by absorbing solution

AsH₃ is collected by porous membrane diffusion scrubber filled with absorbing solution (15 mM KMnO₄ + 10 mM NaOH). Collection efficiency of AsH₃ is dependent on the gas flow rate. In Fig. 2-4 shows the effect of purged gas flow rate on AsH₃ generation/collection and optimized purge gas flow rate is 50 mL min^{-1} .

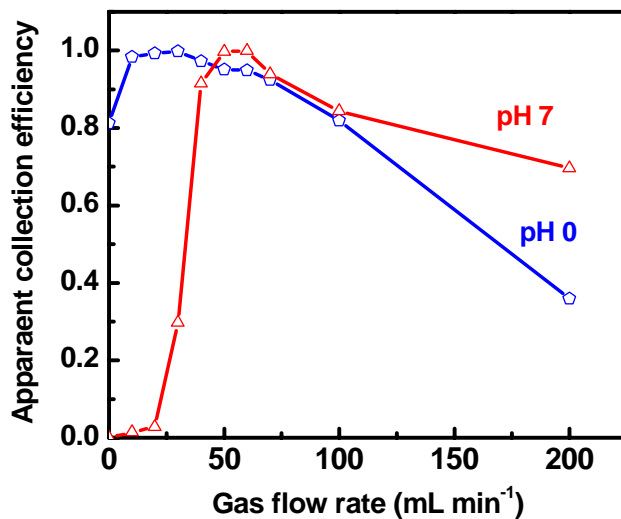


Fig. 2-4. Effect of purged gas flow rate on AsH₃ generation/collection. $50 \mu\text{g L}^{-1}$ As(III) is for pH 0 and pH 7. Arsine generation/collection time was 5 min.

2.3.3. Measurement of collected arsenic by MB chemistry

The formed arsine (AsH_3) is collected as arsenate and flowed to be mixed with molybdenum blue reagent solution which passes through the heating coil (60°C). Absorbance of the reaction product was measured at 870 nm with an UV-VIS spectrophotometer (UV-1570 obtained from JASCO). In Fig. 2-5 shows the response signal during measuring the arsenic standard by SHGFA at different concentrations 0, 100, 200, 400 and 500 $\mu\text{g L}^{-1}$ total As[As(III)+As(V)]. Calibration curves were linear with $R^2=0.9989$ for As(III) and $R^2=0.9997$ for total As. Repeatability was calculated after 3 consecutive measurement of the same standard solution at the same condition with the relative standard deviations and both were 1% for As(III) and total As for 4 different concentrations. The concentration of As(V) was determined by subtracting the concentration of As(III) from total arsenic concentration. The limits of detection (LODs) was estimated from three times standard deviation of blank sample signals were 0.02 and 0.03 $\mu\text{g L}^{-1}$ for As(III) and total As, respectively.

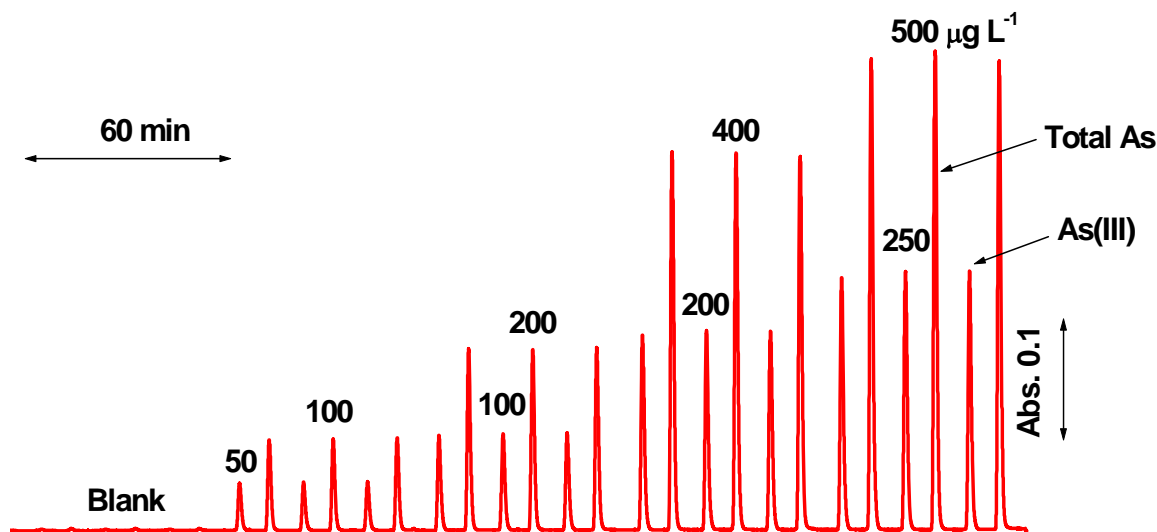


Fig. 2-5. Response signals obtained of the SHGFA system during measuring the arsenic standard solutions of As(III) and total As[As(III)+As(V)] at different concentrations.

2.3.4. Effect of EDTA to retain oxidation state of arsenite and arsenate

In the groundwater and surface water arsenic is predominantly present arsenite [As(III)] and arsenate [As(V)] and used for drinking and irrigation water supplies. Arsenite is the

most toxic inorganic than arsenate [10]. The distribution of arsenite and arsenate in the drinking water source is the main root of arsenic to enter human body and causes health effect. On-site arsenic monitoring is important to distinguish the oxidation state because oxidation state changes during transporting and storage due to precipitation by metals oxyhydroxide (*e.g.* Fe, Mn), As(III) can be oxidation to As(V) photolytically produced free radicals in the many sample matrices [11, 12]. In Fig. 2-6 shows that the oxidation state changed dramatically in the storage while the concentrations of As(III) and As(V) were constant for a few days when EDTA was added into the natural water samples even for such low concentrations. On the contrary, when the water was not treated with EDTA, As(III) was oxidized to As(V) probably due to dissolved oxygen, and then the formed As(V) was gradually converted back to As(III) after 3 days with being anaerobic. Finally the all arsenic was three-valent in two weeks.

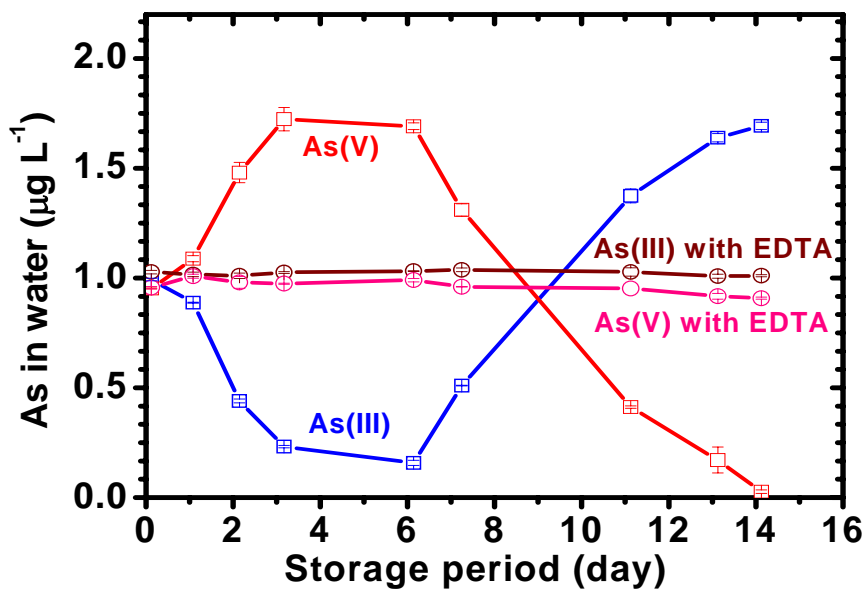


Fig. 2-6. Change in oxidation state of arsenic during storage with EDTA, phosphoric acid and without the stabilizer. Examination was performed using natural water with addition of As to be $1 \mu\text{g L}^{-1}$ and kept at room temperature.

According to the above results, water samples were collected from fifteen points into plastic bottles and EDTA was added to adjust the concentration at 1.25 mM to eliminate the changes oxidation state. Samples were filtrated through the $0.45 \mu\text{m}$ cellulose acetate filters and kept in the dark place at 4°C . In the next day arsenite and

arsenate were determined with sequential hydride generation flow analysis. The water sampling points and arsenic measurements data are shown in Fig. 2-7.

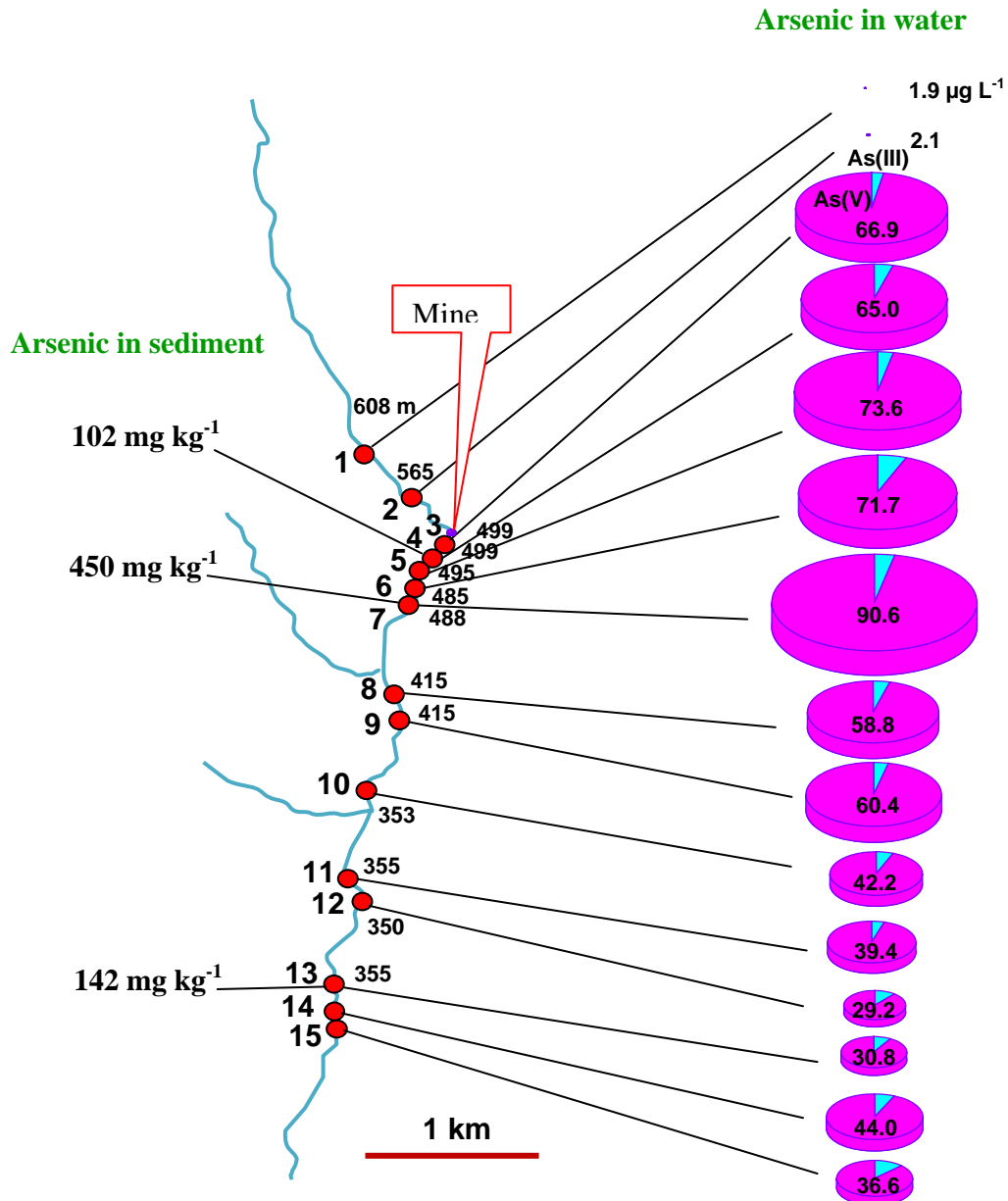


Fig. 2-7. Sampling points of water and sediments. Water samples were collected at 15 points shown as red circles. Numbers for the points indicate their altitudes. Size of circles in the right is proportional to the total arsenic concentration. Ratio of As(III) and As(V) is shown in the circle. Arsenic content in the sediment is shown after washing.

Upstream of the mining at two points, the total arsenic concentrations were around $2 \mu\text{g L}^{-1}$. On the other hand, total arsenic concentration was $66.9 \mu\text{g L}^{-1}$ at the point just next to the mining, which water was flowing out from the mouth of mining (sample No. 3). The ratio of As(III)/total As in water sample No. 3 was 3%. With going downstream from the mining, arsenic level was almost same ($65\text{-}74 \mu\text{g L}^{-1}$ at No. 3-6). At the sample No. 7, arsenic level became high and it was $2.9 \mu\text{g L}^{-1}$ As(III) and $87.6 \mu\text{g L}^{-1}$ As(V), respectively. This is because; sample No. 7 was small place where water was not moving, there might be anaerobic condition and biological activity eluted arsenic from the sediments. Downstream from the sample No. 7, arsenic level decreases went down to $30.8 \mu\text{g L}^{-1}$ at sample No. 13. Dissolved arsenic might deposit to the river sediments and the contaminated water was diluted with water from the branches of the river. However, the arsenic concentrations again increased and were $43.8 \mu\text{g L}^{-1}$ and $36.6 \mu\text{g L}^{-1}$ at No. 14 and No. 15, respectively. Those two points water were not moving and supposed to be under anaerobic, might be enhanced to elute arsenic from the sediments again here. In the last four point (No. 12-15) the ratio of As(III)/total As was higher (7-13%) whereas other points were (3-6% at No. 3-11). Sampling point No. 13 was dam and water stream on the deposited sands. Probably, arsenic was leached from the deposited sands. To investigate the leaching experiment, sediments were collected from three points along the river and brought back to the laboratory. The sediments were washed before leaching experiment with flowing water sieving on an 80-mesh. Arsenic content in the sediments were 218-476 mg kg^{-1} and downed to 102-450 mg kg^{-1} with washing is shown in the Fig. 2-7. The decreased amount of arsenic in sediment was corresponding to adsorb arsenic and fine particles which contained high concentration of arsenic.

2.3.5. Interferences

Interferences from the coexisting species are not large as shown previously [7] and the effects from heavy metals ions can be reduced by the addition of EDTA. In case of iron and copper ions species required attention of interference and the common ions phosphate, silicate, carbonate, sulfate, cyanide, magnesium, calcium, ammonium, nickel ions did not interfere to generate arsine as well as measurement.

2.4. Conclusions

As described the SHGFA system has very little interference with heavy metals and without pretreatment it can measure arsenic by discriminating arsenite and arsenate simultaneously. The system was applied for the arsenic removal as well as leaching of arsenic from the contaminated sediments by speciation automatically and results are described in the respective chapters.

References

1. Naidu, R., Smith, E., Owens, G., Bhattacharya, P., Nadebaum, P. Managing Arsenic in the Environment from Soil to Human Health. CSIRO Publishing. **2006**, p. 3.
2. World Health Organization (WHO), Guidelines for drinking-water quality. **2004**, Vol. 1, Recommendations, 3rd ed. Geneva, Switzerland.
3. Kondo, H., Ishiguro, Y., Ohno, K., Nagase, M., Toba, M., Takagi, M. Naturally occurring in the groundwaters in the southern region of Fukuoka prefecture, Japan. *Water Res.*, **1999**, 33, 1967-1972.
4. Fazal, M. A., Kawachi, T., Ichion, E. Extent and Severity of Groundwater Arsenic Contamination in Bangladesh. *Water Int.*, **2001**, 26, 370-379.
5. Akter, K. F., Chen, Z., Smith, L., Davey, D., Naidu, R. Speciation of arsenic in ground water samples: A comparative study of CE-UV, HG-AAS and LC-ICP-MS. *Talanta*, **2005**, 68, 406-415.
6. Muller, J. Determination of inorganic arsenic(III) in ground water using hydride generation coupled to ICP-AES (HG-ICP-AES) under various sodium boron hydride (NaBH₄) concentrations. *Fresenius' J. Anal. Chem.*, **1999**, 363, 572-576.
7. Toda, K., Ohba, T., Takaki, M., Karthikeyan, S., Hirata, S., Dasgupta, P. K. Speciation-Capable Field Instrument for the Measurement of Arsenite and Arsenate in Water. *Anal. Chem.*, **2005**, 77, 4765-4773
8. Toda, K., Takaki, M., Hashem, M. A. Investigation of arsenic removal in batch wise water treatments by means of sequential hydride generation flow injection analysis. *Chemosphere*, **2008**, 72, 1517-1523.

9. Gormley, P., Kennedy, M. Diffusion for a stream flowing through a cylindrical tube. *Proc. R. Ir. Acad.*, **1949**, 52, 163-167.
10. Zhua, Z., Liub, J., Zhanga, S., Nab, Xing., Zhanga, X. Evaluation of a hydride generation-atomic fluorescence system for the determination of arsenic using a dielectric barrier discharge atomizer. *Anal. Chim. Acta*, **2008**, 607, 136-141.
11. Bednar, A. J., Garbarino, J. R., Ranville, J. F., Wildeman, T. R. Preserving the Distribution of Inorganic Arsenic Species in Groundwater and Acid Mine Drainage Samples. *Environ. Sci. Technol.*, **2002**, 36, 2213-2218.
12. Patricia, A. G., Carol, A. S., Xinyi, W., John, T. C. Speciation and preservation of inorganic arsenic in drinking water sources using EDTA with IC separation and ICP-MS detection. *J. Environ. Monit.*, **2001**, 3, 371-376.

CHAPTER THREE

Investigation of leaching of arsenite and arsenate from contaminated sediments

3.1. Introduction

Widespread the occurrence of arsenic, distribution and its mobilization have received increasing significant attention in the recent years due to its high toxicity. It is distributed throughout the rocks, soil, natural waters and is present in trace amounts in all living matter. In spite of a large number of researches, still it is not clear the mechanism of geochemical occurrence of arsenic in the groundwater different part of the world [1]. Elevated levels of arsenic occur in the environment from the various anthropogenic processes such as agricultural applications, mining activities and mineral processes as well as natural geochemical processes [2, 3]. Due to increasing the industrialization, to dispose the mine tailings [4, 5], metallurgical slags [6] and municipal sewage sludge [7] also increased. In the many countries of the world from the mine spoils, slag dumps, tailings that remained left in the area of manufacturing after industrial process which contained extremely high concentration of arsenic [8]. In those disposing, soil is polluted from where possible mobilization and subsequent leaching of arsenic into groundwater or surface water or enter the human food chain through various chemical and biological reactions. The forms of arsenic present in the soils depend on the type and amounts of sorbing compounds. Soil pH and redox potential is very closely related the adsorbed arsenate fraction but it varies with soil type under the same pH conditions [9].

According to the currently available information on geochemistry of arsenic, it is commonly found in the sulfidic minerals and which is released from the solids through the various process called dissolution, redox reactions, adsorption-desorption. The solubility, mobility, toxicity and bioavailability of arsenic depend on the parent minerals form, oxidation state and mobilization mechanisms [10, 11].

The mobility of arsenic in the environment depends on its interactions with metal oxides (Fe, Al, Mn) that exists as a disperse phases (*e.g.* as a coatings). The binding mechanism of arsenic on the metal oxides is impacted by pH and redox potential of the

environment [12]. Arsenate binds more strongly with metals oxides as compared to arsenite [13]. Arsenate retention on ferrihydrite is usually at low pH compared to the arsenite retention at higher pH values [14]. Arsenic mobility tends to increase due to mineral dissolution, proton competition of surface binding sites and increase the surface potential. Onset of reducing conditions in such environments can lead to the dissolution of iron oxy-hydroxides coating, resulting to release of arsenic into the groundwater [15-17]. Due to the application of phosphate fertilizer in the agricultural activities to the soil surface the releasing of arsenic ions sorbed to the aquifer minerals by the competitive ion exchange with phosphate ions which migrates into aquifer [18]. As mentioned, the mobilization of arsenic under reduced condition iron plays an important role in many subsurface environments. The pH is another major factor to release the arsenic into groundwater.

In the past years various fractionation protocols have been developed for heavy metals. Leaching of heavy metals from the environmental solids samples, a variety of leaching reagents have been proposed to characterize the physiochemical behavior of metals *e.g.* water-soluble, reducible/oxidizable and complex bound fractions [19]. In the leaching of heavy metals oxidation state don't consider but on the other hand leaching of arsenic from the environmental samples oxidation state has to be consider due to the toxicity variation. Arsenite is 60 times more toxic than arsenate [20].

Many researchers have investigated the potential release of arsenic from the solid wastage by the leaching test in the different ways by monitoring many factors like pHs, redox condition, differences in the leaching fluid, liquid-to-solid ratio and long agitation time. The majority of these investigations have been based on to measure the total arsenic from the various environmental samples by the effect of pHs [21], from the natural rock under oxidizing condition [22], from the subsurface sediment sample by the effect of bicarbonate [23], from the soils and wastes using the chelating agent [24] and from the various rocks by controlling the geochemical conditions [25]. The main purpose of their substantial effort was to give rationalization of the mechanism of arsenic leaching from the environmental samples. Most of the leaching process used the conventional techniques which are often expensive and mostly they measure total arsenic. However, the mechanism of arsenic leaching from the contaminated sediments as well as solid

wastage is not well monitored. An investigation has been carried out to have useful information of the mechanisms of arsenic from the contaminated sediments.

