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Speciation of arsenic(III) and arsenic(V) by inductively coupled plasma-atomic emission spectrometry coupled with preconcentration system

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Abstract

A novel and simple flow-based method was developed for the simultaneous determination of As(III) and As(V) in freshwater samples. Two miniature columns with a solid phase anion exchange resin, placed on two 6-way valves were utilized for the solid-phase collection/concentration of arsenic(III) and arsenic(V), respectively. As(III) could be retained on the column after its oxidation to As(V) species with an oxidizing agent. The collected analytes were then sequentially eluted by 2 M nitric acid and introduced into ICP-AES. Potassium permanganate was examined as potential oxidizing agent for conversion of As(III) to As(V). The standard deviation of the analytical signals (peak height) for the replicate analysis ($n = 5$) of 0.5 $\mu g\,l^{-1}$ solution were 3 and 5% for As(III) and As(V), respectively. The limit of detection (3σ) for both As(III) and As(V) were 0.1 $\mu g\,l^{-1}$. The proposed system produced satisfactory results on the application to the direct analysis of inorganic arsenic species in freshwater samples.

Keywords: Speciation; As(III) and As(V); Preconcentration; ICP-AES; Permanganate

1. Introduction

Inorganic arsenic species, i.e. arsenite As(III) and arsenate As(V), are commonly found in natural waters, while the organic arsenic species, such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) occur in marine and other biological samples. Between the two categories, inorganic arsenic species, especially arsenite, are more toxic than their organic counterparts. Therefore, the speciation of arsenic species is very important and necessary for environmental analyses. Water contamination from arsenic is very serious problem in some countries, such as Bangladesh and India, where some parts of the population are exposed to high health risks from drinking water contaminated with arsenic. Based on the regulation of these species in drinking water set by World Health Organization (WHO) [1] and the US Environmental Protection Agency (USEPA) [2], the maximum permissible concentration of As is 10 $\mu g\,l^{-1}$. Consequently, a speciation method as well as a sensitive and selective method is required for the arsenic analyses. The speciation of arsenic species has been intensively studied for more than a decade. Well established methods include the coupling of separation techniques, such as IC [3–9], HPLC [10,11] and CE [12–14], for the separation of arsenic species with element specific detection systems, e.g. ICP-MS, HG-AFS, etc. These methods often require the incorporation of the hydride generation techniques in order to improve the detection sensitivity and also to eliminate matrices interferences. The electrochemical methods have also been reported as a detection system [15,16] or merely as a preconcentration technique prior to the detection of As species by ICP-AES and ICP-MS [17]. However, these sophisticated separation systems are complicated and time-consuming. Some comprehensive reviews on the speciation of arsenic species can be found in the literature

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[18–22], from which it can be concluded that most of fresh waters contain inorganic arsenic, As(III) and As(V), whereas organic arsenic species are very less compared with inorganic arsenic.

As(III) occurs at much lower concentrations compared to As(V) in environmental samples, which makes it difficult to detect directly and inevitably requires preconcentration steps. Thus, the preconcentration of arsenic species is necessary prior to their detection. Ammonium pyrrolidinedithiocarbamate (APDC) [23–25], hexamethylenedithiocarbamate (HMDC) [26] and dimercaptopropane-1-sulfonate (DMPS) [27] have often been used as arsenic complexing agent, forming hydrophobic complexes, which can be retained on a hydrophobic collection media. Trung et al. reported the utilization of metal-loaded chelating resin for collection of As(III) and As(V) [28]. Recently, Dasgupta et al. reported the photometric method for the determination of As(III) and As(V) [29]. The molybdenum blue method was utilized for the determination of As(V) and the potential interference from phosphate for the determination of As(III) and total arsenic (after reducing As(V) to As(III) with cysteine) was eliminated. The concentration of As(V) could be determined from the difference between the total concentration and the concentration of As(III). In this method, As(III) was separated from phosphate and As(V) with anion exchange resin column. As(III) was carried to the detection system, followed by its oxidation to As(V) with $KBrO_3$ and the determination of resulting As(V) by molybdenum blue method. The reaction chemistry used in this work is well-defined. However, the system is somewhat complicated and As(III) could not be enriched: LOD of As was $8\,\mu g\,l^{-1}$. Most of the methods reported so far have used the difference between the total concentrations of arsenic ((III) or (V)) and the concentration of As(III) or As(III). In natural waters, however, the concentration of As(V) are much higher than As(III), which is more important and more toxic than As(V).

