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Talanta 68 (2005) 298–304
Talanta
www.elsevier.com/locate/talanta

On-line preconcentration and speciation of arsenic by flow injection hydride generation atomic absorption spectrophotometry

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Available online 5 October 2005

Abstract

A flow injection-column preconcentration-hydride generation atomic absorption spectrophotometric (FI-column-HGAAS) method was developed for determining μg/l levels of As(III) and As(V) in water samples, with simultaneous preconcentration and speciation. The speciation scheme involved determining As(V) at neutral pH and As(III + V) at pH 12, with As(III) obtained by difference. The enrichment factor (EF) increased with increase in sample loading volume from 2.5 to 10 ml, and for preconcentration using the chloride-form anion exchange column, EFs ranged from 5 to 48 for As(V) and 4 to 24 for As(III + V), with corresponding detection limits of 0.03–0.3 and 0.07–0.3 μg/l. Linear concentration range (LCR) also varied with sample loading volume, and for a 5-ml sample was 0.3–5 and 0.2–8 μg/l for As(V) and As(III + V), respectively. Sample throughput, which decreased with increase in sample volume, was 8–17 samples/h. For the hydroxide-form column, the EFS for 2.5–10 ml samples were 3–23 for As(V) and 2–15 for As(III + V), with corresponding detection limits of 0.07–0.4 and 0.1–0.5 μg/l. The LCR for a 5-ml sample was 0.3–10 μg/l for As(V) and 0.2–20 μg/l for As(III + V). Sample throughput was 10–20 samples/h. The developed method has been effectively applied to tap water and mineral water samples, with recoveries ranging from 90 to 102% for 5-ml samples passed through the two columns.

Keywords: Arsenic speciation; On-line preconcentration; Anion-exchange microcolumns; Hydride generation

1. Introduction

Interest in the detection of arsenic (As) stems from its ubiquitous nature and its toxicity even at low concentrations. It is found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as a range of anthropogenic activities which include mining, combustion of fossil fuels, wood preservation, and the use of arsenical pesticides, herbicides and crop dessicants [1].

Average concentrations of As in open seawater usually show little variation and are typically around 1.5 μg/l. In freshwater, typical concentrations are less than 10 μg/l and frequently less than 1 μg/l. Rarely, much higher concentrations are found, particularly in groundwater [1]. The bioaccumulation and toxicity of arsenic depends on the chemical form, with the toxicity decreasing in the order arsenite > arsenate > monomethylarsonic acid (MMAA) > dimethylarsinic acid (DMAA) [2].

Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health [1]. Depending on local availability, drinking water is derived from a variety of sources such as surface waters (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water, which are variable in terms of As risk. Following the accumulation of evidence for the chronic toxic effects of As in drinking water, recommended and regulatory limits of the World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA) were reduced from 50 to 10 μg/l. The Japanese and European Community (EC) limits for As in drinking water are also 10 μg/l [1].

It has become apparent, in recent years, that the WHO guideline value and national standards are quite frequently exceeded in drinking water sources, such that As is now recognized as among the most serious inorganic contaminants on a worldwide basis [1]. Unlike the other constituents of drinking water which are routinely analyzed, however, information about the distribution of arsenic is not as extensive since As was not often on the list of drinking water constituents routinely analyzed. Many countries, particularly in the developing areas, also still operate using the 50 μg/l standard, in part because of lack of adequate testing facilities for lower As concentrations.

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doi:10.1016/j.talanta.2005.08.055

The well-known toxicity of As and the potential need to routinely determine its low concentrations in natural waters particularly drinking water require the use of a highly sensitive and affordable method of determination. The different toxicities, biochemical and environmental behaviors of arsenic species also require the determination of individual species and not just the "total" concentration.