Several reports have been presented for automated arsenic determination such as Australian group, Sakchai *et al.*, proposed highly sensitive (limit of detection $0.3 \mu\text{g L}^{-1}$) and rapid (150 h^{-1}) flow analysis based on chemiluminescence emission in the reaction with permanganate [26], and Hungary's group, Stefanka *et al.*, developed flow injection method coupled with ICP-TOFMS [27]. Most of arsenic flow analyses recently reported is based on hydride generation with AAS [28-30] and atomic fluorescence spectroscopy [31] or with chromatographic separation [32, 33].

The flow system especially sequential hydride generation flow analysis is used to investigate the leaching of arsenic from the contaminated sediments a) under aerobic and anaerobic b) effect of phosphate to leach arsenic under anaerobic and c) arsenic leached from the sediment by stepwise addition of ions. Leachates arsenic was monitored by discriminatively arsenite and arsenate in near-real time. The purposes of the studies were to investigate the mechanisms of arsenic leaching and/or behavior of arsenic leaching mechanism from the contaminated sediments.

3.2. Experimental

3.2.1. Sediment samples collection

Sediment and water samples were collected from the river near an old mine (N $32^{\circ}77'$, E $31^{\circ}36'$) which was developed in the world war two for chemical warfare development. The water came out from the mining mouth and formed a river stream. Along the river, sediments were sampled at three points is shown in Fig. 2-7. (Chapter two). The first sediment sample was taken just downstream of the closed mining (No. 4) and the second and third were 300 m (No. 7) and 3.5 km (No. 13) downstream, respectively. The sediment samples are shown in the Fig. 3-1. The color of the sediment is yellowish brown to gray. Physical characterization of sediments is inserted in the Table 3-1.

Arsenic content in the sediments were determined by acid digestion followed by the standard method [34]. The each sediment sample (4 g) was digested with 15 mL HNO_3 and 15 mL doubly diluted H_2SO_4 . Occasionally 10 mL of HNO_3 was added and finally 5

mL of HNO₃ and 3 mL of HClO₄ was added and heated until the liquid volume became 5 mL. After cooling at room temperature, 50 mL deionized water (DIW) was added and heated for 60 min again. The resulting suspensions were filtered with 5B filter paper and made up to be 100 mL. Arsenic content in the digested samples were determined by SHGFA.



Fig. 3-1. Sediment samples without wash a) and with wash sieving on 80-mesh b).

Table 3-1. Physical characterization of sediments

Sediment No.	As (mg kg ⁻¹)		Specific surface area (m ² g ⁻¹)*
	Without wash	With wash	
4 (coarse)	422	102	4.29
7 (middle)	476	450	3.57
13 (fine)	218	142	5.19

*Specific surface area for sediments with washed.

3.2.2. Leaching examinations

Before leaching examination, the sediment samples were washed with water on an 80-mesh sieve to remove fine particles. Then, the sediments were dried at 135°C for 3 h to remove adsorbed water in air for aerobic experiments or with introducing N₂ gas at a flow rate of 500 mL min⁻¹ for anaerobic experiments. Thus treated sediment sample (100 g) was added into 800 mL of synthetic groundwater which contained Ca²⁺ 100 mg L⁻¹,

bicarbonate 100 mg L^{-1} , silicate 20 mg L^{-1} , nitrate 2 mg L^{-1} , and phosphate 3 mg L^{-1} , and pH was adjusted to be 9.0 by the addition of $0.1 \text{ M Na}_2\text{CO}_3$. Air or N_2 was purged through the synthetic groundwater at the flow rate of 20 mL min^{-1} since 3 h before the addition of sediment to make the water condition aerobic or anaerobic. Thus, the sediment and water were treated with air and N_2 beforehand for aerobic and anaerobic experiments, respectively. Leached arsenite and total arsenic were measured by SHGFA (Chapter two Fig. 2-1). Dissolved oxygen, redox potential and pH of the water was monitored concurrently with DO meter and ion meter (OM-14 and F-53, both from Horiba, Kyoto, Japan).

3.2.3. Comparative measurement

For comparison measurement, 10 water samples were collected at the same time during leaching with SHGFA and filtered through $0.45 \mu\text{m}$ cellulose acetate filter. Water sample 5 mL was taken into volumetric flask and made up to 50 mL after addition of 0.5 mL nitric acid and $100 \mu\text{L}$ of 0.5 mg L^{-1} yttrium as an internal standard. Arsenic was measured by ICP-MS (Element, Thermo Fisher Scientific) to compare with SHGFA results.

3.2.4. Leaching test with phosphate ions

To investigate the effect of phosphate ions to leach arsenic, sediment No. 7 treated with different concentrations of phosphate ions. Prior to the leaching test, sediment was washed with water on an 80-mesh sieve to remove fine particles. Then, air dried at room temperature and finally at 135°C for 3 h to remove adsorbed water with purging N_2 gas at a flow rate of 500 mL min^{-1} . Thus treated 50 g sediment sample was added into each containing 400 mL of five different concentration of 0 (no addition), 3, 10, 15, and 20 mg L^{-1} phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, Nacalai) solutions. Nitrogen gas was purged at the flow rate of 20 mL min^{-1} since 3 h before to add the sediment through the solution to make it anaerobic. Every 30 minutes arsenite and arsenate was monitored with SHGFA for 3 h. In sequence, arsenite and arsenate were monitored at 24, 48, and 72 h. The experiment was conducted for 72 h under anaerobic. The pH of the solutions was monitored with ion meter (F-53, Horiba, Japan) and was near neutral.

3.2.5. Leaching test with stepwise ions addition

To investigate the effect of stepwise ions addition, 110 g air dried sediment No.7 (with washed) was added into 1000 mL deionized water (DIW) and monitored the leached arsenic. To make the solution aerobic or anaerobic air or N₂ was purged through the solution at the flow rate of 20 mL min⁻¹ since 3 h before the addition of sediment. Gradually, stepwise added the synthetic groundwater compositions (calcium 100 mg L⁻¹, bicarbonate 100 mg L⁻¹, silicate 20 mg L⁻¹, nitrate 2 mg L⁻¹, and phosphate 3 mg L⁻¹) and arsenite and arsenate were monitored. Additional amount of phosphate was added into two steps (7 mg L⁻¹ and 20 mg L⁻¹) and arsenite and arsenate were monitored. Initially, pH of the deionized water (DIW) was 6.68 and stepwise addition of ions pH gradually increased and finally it was above 9. The experiment was conducted for 5 h under aerobic and anaerobic condition.

3.2.6. Leaching test with synthetic As-containing ferric oxide

To investigate the effect of pH effect to leach arsenic, 1 g (7138 mg kg⁻¹) arsenic containing ferric oxide was added each containing 200 mL synthetic groundwater at different pH 3, 5, 7 and 9. The pH of the solutions were adjusted by the addition of 10 mM HCl and 10 mM sodium carbonate and the leachates arsenic were monitored by discriminating arsenite and arsenate for several days.

3.3. Results and discussion

3.3.1. Leaching test with SHGFA

Leaching characteristics of the sediments sampled along the mining river were examined by SHGFA. Examples of raw data are shown in Fig. 3-2. The top panel (a) shows responses for standard solutions containing 0, 1, 5 and 10 µg L⁻¹ of As(III) and As(V). The data for low concentrations of arsenic indicate that the SHGFA system had enough ability to measure arsenic level of sample waters with distinguishing As(III) and As(V). For the same sample, the first peak was corresponding to As(III) and the second peak was for total As (As(III) +As(V)). Limits of detection (LODs) obtained from three

times standard deviation of blank signals were 0.02 and 0.03 $\mu\text{g L}^{-1}$ for As(III) and total As, respectively. Calibration curve was straight from 1 $\mu\text{g L}^{-1}$ to 0.5 mg L^{-1} .

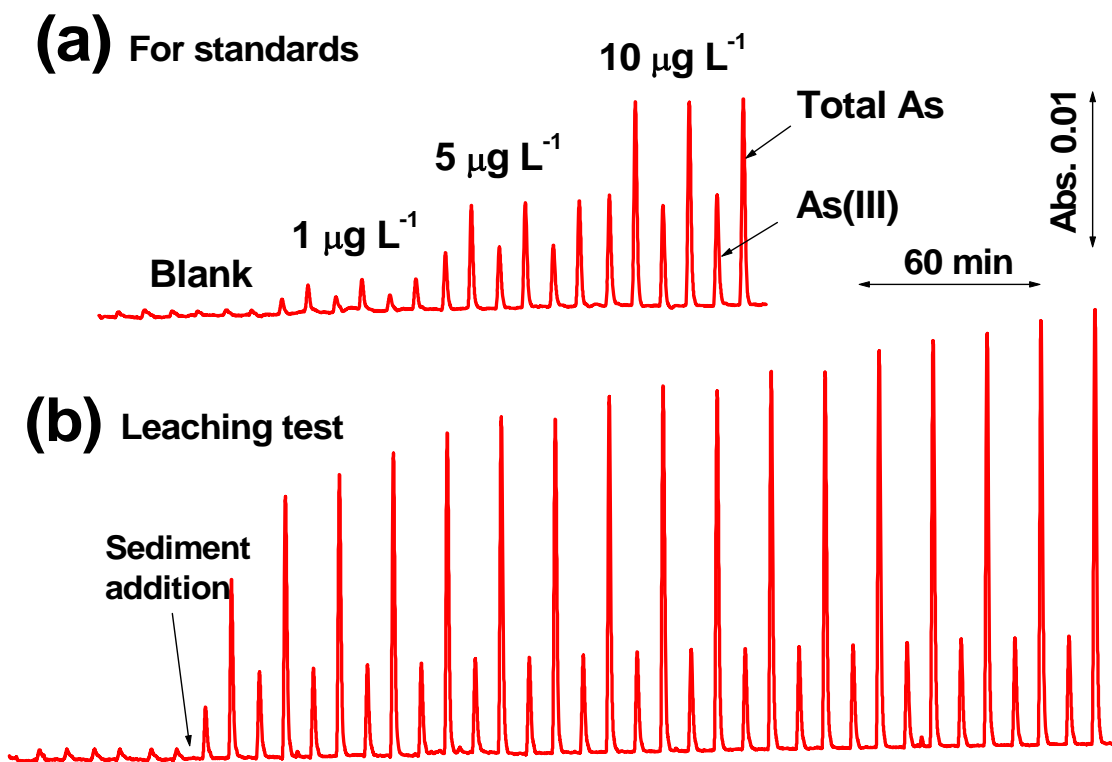


Fig. 3-2. Response signals of the SHGFA system for standard solutions of 0, 1, 5 and 10 $\mu\text{g L}^{-1}$ As(III) + As(V) (a) and for monitoring of leached arsenic from sediment No. 7 in aerobic condition (b).

The panel (b) shows real signals obtained during the leaching test where sediment was added into water and As(III) and As(V) were monitored before and after the sediment addition. After the sediment addition, peaks appeared and their intensities gradually increased with the time. Peaks for As(III) were saturated in a short period of time and concentrations did not increase much while peak for total As continued increasing. Interferences from coexisting species are not large as investigated previously and effects from heavy metal ions can be reduced by addition of EDTA [35, 36]. In case of iron and copper ions species needed attention of interference, and phosphate, silicate, carbonate, sulfate, cyanide, magnesium, calcium, ammonium, nickel ions didn't interfere.

To make sure that there are few effects from these ions, iron, copper and sulfide ions contained in leaching sample solutions was analyzed by AAS, and they were below limits of detection of AAS (0.1 mg L^{-1}). These metals do not exist as free ions in neutral solution due to large formation constants for hydroxide complex. The iron content in the leachates was not high enough to interfere the arsenic analysis. Sulfide could not be detected by the fluorometric method using fluorescence mercuric acetate [37].

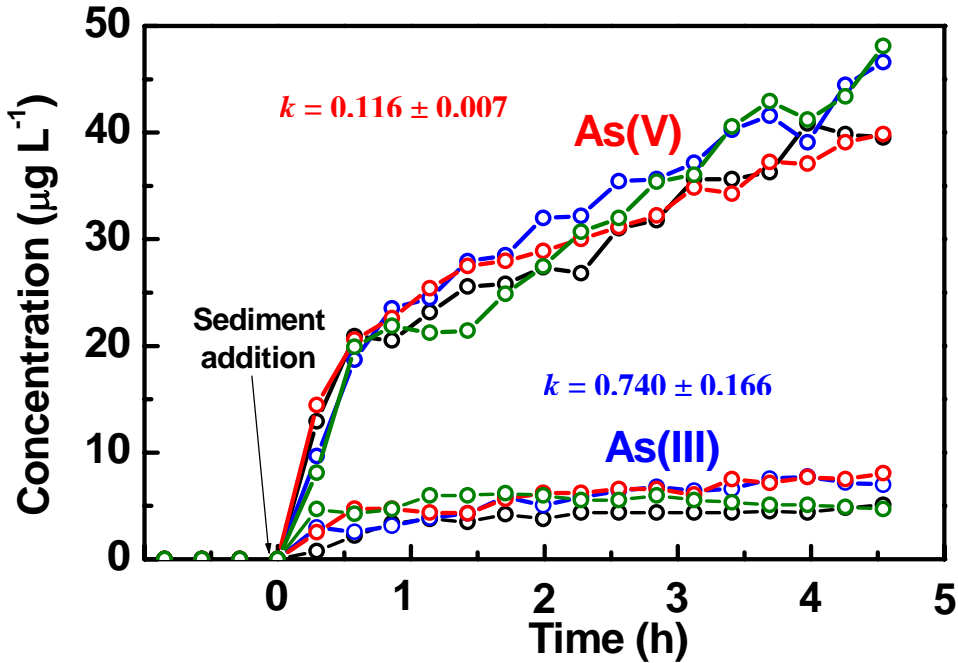


Fig. 3-3. Calculated concentrations of leached As(III) and As(V) obtained by repeating four experiments for sediment No. 7 in aerobic condition.

Plot of As(III) and As(V) concentrations against the leaching time obtained with the sediment No. 7 in aerobic condition is shown in the Fig. 3-3. The measurement was repeated four times and the each run was performed for 4.5 h. It can be seen that repeatability of the leaching examination was good and this method was suitable to investigate leaching property of sediments. Concentration of As(III) reached constant in 30 min to be $\sim 5 \text{ } \mu\text{g L}^{-1}$ in those experiments. On the other hand, As(V) concentration continued increasing and the As(V) level reached $\sim 40 \text{ } \mu\text{g L}^{-1}$ at the end of experiments. It may suggest that leaching of As(III) was faster and most of As(III) contained in the sediment consumed in a short period of time. It was probably due to As(III) is 5-10 times

more soluble than As(V) [38]. In this way interesting results for As(III) and As(V) with relatively good time resolution while so far only total As was monitored in hours or days [39].

The pH of sample solution was adjusted to be 9 by the addition of 0.1 M Na₂CO₃. Effect of pH was tested and it was found that leaching was higher in weekly alkaline solution compared to neutral or slightly acidic solution. The adsorption affinity of arsenate is higher at low pH and for arsenite at higher pH values [40].

3.3.2. Comparative measurement

The comparison measurement data with this method and ICP-MS in µg L⁻¹ was expressed as:

SHGFA data = 0.840 ICP-MS data + 0.002 ($R = 0.973$) for total As.

Particularly, agreements were obtained for comparison analysis ($n = 10$), as the value of the slope being 0.840 approaching unity and it can be said that the present method was reliable in the leaching analysis. ICP-MS showed slightly larger data compared to SHGFA data probably due to solid small particles contained in leaching samples.

3.3.3. Kinetic consideration of the leaching

In the leaching experiments different sediments and synthetic groundwater (pH 9) were used as an extraction fluid. Arsenic concentration in the leachates increased until reach at equilibrium subsequently decreased. It suggests that the kinetics of arsenic desorption from the sediments may be dissolution of minerals or limited by diffusion is the main side reactions, pH changes was negligible and were approximately constant throughout the experiment.

It assumed that the leaching was pseudo first order reaction from the sediment with the rate constant k . Accordingly, the rate of leaching namely decreasing rate of arsenic concentration of sediment $-(dC_{sed} / dt)$ can be expressed as eq. (1).

$$-\frac{dC_{sed}}{dt} = \frac{dC_{sol}}{dt} \frac{W}{V} = k C_{sed} \quad \dots (1)$$

The term C_{sed} is leachable arsenic concentration in sediment in µg kg⁻¹, C_{sol} is leached arsenic concentration in solution in µg L⁻¹, W is weight of sediment in kg and V is volume

of solution in L. Eq. (1) can be changed to Eq. (2) with using initial sediment concentration C_{sed}^0 . The C_{sed} is expressed as subtraction of leached amount of arsenic from the initial arsenic concentration in C_{sed}^0 and Eq. (1) can be changed to Eq. (2).

$$\frac{dC_{sol}}{dt} \frac{W}{V} = k \left(C_{sed}^0 - C_{sol} \frac{W}{V} \right) \quad \dots (2)$$

Both sides are divided by W/V and we obtain Eq. (3).

$$\frac{dC_{sol}}{dt} = k \left(C_{sed}^0 \frac{V}{W} - C_{sol} \right) \quad \dots (3)$$

Eq. (3) shows the rate of increase in solution concentration, which can be measured in the

leaching experiments. Eq. (3) can be converted in integrated form. First, $C_{sed}^0(V/W)$ can be rewritten as C_{sol}^∞ and we obtain Eq. (4).

$$\frac{dC_{sol}}{C_{sol}^\infty - C_{sol}} = k dt \quad \dots (4)$$

Integrated form:

$$\ln(C_{sol}^\infty - C_{sol}) = \ln C_{sol}^\infty - k t \quad \dots (5)$$

or it can be expressed as:

$$\ln \frac{C_{sol}^\infty - C_{sol}}{C_{sol}^\infty} = -k t \quad \dots (6)$$

The term C_{sol}^∞ can be estimated from the $C_{sol} - t$ curve obtained in leaching examination. The concentrations of As(III) and As(V) were almost constant from 24 to 72 h as shown in Fig. 3-4, and 24 h data was taken as C_{sol}^∞ value. Log scale plot is shown in the bottom panel of Fig. 3-4: $\ln\{(C_{sol}^\infty - C_{sol})/C_{sol}^\infty\}$ was plotted against time (t). Good linearity was observed in the first 1 h for both As(III) and As(V).

From the first 1 h data of the four runs (Fig. 3-3), the rate constant k was obtained as 0.740 ± 0.166 for As(III) and 0.116 ± 0.007 for As(V). It can be said that leaching of As(III) was six times faster than that of As(V). However, basically the leaching amount of As(III) was much smaller than that of As(V). It can be said that the leachable As(V) is dominant in the sediment compared to As(III) content.

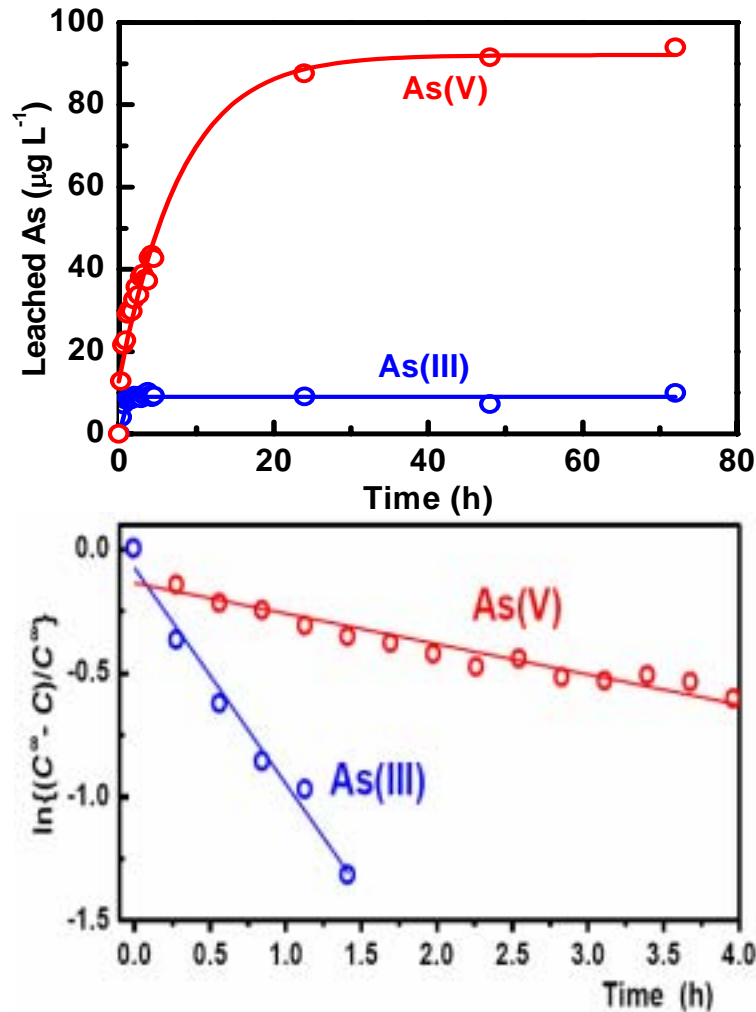


Fig. 3-4. Long term change in leached As(III) and As(V) (top) and log scale plot of the leached arsenic (bottom) obtained with sample No. 7 in aerobic condition.