This work aimed at developing a simple system for the speciation of As species: arsenite, As(III) and arsenate, As(V) were separated based on the difference in acid dissociation constants, pK_a values, between arsenite ($pK_{a1} = 9.2$ and $pK_{a2} = 13.5$) and arsenate ($pK_{a1} = 2.3$, $pK_{a2} = 6.9$ and $pK_{a3} = 11.5$) [30], which facilitates easy collection and separation of these two species on the solid phase via an on-line system following ICP-AES measurement. In the proposed system, the solution containing arsenite and arsenate at particular pH was introduced into the system. Arsenate was collected on the first collection/concentration unit (containing anion exchange resin), while arsenite passed through the unit and then oxidized to arsenate, which can be collected on the second collection/concentration unit. The proposed methods were successfully applied to natural water samples and bottled drinking waters.

2. Experimental

2.1. Apparatus

An inductively coupled plasma atomic emission spectrometry (ICP-AES) (Vista Pro, Seiko Instrument & Varian Instrument) was used for the detection of arsenic. Some of the instrumental conditions used in this work are as follows: RF generator frequency, 40 MHz; plasma power, 1.10 kW; plasma gas flow (Ar), $15\,l\,min^{-1}$; auxiliary gas flow (Ar), $1.5\,l\,min^{-1}$; nebulizer gas flow (Ar), $0.75\,l\,min^{-1}$; glass cyclonic spray chamber with K-style concentric glass nebulizer and one-piece low flow extended torch in the axial view mode. The time scan mode was used to detect As at 188.980 nm of emission line. The PTFE tubing was used for the assembling of flow lines in a flow injection pretreatment system. A double-plunger pump (P_3) (F.I.A. Instruments, Tokyo, Japan) was used to propel an eluent solution and peristaltic pumps (P_1 and P_2) (ALITEA, Sweden) were used for propelling ammonium acetate, a sample and an oxidizing agent solution (see Fig. 1).

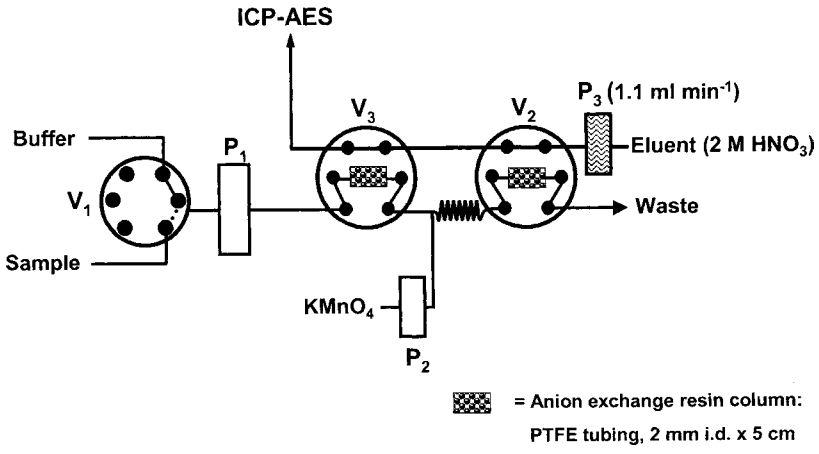

Fig. 1. Flow set up for the speciation of As(III) and As(V) (all valves are in load-position).

