Trace Amounts Determination of Arsenic (III) and Arsenic(V) in Environmental Water Samples by Inductively Coupled Plasma -Atomic Emission Spectrometry (ICP-AES) Coupled with Flow-Injection Solid-Phase Collection/Concentration System

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Abstract

A simple flow-based method for the selective, sensitive and simultaneous determination of As(III) and As(V) was investigated. Two sequentially connected 6-way valves, which each contain a solid-phase collection/concentration unit, were utilized for collecting of As(III) and As(V), respectively. Potassium periodate was examined as a potential oxidizing agent for As(III) to As(V). The collected analytes on the solid phase containing anion exchanger were sequentially eluted by nitric acid and introduced into ICP-AES. The standard deviation of the analytical signals (peak height) for the replicate analysis (n=6) of 10 μg l^{-1} solution were 3% and 5% for As(III) and As(V), respectively. The detection sensitivity for arsenic was improved for ca. 10 times compared with the conventional direct measurement by ICP-AES. The limit of detection (3σ) for both As(III) and As(V) were 1 μg l^{-1}. The proposed system was applied to the speciation of inorganic arsenic in freshwater samples.

Keywords Trace analysis, As(III) and As(V), ICP-AES, solid-phase collection, flow injection

1. Introduction

Speciation analysis is becoming an interesting task, especially in environmental and clinical analysis. Since the toxicity of particular elements is dependent on their species, total concentrations are not sufficient for risk and health assessment as well as the understanding in the metabolic and biological pathway. Arsenic is one of the elements which are very interesting and has frequently been a target element of analysis. Arsenite, As(III), and arsenate, As(V), are the inorganic arsenic species commonly found in natural waters while their organic counterparts such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), etc., occur in marine and other biological samples. Among arsenic species, inorganic arsenic species, especially arsenite, are more toxic than their organic counterparts. The "Blackfoot" is the well known disease resulting from exposure to high arsenic level in drinking waters. This disease is very serious in some countries, i.e. Bangladesh and India, where the unusual concentrations of arsenic can be found in natural drinking waters in some areas. The US Environmental Protection Agency (USEPA) [1] has set the maximum permissible concentration of total arsenic at 10 μg l^{-1}. The World Health Organization (WHO) [2] alternatively provides the information of arsenic contaminations. Since arsenic species present at trace level in uncontaminated waters, the sensitive and selective method is required for the speciation of arsenic. The couplings of techniques such as chromatographic ones with spectroscopy have well been utilized for the speciation. Ion chromatography (IC) [3-9], high performance liquid chromatography (HPLC) [10,11] coupled with element-selective detectors such as AAS, AFS, ICP-AES and ICP-MS, are commonly used methods for the determination of inorganic and organic arsenic species.

Though ICP with a quadrupole mass spectrometer shows very high sensitivity over other detectors, it can be suffered from the interferences from matrices for the direct determination of arsenic. The hydride generation techniques can improve the detection limit of arsenic, as well as other hydride forming elements. The comprehensive reviews on the speciation of arsenic species can be found in the literature [12-16]

Spectrophotometric methods based on the formation of arsenomolybdenum-blue complexes are the alternative approaches for the determination of As(V). However, the potential interferences from phosphate and silicate, which cause the positive errors, and the low sensitivity of the method make it not applicable to uncontaminated water analysis. Recently, Dasgupta et al. [17] reported the strategy for the elimination of interference from phosphate by using an anion exchange resin column. The resin column retained phosphate selectively, as well as As(V), whereas As(III) passed through it. The unretained As(III) was carried to the detection system, being oxidized to As(V) by potassium bromate and followed by the formation of arsenomolybdenum blue complexes, which was detected by LED-based colorimeter. The concentration of As(V) can be calculated by the difference between the concentration of As(III) and the total concentration (after reduction of As(V) to As(III) by cysteine).

In this work, we aimed at developing a simple and sensitive method for the determination of As(III) and As(V) separately. The method was based on the selective collection/concentration of As(V) on an anion exchange resin column and the oxidation of un-retainable As(III) to retainable As(V) prior to their ICP-AES measurement. The concept was applied to the flow injection method, where the simple solution manipulations can be achieved. The proposed method was applied to natural water samples and bottled drinking waters.

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2. Experimental

2.1. Apparatus

An inductively coupled plasma optical emission spectrometry (ICP-AES) (Vista Pro, Seiko Instrument & Varian Instrument) was used for measuring arsenic. Some of the instrumental conditions used in this work are shown in Table 1. In Fig.1, the flow diagram was shown: the PTFE tubing was used for assembling flow lines in a flow-injection pretreatment system. The double-plunger pumps (P_2 and P_4) (F.I.A. Instruments, Tokyo, Japan) was used to propel an eluent and a sample solution, and the peristaltic pumps (P_1 and P_3) (ALITEA, Sweden) were used for propelling an ammonium acetate and an oxidizing agent solution.