3.3.4. Leaching characteristics with different sediments and different conditions

Arsenic leaching was investigated with different sediments sampled along the river is shown in the Fig. A-1. Anaerobic and aerobic conditions were tested for the leaching and solution concentration at 4.5 h leaching and kinetic constants obtained as shown in Table 3-2. Among the samples, sediment sample No. 7, which contained higher amount of arsenic (450 mg kg^{-1}), arsenic leached as $5.1 \mu\text{g L}^{-1}$ As(III) and $39.5 \mu\text{g L}^{-1}$ As(V), respectively under aerobic condition. Under aerobic from the sediment sample No. 4, desorption of arsenic was low because sediment physical properties was almost pebble-stone and adsorbed less amount of arsenic, as a result the minerals dissolution and

desorption of arsenic was also low. In case of sediment sample No. 13, which was in reduced condition in the sampling situation, desorption of As(III) was significant compared to the other sediments. From the sediment sample No. 4 arsenic was leached as 1.0 $\mu\text{g L}^{-1}$ As(III) and 20.6 $\mu\text{g L}^{-1}$ As(V) whereas from the sediment sample No. 13 arsenic was leached as 19.8 $\mu\text{g L}^{-1}$ As(III) and 26.2 $\mu\text{g L}^{-1}$ As(V), respectively. The finer sediment sample was in anaerobic condition released inorganic arsenic significantly in the leaching examination compared to the other sediment samples. In any cases, leached arsenic in 4.5 h was ~3% of sediment arsenic. With this investigation it can be said that most of arsenic was to be in insoluble form.

Table 3-2. Leaching results obtained in aerobic and anaerobic

Sediment	mg kg ⁻¹	Aerobic				Anaerobic			
		As(III)		As(V)		As(III)		As(V)	
No.		Elution* $\mu\text{g L}^{-1}$	<i>k</i> h^{-1}	Elution $\mu\text{g L}^{-1}$	<i>k</i> h^{-1}	Elution $\mu\text{g L}^{-1}$	<i>k</i> h^{-1}	Elution $\mu\text{g L}^{-1}$	<i>k</i> h^{-1}
4	102	0.83	0.554	20.6	0.118	0.77	0.964	16.3	0.157
7	450	5.09	0.740	39.5	0.116	8.71	0.497	49.4	0.153
13	142	19.8	1.15	26.2	0.117	18.1	0.402	45.1	0.142

*Elutions are concentrations at 4.5 h leaching.

The leaching of arsenic concentration in anaerobic is more than leached in aerobic condition. In anaerobic condition, reductive dissolution of metal (Fe, Al, Mn) oxides are more which combine with arsenic, therefore leaching of arsenic also more than in aerobic. This indicates that anaerobic condition enhances the leaching of arsenic from the sediments. Both in aerobic and anaerobic condition the same sediment samples were used for the leaching experiments. Under anaerobic condition from the sediment sample No. 7, 8.71 $\mu\text{g L}^{-1}$ As(III) and 49.4 $\mu\text{g L}^{-1}$ As(V) were obtained, and their levels were more than leached under aerobic condition (5.09 $\mu\text{g L}^{-1}$ As(III) and 39.5 $\mu\text{g L}^{-1}$ As(V)). Sediment sample No. 13 sample was in reduced condition may be As(III) and As(V) coprecipitated/adsorbed with metals oxides. This is why in the both conditions As(III) was leached from the sediment sample No. 13 more than other two sediment samples.

While amounts of elution of As(V) were higher than those of As(III), kinetic constants for As(V) were lower than As(III). Desorbable As(III) leached quickly compared to As(V).

3.3.5. Arsenic leached by the effect of phosphate ions

Leaching behaviors of arsenic leached from the sediment No. 7 was examined by the SHGFA system and obtained response chart is shown in the Fig. 3-5. The response signals obtained during the leaching test where sediment was added into solution and leachate arsenics were monitored before and after the addition of sediment. After addition of the sediment, peaks appeared as well as intensities gradually increased with the elapse of time.

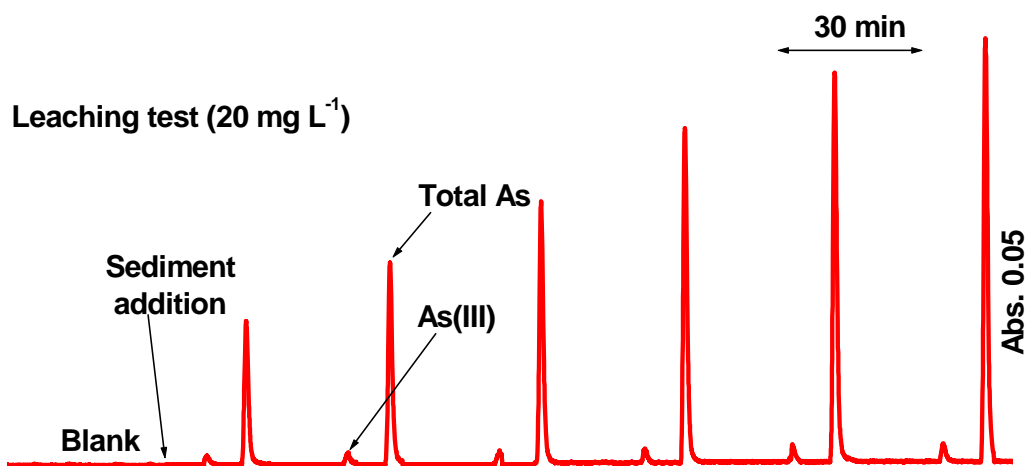


Fig. 3-5. Response signals during leaching test for first 3 h by the effect of 20 mg L⁻¹ phosphate under anaerobic. The first peak correspond to As(III) and the second peak correspond to the total As.

The amount of arsenic leached from the sediment is evidently dependent on the phosphate concentration is shown in the Fig. 3-6. Leaching amount of arsenic gradually increased for As(III) and As(V) until 24 h and 48 h, respectively then decreased. Possibly re-adsorption or co-precipitation may happen with the metal oxides. It should be stated that pH of the solutions were relatively constant during the leaching test and it was near neutral. As(III) and As(V) were equilibrated at different time, because As(III) is normally less strongly adsorbed by metal oxides than As(V) under near neutral pH. At the

equilibrium (24 h), As(III) was almost $10 \mu\text{g L}^{-1}$ for without/with phosphate. Conversely, leaching amount of As(V) was significantly increased with respect to the phosphate concentration and elapse of time. Leached amount of arsenate was very steep for 20 mg L^{-1} phosphate until reach at equilibrium (48 h) and arsenic was leached as As(III) $2.5 \mu\text{g L}^{-1}$ and As(V) $311.4 \mu\text{g L}^{-1}$, respectively.

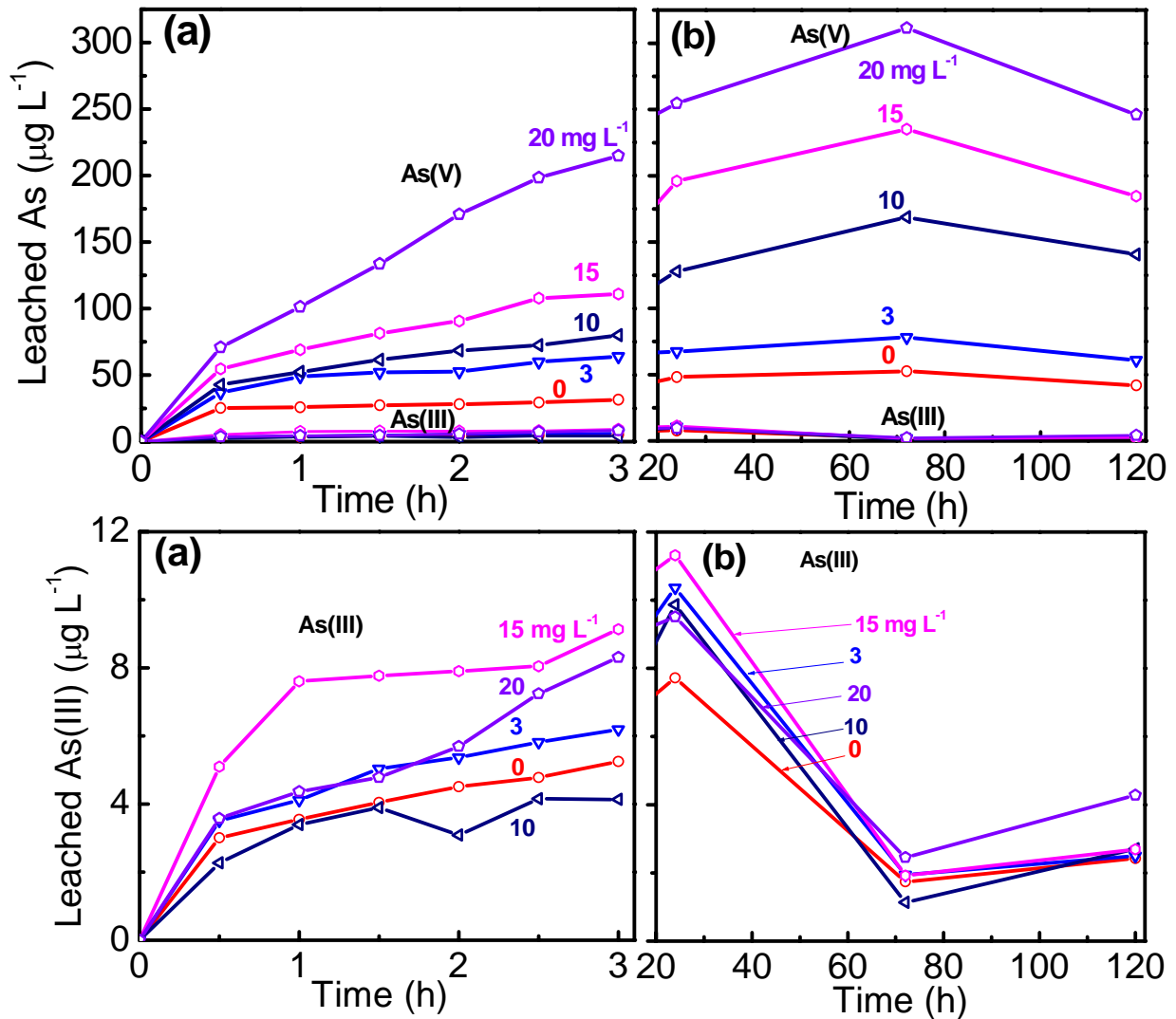


Fig. 3-6. Effect of phosphate concentrations to leach arsenic upper panel first 3 h (a) and successively monitored at 24, 48, and 72 h under anaerobic condition (b). Lower panel only shows leached As(III).

In the all leaching experiment As(V) was dominant in the aqueous phase. As phosphate is smaller in size and has higher charge density [40] as a result, with increasing

the phosphate concentration in the suspension leached amount of arsenate also increased. A good relationship was obtained between the phosphate concentration and leached amount of arsenate in the aqueous phase is shown in the Fig. 3-7, while leached amount of arsenite was same without/with phosphate. It is reported that competitive sorption of arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) can be affected some properties [41], and the binding energy is not the major controlling factor for the competitive effect of phosphate on arsenate sorption on soil and the effect of phosphate was more with less arsenic sorption capacity [42].

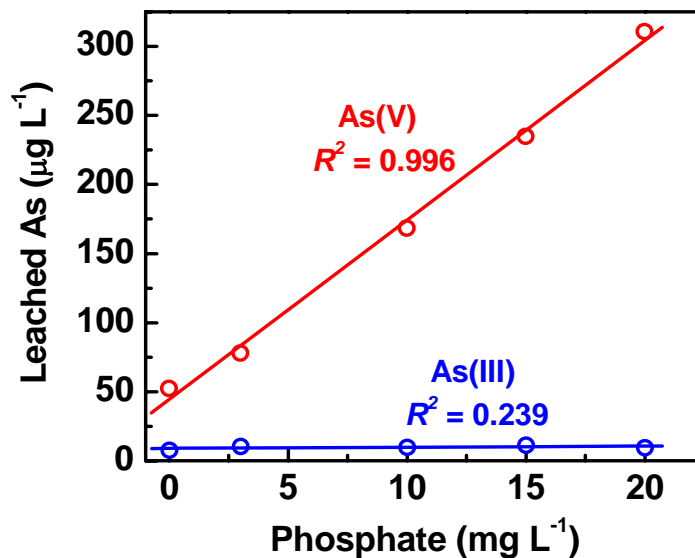


Fig. 3-7. Effect of phosphate concentration to extracts As(III) and As(V) from the sediment sample No. 7 under anaerobic.

Application of phosphate fertilizers for agricultural activities have caused the mobilization of phosphate from the fertilizers down to shallow aquifers, which enhances the mobilization of arsenic due to anion exchange onto the reactive minerals surfaces to increase the groundwater arsenic concentration like India, Bangladesh. It is well known that phosphate promotes growth of sediment biota and it may plays as an eluent for arsenic from the sediment [43]. Thus, phosphate is considered to be one of the most important factors to mobilize arsenic to groundwater from the contaminated sediments.

In Table 3-3 shows the kinetic studies data for arsenic leaching from the sediment by the effect of phosphate ions. In the Fig. 3-8 shows the leaching of arsenic from the sediment was found pseudo first order reaction.

Table 3-3. Leaching results obtained under anaerobic by the effect of phosphate ions

Sediment (mg kg ⁻¹)	Phosphate (mg L ⁻¹)	*Conc. (µg L ⁻¹)		<i>k</i> -value (h ⁻¹)		<i>R</i> ² -value	
		As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
450	0	7.7	52.6	0.330	0.226	0.913	0.659
	3	10.4	78.1	0.269	0.494	0.896	0.912
	10	9.9	168.8	0.166	0.187	0.842	0.890
	15	11.3	235.2	0.450	0.197	0.828	0.928
	20	9.5	311.4	0.601	0.387	0.918	0.996

*Conc. at equilibrium for As(III) 24 h and As(V) 48 h.

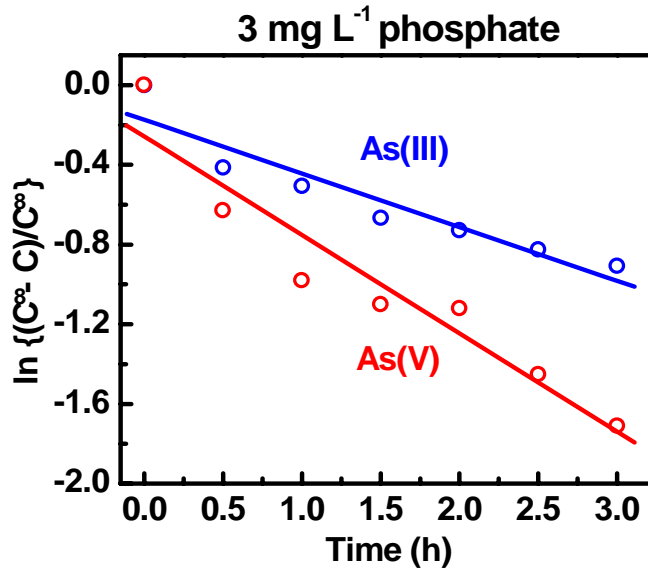


Fig. 3-8. Pseudo first order kinetic for arsenite and arsenate. Data presented for 3 mg L⁻¹ phosphate.

In the section 3.3.4, it was found that leaching rate for As(III) was faster than As(V) where extraction fluid was the synthetic groundwater [44]. In case of phosphate effect, it found that leaching rate of As(III) is faster without phosphate effect. As expected, leaching rate for As(V) will be faster than As(III) and obtained that As(V) was faster than As(III) by the effect of 3 and 10 mg L⁻¹ phosphate, respectively. In case of 15 and 20 mg L⁻¹ phosphate, leaching rate for As(III) was faster than As(V). There may be another reason but not clear. However, with increasing the phosphate concentration leaching

amount of As(V) was increased. In brief, it is obvious that phosphate ion possesses to leach As(V) effectively from the sediment mineral surfaces.

3.3.6. Arsenic leached by the stepwise ions addition

In the Fig. 3-9 shows the arsenic leached by the effect of stepwise ions addition under aerobic and anaerobic. Initially, sediment (No. 7) was added into deionized water (DIW), in both cases the leaching amount of arsenic as As(III) and As(V) was very low. Subsequently, stepwise addition of ions (calcium 100 mg L⁻¹ + bicarbonate 100 mg L⁻¹) and then (silicate 20 mg L⁻¹ + nitrate 2 mg L⁻¹ + phosphate 3 mg L⁻¹) leaching of arsenic also gradually increased. Stepwise addition of synthetic groundwater compositions, at 2.55 h under aerobic, arsenic leached as 2.7 μg L⁻¹ As(III) and 12.9 μg L⁻¹ As(V), respectively. Whereas, at the same time under anaerobic arsenic leached as 2.6 μg L⁻¹ As(III) and 16.6 μg L⁻¹ As(V), respectively.

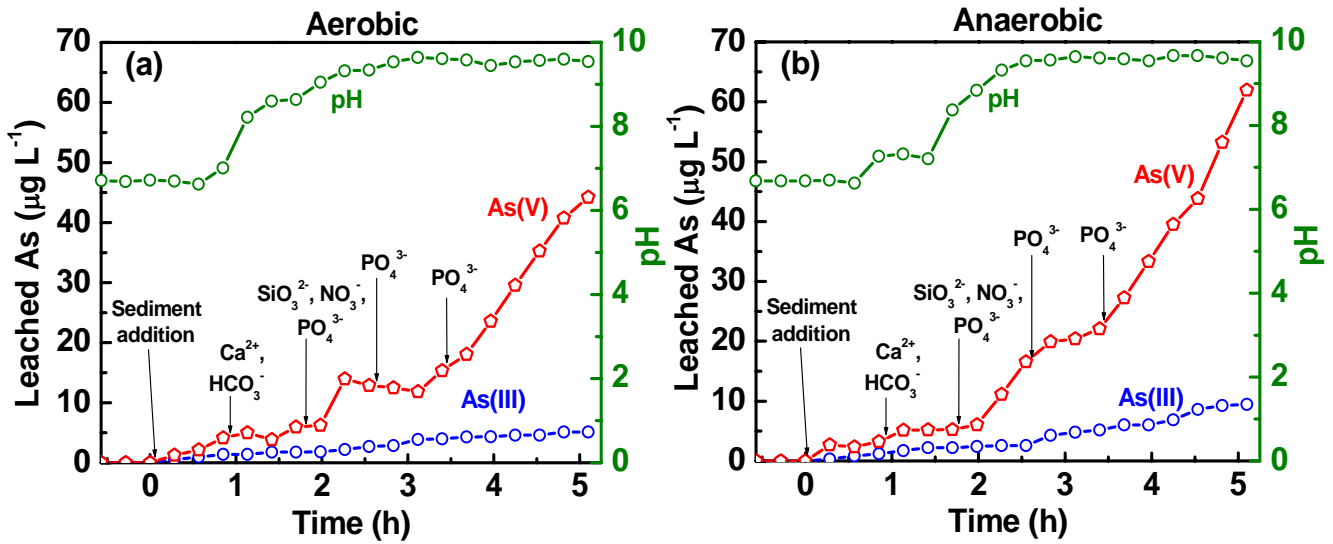


Fig. 3-9. Arsenic leached by the effect of step-wise ions addition under aerobic a) and arsenic leached under anaerobic b). Ions added: (calcium 100 mg L⁻¹ + bicarbonate 100 mg L⁻¹), (silicate 20 mg L⁻¹ + nitrate 2 mg L⁻¹ + phosphate 3 mg L⁻¹), (phosphate 7 mg L⁻¹), and (phosphate 20 mg L⁻¹).

The suspension pH also increased after addition of (calcium 100 mg L⁻¹ + bicarbonate 100 mg L⁻¹) as well as (20 mg L⁻¹ silicate + 2 mg L⁻¹ nitrate + 3 mg L⁻¹) and it was above 9. By the addition of additional amount of phosphate ions in two steps, 7

mg L⁻¹ and 20 mg L⁻¹ pH was constant but in both conditions leaching of As(V) was very steep and leaching of As(III) also increased. In case of anaerobic, leaching amount of arsenic was more than aerobic condition. Of course, pH is an important factor to leach arsenic from the sediment surface, as the adsorption affinity of As(V) is higher at low pH and As(III) at higher pH values [10]. Therefore, at higher the pH the adsorbed arsenic from the sediment surface can be easily desorbed because to increase the suspension pH decreases positive surface charge of the metals oxides as a result increasing the pH aiding the desorption of As oxyanions [45]. Arsenic leached at 5 h, under aerobic as 5.1 µg L⁻¹ As(III) and 44.2 µg L⁻¹ As(V), respectively. Conversely, at the same time under anaerobic, arsenic leached as 9.5 µg L⁻¹ As(III) and 61.9 µg L⁻¹ As(V), respectively. It seems that anaerobic condition enhances to leach arsenic more than leached under aerobic from the sediment minerals surfaces. It is obvious that leaching of arsenic from the sediment not only leached as As(V) but also As(III) by the effect of stepwise ions addition. Increasing the phosphate concentration in the suspension desorption of As(III) and As(V) also increased sufficiently although As(V) was dominant in the aqueous phase.

3.3.7. Arsenic leached from As-containing ferric oxide

In the Table 3-4 shows the arsenic leached from the arsenic containing ferric oxide at different pH. Leaching of arsenics was monitored several days. On 6th day leaching of arsenic was significant and afterwards decreased. The amount of arsenic was leached from the As-containing ferric oxide at the lower pH value was low than leached at higher pH value.