2.2. Reagents

A 1000 mg l^{-1} stock solution of As(III) was prepared by dissolving sodium metaarsenite (analytical reagent grade: Wako Pure Chemical Industries, Japan) in an ultra-purified water (resistivity: more than 18 MΩ cm), which was prepared with an Elix 3/Milli-Q Element System (Nihon Millipore, Japan). Similarly, a 1000 mg l^{-1} stock solution of As(V) was prepared by dissolving disodium hydrogen arsenateheptahydrate (analytical reagent grade: Kanto Chemical Co., Japan) in an ultra-purified water. Accurately diluted solutions of As(III) and As(V) were prepared daily using standard stock solutions. Potassium permanganate solution (analytical reagent grade: Ishizu Pharmaceutical Co., Japan) was prepared by dissolving known amounts in water. The ammonia–ammonium acetate buffers were prepared by appropriate mixing of acetic acid (electronic grade: Mitsubishi Chemicals, Japan) and ammonia water (29%, electronic grade: Mitsubishi Chemicals, Japan). Nitric acid (ultrapure reagent: Kanto Chemical Co., Japan) was used as an eluent after appropriate dilution with water. An anion exchange resin Muromac® 2 × 8, 100–200 mesh in Cl-form (Muromachi Technos Co., Japan) was used for collection and concentration of As(V) species. The solid-phase collection/concentration unit (CU) was prepared by packing the anion exchange resin into the PTFE tubing (2 mm i.d. × 5 cm) with the plugs of glass wool (packing for gas chromatography, Kishida Chemical Co., Japan) at both ends of the tubing to keep the resin in the unit. Smaller PTFE tubings (0.5 mm i.d.) were tightly inserted into the CU at both ends, which enabled the CU to be placed on the 6-way valve.

2.3. Analytical procedures

For the on-line collection/concentration of both As(III) and As(V), the operating steps for the proposed system (Fig. 1) are shown in Table 1; briefly, the procedure involved the conditioning step in which the anion exchange resin in CU was washed with an ammonia–ammonium acetate buffer, followed by the collection step, whereby the analytes were collected in the CU. Valve V_1 was used for the selection of the solution (the buffer or the sample solution) to be propelled to the system. In the pH range 3.0–6.9, As(V) in the sample solution exits as a monovalent anionic species, $H_2AsO_4^-$, while As(III) is present as a nonionic species, H_3AsO_4. Therefore, in the first CU, only As(V) was collected, while the un-retained nonionic As(III) passed through the first CU, subsequently being oxidized by permanganate to As(V), which was collected on the second CU. The collection steps of analytes were followed by the washing step, which involved the introduction of the buffer to wash away matrices as well as analytes remaining in the tubing of the flow system. In the elution step, the collected As(V) and pre-oxidized As(III) were sequentially eluted by switching the valve V_2 for elution of pre-oxidized As(III) and thereafter switching of valve V_3 for As(V). The analytes' zone eluted from the CU was introduced into ICP-AES for their detection. The As signals obtained from the instrument by using time-scan mode measurement were transferred to Excel program, where the flow signals were graphically plotted. The peak height and peak area of the analytical signals were computed by using the Microcal Origin program. The sample solutions were filtered through the membrane filter (mixed nitrocellulose ester, 0.45 μm, Advantec, Toyo Roshi Kaisha, Japan) before injection.

Table 1
Operation steps for the proposed system

Steps	Valve positions			Time (min)
	V_1	V_2	V_3	
Conditioning	Load	Load	Load	0.5
Collection	Inject	Load	Load	10.0
Washing	Load	Load	Load	1.0
Elution for As(III)	Load	Inject	Load	1.5
Elution for As(V)	Load	Inject	Inject	1.5

3. Results and discussion

3.1. Effect of pH on collection/concentration of arsenic

The acidity of sample solutions plays an important role to control the ionic characters of both As(III) and As(V). Since it is aimed to collect anionic species of As(V) on the anion exchange resin, the acidity of sample solution should allow not only for the collection of the existing As(V), but also for the separation from As(III) and the effective oxidation of As(III) to As(V). Both arsenic species can be easily separated by selecting pH of the sample solutions which should be below the first pK_a value of As(III), pK_{a1} = 9.2. Under such a condition, As(III) presents as a nonionic species and can not be retained on the anion exchange resin used, whereas As(V) are present as anionic species and can be retained. The sample solutions containing As(III) and As(V) at pH of 4–7 were examined. The concentration of potassium permanganate and As(III) used in this study was 1×10^{-6} M and 0.27×10^{-6} M (20 μg l^{-1}), respectively. It was found that increase in pH from 4 to 6 led to an increase in As(III) signals, and in the pH range from 6 to 7 the signals become constant. Therefore, pH 6.3 of the sample solution was adopted for further studies.