2.2. Reagents

A 1000 mg l^{-1} stock solution of As(III) and As(V) were prepared by dissolving analytical reagent grade sodium metaarsenite (Wako Pure Chemical Industries, Japan) and disodium hydrogen arsenate heptahydrate (Kanto Chemical Co., Japan), respectively, in ultra-purified water (resistivity = 18 MΩcm), which was prepared with Elix 3/Milli-Q Element System (Nihon Millipore, Japan). The working standard solutions of As(III) and As(V) were prepared daily by accurate dilutions of the standard stock solutions. The oxidizing agent solution was prepared by dissolving known amounts of potassium periodate (Wako Pure Chemical Industries, Japan) in water. The ammonium acetate solution was 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® 2x8, 100-200 mesh in Cl^--form (Muromachi Technos Co., Japan), was used for the collection and the concentration of As(V) species. The solid-phase collection/concentration unit (SCU) was prepared by slurry packing of the anion exchange resin into the PTFE tubing (2 mm i.d. x 5 cm), and both ends of the tubing were plugged with glass wool (Kishida Chemical Co., Japan) for keeping the resin in the unit. The smaller PTFE tubings (0.5 mm i.d.) connected at both ends of SCU were connected to two ports of the 6-way valve. The sample solutions were filtered through the membrane filter (mixed cellulose ester, 0.45 μm, Advantec, Toyo Roshi Co., Japan) before injection.

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 2. The conditioning step involved the washing of anion exchange resin packed in SCU with ammonium acetate solution and followed by the collection of analytes. Valve V_1 was used for the selection of the solution (ammonium acetate or sample solution) being introduced into the system. At a certain pH, i.e. 4.5, only As(V) was present as an anionic species and collected on the first SCU, whereas nonionic arsenic species, As(III), passed through it, and then it was oxidized to As(V) by potassium periodate and collected on the second SCU. The removal of the remained matrices and analytes in the manifold performed in the washing step was followed by the elution of the collected analytes. In the elution step, the sequentially switching of V_2 and V_3 elute and introduce the sample into the detector, and As in SCU on the valve V_2 and valve V_3, which correspond to As(III) and As(V), respectively, can be detected by ICP-AES. The analytical signals of arsenic obtained from the instrument were transferred to Microcal Origin programme, where graphical plots of the flow signals, as well as the computation of peak area and peak height, could be performed.

Table 1 Instrumental conditions for the detection of As by ICP-AES

Parameters	
RF generator frequency	40 MHz
Plasma power	1.10 kW
Gas flow rate	
plasma gas	Ar; 15 l min^{-1}
auxiliary gas	Ar; 1.5 l min^{-1}
nebulizer gas	Ar; 0.75 l min^{-1}
Spray chamber	Glass cyclonic type
Nebulizer	K-style concentric type
Torch	One-piece glass type in axial view mode
Emission line for As	188.980 nm

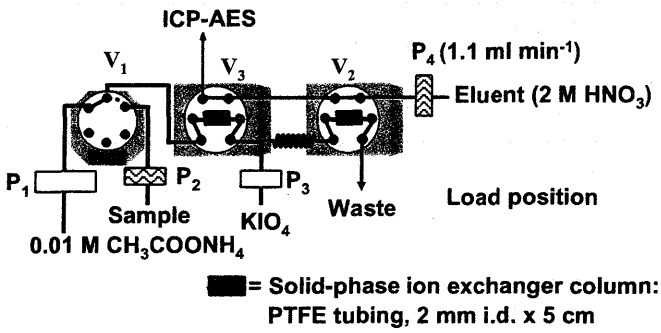

Fig.1 Flow set up for the speciation of As(III) and As(V)

Table 2 Operating steps for the proposed system

Steps	Valve positions			Time , min
	V_1	V_2	V_3	
Conditioning	Load	Load	Load	1.0
Collection	Inject	Load	Load	5.0
Washing	Load	Load	Load	2.0
Elution ; As(III)	Load	Inject	Load	1.5
Elution; As(V)	Load	Inject	Inject	1.5

Note:
"Inject" refers to injection of sample solution and of eluent (2 M HNO_3).
"Load" refers to introduction of CH_3COONH_4 solution.