Table 3-4. Leaching results for As-containing ferric oxide

Solution		As-containing ferric oxide (mg kg ⁻¹)	Leached As (µg L ⁻¹)	
(mL)	pH		As(III)	As(V)
200	3.0	7138	1.7	20.3
200	5.0		0.0	21.2
200	7.0		1.3	18.7
200	9.0		2.5	41.5

Leaching amount of total arsenic was from the As-containing ferric oxide at the pH 3.0, 5.0 and 7.0 were $22.0 \mu\text{g L}^{-1}$, $21.2 \mu\text{g L}^{-1}$ and $20.0 \mu\text{g L}^{-1}$, respectively. The leaching amounts of arsenics at those pHs were almost same. Whereas at higher pH (9.0) total amount of arsenic was leached $44.0 \mu\text{g L}^{-1}$ which was almost 2-fold than leached at the lower pHs. The adsorption affinity of As(V) is higher at low pH and for As(III) at higher pH value. At higher the pH vales (8.5-9.5) arsenic is bound less strongly to ferric oxides than at lower pH values [39] as a result desorption of arsenic at pH 9.0 was higher than those of acidic to neutral pHs.

3.4. Conclusions

The sequential hydride generation flow analysis is useful tool to analysis leached arsenic by discriminating arsenite and arsenate. Leaching rate for As(III) was faster than As(V) where extraction fluid was synthetic groundwater. In case of phosphate effect for 3 and 10 mg L^{-1} leaching rate of As(V) was faster than As(III). On the other hand, by effect of 15 and 20 mg L^{-1} phosphate leaching rate of As(III) was faster than As(V). However, phosphate ion effectively leached arsenic from the sediment surface especially As(V). The amount of leached arsenic as As(V) strongly depended on the phosphate concentration. However, in the all leaching experiments arsenic leached as As(III) and As(V) but mostly was As(V).

References

1. Anawar, H. M., Akai, J., Komaki, K., Terao, H., Yoshida, T., Ishizuka, T., Safiullah, S., Kato, K. Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *J. Geochem. Explor.*, **2003**, 77, 109-131.
2. Smedley, P. L., Kinniburgh, D. G. A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.*, **2002**, 17, 517-568
3. Roussel, C., Neel C., Bril, H. Minerals controlling arsenic and lead solubility in an abandoned gold mine tailings. *Sci. Total Environ.*, **2000**, 263, 209-219.
4. Jacob DL., Otte ML. Influence of *Typha latifolia* and fertilization on metal mobility

- in two different Pb-Zn mine tailings types. *Sci. Total Environ.*, **2004**, 333, 9-24.
5. Stoltz, E., Greger, M. Release of metals and arsenic from various mine tailings by *Eriophorum angustifolium*. *Plant Soil*, **2006**, 289, 199-210.
 6. Ettler, V., Komarkova, M., Jehlicka, J., Coufal, P., Hradil, D., Machovic, V., Delorme, F. Leaching of lead metallurgical slag in citric solutions-implications for disposal and weathering in soil environments. *Chemosphere*, **2004**, 57, 567-577.
 7. Carbonel-Barrachina, A. A., Jugsujinda, A, Burlo, F., Delaune, R. D., Patrick JR, W. H. Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH. *Water Res.*, **1999**, 34, 216-224.
 8. Krysiak, A., Karczewska, A. Arsenic extractability in soils in the areas of former arsenic mining and smelting, SW Poland. *Sci. Total Environ.*, **2007**, 379, 190-200.
 9. Mandal, B. K., Suzuki, K. T. Arsenic round the world: a review. *Talanta*, **2002**, 58, 201-235.
 10. Al-Abed, S. R., Jegadeesan G., Purandare, J., Allen, D. Arsenic release from the iron rich mineral processing waste: Influence of pH and redox potential. *Chemosphere*, **2007**, 66, 775-782.
 11. La Force, M. J., Hansel, C. M., Fendorf, S. Arsenic Speciation, Seasonal Transformations, and Co-distribution with Iron in a Mine Waste-Influenced Palustrine Emergent Wetland. *Environ. Sci. Technol.*, **2000**, 34, 3937-3943.
 12. Masue, Y., Loeppert, R. H., Kramer, T. A. Arsenate and Arsenite Adsorption and Desorption Behavior on Coprecipitated Aluminum: Iron Hydroxides. *Environ. Sci. Technol.*, **2007**, 41, 837-842.
 13. Yang, J. K., Barnett, M. O., Jardine, P. M., Basta, N. T., Casteel, S. W. Adsorption, Sequestration and Bioaccessibility of As(V) in Soils. *Environ. Sci. Technol.*, **2002**, 36, 4562-4569.
 14. Dixit, S., Hering, J. G. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. *Environ. Sci. Technol.*, **2003**, 37, 4182-4189.
 15. Nickson, R. T., McArthur, J. M., Ravenscroft, P., Burgess, W. G., Ahmed, K. M. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.*, **2000**, 15, 403-413.

16. Meng, X., Korfiatis, G. P., Jing, C., Christodoulatos, C. Redox Transformations of Arsenic and Iron in Water Treatment Sludge during Aging and TCLP Extraction. *Environ. Sci. Technol.*, **2001**, *35*, 3476-3481.
17. Technical report, *The World Bank, Vol-II*, Report No. 31303.
18. Acharyya, S. K., Chakraborty, P., Lahiri, S., Raymahashay, B. C., Guha, S., Bhowmik, A. Arsenic poisoning in Ganges delta. *Nature*, **1999**, *401*, 545-546.
19. Jimoh, M., Frenzel, W., Muller, V., Stephanowitz, H., Hoffmann, E. Development of a Hyphenated Microanalytical System for the Investigation of Leaching Kinetics of Heavy Metals in Environmental Samples. *Anal. Chem.*, **2004**, *76*, 1197-1203.
20. Fazal, M. A., Kawachi. T., Ichion. E. Extend and Severity of Groundwater Arsenic Contamination in Bangladesh. *Water Int.*, **2001**, *26*, 370-379.
21. Rigol, A., Mateu, J., Gonzalez-Nu nez, R., Rauret. G., Vidal, M. pHstat vs. single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. *Anal. Chim. Acta*, **2009**, *632*, 69-79.
22. Noubactep, C., Chen-Braucher, D., Schlothauer, T. Arsenic Release from a Natural Rock under Near-natural Oxidizing Conditions. *Eng. Life Sci.*, **2008**, *8*, 622-630.
23. Anawar, H. M., Akai, J., Sakugawa, H. Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere*, **2004**, *54*, 753-762.
24. Garrabrants, A. C., Kosson, D. S. Use of the chelating agent to determine the metals availability for leaching soils and wastes. *Waste Manage.*, **2000**, *20*, 155-165.
25. Igarashi, T., Imagawa, H., Uchiyama, H., Asakura, K. Leaching behavior of arsenic from various rocks by controlling geochemical conditions. *Miner. Eng.*, **2008**, *21*, 191-199.
26. Satienerakul, S., Cardwell, T. J., Kolev, S. D., Lenehan, C. E., Barnett, N. W. A sensitive procedure for the rapid determination of arsenic(III) by flow injection analysis and chemiluminescence detection. *Anal. Chim. Acta*, **2005**, *554*, 25-30.
27. Stefanka, Z., Abranko, L., Dernovics, M., Fodor, P. Characterisation of a hydraulic high-pressure sample introduction assisted flow injection-inductively coupled plasma time-of-flight mass spectrometry system and its application to the analysis. *Talanta*, **2004**, *63*, 705-712.

28. Hsiung, T. -M., Wang, J. -M. Cryogenic trapping with a packed cold finger trap for the determination and speciation of arsenic by flow injection/hydride generation/atomic absorption spectrometry of biological samples. *J. Anal. At. Spectrom.*, **2004**, *19*, 923-928.
29. Anthemidis, A. N., Martavaltzoglou, E. K. Determination of arsenic(III) by flow injection solid phase extraction coupled with on-line hydride generation atomic absorption spectrometry using a PTFE turnings-packed micro-column. *Anal. Chim. Acta*, **2006**, *573-574*, 413-418.
30. Tsalev, D. L., Sperling, M., Welz, B. Flow-injection hydride generation atomic absorption spectrometric study of the automated on-line pre-reduction of arsenate, methylarsonate and dimethylarsinate and high-performance liquid chromatographic separation of their L-cysteine complexes. *Talanta*, **2000**, *51*, 1059-1068.
31. Yan, X. -P., Yin, X. -B., He, X. -W., Jing, Y. Flow Injection On-Line Sorption Preconcentration Coupled with Hydride Generation Atomic Fluorescence Spectrometry for Determination of (Ultra)trace Amounts of Arsenic(III) and Arsenic(V) in Natural Water Samples. *Anal. Chem.*, **2002**, *74*, 2162-2166.
32. Simon, S., Tran, H., Pannier, F., Poten-Gautier, M. Simultaneous determination of twelve inorganic and organic arsenic compounds by liquid chromatography-ultraviolet irradiation-hydride generation atomic fluorescence spectrometry. *J. Chromatogr. A*, **2004**, *1024*, 105-113.
33. Gomez-Ariza, J. L., Lorenzo, F., Garcia-Barrera, T. Simultaneous determination of mercury and arsenic species in natural freshwater by liquid chromatography with on-line UV irradiation, generation of hydrides and cold vapor and tandem atomic fluorescence detection. *J. Chromatogr. A*, **2004**, *1056*, 139-144.
34. Kagaku Jikken Tekisuto Kenkyukai (Ed.), Heavy Metals in Sediments (Pretreatments) (in Japanese), Kankyo Kagaku, Sangyo Tosho Co., Tokyo. **1997**, pp. 66-73.
35. Toda, K., Ohba, T., Takaki, M., Karthikeyan, S., Hirata, S., Dasgupta, P. K. Speciation-Capable Field Instrument for the Measurement of Arsenite and Arsenate in Water. *Anal. Chem.*, **2005**, *77*, 4765-4773.
36. Idowu, A. D., Dasgupta, P. K., Genfa, Z., Toda, K., Garbarino, J. R. A Gas-Phase

- Chemiluminescence-Based Analyzer for Waterborne Arsenic. *Anal. Chem.*, **2006**, *78*, 7088-7097.
37. Ohira, S., Toda, K. Ion chromatographic measurement of sulfide, methanethiolate, sulfite and sulfate in aqueous and air samples. *J. Chromatogr. A*, **2006**, *1121*, 280-284.
38. Singh, A. K. Chemistry of arsenic in groundwater of Ganges-Brahmaputra river basin. *Curr. Sci.*, **2006**, *91*, 599-606.
39. Anawar, H. M., Akai, J., Sakugawa, H. Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere*, **2004**, *54*, 753-762.
40. Wenzel, W. W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D. C. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal. Chim. Acta*, **2001**, *436*, 309-323.
41. Zhang, H., Selim, H. M. Competitive sorption-desorption kinetics of arsenate and phosphate in soils. *Soil Science*, **2008**, *173*, 3-12.
42. Violante, A., Pigna, M. Competitive Sorption of Arsenate and Phosphate on Different Clay Minerals and Soils. *Soil Sci. Soc. Am. J.*, **2002**, *66*, 1788-1796.
43. Acharyya, S. K., Lahiri, S., Ramahashay, B. C., Bhowmik, A. Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environ. Geol.*, **2000**, *39*, 1127-1137.
44. Hashem, M. A., Takaki, M., Jodai, T., Toda, K. Measurement of arsenite and arsenate contained in mining river waters and leached from contaminated sediments by sequential hydride generation flow injection analysis. *Talanta*, **2011**, *84*, 1336-1341.
45. Masscheleyn, P. H., Delaune, R. D., Patrick, Jr., W. H. Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil. *Environ. Sci. Technol.*, **1991**, *25*, 1414-1419.

CHAPTER FOUR

Investigation of arsenic removal in batch wise water treatments

4.1. Introduction

Nowadays, arsenic groundwater pollution is a serious problem around the world [1-3]. In Bangladesh and West Bengal in India, Kolshi filters are commonly used and consist of multiple earthenware pots containing sands and nails as adsorbents [4]. The removal by the Kolshi filters is based on coagulation with ferric hydroxide and filtration. This removal mechanism has been well studied [5-7]. Arsenic is mainly released from arsenopyrite and ferric hydroxide [8-10]. Most arsenic in ground water is inorganic, and it is well known that As(III) is much more toxic than As(V) [11, 12]. The valence composition changes with time. Most investigations on arsenic removal have monitored total arsenic. Water treatment should reduce the arsenic level to below $10 \mu\text{g L}^{-1}$ or at least to below $50 \mu\text{g L}^{-1}$. However, there is no regulation for individual valence arsenics. In particular, the concentration of As(III) needs to be reduced. High concentrations of arsenic in water usually exist with high levels of iron and other heavy metals. These metals present as cations underground and precipitate by coming into contact with air after the water is taken from the tube well. In the precipitations, arsenic is supposed to co-precipitate to the bottom with the metal hydroxides. Thus, arsenic should be able to be removed by simply standing water for several hours after the water has been taken from the ground. In this work, the behaviors of As(III) and As(V) in artificial groundwater were individually monitored during standing.

Previously, the authors have proposed a highly sensitive arsenic measurement method based on the vaporization and collection of arsenic [13] and applied it as a field affordable instrument to determine As(III) and As(V) at microgram and sub-microgram per liter levels contained in natural waters [14]. In the method, arsenic from the sample water is completely vaporized as AsH_3 and collected/preconcentrated by a miniature diffusion scrubber. The collected arsenic is determined by flow-based analysis with molybdenum blue (MB) chemistry. Interference from heavy metals, which has been noted as a problem in hydride generation [15] is made negligible by optimizing the conditions. However, manual preparation is required in the setup of the

AsH₃ generator in such systems. Idowu *et al.* [16], including one of the authors of the present study, used sequential analysis to make the system fully automatic. The detection method was replaced with ozone induced chemiluminescence (CL) analysis from the MB wet chemistry.

In this work, sequential analysis and the previous vaporization/collection with detection by MB chemistry were combined because the interference from the heavy metals can be eliminated more effectively by mild and long vaporization. This method enabled investigation of the variation in individual inorganic arsenics at $\mu\text{g L}^{-1}$ levels during batch process water treatment with good time resolution. The possibility of arsenic removal by simple overnight standing was investigated by the monitoring process.

4.2. Methodology

4.2.1. Reactor

The reactor was made with a 2-L polyethylene plastic bottle containing 1.5 L of artificial groundwater. The composition of the water sample was set as typical groundwater in Bangladesh in accordance with reported data [6, 17, 18]: 100 mg L^{-1} Ca²⁺, 5, 20 or 100 mg L^{-1} Fe(II) or Fe(III), 0 or 3 mg L^{-1} phosphate, and the pH was adjusted to be 7 with the addition of bicarbonate (100 mg L^{-1}). Arsenic was added to be $500 \mu\text{g L}^{-1}$ ($250 \mu\text{g L}^{-1}$ As(III) and $250 \mu\text{g L}^{-1}$ As(V)) and the change in each arsenic concentration was monitored. Dissolved oxygen (DO) and redox potential were monitored by a DO meter (OM-14, Horiba) and a Pt wire coupled with an Ag/AgCl reference electrode.

4.2.2. Arsenic monitoring

Arsenic contained in the reactor solution was monitored by flow analysis coupled with preconcentration by sequential vaporization and collection of the arsenic. The sequential hydride generation flow analysis (SHGFA) system was designed for this investigation. The flow system is shown in Fig. 2-1 (Chapter two).

4.2.3. Batch test

Artificial groundwater (1.5 L) containing $250 \mu\text{g L}^{-1}$ As(III) and $250 \mu\text{g L}^{-1}$ As(V) was placed in the reactor. The solution was made anaerobic or aerobic prior to the iron precipitation by bubbling nitrogen or air through the solution at a rate of 0.2 L min^{-1} . The original pH was below 4 because Fe and As stock solutions were acidic. The reactor pH was adjusted to be 7 by the addition of bicarbonate, and then the iron precipitation commenced. The As concentration decreased with the precipitation and it was monitored by the SHGFA. All data including DO and redox potential were monitored by a data logger (8420, Hioki).

Oxidants to accelerate the removal were tested. Hydrogen peroxide was added to be 0.3, 3 and 30 mg L^{-1} , and NaClO was added to be 0.1, 0.5, 1 and 5 mg L^{-1} in the sample water. In addition, O_3 was bubbled through the sample water at a flow rate of 0.2 L min^{-1} . Ozone was prepared from air using an arch discharge electrode (1100 N) powered by a pulse supplier (LHV09, both from Logy Electric). The O_3 concentration was 3500 ppmv. Steel wool used as zero valent iron was steel scour (Three Ace, Yamazaki Sangyo), and 8.8 g of the steel wool was spread over the reactor walls.

4.3. Results and discussion

4.3.1. Sequential measurement of As(III) and As(V)

The authors have developed a field affordable high sensitivity analysis system for discriminative determination of As(III) and As(V) [14]. The principle of the method used in the current work is the same as that used previously, but changes in As(III) and As(V) concentrations were monitored automatically with the help of sequential hydride generation. The AsH_3 formations from total As and from only As(III) can be controlled by the pH of the generators [19, 20]. In the conventional arsenic analysis with hydride generation, the measurement is sometimes affected by heavy metals. To overcome this problem in the current work, the hydride generation was performed over a much longer time at a slower rate. Addition of EDTA also helped reduce the effects on the measurements. As a result, the effect of heavy metals can be minimized to within 2% in most natural water conditions [14]. In the previous system, the generation time was 5 min. This was sufficient at pH 0 for total As, but the

gasifying/collection efficiency at pH 7 for As(III) was 77%. The above generation time was preferred in that it saved analysis time. On the other hand, in the current work, a fast measurement was not important and perfect As generation was considered ideal. Fig. 4-1 shows the signal intensity against generation time for As(III + V) at pH 0 and As(III) at pH 7. From the data, it was decided to set the generation time at 4 and 8 min for As(III + V) and As(III), respectively. Each generation time was set by the sequential program.

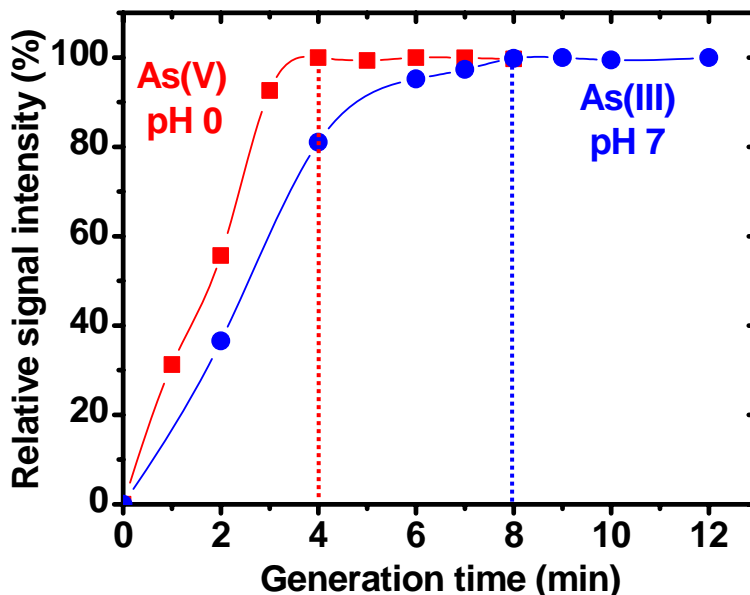


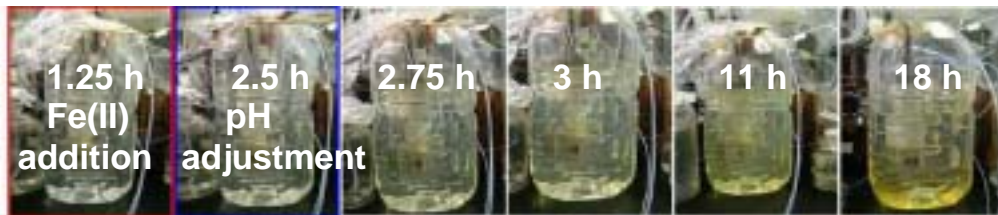
Fig. 4-1. AsH₃ generation as a function of generation time. The signals were obtained for 50 µg L⁻¹ As(III) and As(V) at pH values of 7 and 0, respectively.

In this condition, samples containing 0-250 µg L⁻¹ of As(III) and As(V) with 20 mg L⁻¹ of Fe(III) and 3 mg L⁻¹ of phosphate were successfully determined by SHGFA. Recoveries of As(III) and As(V) in these typical sample conditions were 96-101%. Thus the proposed method has the potential to individually analyze As(III) and As(V) contained in the water samples. Detailed validation is described in previous papers for the manual hydride generation flow analysis [13, 14] and the sequential hydride generation-chemiluminescence detection [16]. The method of SHGFA proposed here is the combination of those methods.

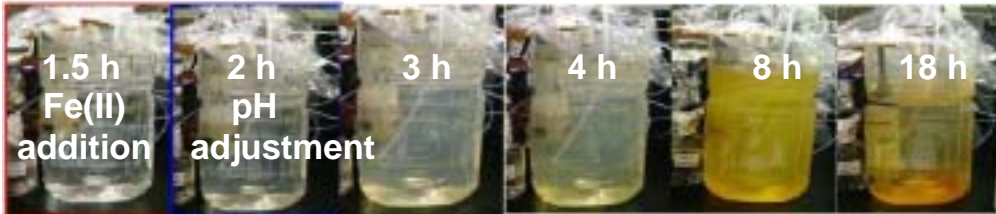
4.3.2. Trends of arsenic removal from anaerobic water samples

The natural removal of arsenic would be very convenient for people taking contaminated water from family wells. First, the change in As level during water standing was examined, starting with an anaerobic condition because groundwater is usually insulated from air and not supposed to contain much oxygen. Oxygen in the experimental water was removed by nitrogen bubbling, and the pH was adjusted to be neutral. The precipitation of ferric hydroxide then commenced. The water color became light green then changed to yellowish after several hours. After half a day, the colored precipitation was only in the bottom of the reactor. Changes in the water color are shown in the Fig. 4-2 and Fig. 4-3 under anaerobic and aerobic conditions.