3.2. Effect of concentration of potassium permanganate on the collection/concentration of arsenic

The results showed that the increase in the concentrations of potassium permanganate from 0.1×10^{-6} to 0.5×10^{-6} M resulted in an increase in the intensity of As(III) signals, and further increase in the concentrations of $KMnO_4$ from 1×10^{-6} to 5×10^{-6} M resulted in gradual decrease in the As(III) signals. Therefore, 1×10^{-6} M was selected as an optimum concentration of $KMnO_4$.

3.3. Effect of length of reaction coil on oxidation of As(III) to As(V)

The oxidation reaction of As(III) with $KMnO_4$ was found to proceed rapidly. By using 1×10^{-6} M $KMnO_4$ at flow rate of 0.4 ml min^{-1} and the sample flow rate of 1.0 ml min^{-1}, the effect of the length of reaction coil (20 cm to 10 m) on the oxidation of As(III) to As(V) was examined. The oxidation of As(III) to As(V) was effective despite using a short reaction coil (length = 20 cm). Furthermore, the analytical signals (peak heights) for As(III) remained almost constant when the reaction coil was increased up to 10 m. As a result, the length of reaction coil of 20 cm was selected with respect of analysis time and of less consuming permanganate to oxidize organic substances in sample solutions.

3.4. Effect of flow rate of potassium permanganate solution on collection/concentration of As(III)

The flow rate of potassium permanganate solution in the range of 0.1 to 0.8 ml min^{-1} was examined. The flow rate of 0.2 ml min^{-1} was resulting in the highest signals of As(III) and was sufficient for the oxidation of As(III) (0.27×10^{-6} M). Further increase in the flow rate up to 0.8 ml min^{-1} did not affect the analytical signals of As(III). The flow rate of 0.4 ml min^{-1} was therefore selected.

3.5. Effect of sample size and sampling flow rate on the analytical signals

The effect of sample size on the analytical signals of As(III) and As(V) was also studied. The results showed that the analytical signals of both species increased linearly with an increase in sample size up to at least 20 ml. The sample size of 20 ml was selected with respect of sensitivity.

Since the oxidation of As(III) to As(V) proceeded rapidly and effectively, the optimum flow rate of the sample was examined for shortening the analysis time and introducing large sample size in a short period. Due to the back-pressure generated from two CUs, the maximum sampling flow rate that can be applied to the system was 3 ml min^{-1}. In the present study, however, the flow rate of 2 ml min^{-1} was adopted as the sampling flow rate in order to avoid any leakage of sample solutions.

Under such conditions, the effect of concentration of potassium permanganate was re-examined. The results showed that an increase in the concentration of potassium permanganate increased the signals of As(III) which was maximum at 1×10^{-6} M potassium permanganate. Further increase in the concentration of potassium permanganate up to 4×10^{-6} M did not significantly change the signals of As(III). The concentration of potassium permanganate in the range of 1×10^{-6} to 4×10^{-6} M was effective for the oxidation and collection of 0.27×10^{-6} M As(III). Therefore, 2×10^{-6} M of potassium permanganate was selected.

