# Monitoring of Arsenite and Arsenate by Flow Injection-Hydride Generation Atomic-Fluorescence Spectrometry I: System Development

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#### Abstract

A flow injection-hydride generation-atomic fluorescence spectrometry system has been developed for monitoring arsenite and arsenate in aqueous samples. The system involves injection of a 120- $\mu$ L water sample in a carrier stream, mixing with 1.0 M phosphate buffer or 3 M HCl followed by 3.0% alkaline reducing agent NaBH<sub>4</sub>, passing through a mixing coil and feeding into a gas liquid separator with Ar carrier gas. The generated arsenic trihydride (AsH<sub>3</sub>) was fed to an atomizer by the carrier gas and the fluorescence intensity monitored using a photomultiplier tube. Under optimized conditions, the detection limit was 0.2  $\mu$ g/L with a linear range of 0.5–300  $\mu$ g/L. A distinction between As(III) and As(V) measurements was possible with a sampling frequency of 30/h. Repeatability (*n* = 20) for As(III) and total arsenic was 1.7 and 1.0%, respectively, for standard mixture solutions of [10  $\mu$ g/L As(III) + 10  $\mu$ g/L As(V)].

Keywords Flow injection analysis, hydride generation, arsenite, arsenate, atomic fluorescence spectrometry

## 1. Introduction

Arsenic occurrence in water and its toxic effect on human health through drinking and agricultural practice is a serious worldwide environmental problem. Humans may be exposed to arsenic through food, air, water, and skin contact. Drinking water contaminated with arsenic is the most common cause of arsenic poisoning in humans. Inorganic arsenic is found mostly in groundwater and exists typically in either trivalent arsenite As(III) or pentavalent arsenate As(V) form with arsenite being more toxic than arsenate [2]. Millions of people are exposed to inorganic arsenic, which occurs naturally in many parts of the world [3]. Long-term ingestion of inorganic arsenic causes serious disorders and may lead to lung, liver, renal, and skin cancers with other adverse health effects [4].

In 20 countries worldwide, groundwater is contaminated with arsenic [5] with the most severely affected countries including Bangladesh, India, Taiwan, Vietnam, Cambodia, and Argentina. While the WHO guideline value for arsenic in drinking water is 10  $\mu$ g/L [6], in the countries mentioned above, groundwater arsenic concentrations are higher than the permissible level and sometimes are at a level of several thousand micrograms per liter.

Although the mechanism of arsenic occurrence in groundwater is of great interest in understanding the pollution, little work has been done to investigate the kinetics of arsenic leaching. We have developed a flow analysis system for arsenic field analysis based on molybdenum blue chemistry [7] and ozone induced chemiluminescence detection [8]. A sequential automated system (sequential hydride-generation flow injection analysis, SHG-FIA) was developed based on the same principle as the former for

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<sup>†</sup>Current address: Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna 9203, Bangladesh (M.A. Hashem). speciation analysis of arsenite and arsenate in the leachate [11]. Although the limit of detection (LOD) of 0.02  $\mu$ g/L was acceptable, the 3.5/h sampling frequency of the SHG-FIA was too small for monitoring during rapid leaching and a sample consumption of 2 mL/analysis was too large for long-term monitoring.

To improve performance, other detection methods were explored and atomic fluorescence spectrometry (AFS) considered to be an attractive alternative for the high sensitivity detection of heavy metals. AFS is much more sensitive than the commonly used atomic absorption spectrometry and inductively coupled plasma optical emission spectroscopy. Recently, several attempts using AFS have been made for speciation measurement with hydride generation (HG-AFS) [9] coupled with high performance liquid chromatography [10], ion chromatography [11] and multi-syringe flow injection analysis [10]. Arsenite and arsenate were measured successfully with a throughput of 6–10 samples/h. Leal et al. demonstrated that the performance of HG-AFS was 20 samples/h with 8 mL sample consumption per analysis [12]. The LODs for arsenite and total arsenic were 2.9 and 3.1  $\mu$ g/L, respectively.

Here we demonstrate a faster and more sensitive method without pre-reduction of As(V) to As(III) for simultaneous speciation monitoring of arsenite and arsenate with high sample throughput (30/h) and low sample consumption by flow injection-hydride generation-atomic fluorescence spectrometry (FI-HG-AFS). This test work demonstrates the viability of using this technique over the long term for analysis of products from a leaching reactor. Arsine was generated at a selective pH 5.6 and pH 0 for As(III) and total As [As(III) + As(V)], respectively.