The most commonly used method in arsenic determination is hydride generation. Introduced by Holak in 1969 [3], hydride generation (HG) involves the formation of arsine (AsH_3), a gaseous hydride of arsenic, upon its reaction with a reducing agent (typically sodium borohydride), the separation of arsine from the liquid products of the reaction, and subsequent detection using a variety of detectors. Determination of As using this method has since then advanced with regard to sensitivity, selectivity and ease of application, particularly with the advent of flow techniques [4,5]. Various combinations of separation techniques and detection instruments have also been applied to improve the specificity and detection for individual arsenic species [6]. Amidst the innovations and advances, the combination of HG with atomic absorption spectrophotometry (AAS), in one of its numerous variants, the quartz tube HG-AAS, is still the most frequently used system owing to its versatility and availability in most laboratories.

In marine/natural waters, As(III) and As(V) exist dominantly in oxoanionic forms with As(V) as $H_2AsO_4^-$ and $HAsO_4^{2-}$ and As(III) in neutral form ($HAsO_2$) [1,7,8]. The formation of anions by these arsenic species enable their uptake and preconcentration by anion exchange resins [8,9], while the different acid dissociation constants (pK_a) for the formation of these anions enable their simultaneous speciation [8–10]. The pK_as of H_3AsO_4 and $HAsO_2$ are 2.3 and 9.3 [9,10], respectively, while the usual pH range of seawater is 7.4–8.4. The As(III) species, $HAsO_2$, can be converted to anionic form by adjusting the pH of the solution above the pK_a of $HAsO_2$ [6,8]. The analytes are released from the resin by protonation of the sorbed arsenic species, which is at pH below the respective pK_as. This suggests that the pH of samples can be controlled to allow the separation and preconcentration of As(V) alone and the determination of both inorganic arsenic species.

This study aims to develop a flow injection system with simultaneous on-line preconcentration and speciation of inorganic arsenic species using anion exchange microcolumn and pH control of sample based on pK_a prior to hydride generation and detection by AAS. AAS is relatively inexpensive to operate and is easily available in most laboratories. The use of an inexpensive ion-exchange column for on-line preconcentration and speciation will extend the detection limit of HG-AAS and enable the cost-effective determination of low levels of arsenic in the environment.

2. Experimental

2.1. Instrumentation

A Shimadzu AA-680 atomic absorption spectrophotometer was used as detector with hollow cathode lamp (Hamamatsu Phototronics and Koto Bunkogen) light source set at 193.7 nm wavelength, using 7 mA lamp current and 0.6 nm slit width, and with deuterium lamp for background correction. Instrument grade (99.5%) acetylene (CIGI), delivered at 4.2 l/min at a pressure of 0.5 kg/cm^2, was used to generate the flame for the AAS together with compressed air supplied at 8 l/min flow rate and 2.5 kg/cm^2 gas pressure.

For hydride generation, the basic unit was the Shimadzu HVG-1, a continuous flow hydride generator which is linked to the AAS (CF-HGAAS). This system was modified stepwise to produce a flow injection-HGAAS system with on-line preconcentration through anion-exchange (FI-column-HGAAS). High purity (99.99%) argon (CIGI) was used as purge gas at a rate of 70 ml/min and supply pressure of 3.2 ± 0.2 kgf/cm^2.

2.2. Reagents and chemicals

2.2.1. Standards

All reagents used in the experiments were of analytical reagent grade. Deionized distilled water (DDW) was used as matrix for reagent and standard solutions.

A 1000-mg/l stock solution of As(III) was prepared by dissolving 1.32 g of arsenic trioxide (Merck) in 1 l of 0.4% NaOH. The stock solution of 1000 μg/l As(V) was obtained from Merck (Titrisol). Working standards for As(III) and As(V) were prepared by serial dilution with deionized distilled water. Standard solutions were prepared immediately before the measurement.

2.2.2. HG-AAS

The sodium borohydride ($NaBH_4$) solution was made up of a mixture of 0.5% (w/v) $NaBH_4$ and 0.75% (w/v) NaOH. The 500-ml $NaBH_4$ solution was prepared by dissolving 3.75 g NaOH and 2.5 g $NaBH_4$, in this order, in deionized distilled water and diluting to mark. The $NaBH_4$ reagent was always prepared immediately before use.