3. Results and Discussion

3.1. Effect of pH on the collection/ concentration of arsenic species

The collection/concentration and the separation of As(III) and As(V) can be achieved by controlling the acidity of the solution. As(III) and As(V) were separated by using the difference in acid dissociation constants: the pKa values for As(III) are $pKa_1 = 9.2$ and $pKa_2 = 13.5$ and for As(V) are $pKa_1 = 2.3$, $pKa_2 = 6.9$ and $pKa_3 = 11.5$. From such pKa values, in the pH region below (4.9) and above (4.3), more than 99% of As(V) is present as an anionic species, $H_2AsO_4^-$, whereas As(III) is present as nonionic species, H_3AsO_3, in such pH region. Taking into consideration of the acid dissociation, the sample solutions were adjusted to pH 4.5.

3.2. Effect of the concentration of potassium periodate on oxidation and collection of As(III)

The effect of the concentration of KIO_4 solution was examined in the range of 0.5 $x10^{-3}$ to 2.0 $x10^{-3}$ M. The concentrations of KIO_4 in the range of $0.5x10^{-3}$ M to $1x10^{-3}$ M resulted in better sensitivity and linearity of calibration graphs for the concentration range from 5 to 50 μg l^{-1} of As(III) with sensitivity remaining constant. However, when the lower calibration range is concerned, i.e. 5 to 20 μg l^{-1}, the sensitivity of the calibration graphs decreased significantly. A concentration of $1x10^{-3}$ M potassium periodate was selected as a compromise with respect of the sensitivity and the dynamic range.

3.3. Effect of length of reaction coil and flow rate of KIO_4 on the collection/ concentration of As(III)

The oxidation of As(III) with potassium periodate seemed to proceed at slow rate. The oxidation efficiency of 20 μg l^{-1} As(III) with 1 mM KIO_4 at the flow rate of 0.4 ml min^{-1} with different length of reaction coil were therefore studied. The reaction coils (PTFE tubing, 1.2 mm i.d.) with the length of 1 to 5 m were examined. The longer the reaction coil (longer sample residence time), the lower the analytical signals corresponding to As(III) became. The analytical signals correspond to As(III) reach maximum when using the reaction coil length of 2 m. Further increase in the reaction coil length resulted in gradual decrease of As(III) signals. This is probably due to the lower adsorption efficiency of the analyte. The lower adsorption efficiency of the analyte could be attributed to the competition of the adsorption on anion exchange resin between the periodate ion and the analyte ion for the exchange site.

At the flow rate of potassium periodate higher than 0.4 ml min^{-1}, a better sensitivity for As(III) was obtained. However, there was no significant improvement in analytical signals of As(III) at the flow rate ranging from 0.5 to 0.8 ml min^{-1}. Therefore, the flow rate of the KIO_4 solution at 0.6 ml min^{-1} was adopted. The reaction temperature from 25 to 60 °C was tested: it did not affect the oxidation/collection efficiency of As(III). Therefore, the reaction was allowed to proceed at room temperature (25 °C).

3.4. Effect of eluent concentration on the analytical signals of As(III) and As(V)

The effective elution of collected analytes could be achieved by using nitric acid solutions in the range of 1 M to 2 M, where analytical signals for As(III) and As(V) were constant. The lower the nitric acid concentration, 0.5 M and 0.1 M, the poorer the elution efficiency and the lower the analytical signals became. As a result, 2 M nitric acid was selected as an eluent.

3.5. Effect of sample size on the analytical signals

The effect of sample size on the analytical signals of both As(III) and As(V) were examined. At a sample flow rate of 1 ml min^{-1}, the collections of 10 μg l^{-1} of As(III) and As(V) for the sample size of 3 to 30 ml were examined: the results are shown in Fig.2. The analytical signals (peak height and peak area) of As(V) linearly increased with an increase in the sample size up to 30 ml. On the other hand, As(III) showed a slight decrease above the sample size of 15 ml. Therefore, sample size of 5 ml was adopted for the present purposes. However, the larger sample size is useful when higher sensitivity is desired.

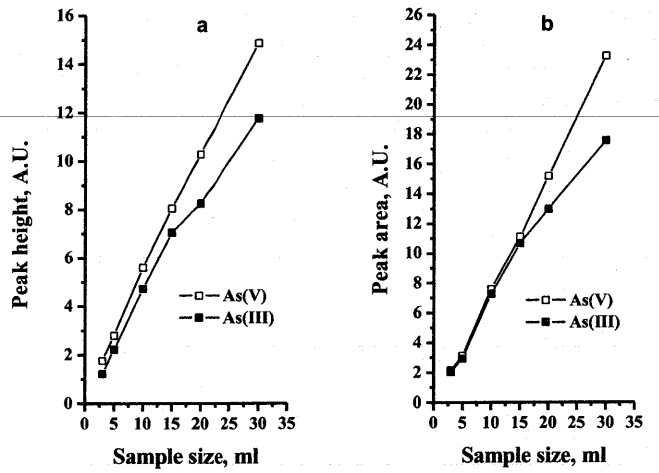

Fig.2 The effect of sample size on analytical signals; (a) peak height and (b) peak area of As(III) and As(V).