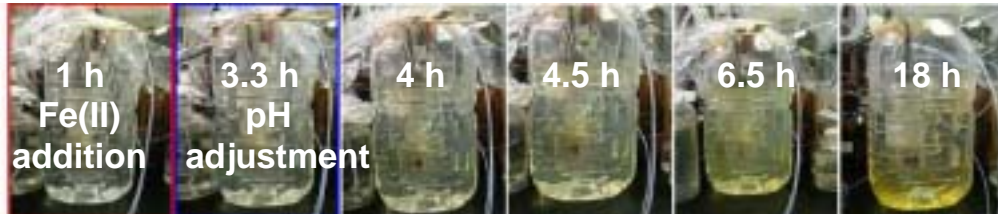
Fe(II): 5 mg/L (without phosphate)



Fe(II): 20 mg/L (without phosphate)



Fe(II): 5 mg/L (with phosphate)



Fe(II): 20 mg/L (with phosphate)

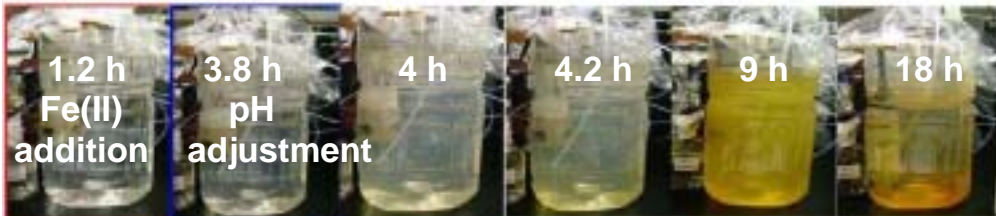
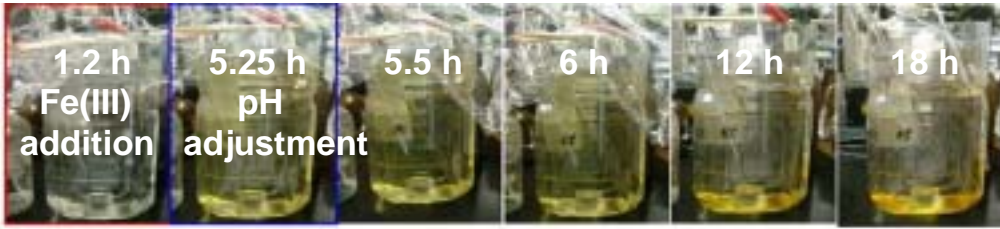
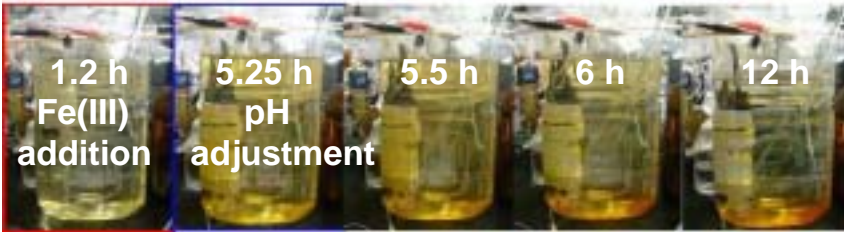


Fig. 4-2. Changes in the water color with/without phosphate and Fe(II) under anaerobic.

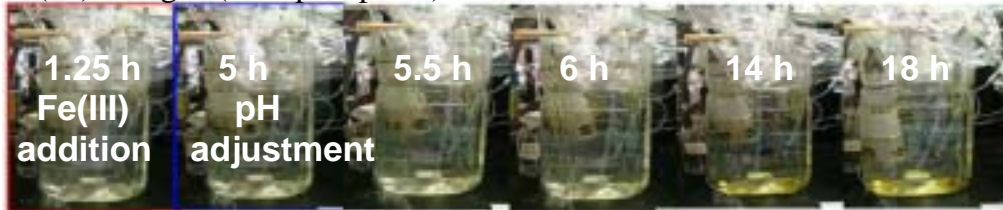
Fe(III): 5 mg/L (without phosphate)



Fe(III): 20 mg/L (without phosphate)



Fe(III): 5 mg/L (with phosphate)



Fe(III): 20 mg/L (with phosphate)

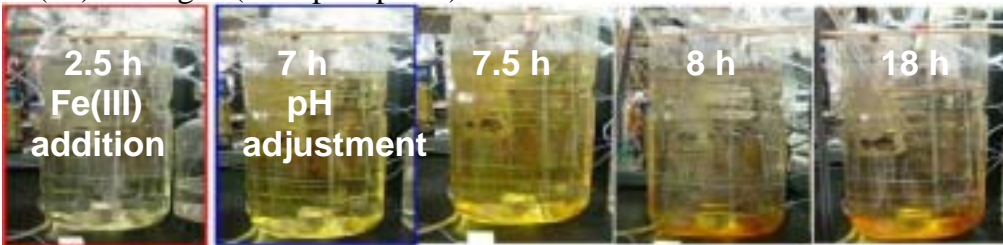


Fig. 4-3. Changes in the water color with/without phosphate and Fe(III) under aerobic.

The changes in As(III) and As(V) concentrations are shown in Fig. 4-4. The tests were examined without and with (3 mg L^{-1}) phosphate and with 5 and 20 mg L^{-1} Fe(II). When there was no phosphate, the ratio of As(V)/As(III) did not change with the addition of Fe(II) while the pH was 4.9. After adjusting the pH to be neutral, it was interesting that only the As(III) concentration decreased while the As(V) concentration was almost constant. The decrease in As(III) concentration stopped after a few hours, and the As(V) concentration began decreasing 3-5 h after neutralization. Here, the delay in the start of As(V) removal is referred to as “the dead time”. The dead time was longer with lower concentrations of Fe(II). In addition, the dead time became longer

with the presence of phosphate. Since the As(V) concentrations were constant, decreases in As(III) concentrations during the dead times were unlikely to be caused by oxidation. Leupin and Hug [21] suggested As(III) can be oxidized with Fe(II) during the oxidation of iron with dissolved oxygen. From our results, however, it is reasonable to believe only the As(III) concentration decreases in the beginning of anaerobic experiments, and this decrease is slow. To the best of our knowledge, this is rare work showing that the removal occurs preferably for As(III) over As(V). This phenomenon suggests there might be an interaction between Fe(II) and As(III). After the dead time, coprecipitation of As(V) started probably due to the formation of Fe(III) from Fe(II) by oxygen naturally and slowly dissolving from the water/air interface. The start of ferric hydroxide precipitation could be seen from the change in color of the water sample. Further investigations are needed to make this clear in future.

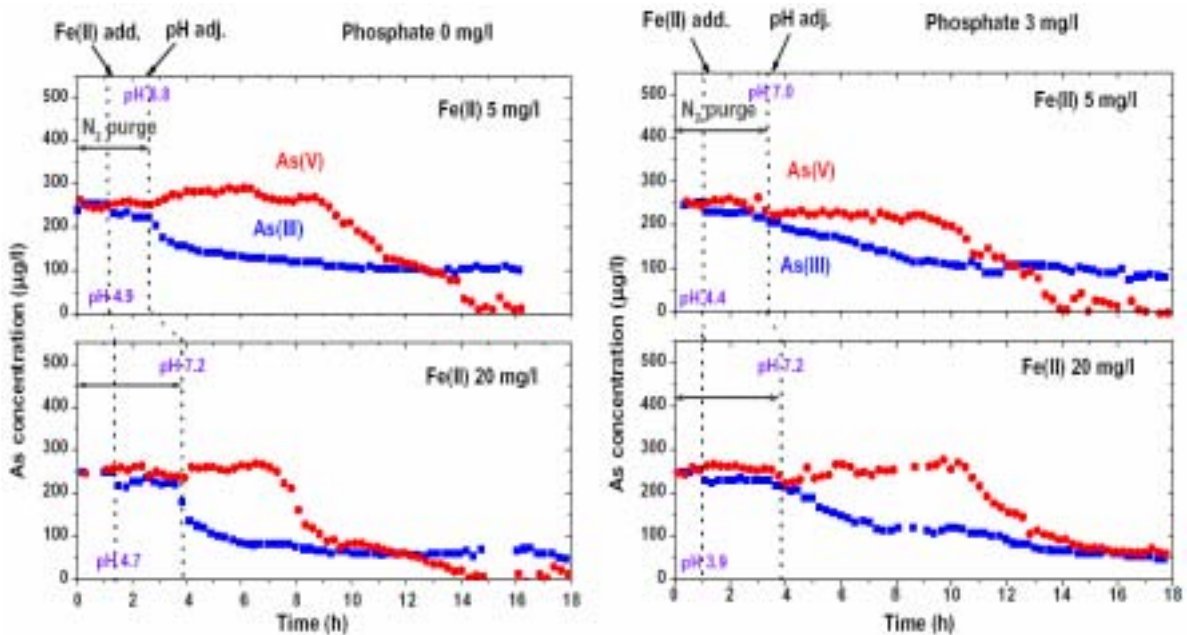


Fig. 4-4. Changes in As(III) and As(V) concentrations in the standing water under reducing condition. Left and right panels are the data without and with phosphate. Iron was added as Fe(II); 5 (upper panel) and 20 mg/L (lower panel).

The rate of decrease in the As(V) concentration after the dead time was higher with richer Fe content. For both Fe(II) contents, As(V) was almost completely removed from the top clear water. On the other hand, toxic As(III) remained in the water after over-

night standing. The final As(III) level, $110 \mu\text{g L}^{-1}$, with lower Fe content (5 mg L^{-1}) was higher than that of As(III), $\sim 70 \mu\text{g L}^{-1}$, with 20 mg L^{-1} Fe. When phosphate coexisted in the normal groundwater, the rate at which As(III) decreased was much slower in the beginning of coprecipitation than was the case for groundwater without phosphate.

Some arsenic was removed simply by overnight standing. Water taken from a tube well should be able to be refined by storage in a tall bottle. However, the extent of the removal is dependent on the Fe and phosphate contents. Arsenic removal profile with aeration

4.3.3. Arsenic removal profile with aeration

Behaviors of As(III) and As(V) were examined in the treatment with aeration, which was performed for acceleration of the removal. The results are shown in Fig. 4-5.

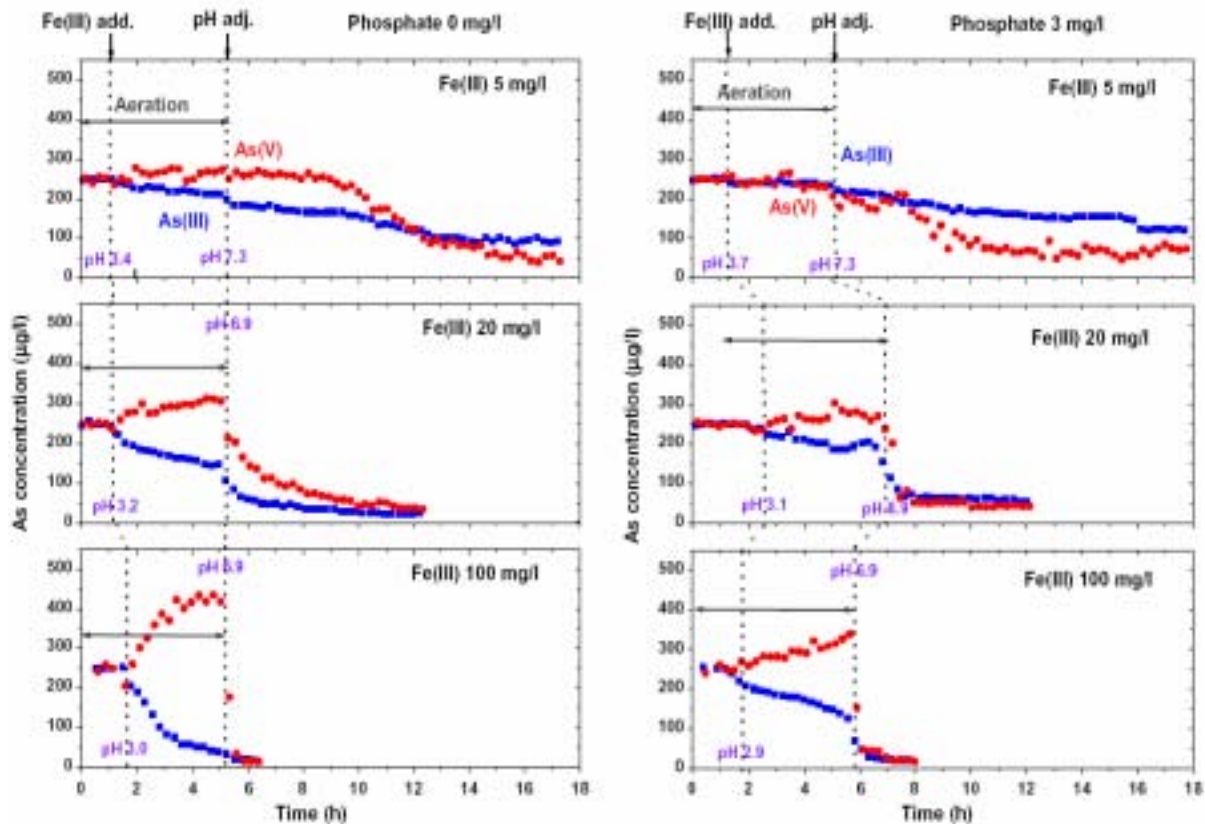


Fig. 4-5. Changes in As(III) and As(V) concentrations in the standing water under aerobic condition. Left and right panels are the data without and with phosphate. Iron was added as Fe(III); $5, 20$ and 100 mg L^{-1} .

As for the anaerobic examinations, bubbling was performed before the pH adjustment, but with air instead of nitrogen. An increase in the As(V)/As(III) ratio was observed during the air bubbling in contrast to the nitrogen bubbling in the anaerobic experiments. The aeration converted As(III)-As(V) but this oxidation was obviously dependent on the Fe(III) concentration. There was no oxidation of As(III) without Fe(III) even with air bubbling in our preliminary experiments. Hence, it can be said that Fe(III) had an important role in the oxidation of As(III).

There was no dead time in aerobic conditions, whereas dead time was observed in anaerobic conditions. When the Fe(III) concentration was low (5 mg/l), only 60–70% of As was removed after the overnight standing. However, there was good removal of As with higher Fe concentrations. Commonly, arsenic exists high in groundwater with a high concentration of Fe. The higher Fe(III) concentration of 20 mg L⁻¹ removed As reasonably well, and As was removed quickly and completely with 100 mg L⁻¹ Fe(III). It is noted As(V) is coordinated by ferric hydroxide sites before crystallite growth and coagulation processes can proceed [22, 23]. The presence of phosphate interfered with the As removal in aerobic conditions as well as in anaerobic conditions. The oxidation rates of As(III) decreased to one third to one fifth with the addition of phosphate. The final concentration of As was still not sufficiently low even with 20 mg L⁻¹ Fe(III) when phosphate coexisted. There is a concern relating to the combined effects of anions on As removal by iron hydroxides, as noted by Meng *et al.* [24, 25]. However, the removal was obviously improved by the aeration.

4.3.4. Addition of oxidizing agent

As in previous experiments, removal of As(III) with Fe precipitation was sometimes difficult, and only As(V) was effectively removed in the standing processes. As(III) was oxidized with coexisting Fe(III), but the Fe content may be different in water samples. Furthermore, addition of Fe(III) is not suitable as a drinking water treatment due to its bad taste. The addition of oxidants is another option to be considered. Here, the As oxidation profiles for simple and common processes were examined, with H₂O₂ [26] hypochlorite and ozone being tested. These oxidants are not stable and would disappear upon standing.

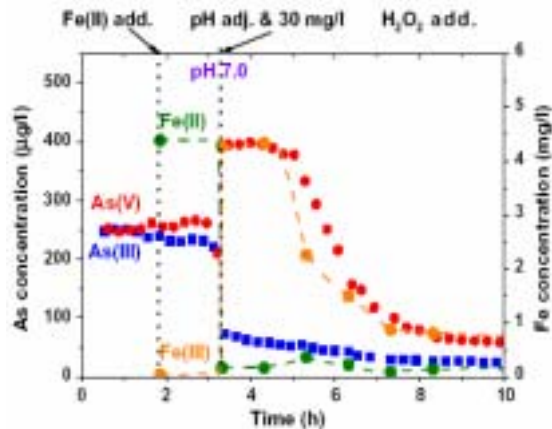


Fig. 4-6. Changes in concentrations of iron and arsenic ions in batch treatment with hydrogen peroxide.

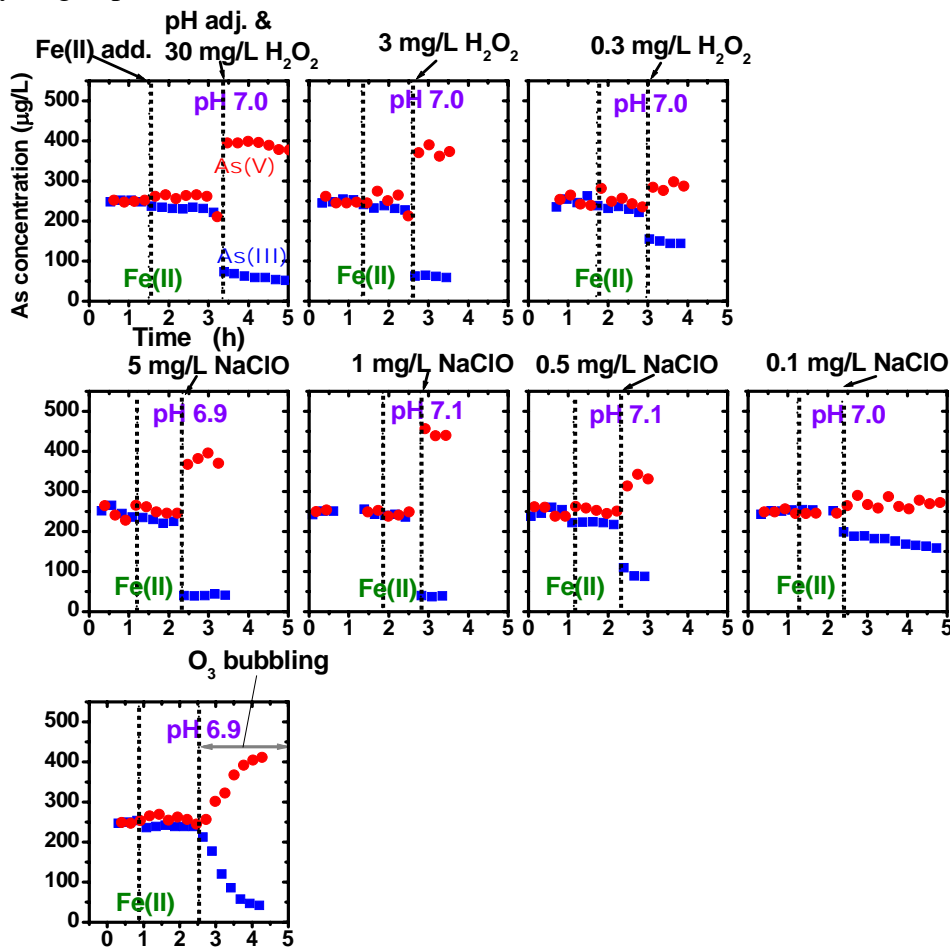


Fig. 4-7. Oxidant test results. Original As(III) and As(V) concentrations were both 250 µg/l and 5 mg/l Fe(II) was added. One or two hours later, the pH was adjusted to be neutral with Na₂CO₃, and at the same time, each oxidant was added. In the case of O₃, the gas was continuously bubbled through the sample.

Water containing 3 mg L⁻¹ phosphate and 5 mg L⁻¹ Fe(II) was used. The oxidants were added at the same time as the pH adjustment was made. When H₂O₂ was added to the sample water, all Fe(II) and 70% of As(III) oxidized within a minute, and the decrease in As(V) was synchronized with the decrease in ionic Fe(III) as shown in Fig. 4-6. Nishimura and Umetsu [27] succeeded in preparing an oxidative arsenic precipitation with O₃. However, oxidation of As(III) by O₃ was relatively slow as shown in Fig. 4-7, and in our experimental conditions, it took a few hours.

On the other hand, oxidations by H₂O₂ and hypochlorite were much faster. In particular, hypochlorite works at low concentrations. Japan Water Works and the World Health Organization recommend the hypochlorite concentration of tap water to be more than 1 mg L⁻¹ and 5 mg L⁻¹, respectively. These hypochlorite concentrations in tap water would be sufficient for As(III) oxidation. The removal of arsenic by standing would be made effective by the addition of hypochlorite at a tap water level.

4.3.5. Arsenic removal with zero valent

Recently, attention has been paid to As removal by zero valent Fe as an effective and low cost method for the treatment of As contaminated water [28-33]. Zero valent iron is used in column treatments and Kolshi filters. In the current work, As removal was examined for the simple placement of metal iron in a water sample in a batch wise treatment.