The 5-mol/l hydrochloric acid solution was prepared with 208.33 ml of concentrated HCl diluted to 500 ml.

2.2.3. Microcolumns

The hydroxide-form anion exchange microcolumn (JT Baker Anion Exchange Resin, IONAC Na-38, OH^--form, 16–50 mesh or 0.3–1.18 mm) was prepared by packing approximately 60 mg resin in a 70 mm × 1 mm i.d. glass tubing. The resins were held in the column with high purity glass wool. The column was pre-conditioned using 0.01 mol/l NaOH solution. The chloride-form anion exchange microcolumn (Merck strong base anion exchanger with color indicator, 60–150 mesh ASTM, 0.1–0.25 mm) was prepared by packing approximately 30 mg resin in a 70 mm × 1 mm i.d. glass tubing, held by high purity glass wool at the ends. The column was preconditioned with 1 mol/l HCl.

2.3. FI-column-HGAAS

The anion-exchange microcolumn was incorporated in a FI-column-HGAAS set-up along the path of the carrier solution, between the injection valve (4-way Rheodyne 5020 manual

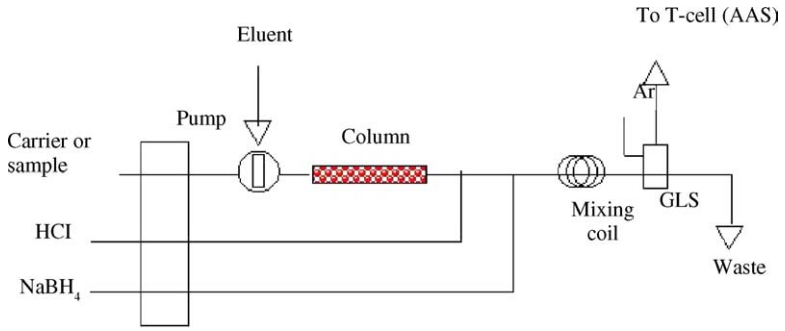

Fig. 1. FI-column-HGAAS.

Teflon injector) and the mixing coil (1 m Teflon mixing coil with 1 mm i.d.) as shown in Fig. 1.

In this set-up, a known volume of sample was aspirated directly through the carrier channel and while the injection valve was in the load position, passed through the microcolumn where arsenic species were sorbed onto the ion-exchange resins. After sample aspiration, the carrier solution was run through the same channel and the eluent was injected into the carrier stream, eluting the sorbed species as it passed through the microcolumn and after reaction with HCl and $NaBH_4$, producing a transient peak signal that was printed out. Hydroxide-form and chloride-form anion exchange microcolumns were evaluated for the preconcentration and speciation of As(III) and As(V). Chemical and physical parameters such as the dimensions of the microcolumn, preconcentration and elution flow rates, type, concentration and volume of eluent and volume of the sample and conditions in the hydride generation step such as reagent concentration and flow rates and length of mixing coil were optimized using a univariate approach.

2.4. Performance characteristics of the FI-column-HGAAS

Figures of merit such as enrichment factor, linear concentration range, limit of detection, precision, interferences and sample throughput were evaluated to characterize the performance of the FI-column-HGAAS method for the on-line preconcentration and speciation of inorganic arsenic species. The performance characteristics of the FI-column-HGAAS were assessed relative to other optimized in-house modifications of the Shimadzu HVG-1 including an FI-HGAAS and an on-line FI-KI-HGAAS, which uses 8 mol/l HCl and 50% KI (w/v) delivered at 1.8 ml/min, and a 1-m (1 mm i.d.) mixing fcoil immersed in a hot water bath (>53 °C) for As(V) pre-reduction. Both systems require 0.25 mol/l HCl and 0.5% (w/v) $NaBH_4$ delivered at 2.5 ml/min for hydride generation.