## 2. Experimental

#### 2.1. Reagents

All stock solutions were prepared from analytical grade reagents. Arsenic stock solutions of As(III) and As(V), each containing 100 mg/L arsenic, were prepared from sodium metaarsenite (Wako) and disodium hydrogen arsenate heptahydrate (Nacalai) in 0.18 M  $H_2SO_4$  (Nacalai). Standard solutions of As(III) and As(V) were made up daily from appropriate dilutions of the stock solutions. The stock solutions were refrigerated when not in use. Arsenic trihydride (AsH<sub>3</sub>) was generated with 3.0% NaBH<sub>4</sub> (Nacalai) and prepared by dissolution in 10 mM NaOH. Phosphate buffer (1 M, pH 5.6) was prepared by mixing 1 M NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and 1 M Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O (both Nacalai) at a ratio of 2:1.

#### 2.2. System setup and operation

Using a peristaltic pump, sample water was fed continuously at 6 mL/min through a DC driven 6-port valve (C22Z-3186D, Valco, Houston, TX) equipped with 120-µL sample loop (1 mm i.d.  $\times$  1/16" o.d.  $\times$  150 mm). Reagent solutions of NaBH<sub>4</sub>, 3 M HCl, pH 5.6 buffer, and water were fed by a four-channel peristaltic pump (MP-3, Gilson, Middleton, WI) with 0.76 mm i.d.  $\times$  2.46 mm Tygon tubes at 2 mL/min each. The HCl and buffer solutions were switched by two three-way solenoid valves 3SV1 and 3SV2 (MTV-3-1/4 UFH-S, 12V dc, PCTFE, Takasago Electric, Nagoya, Japan) to introduce them alternately. When the solution was not introduced to the main reaction system, it was returned to the storage bottle. The injector and solenoid valves were controlled by a sequencer (ZEN-10C2DR-D-V2, Omron, Kyoto). Typically, the 3SVs were switched every 60 s. The injector was maintained in the loading mode 25 s after the 3SV switching and then in the injection mode for 15 s.

The aqueous sample was transported by the water carrier and mixed with HCl or buffer at T2 and merged with NaBH<sub>4</sub> solution at T3 (T1~3: P-712, UpChurch, Oak Harbor, WA). AsH<sub>3</sub> gas produced in the reaction coil (1 mm i.d.  $\times$  1.00 m) was introduced to a gas/liquid separator GLS1 and the vapor was transported by Ar gas flow (0.3 L/min) to an AFS instrument (AI3300, Aurora Instruments, Vancouver, BC). Arsenic from

AsH<sub>3</sub> was atomized using a NiCr wire heater and fluorescence formed by radiation of a 193.7-nm hollow cathode lamp (Aurora Instrument) was monitored by a photomultiplier tube. All flow conduits were polytetrafluoroethylene tubes (1.0 mm i.d.  $\times$  1/16" o.d.).

For the As(III) measurement, 3SV1 and 2 were turned off to introduce the buffer into the flow system and HCl was by-passed via 3SV1 and returned to the reagent container. Total As [As(III)+As(V)] was measured in the same way by switching 3SVs on to obtain a peak for total As [As(III)+As(V)]. A set of two signals for As(III) and total As [As(III)+As(V)] were obtained every 2 minutes. The concentration of As(V) was determined by subtracting the As(III) concentration from the total As concentration. The optimized parameters for the FI-HG-AFS are listed in Table 1.

Table 1 Parameters optimized for FI-HG-AFS

Parameter	Setting			
Water	2 mL/min			
Buffer <sup>a</sup>	1 M phosphate buffer pH 5.6			
	2 mL/min			
Acid <sup>b</sup>	3 M HCl, 2 mL/min			
Reducing agent	3% (w/v) NaBH <sub>4</sub> /0.1 M NaOH			
	2 mL/min			
3SV 1 and 2	$0\sim60 \text{ s off} \leftrightarrow 360\sim120 \text{ s on}$			
Injector	25~40 s, 85~100 s: on (injection)			
AFS carrier gas	Ar 0.3 L/min			
AFS shield gas	Ar 0.7 L/min			
AFS PMT voltage	295 V			
AFS HCL current	100 mA (high intensity)			
	<b>b</b>			

<sup>a</sup> for As(III) measurement, <sup>b</sup> for total As measurement.



Fig. 1 Flow diagram of FI-HG-AFS system. P1 and P2: peristaltic pumps; GLS1 and GLS2: gas liquid separators; 3SV1 and 3SV2: three-way solenoid valves; T1, T2, and T3: tee connectors (PEEK); AF chamber: atomic fluorescence chamber; HCL: hollow cathode lamp; PMT: photomultiplier tube.



Fig. 2 Effect of pH on fluorescence intensity for 50  $\mu$ g/L As(III) and As(V). Reducing agent was 3 % (w/v) NaBH<sub>4</sub> in 0.01 M NaOH. Both carrier and shield gas flow rates were 0.6 L/min.

#### 3. Results and discussion

#### 3.1. Optimization of pH

The effect of pH on AsH<sub>3</sub> generation from arsenite and arsenate was investigated. As shown in Fig. 2, As(V) was vaporized as AsH<sub>3</sub> at low pH because the p $K_1$  of arsenic acid is 2.2 [8] and the reaction must be carried out below this pH. On the other hand, arsenous acid is formed below pH 7 and As(III) could be vaporized over a wide pH range. The optimized HCl concentration for arsine both from As(III) and As(V) is 3 M (pH < 0) and from As(III), 1 M phosphate buffer at pH 5.6.