Initially, an iron mesh (58 g) was placed in a 1.5 L water sample but this method did not work effectively. Secondly, the use of steel wool was examined. Only 8.8 g of steel wool was pasted on the reactor walls. The water samples contained 3 mg L⁻¹ phosphate, 250 µg L⁻¹ As(III) and 250 µg L⁻¹ As(V). As shown in Fig. 4-8, both As(III) and As(V) were quickly removed from the water with the steel wool and aeration. The As(III) and As(V) concentrations decreased to only 6.9 and 2.4 µg L⁻¹, respectively, in 2 h. It can be seen that As(III) was removed faster than As(V), which is similar to the trend found in the standing of anaerobic water samples. Fe(0) forms Fe(II) from the reaction with dissolved oxygen [34, 24, 25]. The formed Fe(II) becomes Fe(III) and Fe(OH)₃ in the aerobic condition. As(III) may be trapped with Fe(II) as suggested in our anaerobic experiments or oxidation from As(III) to As(V) may occur faster than the

removal of As(V). Therefore, the As(III) concentration decreased faster than did that of As(V).

When aeration was not performed, there was no effective decrease in arsenic concentration. A fast decrease was observed, as for aeration, when nitrogen was bubbled through the reactor instead of air. Therefore, the aeration worked mainly through agitation rather than through the supply of oxygen. Other agitation methods could be used instead of aeration such as employing a stirrer bar or propeller mixer, yet aeration is one of the easiest ways to agitate a sample water.

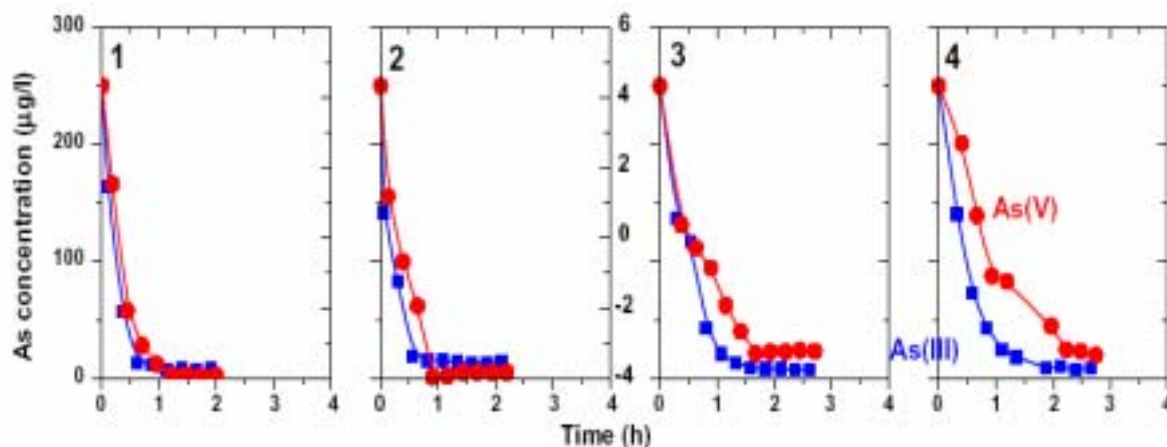


Fig. 4-8. Batch wise removal of As with steel wool. The same steel wool (8.8 g) was repeatedly used four times. The decreases in As concentration in the first use of the steel wool to the fourth use are shown in the panels 1- 4.

It has been found that high concentrations of arsenic can be removed with a cheap material in a short time. After four water treatments, the steel wool weight decreased 12%, the wool surface became brown with the formation of ferric oxide, and the elimination rate decreased. However, the same steel wool could be used repeatedly. Batch wise treatment with steel wool and agitation was found to be an effective water treatment.

4.4. Conclusions

Trends for As(III) and As(V) concentrations were investigated in the batch treatments of artificial groundwater. Reductions from harmful concentrations to safe

concentrations for drinking were successfully monitored by a hydride generation/collection hybrid flow analysis, SHGFA, developed for this investigation. When the Fe concentration was relatively high (arsenic is often present with high Fe concentrations), the arsenic was removed from the water simply by standing overnight. In this study, it was clearly demonstrated that oxidation of As(III) was necessary in arsenic removal water treatment. However, dead time (two to five hours) was observed at the beginning of anaerobic experiments where the As(III) concentration decreased gradually yet the As(V) concentration was constant. The removal was interfered with phosphate. The addition of oxidant was effective in ensuring removal. In particular, hypochlorite at a tap water concentration oxidized As(III) to As(V) so that it is removed effectively by coprecipitation. A small amount of steel wool is very effective in As removal, adsorbing As quantitatively within 2 h. The batch process is easily carried out, requiring only a water container such as a plastic soft drink bottle.

References

1. Das, D., Samanta, G., Mandal, B. K., Chowdhury, T. R., Chanda, C. R., Chowdhury, P. P., Basu, G. K., Chakraborti, D. Arsenic in groundwater in six districts of West Bengal, India. *Environ. Geochem. Health*, **1996**, *18*, 5-15.
2. Acharyya, S. K., Chakraborty, P., Lahiri, S., Raymahashay, B. C., Guha, S., Bhowmik, A. Arsenic poisoning in the Ganges delta. *Nature*, **1999**, *401*, 545-546.
3. Karim, M. M. Arsenic in groundwater and health problems in Bangladesh. *Water Res.*, **2000**, *34*, 304-310.
4. Khan, A. H., Rasul, S. B., Munir, A. K. M., Habibuddowla, M., Alauddin, M., Newaz, S. S., Hussam, A. Appraisal of a simple arsenic removal method for groundwater of Bangladesh. *J. Environ. Sci., Health Part A-Toxic/Hazard Subst. Environ. Eng.*, **2000**, *35*, 1021-1041.
5. Meng, X., Korfiatis, G. P., Christodoulatos, C., Bang, S. Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system. *Water Res.*, **2001**, *35*, 2805-2810.

6. Wickramasinghe, S. R., Han, B., Zimbron, J., Shen, Z., Karim, M. N. Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. *Desalination*, **2004**, *169*, 231-244.
7. Song, S., Lopez-Valdivieso, A., Hernandez-Campos, D. J., Peng, C., Monroy-Fernandez, M. G., Razo-Soto, I. Arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite. *Water Res.*, **2006**, *40*, 364-372.
8. Nickson, R., McArthur, J., Burgess, W., Ahmed, K. Z., Ravenscroft, P., Rahman, M. Arsenic poisoning of Bangladesh groundwater. *Nature*, **1998**, *395*, 338.
9. Kondo, H., Ishiguro, Y., Ohno, K., Nagase, M., Toba, M., Takagi, M. Naturally occurring arsenic in the groundwaters in the southern region of Fukuoka prefecture, Japan. *Water Res.*, **1999**, *33*, 1967-1972.
10. Nickson, R. T., McArthur, J. M., Ravenscroft, P., Burgess, W. G., Ahmed, K. M. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.*, **2000**, *15*, 403-413.
11. Tabacova, S., Hunter III, E. S., Gladen, B. C. Developmental toxicity of inorganic arsenic in whole embryo culture: oxidation state, dose, time, and gestational age dependence. *Toxicol. Appl. Pharmacol.*, **1996**, *138*, 298-307.
12. Jain, C. K., Ali, I. Arsenic: occurrence, toxicity and speciation techniques. *Water Res.*, **2000**, *34*, 4304-4312.
13. Toda, K., Ohba, T. Highly Sensitive Flow Analysis of Trace Level Arsenic in Water Based on Vaporization-collection In-line Preconcentration. *Chem. Lett.*, **2005**, *34*, 176-177.
14. Toda, K., Ohba, T., Takaki, M., Karthikeyan, S., Hirata, S., Dasgupta, P. K. Speciation-capable field instrument for the measurement of arsenite and arsenate in water. *Anal. Chem.*, **2005**, *77*, 4765-4773.
15. Tao, H. Analytical methods of hydride generation/atomic spectroscopy. *Bunseki*, **2004**, *2004*, 257-263 (in Japanese).
16. Idowu, A. D., Dasgupta, P. K., Genfa, Z., Toda, K., Garbarino, J. R. A gas-phase chemiluminescence-based analyzer for waterborne arsenic. *Anal. Chem.*, **2006**, *78*, 7088-7097.

17. Robert, L. C., Hug, S. J., Ruettimann, T., Billah, M. M., Khan, A. W., Rahman, M. T. Arsenic removal with iron(II) and iron(III) in waters with high silicate and phosphate concentrations. *Environ. Sci. Technol.*, **2004**, *38*, 307-315.
18. Leupin, O. X., Hug, S. J., Badruzzaman, A. B. M. Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filling and sand. *Environ. Sci. Technol.*, **2005**, *39*, 8032–8037
19. Shaikh, A. U., Tallman, D. E. Species-specific analysis for nanogram quantities of arsenic in natural waters by arsine generation followed by graphite furnace atomic absorption spectrometry. *Anal. Chim. Acta*, **1978**, *98*, 251-259.
20. Feldman, C. Improvements in the arsenic accumulation-helium glow detector procedure for determining traces of arsenic. *Anal. Chem.*, **1979**, *51*, 664-669.
21. Leupin, O. X., Hug, S. J. Oxidation and removal of arsenic(III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.*, **2005**, *39*, 1729-1740.
22. Fuller, C. C., Davis, J. A., Waychunas, G. A. Surface chemistry of ferrihydrite: part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta*, **1993**, *57*, 2271-2282.
23. Meng, X., Bang, S., Korfiatis, G. P. Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Water Res.*, **2000**, *34*, 1255-1261.
24. Meng, X., Korfiatis, G. P., Bang, S., Bang, K. W. Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol. Lett.*, **2002**, *133*, 103-111.
25. Meng, X., Bang, S., Korfiatis, G. P. Removal of selenocyanate from water using elemental iron. *Water Res.*, **2002**, *36*, 3867-3873.
26. Hug, S. J., Leupin, O. Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidation in the Fenton reaction. *Environ. Sci. Technol.*, **2003**, *37*, 27340-2742.
27. Nishimura, T., Umetsu, Y. Oxidative precipitation of arsenic(III) with manganese(II) and iron(II) in dilute acidic solution by ozone. *Hydrometallurgy*, **2001**, *62*, 83-92.
28. Nikolaidis, N. P., Dobbs, G. M., Lackovic, J. A. Arsenic removal by zero-valent iron: field, laboratory and modeling studies. *Water Res.*, **2003**, *37*, 1417-1425.

29. Gupta, V. K., Saini, V. K., Jain, N. Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *J. Colloid Interface Sci.*, **2005**, 288, 55-60.
30. Bang, S., Korfiatis, G. P., Meng, X. Removal of arsenic from water by zerovalent iron. *J. Hazard. Mater.*, **2005**, 121, 61-67.
31. Bang, S., Johnson, M. D., Korfiatis, G. P., Meng, X. Chemical reactions between arsenic and zero-valent iron in water. *Water Res.*, **2005**, 39, 763-770.
32. Lien, H. -L., Wilkin, R. T. High-level arsenite removal from groundwater by zerovalent iron. *Chemosphere*, **2005**, 59, 377-386.
33. Tyrovola, K., Nikolaidis, N. P., Veranis, N., Kallithrakas-Kontos, N., Koulouridakis, P. E. Arsenic removal from geothermal waters with zero-valent iron-effect of temperature, phosphate and nitrate. *Water Res.*, **2006**, 40, 2375-2386.
34. Su, C., Puls, R. W. Arsenate and arsenite removal by zerovalent iron: redox transformation, and implications for in situ groundwater remediation. *Environ. Sci. Technol.*, **2001**, 35, 1487-1492.

CHAPTER FIVE

High sensitivity arsenic analyzer based on liquid-reagent-free hydride generation and chemiluminescence detection for on-site water analysis

5.1. Introduction

Arsenic occurrence in the water and its toxic effect on human health through by drinking and agricultural practices is a serious environmental problem throughout the world. Human may be exposed to arsenic through food, air, water, or through skin contact. Drinking water contamination with arsenic is the most common cause of arsenic poisoning in human. Chemically, there are two types of arsenic compounds: inorganic and organic. Inorganic arsenic is typically present in either trivalent or pentavalent form and tends to be more toxic than organic arsenic. Arsenite binds to sulfhydryl (-SH) groups and has broad toxicity [1], which impairs the function of many proteins [2]. In the case of organic arsenic, increasing the degree of methylation acute toxicity generally decreases only exception the tetramethylarsonium (TeMA) ion [3]. The International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA) is classified arsenic as a group 'A' known as human carcinogen [4]. Chronic ingestion of inorganic arsenic causes cancer of the skin, bladder, and lungs, as well as neurological and cardiovascular problems [5]. The presence of arsenic in water and its toxic effect on humans through drinking and agricultural practices is a serious global environmental problem.

Generally arsenic concentration in surface and groundwater ranges from 1 to 10 $\mu\text{g L}^{-1}$ but the elevated levels of arsenic accounted into groundwater in China [6], India and Bangladesh [7] is 100-5000 $\mu\text{g L}^{-1}$, in Vietnam is 1-3500 $\mu\text{g L}^{-1}$ [8]. The WHO provisional guideline value for arsenic in drinking water is 10 $\mu\text{g L}^{-1}$ [9] and has been adopted as a national standard by the most countries including Japan, Laos, Mongolia, the USA, Jordan and by the European Union (EU). On the other hand, to implement the new guideline is not currently feasible for a number of countries strongly affected including Bangladesh, India, and Vietnam. Those countries retained their national standard 50 μg

L⁻¹. But most of the arsenic affected areas where people consume drinking water with arsenic content over 50 µg L⁻¹.

In the past decades, many technologies have been developed to remove arsenic from the water based on metal base adsorbents, including aluminum, iron, titanium, zirconium, and manganese, have been extensively studied. Many oxidants like ozone, chlorine, hydrogen peroxide use to oxidize As(III) to As(V) and finally arsenic is removed by adsorption process. Removal of arsenite and arsenate from the drinking water adsorption on hydrous ferric oxide is simple and cost-effective [10].

Many analytical methods have been developed to measure arsenic in water samples, including electrospray ionization mass spectrometry [11], ion chromatography-hydride generation-atomic fluorescence spectrometry [12], and automated hydride generation interfaced to ICP-MS [13]. Although these methods are highly sensitive, unfortunately they cannot be used in villages because they are time consuming and expensive. Nearly all of the water treatment utilities do not have such expensive instruments and they have to send the samples state to laboratory for off-site analysis. Off-site analysis is expensive, time consuming between sample collections and obtaining the test results. As a result it makes difficult to monitor those treatment utilizes to optimize the arsenic removal.

As simpler methods, flow analysis and sequential analysis were applied to determine trace arsenic with arsine vapor generation and applied to field analysis [14, 15], investigation of arsenic removal [16], and leaching of arsenic from the contaminated sediments [17]. Generated arsine vapor can also be analyzed by chemiluminescence (CL) detection. [18, 19]. Arsine vapor has been generated electrochemically, which eliminates the need for a chemical reducing agent [20]. For on-site analysis of arsenic, several approaches have been reported such as electrochemical micro determinations [21, 22] colorimetric assay using nanoparticle formation [23], and selective co-precipitation with BaSO₄ [24]. 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 (NaBH₄) 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 [25]. 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 for reagents preparation.

A simple, fast, inexpensive and low operating cost method is developed based on manually hydride generation and chemiluminescence detection (HG-CL). Arsine is generated manually with solid reagents to avoid using the high concentrated inorganic acid. Purge gas is not required for arsine generation or delivery. Besides, in the field measurement for blank test, we developed an adsorbents base technique to get arsenic free water relatively in short time. To develop this method, a variety of organic acids were tested for arsine generation, different photodetectors were investigated and finally the most favorable procedures were combined into one method. The interferences of various diverse ions and possibilities for their removal as reagent were investigated. The method then tested to measure natural water samples and validated with accepted analytical method ICP-MS.

5.2. Experimental

5.2.1. Reagents

Standard stock solutions of 100 mg L⁻¹ As(III) and As(V) were prepared using sodium metaarsenite (Wako Pure Chemical Industries, Osaka, Japan) and disodium hydrogen arsenate heptahydrate (Nacalai Tesque, Kyoto, Japan), respectively, along with 0.18 mol L⁻¹ H₂SO₄. 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; EDTA2Na was for elimination of interference from heavy metal ions. Sodium borohydride (NaBH₄, 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).

5.2.2. Instrumental system

The HG-CL system is illustrated in Fig. 5-1. 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 Harbor, 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 the 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 to make the cell opaque. During the metal-film coating and painting, an 11 mm × 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 ozone were introduced into the cell *via* the tube-in-tube insert. The formed arsine gas and introduced ozone were mixed 80 mm far away in front of the optical window. A small air pump (CM-15-12, Enomoto Micro Pump, Tokyo, Japan) was used to supply air at 100 mL min⁻¹ for ozone formation. After the air passed through a silica gel column (ϕ 15 mm × 110 mm) and flow restriction tube (PTFE, 0.3 mm i.d. × 460 mm), ozone was formed by an ozone generator that used a corona discharge-cylindrical tube (Cylindrical A, 1000BT-12 (300 mg h⁻¹), Enaly, Shanghai, China). Other ozone 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.

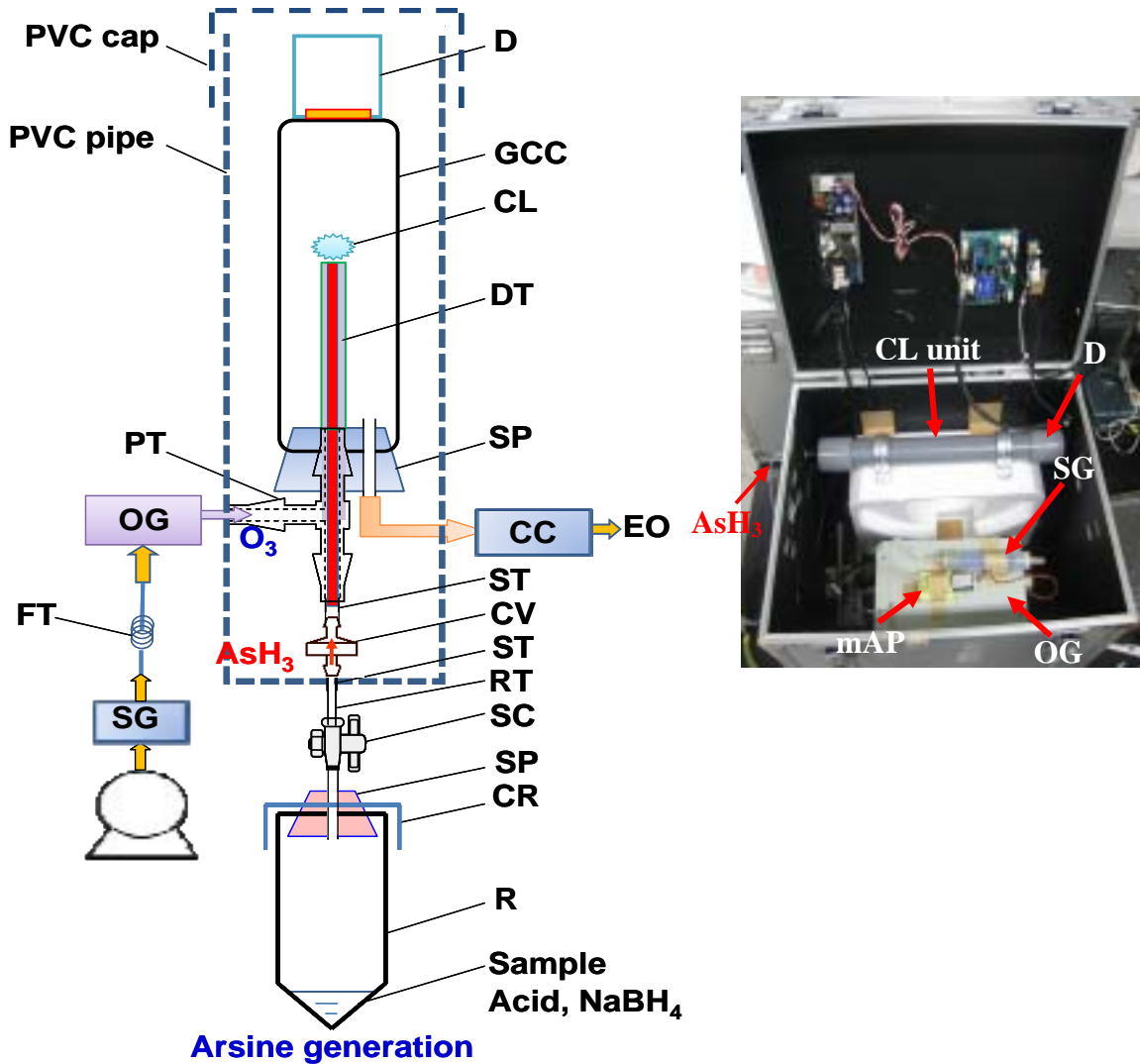


Fig. 5-1. The HG-CL system. mAP: miniature air pump; SG: silica gel column; FT: flow restricting tube for O_3 air flow; OG: ozone generator; PT: polyether ether ketone tee connector; R: reactor for AsH_3 generation; CR: cap for reactor; SP: silicone plug; SC: stopcock; RT: restrictor tube for AsH_3 introduction; 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.