2.5. Ensuring selectivity for inorganic arsenic species

For the determination of preconcentrated inorganic species in the presence of the methylated species, hydride generation conditions and preconcentration conditions should be controlled such that the generation of arsine from the methylated species is not favored. It has been reported that only dimethylarsinic acid (DMAA) has a strong affinity for acid-charged cation exchange resins [11]. In this study, to ensure that DMAA will not be retained in the anion exchange column, it was isolated by passing the sample through a strong acid cation exchange column incorporated before the injection valve before going through through the anion exchange column. In similar studies [11,12], where MMAA and As(V) were both present in anion exchange columns, the two species were resolved by eluting first with 0.06–0.1 mol/l HOAc to elute MMAA followed by 1 mol/l HCl to elute the As(V). Standards for DMAA and MMAA were not available to verify the effectiveness of these steps in separating these methylated arsenic species from As(III) and As(V) but confirmatory tests were carried out to ensure that the preconcentration and elution of the inorganic arsenic species will not be affected by the inclusion of the cation exchange column or by the passage of HOAc through the column. The effect on the As(V) signal of incorporating a cation exchange column consisting of Na^+-form strong acid cation exchange resins (Merck) before the injection valve and anion exchange column was investigated by passing 5 ml of 1 μg/l As(V) through the two columns at 2.5 ml/min and eluting with 1 mol/l HCl and comparing against the As(V) signals obtained without the cation exchange column. Similarly, the effect on As(V) signals of injecting a 0.1 mol/l HOAc eluent prior to the 1 mol/l HCl eluent was also investigated for a 5 ml As(V) sample preconcentrated at 2.5 ml/min. The peak signals obtained were compared with signals generated without the use of HOAc.

2.6. Application

The suitability of the method for determining inorganic arsenic species in natural water samples was checked by passing through the microcolumns tap water and mineral water spiked with 2 μg/l each of As(III) and As(V), and elution by 250 μl of 1 mol/l HCl. The recoveries obtained were evaluated against the acceptable recoveries as specified in the Manual on Policies and Procedures of the Association of Analytical Chemists (AOAC) Peer Verified Method Program [13] and the American Public Health Association (APHA) Standard Methods for Examination of Water and Wastewater [14].

3. Results and discussion

3.1. Optimum conditions for the FI-column-HGAAS

The optimized conditions for the FI-column-HGAAS manifold shown in Fig. 1 are 5 mol/l HCl (at 2.5 ml/min), 0.5% (w/v) $NaBH_4$ (at 2.5 ml/min) and mixing coil length of 1 m (1 mm i.d.) for the hydride generation step; and a flow rate of 2.5 ml/min for both column preconcentration and elution, using 250 μl of 1 mol/l HCl eluent.

3.2. Effect of sample pH on ion-exchange

As(V) was taken up by both the OH^-- and Cl^--form anion exchange columns from the standard solutions prepared at neutral pH, pH 10, 11 and 12. Uptake of As(III) by both resins on the other hand, only occurred at pH > 11. The recommended sample pH therefore for the preconcentration of As(III) is pH 12. At this pH, the peak heights and peak forms for As(V) were comparable to those obtained at neutral pH. Since both species were retained by the anion exchange resins at pH 12 and only As(V) was retained at neutral pH, As(III) could be obtained as the difference between these two measurements.

3.3. Selectivity of column preconcentration for inorganic arsenic species in the presence of organic arsenic species

Inorganic species of As typically dominate in natural waters and organic forms are usually minor. In marine, estuarine, lake and river waters, the organic forms, which are dominated by DMAA and MMAA, are found in zones where methylation reactions occur due to phytoplankton and microbial activity. In groundwaters, concentrations of organic forms are generally low or negligible [1].