## 3.2. Optimization of Ar flow rates

Figure 3 shows the effect of carrier and shield gas flow rates on the signal intensity obtained for mixtures of 50  $\mu$ g/L each of As(III) and As(V). At lower carrier flow ranges of 0.1 to 0.3 L/min, the signal intensity was higher. A higher carrier gas may dilute the AsH<sub>3</sub> vapor. In the case of the shield gas, with increasing gas flow, the signal intensity also increased and stabilized from 0.7 to 1.0 L/min. The higher Ar flow rate probably serves to shield the sample stream from air. The optimized argon gas flow rates were 0.3 and 0.7 L/min for the carrier and shield, respectively.

#### 3.3. Performance of FI-HG-AFS

Figure 4 shows the fluorescence signal peaks of the FI-HG-AFS system recorded under optimum conditions. Responses are for standard solutions containing 0, 0.5, 1, 3, 5 and 10  $\mu$ g/L of As(III) and measurements were performed with 3 M HCl and 1 M phosphate buffer alternated every minute. There was no difference in response intensity for As(III) and As(V). This indicates that the present system was suitable for the discriminative measurement of As(III) and As(V).

#### 3.4. Calibration graph

Calibration curves were linear from 0.5 to 300  $\mu$ g/L for both As(III) and total As (Fig. 5). Calibration curves for lower concentrations are shown in the inset.

The correlation coefficients were 0.9996 and 0.9989 for As(III)



Fig. 3 Effect of gas flow rates on signal intensity for 50  $\mu$ g/L As(III) and As(V).

when measurements were performed with 3 M HCl and 1 M phosphate buffer, respectively.

The measurement repeatability is shown in Fig. 6. Responses for As(III) and total As were obtained 20 times, for a test sample containing 10 µg each of As(III) and 10 µg As(V). The relative standard deviation (n = 20) was 1.7% for As(III) and 1.0% for total arsenic. The LOD estimated from three times the standard deviation of the blank signal was 0.20 µg/L. The sample frequency for the FI-HG-AFS system was 30/h.



Fig. 4 Signals for As(III) at different concentrations, measurement with 3 M HCl and 1 M phosphate buffer.



Fig. 5 Calibration curves obtained by FI-HG-AFS for As(III).

#### 3.5. Comparison of FI-HG-AFS and reported methods

In Table 2, the FI-HG-AFS performance is compared with that of the reported methods SHG-FIA [13] and HG-AFS [9]. The proposed FI-HG-AFS has a linear range for both As(III) and total As of 0.5-300 µg/L. HG-AFS has a smaller linear range for As(III) of 0.2–15 µg/L and 0.1–10 µg/L for total As. All methods have sufficient sensitivity for the determination of arsenic contained in natural and drinking water. The LODs for both the FI-HG-AFS and HG-AFS system are almost the same. The FI-HG-AFS has a higher sample frequency than the HG-AFS and SHG-FIA with low sample consumption (0.12 mL). Furthermore the FI-HG-AES required less concentrated HCl (3 M) while SHG-FIA and HG-AFS required more concentrated HCl (9 M). The small sample consumption and high throughput of the proposed FI-HG-AFS system are major advantages to investigating arsenic removal and leaching from contaminated sediments.



Fig. 6 Repeatability for standard mixture solution of [As(III)  $10 \ \mu g/L + As(V) \ 10 \ \mu g/L$ ], n = 20.

Table 2 Performance of FI-HG-AFS and other reported methods

	FI-HG-AFS (this work)		SHG-I	SHG-FIA [13]		HG-AFS [9]	
	As(III)	Total As	As(III)	Total As	As(III)	Total As	
LOD (µg/L)	0.2	0.2	0.02	0.03	0.1	0.06	
Repeatability (%)	1.7	1.0	—	-	2.9	3.1	
Linear range (µg/L)	0.5-300	0.5-300	1-500	1-500	0.2–15	0.1-10	
Sample consumption (mL)	0.12	0.12	2	2	8	8	
Sample frequency (/h)	30		3.5		20		
HCl (M)	-	3.0	—	9.0	1.5	9.0	
NaBH <sub>4</sub> (%)	3.0	3.0	1.25	1.25	0.5	3.0	
Phosphate buffer (M)	1.0 (pH 5.6)	_	1.0 (pH 7.0)	_	_	_	

## 4. Conclusion

The developed FI-HG-AFS system offers the potential of measuring arsenic in an aqueous sample by arsenite and arsenate speciation in a short time without any pre-reduction of As(V). The system could be used for the high precision monitoring of the leaching behavior of arsenic or water samples.

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