The waste from the CL cell was treated with a small charcoal column to remove ozone. The PMT module and CL cell were placed in a polyvinylchloride (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 chemiluminescence cell unit (ϕ 38 mm × 307 mm, 0.4 kg), an arsine generator (50 mL sample tube) and an ozone generator (200 mm × 210 mm × 110 mm, 2.6 kg, including the air pump, air dryer tube) and was operated by 12 V dc or 100 V ac.

5.2.3. Measurement procedure

First, the instrument was turned on and ozone 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 NaBH₄ was added, and a silicone cap was placed on the tube immediately. The tube was shaken for 20-30 s to generate H₂ and AsH₃, and then the stopcock was opened to introduce AsH₃ into the CL cell. The AsH₃ reacted with O₃ in the cell and CL was detected with the photodetector. The response peak appeared in the CL signal within a minute. After closed 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 through the acidified water sample before addition of NaBH₄.

5.2.4. Comparative sample measurements

For comparison of data with other methods, fifteen river water samples were collected from a river near a closed mine, and five groundwater 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 through 0.45 μ m 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) [26], by sequential hydride generation flow analysis (SHGFA) 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 AsH₃ to vaporize. After 20 min of AsH₃ generation, the color formed on a paper strip placed above the AsH₃ 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.

Arsenic analysis by SHGFA was performed as described previously in the chapter two. Detection is based on slow generation of AsH₃, collection of all the generated AsH₃, and subsequent flow based analysis with molybdenum blue chemistry. AsH₃ generation/collection and measurement was carried out automatically.

5.3. Results and discussion

5.3.1. Optimization of reagents

The aim of this work was to develop an instrument that could be used in the field for arsenic analysis. In the rural areas of developing countries, it is difficult to obtain pure water, which makes it difficult to prepare reagent solutions. Therefore, initially tried was 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 [27]. The results for 100 µg L⁻¹ As(III) and As(V) with the acids tested are summarized in Table 5-1. 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) → AsH₃) 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 ($pK_{a1} = 2.3$) [28]. Citric, malonic, and ascorbic acids did not make pH low enough for arsenate protonation. 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 M tartaric acid was used, the response signals for As(III) and As(V) were almost constant and equivalent to each other is shown in the Fig. 5-2. 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).

Table 5-1. Response of the HG-CL method with various acids for $100 \mu\text{g L}^{-1}$ arsenic

Acid	Concentration/ 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 ± 0.030	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

^a pH after AsH_3 generation

^b Data are presented as the average \pm standard deviation after normalization with 1.5 M tartaric acid data.

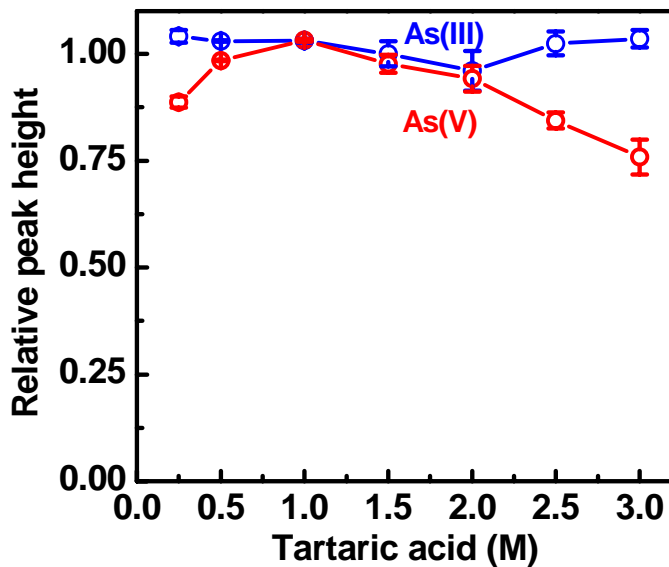
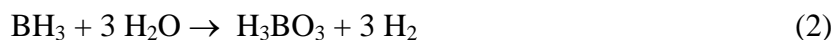


Fig. 5-2. Effect of tartaric acid concentration to signal intensity for HG-CL system, arsine was generated from $100 \mu\text{g L}^{-1}$ each containing standard solution of As(III) and As(V).

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 [16]. 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 [29]:



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. In the Fig. 5-3 shows 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.

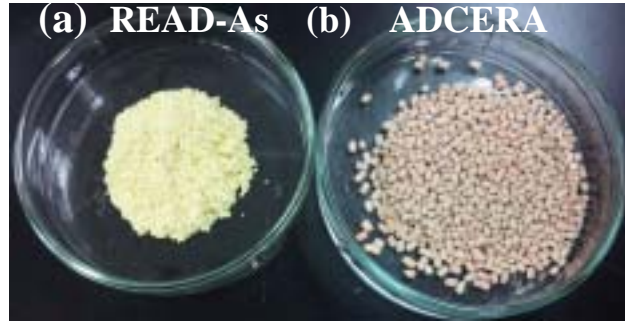
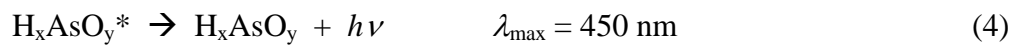
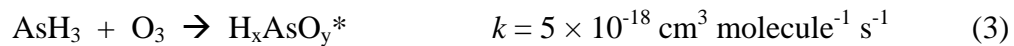


Fig. 5-3. Arsenic adsorbent READ-As (cerium hydroxide) a) and ADCERA (porous ceramic-rare earth compounds) b)

When $100 \mu\text{g L}^{-1}$ 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 $5.9 \mu\text{g L}^{-1}$, respectively. When the column was packed with ADCERA, the As(III) and As(V) concentrations in the eluent were 14.8 and $0.5 \mu\text{g L}^{-1}$, 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 ($100 \mu\text{g L}^{-1}$ 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 $>99\%$.

5.3.2. Investigation of CL cell

Arsine reacts with O_3 to produce CL [30] as follows:



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. 5-4) made of different materials were tested, including cells made of stainless steel (Fig. 5-4(a)), polypropylene (Fig. 5-4(b)) and glass (Figs. 5-4(c)–(e)). The cell made of stainless steel was the same as that used in our previous studies for sulfur gases [31, 32] and isoprene [33, 34].

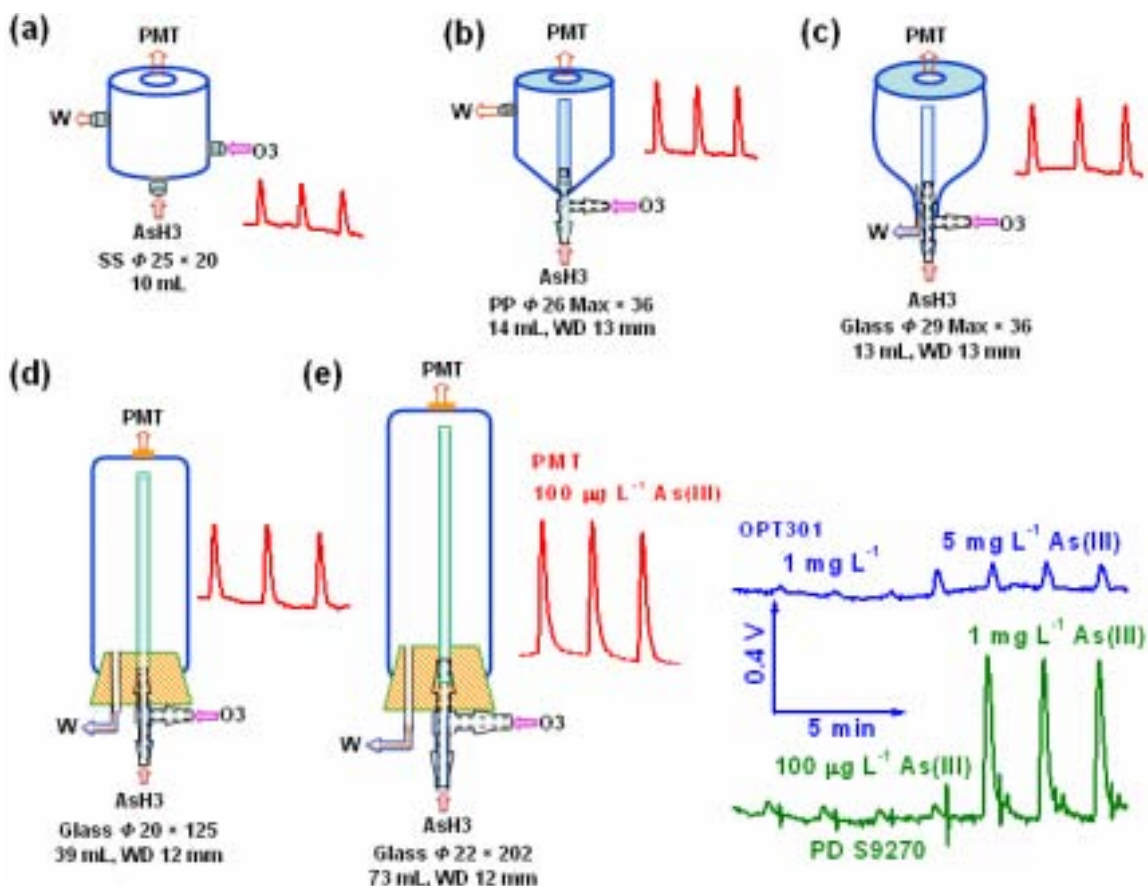


Fig. 5-4. Testing of CL cells and their performance. Response signals shown were obtained for $100 \mu\text{g L}^{-1}$ As(III) . AsH_3 gas was generated as reported previously [16]. The cell in Fig. (e) was tested with the following photodetectors: small PMT module H5784, miniature photodiode integrated 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.

AsH₃ and O₃ 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 AsH₃ 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. AsH₃ and O₃ 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 O₃ flow rate were optimized for each cell. Among the cells tested, the glass cell in Fig. 5-4(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 AsH₃ and O₃. The O₃-reaction rate of AsH₃, 5 × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹ [35, 36] is five orders of magnitude smaller than that of NO (2 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹) [37], and even smaller than that of isoprene (1.4 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹) [38]. Consequently, a long residence time is required for the reaction and a large cell is better for this. The sample gas (50 mL, mostly H₂) was introduced in a short time, and if the cell was smaller than the sample gas volume it could not hold all the introduced AsH₃. For these reasons, the long glass cell (cell volume 73 mL) coated with chromium was adopted as the cell for subsequent experiments.

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 mm × 2.29 mm optical area), which is used for fluorescence detection in micro gas analysis systems [39], a large optical area photodiode (S9270, Hamamatsu, 10 mm × 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. 5-4(e), right). Consequently, the small PMT module was adopted for subsequent use.

5.3.3. Effect of check valve on signal intensity

In the instrumental system (section 5.2.2.) mentioned that during AsH_3 generation stopcock used to keep close and no purge air/gas is used for arsine generation or for delivery. Outlet of the arsine delivery tube from the reactor is connected to the diaphragm check valve ($\phi 19 \times 32.7$ mm) to protect the ozone that can't reach to the reactor which can decrease the signal intensity.

To make sure the effect of check valve on chemiluminescence signals intensity, responses signals (Fig. 5-5) were obtained with and without check valves for blank as well as for $50 \mu\text{g L}^{-1}$ As(III), respectively.

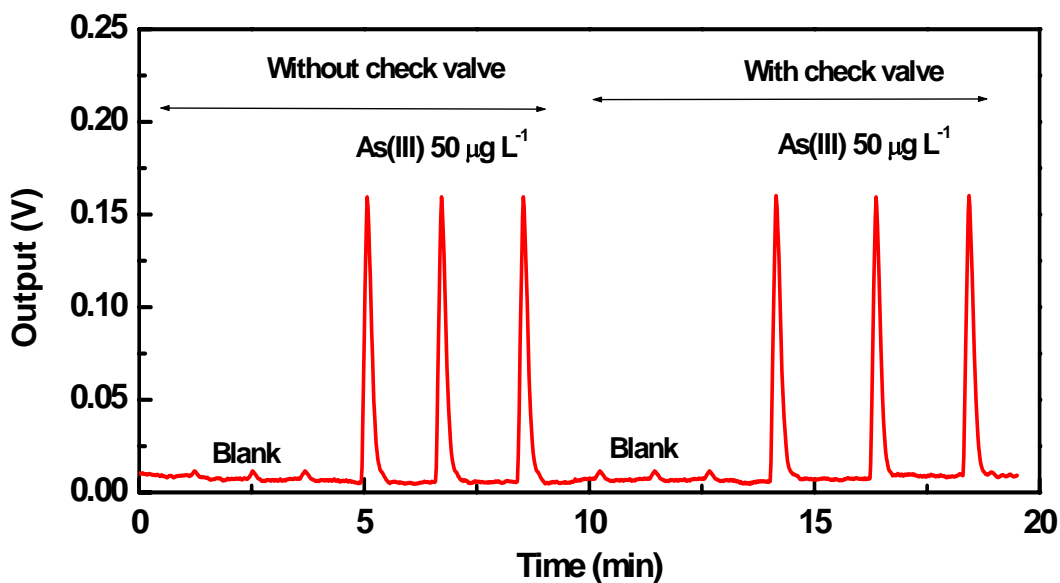


Fig. 5-5. Effect of check valve on chemiluminescence signals intensity.

The peak height of the responses were (0.171 ± 0.001) V and (0.168 ± 0.001) V for without and with check valve, for $50 \mu\text{g L}^{-1}$ As(III), respectively. It seems that there is no effect for check valve on chemiluminescence signal intensity. However, for the safety operation check valve is used in HG-CL system.

5.3.4. Ozone generation and optimization of ozone air flow

O₃ generation was examined with different ozonators. For the field CL detection, high O₃ concentration generated from air at low flow rate is required. In Fig. 5-6a, O₃ concentrations generated by different ozonators are shown as a function of air flow 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 air flow, 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.

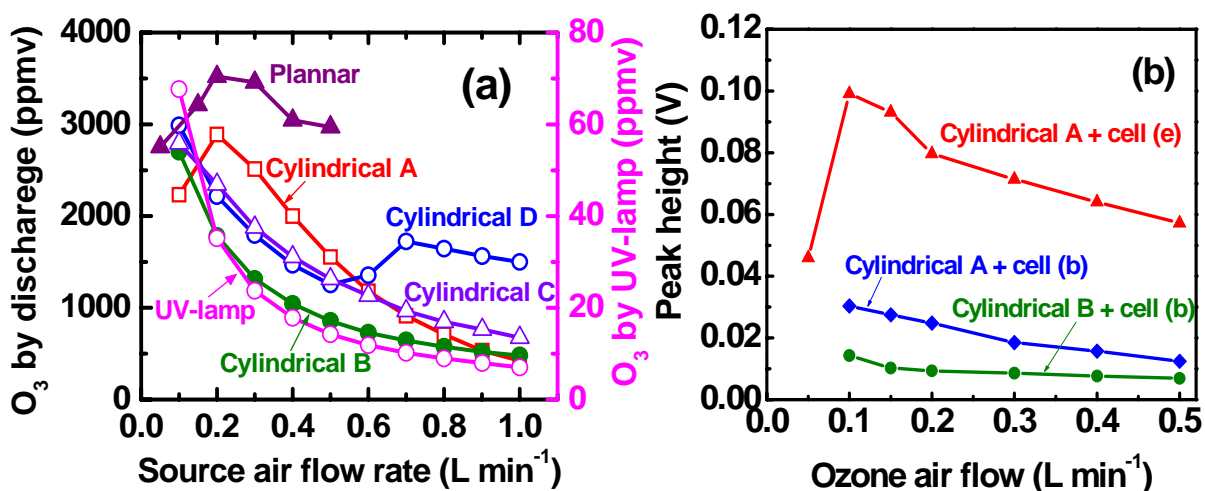


Fig. 5-6. Ozone concentration generated (a) and peak height for 50 µg L⁻¹ As(III) (b) with different ozonators at different air flow rate.

In Fig. 5-6b, effect of ozonator air flow 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 air flow through the ozonator.

5.3.5. 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. 5-7). 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 $1000 \mu\text{g L}^{-1}$.

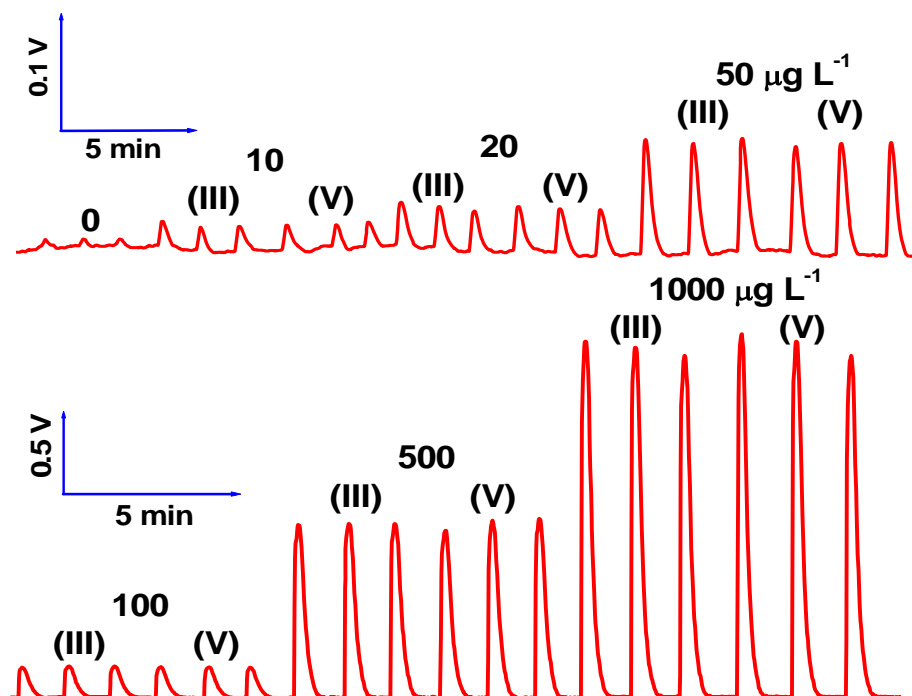


Fig. 5-7. Response signals obtained by HG-CL for 0, 10, 20, 50, 100, 500 and $1000 \mu\text{g L}^{-1}$ arsenic standard solutions of As(III) and As(V).

Calibration curves obtained for As(III) and As(V) were:

$$\text{Peak height (mV)} = 2.11 \text{ As(III)} (\mu\text{g L}^{-1}) - 5.65 \quad R^2 0.9998 \quad (5)$$

$$\text{Peak height (mV)} = 2.13 \text{ As(V)} (\mu\text{g L}^{-1}) - 7.28 \quad R^2 0.9998 \quad (6)$$

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 $0.4 \mu\text{g L}^{-1}$.

Repeatability of the method was excellent even though it was operated manually, and the relative standard deviation for a $10 \mu\text{g L}^{-1}$ arsenic solution was 3.0% over 30 measurements. Measurements were simple and easy, which would allow high throughput.

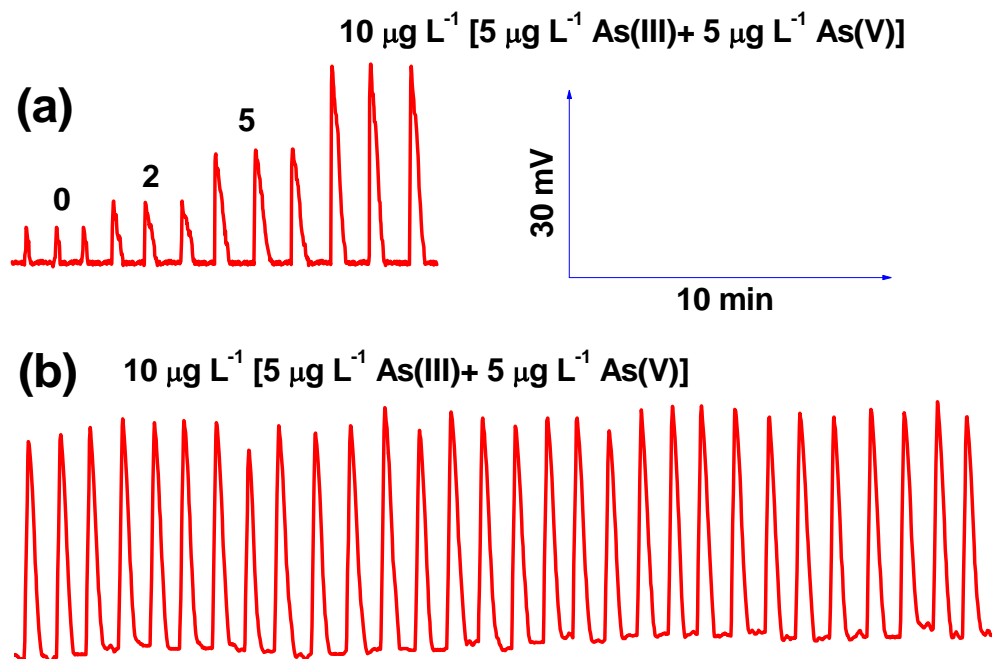


Fig. 5-8. Response signals for low concentration As solutions (a) and for 30 repeat analyses of 5 µg L⁻¹ As(III) + 5 µg L⁻¹ As(V) (b).

In Fig. 5-8 upper panel shows the low concentration measurements were performed for 2, 5, and 10 µg L⁻¹ arsenic mixtures (As(III):As(V) = 1:1) and lower panel shows continuous measurements for As(III) + As(V) (total concentration 10 µg L⁻¹) 30 times in 30 min, 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.