At the pH conditions optimized for As(III) and As(V) sorption in anion exchange columns, the organic hydride-forming species of arsenic, MMAA and DMAA, are also in anionic form and are also retained in anion exchange [11] and alumina [12] columns. At neutral pH, As(V), MMAA and DMAA are sorbed in the column, while at pH 12, all the four species may be taken up. DMAA, however, has been reported to have a strong affinity for acid-charged cation exchange resins [11], which enables the isolation of DMAA through a cation ion exchange column prior to the preconcentration of inorganic species through the anion exchange column. Since DMAA standards were not available to verify the effective separation of DMAA from As(III) and As(V) using this process, confirmatory tests were carried out to ensure that the inclusion of a cation exchange column in the FI-column-HGAAS set up will not affect the preconcentration and elution of the inorganic arsenic species. Following the incorporation of a cation exchange column packed with Na form strong acid cation exchange resins (Merck) before the injection valve and the anion exchange column, 5 ml of 1 μg/l As(V) was passed through the modified system at 2.5 ml/min and eluted with 1 mol/l HCl, then resulting As(V) signals were compared with As(V) signals obtained without the cation exchange column. Retention of As(V) in the anion exchange column was not affected but distortion of analyte signals generated in the presence of the cation exchange column was observed even if the eluent was injected after the cation exchange column. The flow rate measured after the anion exchange column actually was not changed by the inclusion of the cation exchange column into the system. However, the addition of the cation exchange column may have caused some imperceptible effects on the carrier flow rate that led to the distortion of analyte signals. When the cation exchanger was detached from the system before injecting the eluent, signals that were equivalent in peak height and peak form to the reference signals were obtained. No arsenic was detected after injection of 1.0 mol/l HCl or 0.01 mol/l NaOH to the cation exchange column. For this reason, in samples where DMAA is expected to be significant, a cation exchange column, can be incorporated within the loop of an injection or switching valve such that the carrier flow can be directed toward the cation exchange column during preconcentration and bypass this column during elution.

Unlike the DMAA which can be directly isolated from the other hydride-forming arsenic species by controlling hydride generation conditions and by sorption in a cation exchange column, MMAA is retained along with As(V) in the anion exchange column at the hydride generation and preconcentration conditions used in this study. Speciation studies [11,12] have shown that MMAA and As(V) can be collected separately by sequentially eluting with portions of 0.10 mol/l HOAc (for MMAA) and 1.0 mol/l HCl (for As(V)). MMAA standards were not available so the separation could not be verified, but the effect on As(V) signals of injecting a 0.1 mol/l HOAc eluent prior to the 1 mol/l HCl eluent was investigated. For a 5-ml As(V) sample preconcentrated at 2.5 ml/min, the peak signals obtained with the use of HOAc prior to elution were comparable to signals generated without the use of HOAc. The HOAc eluent did not produce a distinguishable peak although a slight rise in signal relative to the baseline was observed. Thus, for the selective determination of As(V) in natural water samples containing MMAA, assuming prior removal of DMAA in a cation exchange resin and preconcentration of As(V) and MMAA in an anion exchange column, 0.1 M HOAc will be injected first as eluent to release MMAA from the resins to be followed by 1 M HCl to desorb the As(V).

3.4. Interferences

When preconcentration of anionic arsenic species using a microcolumn is done before HG-AAS, interference from cations during hydride generation becomes negligible but interference may be encountered from the competitive uptake of other anions by the column. Table 1 shows the levels at which selected anions such as SO_4^{2-}, NO_3^-, PO_4^{3-}, and Cl^- interfere with arsenic preconcentration. For both the Cl^-- and OH^--form columns, the interference from Cl^-, which is present in parts per thousand levels in seawater, in the retention of As in the microcolumn makes the system inoperable for extension to seawater samples. Attempts were made to dilute seawater containing 1 and 2 μg/l As to levels where Cl^- was shown not to affect quantitative retention of As (100× dilution), but the resulting arsenic

Table 1
Interferences of anions in the preconcentration of inorganic arsenic species

Analyte	Cl^--form	OH^--form
As(V)	100 mg/l Cl^-, NO_3^- and SO_4^{2-}	10 mg/l PO_4^{3-} 100 mg/l Cl^-, NO_3^- and SO_4^{2}
As(III + V)	10 mg/l PO_4^{3-} and SO_4^{2-} 100 mg/l NO_3^- and Cl^-	10 mg/l PO_4^{3-} 100 mg/l Cl^-, NO_3^- and SO_4^{2}

concentration became too low for detection even with the use of 25–50 ml sample for preconcentration.