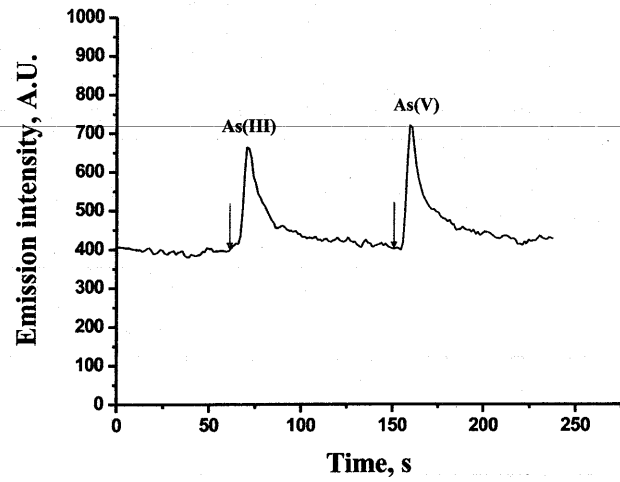

Fig.3 Flow signals for 10 μg l^{-1} solution of As(III) and As(V) obtained by the proposed method
(The arrows indicate the start of elution with 2 M HNO_3)

Table 3 Analysis of freshwater samples by the proposed method

Sample	Add (μg l^{-1})		Found (μg l^{-1}) (n=3)		% Recovery		Found (μg l^{-1}) by ICP-AES [a]
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	Total As (n=2)
River water [b]	0	0	n.d.	n.d.			
	5.2	5.2	5.4 ± 0.3	5.4 ± 0.3	103	101	
Tap water [c]	0	0	n.d.	n.d.			
	5.2	5.0	4.5 ± 0.3	4.7 ± 0.4	90	90	
Bottled mineral drinking water (BW) 1 [d]	0	0	n.d.	n.d.			
	5.1	4.9	5.6 ± 0.2	9.4 ± 0.2	109	110	
BW 2	0	0	n.d.	4.2 ± 0.4			4.0 ± 0.4
BW 3	0	0	n.d.	2.8 ± 0.3			2.9 ± 0.1
BW 4	0	0	n.d.	6.0 ± 0.2			6.1 ± 0.5

n.d.: not detected.
a: Analysis by direct measurement after the samples were 5 times concentrated by evaporation.
b: River water sample were sampled on November 17, 2003, from the river located near Okayama University, Okayama, Japan.
c: Storage water in the laboratory building(Venture Business Laboratory; VBL, in Okayama University, Okayama, Japan).
d: Bottled mineral drinking waters were purchased from a local super market.

3.6. Application of the proposed method to freshwater samples

The calibration graphs obtained by using peak area and peak height, respectively, for the injection of 5 ml sample in the concentration range of 2 to 50 μg l^{-1} were Y= 313X + 105, r^2=0.9998 and Y= 24X + 8, r^2=0.9994 for As(V), and Y= 300X + 122, r^2=0.9997 and Y= 22X + 7, r^2=0.9999 for As(III), respectively. In the determination of As(III) and As(V), however, calibration graphs using peak height were used for the quantitative analysis because of simplicity and better reproducibility. The flow signals obtained by using potassium periodate method are shown in Fig.3. The freshwater samples were collected at local area near our university, filtered through the membrane filter (0.45 μm) and adjusted to pH 4.5 with ammonium acetate solution prior to analysis. The analytical results in Table 3 shows that quantitative recovery for As(III) and As(V) in all samples tested in this study was attained. The good recovery for As(III) in tap water (Table 3) may lead to some misunderstanding: basically As(III) in tap water may not be recovered since the water contains residual chlorine, which can readily oxidize As(III) to As(V). However, the tap water analyzed in this study showed good recovery. The reason why the As(III) was recovered was that the tap water tested came from the storage tank in the building and did not contain any residual chlorine for long storage in the tank. The analytical results for As(V) in some bottled mineral drinking waters are in good agreement with those obtained by measuring using ICP-AES: 50 ml of sample was evaporated to nearly dryness and the residue was diluted to 10 ml with 1 M nitric acid prior to measurement.

4. Conclusion

The simple method for the simultaneous determination of As(III) and As(V) by ICP-AES and flow injection solid-phase collection/ concentration system was developed. As advantages over the other reported methods, As(III) and As(V) can be determined in a single analysis run, and the detection sensitivity for arsenic was improved for about 10 times compared with the conventional direct measurement by ICP-AES.

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