5.3.6. Interferences from the diverse ions

The effect of a number of ions on the arsenic measurement by HG-CL was investigated. These results are detailed in Table 5-2. Interference from Cu²⁺, Ni²⁺, Fe²⁺,

and Fe^{3+} were found but were masked by EDTA2Na. Serious interference was not observed in the optimized condition.

Table 5-2. 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 ± 2	100 ± 2		
	4	115 ± 2	113 ± 2		
PO_4^{3-}	20	100 ± 2	94 ± 2		
SiO_3^{2-}	20	98 ± 2	93 ± 2		
CO_3^{2-}	200	98 ± 2	104 ± 2		
SO_4^{2-}	2000	102 ± 2	105 ± 2		
Mg^{2+}	2000	91 ± 2	102 ± 2		
Ca^{2+}	200	109 ± 2	88 ± 2		
CN^-	20	102 ± 2	95 ± 5		
NH_4^+	20	100 ± 2	109 ± 2		
SeO_4^{2-}	20	117 ± 2	97 ± 2		
ClO^-	2	104 ± 2	85 ± 6		
Cu^{2+}	2	102 ± 2	84 ± 2	104 ± 4	98 ± 1
Ni^{2+}	2	108 ± 2	91 ± 2	100 ± 2	98 ± 5
Fe^{2+}	10	63 ± 2	79 ± 2	104 ± 4	108 ± 1
	20	68 ± 2	71 ± 2	98 ± 3	102 ± 4
Fe^{3+}	10	57 ± 2		105 ± 3	103 ± 0
	20	41 ± 2		93 ± 0	96 ± 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 .

There were no interferences from the common anions and cations such as phosphate, silicate, sulfate, Ca^{2+} , Mg^{2+} , and NH_4^+ . The divalent Cu^{2+} and Ni^{2+} made the As(V) signal smaller, and Fe^{2+} and Fe^{3+} made the recoveries for both As(III) and As(V) small. These problems were solved by the 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 addition of acid 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.

5.3.7. 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, SHGFA, 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. 5-9 and Table 5-3.

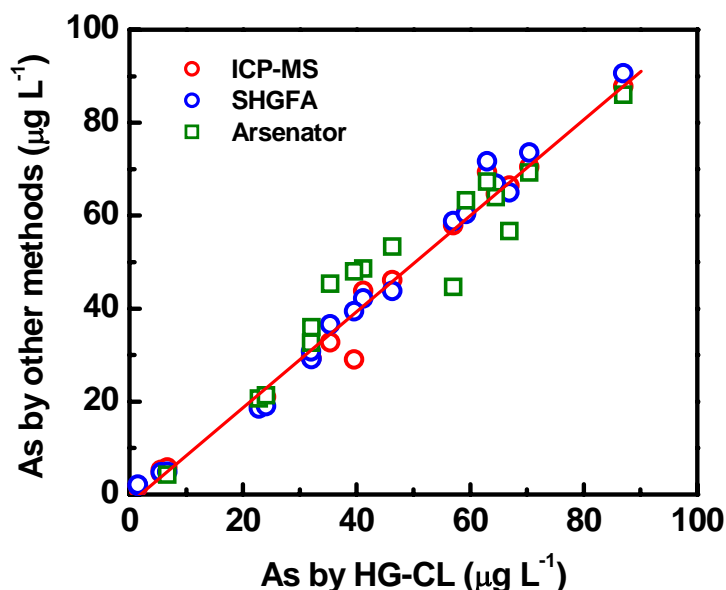


Fig. 5-9. Comparison of arsenic results obtained with HG-CL, ICP-MS, SHGFA and the Arsenator test kit. Data from the other methods are plotted against the values obtained by HG-CL. Red line is a fitted linear line for ICP-MS data plotted against the HG-CL data.

Measurements were repeated in triplicate. The HG-CL data agreed with that from ICP-MS and SHGFA with correlation coefficients of 0.987 and 0.991, 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 5-3) by the Arsenator kit although it has the critical range 2 to 100 $\mu\text{g L}^{-1}$ while arsenic was detected by all the other methods.

Table 5-3. Results of comparative measurement.

No.	Concentration ($\mu\text{g L}^{-1}$)			
	ICP-MS	SHGFA	Arsenator	HG-CL
River water				
1	1.4 ± 0.8	1.9 ± 0.1	ND*	1.5 ± 0.4
2	2.0 ± 0.0	2.1 ± 0.3	ND	1.5 ± 0.0
3	64.7 ± 2.5	66.9 ± 0.4	64 ± 2	64.5 ± 0.5
4	66.5 ± 3.0	65.0 ± 0.1	57 ± 2	66.9 ± 0.3
5	70.5 ± 4.5	73.6 ± 0.6	69 ± 2	70.4 ± 0.6
6	69.4 ± 1.3	71.7 ± 0.3	67 ± 1	63.0 ± 0.5
7	87.8 ± 1.9	90.6 ± 0.0	86 ± 2	87.0 ± 0.2
8	58.0 ± 3.9	58.8 ± 0.2	45 ± 2	57.0 ± 0.2
9	60.6 ± 1.8	60.4 ± 0.7	63 ± 3	59.2 ± 0.7
10	43.9 ± 1.3	42.2 ± 1.0	49 ± 2	41.1 ± 0.8
11	29.1 ± 0.3	39.4 ± 0.2	48 ± 1	39.6 ± 0.9
12	29.3 ± 1.8	29.2 ± 0.3	36 ± 2	32.1 ± 0.3
13	29.6 ± 2.4	30.8 ± 0.7	33 ± 3	32.0 ± 0.5
14	46.1 ± 1.3	43.8 ± 0.1	53 ± 2	46.3 ± 0.4
15	32.8 ± 1.3	36.6 ± 0.2	45 ± 2	35.3 ± 0.7
Well water				
16	5.3 ± 0.2	4.8 ± 0.3	ND	5.6 ± 0.5
17	4.6 ± 0.1	4.8 ± 0.4	ND	5.5 ± 0.5
18	19.2 ± 0.1	18.5 ± 0.3	21 ± 1	22.8 ± 0.6
19	21.0 ± 0.1	19.1 ± 0.0	21 ± 1	24.0 ± 0.2
20	5.8 ± 0.1	4.9 ± 0.0	4 ± 1	6.7 ± 0.4
Values with respect to HG-CL				
Slope	1.033	1.061	0.946	
Intercept	-1.984	-2.133	3.398	
R^2	0.987	0.991	0.914	

*ND: Not detected

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 (0.9136) than the other correlation coefficients. The HG-CL method developed in this 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.

5.4. 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 $\mu\text{g L}^{-1}$ 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.

References

1. National Research Council, *Arsenic in Drinking Water*, **1999**, National Academy Press, Washington, DC.
2. Kumaresan, M., Riyazuddin, P. Overview of speciation chemistry of arsenic. *Curr. Sci.*, **2001**, *80*, 837-846.
3. Leermakers, M., Baeyens, W., De Gieter, M., Smedts, B., Meert, C., De Bisschop, H. C., Morabito, R., Quevauviller, P. Toxic arsenic compounds in environmental samples: Speciation and validation. *Trends Anal. Chem.*, 2006, **25**, 1-10.
4. Dasgupta, P. K., Huang, H., Zhang, G., Cobb, G. P., Photometric measurement of trace As(III) and As(V) in drinking water. *Talanta*, 2002, **58**, 153-164.
5. Fazal, M. A., Kawachi, T., Ichion, E. Extent and severity of groundwater arsenic in Bangladesh. *Water Int.*, **2001**, *26*, 370-379.

6. Lin, N. -F., Tang, Bian, J. -M. Characteristics of environmental geochemistry in the arseniasis area of the Inner Mongolia of China. *Environ. Geochem. Health*, **2002**, *24*, 249-259.
7. Harvey, C. F., Swartz, C. H., Badruzzaman, A. B. M., Keon-Blue, N., Yu, W., Ali, M. A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P. M., Ashfaque, K. A., Islam, S., Ahmed, H. F. Arsenic Mobility and Groundwater Extraction in Bangladesh. *Science*, **2002**, *298*, 1602-1606.
8. Berg, M., Tran, H. C., Guyen, T. C., Pham, H. V., Schertenleib, R., Giger, W. Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat. *Environ. Sci. Technol.*, **2001**, *35*, 2621-2626.
9. World Health Organization (WHO), Guidelines for drinking-water quality, **2004**, *Vol. 1*, Recommendations, 3rd ed. Geneva, Switzerland.
http://www.who.int/water_sanitation_health/dwq/gdwq3/en/
10. Jang, M., Min, S. -H., Kim, T. -H., Park, J. K. Removal of arsenite and arsenate using hydrous ferric oxide incorporated into naturally occurring porous diatomite. *Environ. Sci. Technol.*, **2006**, *40*, 1636- 1643.
11. Minakata, K., Suzuki, M., Suzuki, O. Simple and selective determination of arsenite and arsenate by electrospray ionization mass spectrometry. *Anal. Chim. Acta*, **2009**, *631*, 87-90.
12. Wei, C., Liu, J. A new hydride generation system applied in determination of arsenic species with ion chromatography-hydride generation-atomic fluorescence spectrometry (IC-HG-AFS). *Talanta*, **2007**, *73*, 540-545.
13. Sengupta, M. K., Dasgupta, P. K. An Automated Hydride Generation Interface to ICPMS for Measuring Total Arsenic in Environmental Samples. *Anal. Chem.*, **2009**, *81*, 9737-9743.
14. Toda, K., Ohba, T. Highly Sensitive Flow Analysis of Trace Level Arsenic in Water Based on Vaporization-collection In-line Preconcentration. *Chem. Lett.*, **2005**, *34*, 176-177.
15. Toda, K., Ohba, T., Takaki, M., Karthikeyan, S., Hirata, S., Dasgupta, P. K. Speciation-Capable Field Instrument for the Measurement of Arsenite and Arsenate in Water. *Anal. Chem.*, **2005**, *77*, 4765-4773.

16. Toda, K., Takaki, M., Hashem, M. A. Investigation of arsenic removal in batch wise water treatments by means of sequential hydride generation flow injection analysis. *Chemosphere*, **2008**, 72, 1517-1523.
17. Hashem, M. A., Takaki, M., Jodai, T., Toda, K. Measurement of arsenite and arsenate contained in mining river waters and leached from contaminated sediments by sequential hydride generation flow injection analysis. *Talanta*, **2011**, 84, 1336-1341.
18. Idowu, A. D., Dasgupta, P. K., Genfa, Z., Toda, K., Garbarino, J. R. A Gas-Phase Chemiluminescence-Based Analyzer for Waterborne Arsenic. *Anal. Chem.*, **2006**, 78, 7088-7097.
19. Sengupta, M. K., Hossain, Z. A., Ohira, S. I., Dasgupta, P. K. A simple inexpensive gas phase chemiluminescence analyzer for measuring trace levels of arsenic in drinking water. *Environ. Pollut.*, **2010**, 158, 252-257.
20. Sengupta, M. K., Sawalha, M. F., Ohira, S. I., Idowu, A. D., Dasgupta, P. K. Green Analyzer for the Measurement of Total Arsenic in Drinking Water: Electrochemical Reduction of Arsenate to Arsine and Gas Phase Chemiluminescence with Ozone. *Anal. Chem.*, **2010**, 82, 3467-3473.
21. Ishiyama, T., Takahashi, M. On-Site Speciation Analysis of Inorganic Arsenic in Groundwater by Anodic Stripping Voltammetry. *J. Jpn. Soc. Water Environ.*, **2009**, 32, 93-98.
22. Furusho, Y., Makita, N., Ono, M., Ishiyama, T., Takahashi, M., Motomizu, S. On-Site Determination of Arsenic in Soil Extract by Anodic Stripping Voltammetry with Gold Film Electrode after Solid Phase Pretreatment. *Bunseki Kagaku*, **2007**, 56, 1165-1169.
23. Morita, K., Kaneko, E. Spectrophotometric Determination of Trace Arsenic in Water Samples Using a Nanoparticle of Ethyl Violet with a Molybdate-Iodine Tetrachloride Complex as a Probe for Molybdoarsenate. *Anal. Chem.*, **2006**, 78, 7682-7688.
24. Okamoto, K., Seike, Y., Okumura, M. A Simple Speciation Analysis Using Tristimulus Colorimetry for Arsenic(III) and Arsenic(V) in Environmental Water after Selective Coprecipitation with Barium Sulfate. *Bunseki Kagaku*, **2010**, 59, 653-658.

25. Kinniburgh, D. G., Kosmus, W. Arsenic contamination in groundwater: some analytical considerations. *Talanta*, **2002**, *58*, 165-180.
26. Arsenator digital arsenic test kit: <http://www.wagtech.co.uk/products/water-and-environmental/water-test-kits/arsenator%C2%AE-digital-arsenic-test-kit>
27. Baghel, A., Singh, B., Pandey, P., Sekhar, A. Rapid Field Detection Method for Arsenic in Drinking Water. *Anal. Sci.*, **2007**, *23*, 135-137.
28. Howard, A. G. (Boro)Hydride Techniques in Trace Element Speciation. *J. Anal. Atom. Spectrum.*, **1997**, *12*, 267-272.
29. Hung, D. Q., Nekrassova, O., Compton, R. G. Analytical methods for inorganic arsenic in water: a review. *Talanta*, **2004**, *64*, 269-277.
30. Fujiwara, K., Watanabe, Y., Fuwa, K., Winefordner, J. D. Gas-Phase Chemiluminescence with Ozone Oxidation for the Determination of Arsenic, Antimony, Tin, and Selenium. *Anal. Chem.*, **1982**, *54*, 125-128.
31. Azad, M. A. K., Ohira, S., Toda, K. Single Column Trapping/Separation and Chemiluminescence Detection for On-Site Measurement of Methyl Mercaptan and Dimethyl Sulfide. *Anal. Chem.*, **2006**, *78*, 6252-6259.
32. Toda, K., Obata, T., Obolkin, V. A., Potemkin, V. L., Hirota, K., Takeuchi, M., Arita, S., Khodzher, T. V., Grachev, M. A. Atmospheric methanethiol emitted from a pulp and paper plant on the shore of Lake Baikal. *Atmos. Environ.*, **2010**, *44*, 2427-2433.
33. Ohira, S., Li, J., Lonneman, W. A., Dasgupta, P. K., Toda, K. Can Breath Isoprene Be Measured by Ozone Chemiluminescence? *Anal. Chem.*, **2007**, *79*, 2641-3649.
34. Toda, K., Hirota, K., Tokunaga, W., Suda, D., Gushiken, Y., Ohira, S. On-site Multi Monitoring of Isoprene and Related Compounds in Forest Air. *Bunseki Kagaku*, **2011**, *60*, 489-498.
35. Fraser, M. E., Stedman, D. H., Nazeeri, M., Nelson, M. Chemiluminescent Detection of Arsine Oxidation. *Anal. Chem.*, **1983**, *55*, 1809-1810.
36. Toda, K. Dasgupta, P. K. New Applications of Chemiluminescence for Selective Gas Analysis. *Chem. Eng. Commun.*, **2008**, *195*, 82-97.
37. Clyne, M. A. A., Thrush, B. A., Wayne, R. P. Kinetics of the chemiluminescent reaction between nitric oxide and ozone. *Trans. Faraday Soc.*, **1964**, *60*, 359.
38. Atkinson, R., Winer, A. M., Pitts Jr, J. N. *Atmos. Environ.*, **1982**, *16*, 1017.

39. Ohira, S., Toda, K. Micro gas analysis system for measurement of atmospheric hydrogen sulfide and sulfur dioxide. *Lab Chip*, **2005**, 5, 1374-1379.

CHAPTER SIX

Suggestion for future work as on research

Leaching of arsenic from the contaminated sediments has been investigated in different conditions and leachates were successfully determined as arsenite and arsenate. Anaerobic condition enhances the mobilization of arsenic than aerobic condition due to dissolution of metals oxide/hydroxide. Phosphate was effectively to leach arsenic from the sediments surface especially arsenate. In the leaching experiments arsenic was leached as arsenite and arsenate but mostly was arsenate.

The developed system was reliable to monitor the speciation of arsenite and arsenate. During leaching experiment only inorganic arsenic was monitored, there might be microbiological activity and inorganic arsenic can convert to organic arsenic and finally emit to the atmosphere. It is necessary to investigate the organic arsenics during leaching experiment.

Appendix

Appendix-1

Table A-1. Sequence of analyses for As(III) and As(III+V)

No.	Port name	Operation	Rate (mL/s)	Notes
As(III)				
1	7	Sample		Sample line refresh
2	2	Waste		
3	7	Sample		Sample intake
4	5	EDTA		EDTA addition
5	6	pH 7 buffer		Buffer addition
6	8	Generator bottom		Transfer to generator
7	3	Water	} twice	Syringe cleaning
8	2	Waste		↓
9	11	NaBH ₄		
10	12	Generator top	0.021	AsH ₃ generation
11	8	Generator bottom	} twice	Generator cleaning
12	2	Waste		↓
13	3	Water	} twice	↓
14	8	Generator bottom		↓
15	8	Generator bottom	} twice	Syringe cleaning
16	2	Waste		↓
As(III+V)				
17	7	Sample		Sample intake
18	5	EDTA		EDTA addition
19	6	HCl		HCl addition
20	8	Generator bottom		Transfer to generator
21	3	Water	} twice	Syringe cleaning
22	2	Waste		↓
23	11	NaBH ₄		
24	12	Generator top	0.025	AsH ₃ generation
25	8	Generator bottom	} twice	Generator cleaning
26	2	Waste		↓
27	3	Water	} twice	↓
28	8	Generator bottom		↓
29	8	Generator bottom	} twice	Syringe cleaning
30	2	Waste		↓

Appendix-2: Arsenic leaching from sediments at different conditions

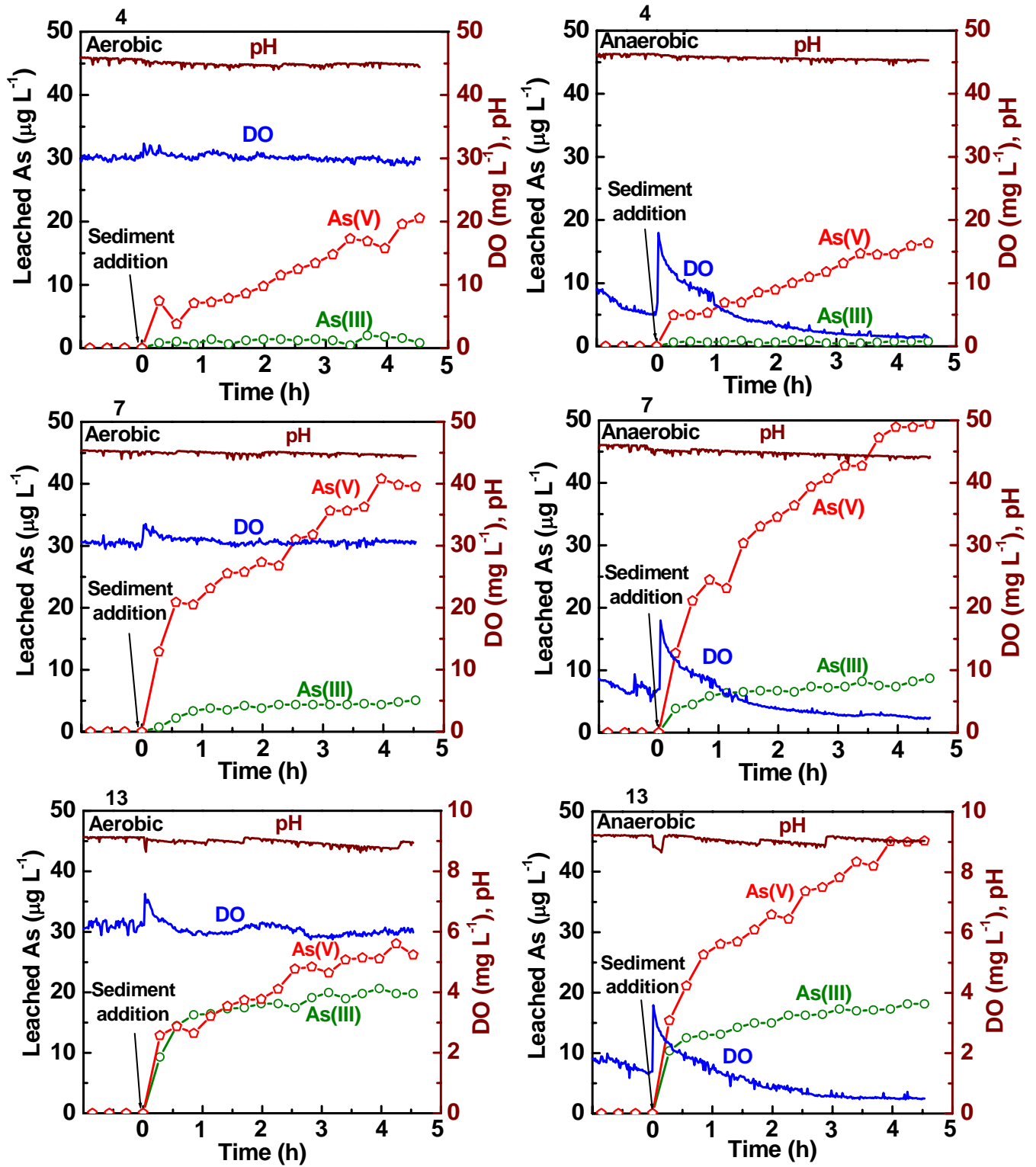


Fig. A-1. Arsenic leached from the different sediments under aerobic left site and under anaerobic in the right site.