3.5. Enrichment factor (EF)

The main figure of merit used in optimizing the FI-column-HGAAS is the enrichment factor (EF) which was approximated as the ratio of the slopes of the linear section of the calibration curves before and after preconcentration [15]. Strictly speaking, the EF should be defined as the ratio of the analyte concentrations before and after preconcentration. In practice, however, such evaluations are not feasible because the actual concentrations are unknown [15]. Thus, EFs were obtained by comparing the slopes of the calibration curves for the FI-column-HGAAS with similar systems that are able to measure the arsenic species without column preconcentration. The EF for As(III) was evaluated relative to the FI-HGAAS system while the EFs for As(V) and As(III + V) were evaluated relative to the FI-HGAAS set up with on-line As(V) pre-reduction using KI. The enrichment factors for the preconcentration of inorganic arsenic species using 2.5, 5 and 10 ml sample preconcentration volumes for the two microcolumns are shown in Table 2.

It is noteworthy that As(V), which requires pre-reduction prior to quantitative measurement by HGAAS, could be determined at the sub-μg/l levels without pre-reduction using this method. Table 2 also shows the dependence of the EF on the sample volume. The highest enrichment factors were achieved using 10 ml of sample at a sample loading rate of 2.5 ml/min (4 min). Depending on the expected concentration of analytes of interest, smaller volume of samples can be used to achieve a reasonably high throughput, although higher sample volumes may be used when higher preconcentration needs to be pursued, with some sacrifice on sampling frequency. Higher EFs were obtained for the determination of As(V) and As(III + V) using the Cl^--form column due to the higher exchange capacity of the Cl^--form resins. The chloride-form resin (30 mg) has an exchange capacity, or maximum amount of arsenic ions that could be taken in by a given weight of resin, of 12.9 ng As(III)/mg resin and 11.3 ng As(V)/mg resin, while the same amount of hydroxide-form resin has a capacity of 4.6 ng As(III)/mg resin and 6.2 ng As(V)/mg resin. The higher resin capacity of the Cl^--form column may be attributed to the smaller size of the Cl^--form resins (0.1–0.25 mm) compared to the OH^--form resins (0.3–1.18 mm), which provides greater number of ion exchange sites.

3.6. Linear concentration range and precision

The linear concentration range for the determination of As(V) and total inorganic arsenic in the FI-column-HGAAS were evaluated by plotting absorbance peak heights versus analyte concentrations, and determining the linear portion of the calibration curves. The correlation coefficient generated using the method of linear regression was used to estimate the degree of linearity. A value of $R^2 > 0.99$ is commonly accepted [13]. The linear concentration ranges ($R^2 > 0.99$) for different sample volumes of As(V) and As(III + V) for the two microcolumns evaluated are shown in Table 3. Higher slope was obtained with higher sample volume but linear range was shorter. For the lowest volume evaluated, the entire linear concentration range was not evaluated but the response was linear up to 4.0 μg/l As(V) and 8 μg/l As(III + V) for both microcolumns. It is highly possible for the linear range to extend to or beyond the maximum concentration value obtained using 5 ml sample. The within-run precision for the determination of As(V) and As(III + V) at the 1 μg/l using 5 ml of sample for the two microcolumns were both less than 5%.

3.7. Limit of detection

The limit of detection was determined by measuring the analytical signals generated by 10 blank measurements and taking

Table 2
Enrichment factors obtained using the chloride-form and hydroxide-form anion exchange columns in FI-HGAAS

Sample volume (ml)	Analyte	Enrichment factor			
		OH^--form column		Cl^--form column	
		Relative to FI-HGAAS with pre-reduction	Relative to FI-HGAAS	Relative to FI-HGAAS with pre-reduction	Relative to FI-HGAAS
10	As(III + V)	15		24	
5	As(III + V)	3		5	
2.5	As(III + V)	2		4	
10	As(V)	23		48	
5	As(V)	4		8	
2.5	As(V)	3		5	
10	As(III)		41		35
2.5	As(III)		10		16