Table 2
Selected conditions for the proposed system and analytical figures of merit

Parameters	
Sample/standard	
Acidity (pH)	6.3
Flow rate (ml min^{-1})	2.0
Loading time (min)	10
Oxidizing agent	$KMnO_4$
Concentration (M)	2×10^{-6}
Flow rate (ml min^{-1})	0.4
Reaction coil	PTFE tubing, 0.5 mm i.d. × 3 m
Eluent	2 M HNO_3
Flow rate (ml min^{-1})	1.1
Analysis time (min)	15
%R.S.D. ($n = 5$, 0.5 μg l^{-1} As(III) and As(V))	5% in peak height
Limit of detection (3σ)	0.1 μg l^{-1} for both As(III) and As(V)

3.6. Analysis of freshwater samples by the proposed method

The calibration graphs by using peak area and peak height, respectively, for 20 ml sample in the range of 0.5–20 μg l^{-1}

Table 3
Analysis of some freshwater samples by the proposed method

Sample	As(III) and As(V) add (μg l^{-1})	Found (μg l^{-1}, $n = 3$)		Recovery (%)	
		As(III)	As(V)	As(III)	As(V)
Asahi river	0	0.30 ± 0.00	0.67 ± 0.06		
	1.00	1.26 ± 0.00	1.66 ± 0.06	96	99
Zasu river	0	0.29 ± 0.03	0.75 ± 0.04		
	1.00	1.34 ± 0.01	1.75 ± 0.10	109	96
Tap water	0	n.d.	0.53 ± 0.02		
	1.00	n.d.	2.62 ± 0.12	0	209
Bottled mineral drinking water (A)	0	0.50 ± 0.06	3.47 ± 0.05		
	1.00	1.43 ± 0.03	4.51 ± 0.05	93	104
Bottled mineral drinking water (B)	0	0.82 ± 0.06	2.17 ± 0.06		

n.d.: not detected. River water sample were sampled on May 23, 2004, from the river located near Okayama University, Okayama, Japan. Tap water was sampled from the tap water supply in Okayama City, Japan. Bottled mineral drinking waters were purchased from a local super market.

were, $Y = 2543X + 177$, $r^2 = 0.9999$ and $Y = 210X + 18$, $r^2 = 0.9999$ for As(III), while $Y = 2456X + 1325$, $r^2 = 0.9988$ and $Y = 234X + 122$, $r^2 = 0.9983$ were for As(V), respectively. However, calibration graphs plotted by using peak height were used for the quantitative analysis because of simplicity and better reproducibility. The flow signals obtained by using the proposed method consisted of two separated-peaks; first and second peak corresponded to As(III) and As(V), respectively. The optimal conditions and analytical figures of merit for the proposed system are summarized in Table 2. The conventional ICP-AES (used in this work) measurement has a detection limit of 10 $\mu g\,l^{-1}$ for As. This detection limit was about two orders of magnitude higher than that obtained by this proposed method.

The developed method was applied for the speciation of As(III) and As(V) in freshwater samples. The spiked samples were also analyzed for the recovery test. The analytical results are summarized in Table 3. Quantitative recovery of As(III) and As(V) can be attained for all examined freshwater samples, except for tap water. The addition of As(III) to this sample significantly increased the amount of As(V) which yielded recovery of As(V) as 209%. The tap water could contained residual chlorine which will rapidly oxidized As(III), and the results are in consistent with the results reported by Dasgupta [29]: the 209% recovery of As(V) was contributed from the added As(V) and As(III) initially spiked to the sample. As expected, As(III) could not be found in tap water.

4. Conclusion

The flow set up for the simultaneous determination of As(III) and As(V) was established. Potassium permanganate was an effective agent for the oxidation of As(III) to As(V). The rapid oxidation reaction of As(III) with potassium permanganate allows for simple set up of the system. The proposed system provides an on-line separation of As(III) and As(V), and the preconcentration of both species in which both species can be determined simultaneously in a single analysis run. The detection sensitivities for As(III) and As(V) were improved for by about two order of magnitudes compared to conventional ICP-AES determination. As an advantage over other As determination techniques, the developed method can be used for sensitive determination of As(III) and As(V) at sub-$\mu g\,l^{-1}$ level, without coupling it with the well-known hydride generation techniques. In addition, the proposed technique will be adapted for the on-site collection/separation of As(III) and As(V) prior to their determinations at laboratories.

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