Table 3
Performance characteristics for the FI-column-HGAAS of arsenic for different sample volumes

Sample volume (ml)	Performance characteristics	Chloride-form column		Hydroxide-form column	
		As(V)	As(III + V)	As(V)	As(III + V)
2.5	LOD (μg/l)	0.3	0.3	0.4	0.5
	LCR (μg/l)	0.5–4.0 (or greater)	0.3–8 (or greater)	0.3–4 (or greater)	0.5–8 (or greater)
	Linear equation	$Y = 3.20x + 1.59$	$Y = 3.51x + 2.64$	$Y = 2.84x + 3.57$	$Y = 1.94x + 4.07$
	R^2	0.9930	0.9925	0.9975	0.9979
5	LOD (μg/l)	0.2	0.2	0.3	0.4
	LCR (μg/l)	0.3–5	0.2–8	0.3–10	0.2–20
	Linear equation	$Y = 5.95x + 2.46$	$Y = 4.62x + 6.02$	$Y = 3.07x + 6.77$	$Y = 2.35x + 5.75$
	R^2	0.9979	0.9924	0.9975	0.9985
	R.S.D.[a,b]	3.1 ($n = 3$)	2.6 ($n = 3$)	4.4 ($n = 2$)	4.9 ($n = 3$)
10	LOD (μg/l)	0.03	0.07	0.07	0.1
	LCR (μg/l)	0.1–1.0	0.05–2.0	0.1–1.0	0.05–2.0
	Linear equation	$Y = 43.85x + 0.69$	$Y = 21.58x + 5.68$	$Y = 21.12x + 2.47$	$Y = 13.64x + 4.16$
	R^2	0.9918	0.9935	0.9928	0.9943

[a] Measured 1 μg/l As(V) in deionized distilled water.
[b] Measured 1 μg/l As(III) + 1 μg/l As(V) in deionized distilled water.

the analyte concentrations that would generate signals which are three times the standard deviation of the blank signals [16].

The limits of detection for the determination of As(V) and As(III + V) using the two microcolumns and different sample volumes are presented also in Table 3. Lower detection limits were obtained for the Cl^--form column, which is consistent with the higher approximated enrichment factors and resin capacity. The detection limits of the FI-column-HGAAS system in this study were found to be comparable with values reported from other studies (Table 4), including one that used off-line ion exchange preconcentration prior to HGAAS [11]. Other studies applied various on-line preconcentration methods and hydride generation in combination with various detectors using solid phase extraction (SPE) and HGAFS [12]; sorbent extraction (SE) and HGAFS [17]; knotted reactor (KR) and HGAFS [18]; and cryogenic trapping (liquid N_2) and HGAAS [19]. Also included in the table are studies that applied on-line preconcentration and direct determination, without hydride generation, by ICP-MS [20] and ICP-AES [21], which are recognized as more sensitive detectors than the AAS.

3.8. Recovery

Validation of the proposed method using samples with certified As contents could not be done due to the lack of certified reference materials (CRM). Furthermore, the CRMs do not provide certified values for separate arsenic species. The suitability of the method for determining inorganic arsenic species in natural water samples was checked by passing through the microcolumn 5 ml of tap water and mineral water spiked with 2 μg/l each of As(III) and As(V), and elution by 250 μl of 1 mol/l HCl. The samples were obtained directly from the laboratory tap water supply after flushing for 1 min and from a commercially available bottled drinking water, and immediately used for analysis without filtration and preservation. Analysis of As(V) and As(III + V) in unspiked samples using the Cl^--form column yielded 0.3 μg/l As(V) and 0.4 μg/l As(III + V) in tap water and 0.3 μg/l As(V) and 0.3 μg/l As(III + V) in mineral water. Using the OH^--form column, however, no measurable peaks were obtained for both samples, indicating that inorganic As in the water samples analyzed were below the detection limit of the developed method using the OH^--form column. Table 5 shows that the method has been effectively applied to tap water and mineral water samples, which were spiked to simulate concentrations falling at the lower end of the 10 μg/l drinking water limits of the WHO, USEPA, EC and Japan [1]. Acceptable recoveries ranging from 90 to 102% for 5 ml samples passed through the two columns were obtained. The AOAC [10] finds as acceptable recoveries within 40–120% and 60–115% for analytes present at 1 and 10 μg/l, respectively, while the APHA [11] recommends the use of methods for trace metal analysis that provide at least 90% recovery and recommends the use of other methods if this is not achieved. Recovery studies for a similar FI-column-HGAAS system [9] presented varying levels of As(III) and As(V) in tap water and mineral water samples, ranging from not detectable in both types of samples to 3.4 μg/l As(V) in tap water and 1.6 μg/l As(III) and 7.8 μg/l As(V) in bottled water samples. Spikes of 2 μg/l As(III) and 2.7 μg/l As(V) were also used to test the recovery.

Table 4
Detection limits of other systems for preconcentration and speciation of arsenic

Other studies	LOD (μg/l)
IEC&FI-HGAAS [11]	As(III), As(V), MMAA, DMAA: 1–2
IE-FI-HGAFS [12]	As(III), As(V), MMAA, DMAA: 0.05
FI-SE-HGAFS [17]	As(III): 0.05; As(V): 2
FI-KR-HGAFS [18]	As(III): 0.023
FI-N2-HGAAS [19]	As(III) and As(V): 0.02–0.06
FI-KR-ICPMS [20]	As(III): 0.021; As(V): 0.029
IE-ICP-AES [21]	As(III): 0.8; As(V): 0.7

3.9. Sample throughput

With properly packed anion exchange columns and well-connected manifold set-up, preconcentration and speciation of

Table 5
Results of recovery tests for As(V) and As(III + V) using the FI-column-HGAAS method

Analyte	Tap water			Mineral water		
	Amount spiked	Amount determined (μg/l)	Recovery (%)	Amount spiked	Amount determined (μg/l)	Recovery (%)
Cl^--form column						
As(V)	0	0.3		0	0.3	
As(V)	2	2.0	98.6 ± 2.9 (n = 3)	2	2.1	102.5 ± 4.8 (n = 3)
As(III + V)	0	0.4		0	0.3	
As(III + V)	2	4.1	102.6 ± 1.6 (n = 3)	2	4.0	101.2 ± 4.0 (n = 3)
OH^--form column						
As(V)	0	nd		0	nd	
As(V)	2	1.9	94.5 ± 1.4 (n = 4)	2	1.8	90.1 ± 4.4 (n = 4)
As(III + V)	0	nd		0	nd	
As(III + V)	2	3.7	91.5 ± 5.6 (n = 2)	2	3.6	90.8 ± 5.0 (n = 4)

nd: not detectable.

samples is simple and easy using this method. Relative to the FI-HGAAS, sample throughput was lower, ranging from 8 to 17 samples/h for the Cl^--form column and 10–20 samples/h for the OH^--form column for sample volumes of 2.5–10 ml. However, this is compensated by the higher sensitivity and ease of determining the different inorganic As species.

4. Conclusion

The FI-column-HGAAS system provides a fast and accurate method of determining μg/l levels of As(III) and As(V) in natural waters. It enables the on-line preconcentration and speciation of inorganic As species prior to determination using AAS and other methods, without the need for As(V) pre-reduction using KI or other reducing agents. This largely simplifies the scheme for As(V) determination and reduces the type and amount of reagents required, although at some cost on sample throughput. The chloride-form column exhibited better performance with regard to EF and detection limit, and is recommended for use if greater than 20-fold analyte enrichment is required. The recommended sample loading volume is 5 ml (for a sample throughput of 15/h) but higher sample volumes may be used to achieve higher sensitivity. This method is not applicable to seawater samples due to interferences from chloride ions in the preconcentration stage.

Acknowledgement

The authors are thankful to the University of the Philippines Office of the Vice-Chancellor for Research and Development for the MS Thesis Grant to Ms. Narcise.

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