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Speciation of inorganic arsenic in a sequential injection dual mini-column system coupled with hydride generation atomic fluorescence spectrometry

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ABSTRACT

The separation and speciation of inorganic arsenic(III) and arsenic(V) are facilitated by employing a novel sequential injection system incorporating two mini-columns followed by detection with hydride generation atomic fluorescence spectrometry. An octadecyl immobilized silica mini-column is used for selective retention of the complex between As(III) and APDC, while the sorption of As(V) is readily accomplished by a 717 anion exchange resin mini-column. The retained As(III)–PDC complex and As(V) are effectively eluted with a 3.0 mol L^{-1} hydrochloric acid solution as stripping reagent, which well facilitates the ensuing hydride generation process via reaction with tetrahydroborate. With a sampling volume of 1.0 mL and an eluent volume of 100 μL for both species, linear ranges of 0.05–1.5 μg L^{-1} for As(III) and 0.1–1.5 μg L^{-1} for As(V) are obtained, along with enrichment factors of 7.0 and 8.2, respectively. Precisions of 2.8% for As(III) and 2.9% for As(V) are derived at the concentration level of 1.0 μg L^{-1}. The practical applicability of the procedure has been demonstrated by analyzing a certified reference material of riverine water (SLRS-4), in addition to spiking recovery in a lake water sample matrix.

1. Introduction

The toxic effects of arsenic have been widely demonstrated in some areas like environment, dairy food, etc. [1,2]. Recently, extensive attentions have been focused on the arsenic pollution of surface water [3]. In some cases, excessive high concentrations of arsenic caused serious health problems [4–6]. Thus, the World Health Organization is currently conducting the guidelines for drinking and environmental waters [3]. The wide distribution of arsenic in biosphere and its pronounced detrimental effects on the ecological system, biological organisms as well as human health not only depend on the total amount, but most significantly, depend strongly on its chemical forms and distribution [1,7]. It is well recognized that inorganic arsenic compounds are far more toxic than their organic counterparts [8], while as refer to the two inorganic arsenic forms, arsenite is more toxic than arsenate [9]. In this respect, it is highly desirable to develop suitable speciation approaches for arsenic in order to provide reliable information concerning the toxicity of arsenic in the sample matrices [10].

Atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICPMS) have been widely employed for the evaluation of total amount of arsenic as well as arsenic speciation hyphenated with various separation and preconcentration protocols [11,12]. ICPMS provides very high sensitivity for arsenic determination, but the operation and maintenance of the instrumentation is quite costly, thus limited its wide applications in routine laboratories. On the other hand, the detection sensitivity for arsenic species by using atomic absorption spectrometry is so far not favorable. In the last decade, a lot of efforts have been dedicated to the development of analytical procedures for hydride forming elements including arsenic with detection by atomic fluorescence spectrometry (AFS), which offers competitive sensitivity with ICPMS for their determination, while requires much lower running cost [13–15].

For many of real world samples, arsenic concentrations might be very low in the presence of complex sample matrices. In such circumstances, the insufficient detection sensitivity in addition to the matrix effects tends to block the accurate determination of arsenic and its speciation. Therefore, pertinent sample pretreatment schemes are required [16]. In this respect, flow/sequential injection on-line separation and preconcentration protocols are most suitable for this purpose, which provide extensive flexibilities in flow manifold design [17]. Among those the hyphenation of sample clean-up with hydride generation atomic fluorescence spectrometry has vast potentials because of its low running cost, ease of operation, improved selectivity and sensitivity [10,14]. In addition, the flow through characteristic of AFS well facilitates

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its incorporation into various on-line separation/preconcentration and speciation systems [15,18,19].

Conventionally, the speciation of inorganic arsenic without employing chromatographic separation is performed by direct analysis of As(III) followed by quantification of total inorganic arsenic after reduction of As(V), and the amount of As(V) is thus obtained by subtraction [20,21]. In the present work, we developed a novel separation and preconcentration procedure for inorganic arsenic by designing a sequential injection system which incorporates two mini-columns packed with C18 and 717 anion exchange resin for selective retention of As(III)-APDC complex and As(V), respectively. Both species were collected with an appropriate eluent followed by quantification with hydride generation atomic fluorescence spectrometry.

2. Experimental

2.1. Instrumentation

A FIAlab-3000 sequential injection system (FIAlab Instruments, Bellevue, WA, USA) equipped with two syringe pumps (5.0 and 1.0 mL) and an 8-port selection valve was employed for fluids delivery and sample processing. An AFS-920 atomic fluorescence spectrometer equipped with two syringe pumps (5.0 mL) and a selection valve (Beijing Titan Instruments, China) was employed for hydride generation and quantification. A high-intensity arsenic hollow cathode lamp at 193.7 nm (Beijing General Research Institute for Nonferrous Metals, China) was used as radiation source. An argon flow was used to sweep the separated arsine from the gas–liquid separator to the quartz tube atomizer. A single computer was used to control both the atomic fluorescence spectrometer and the sequential injection system in order to synchronize the sample processing and the AFS determination.

All the external channels were made of PTFE tubing (0.8 mm i.d./1.0 mm o.d.). The mini-columns were made by filling 5 mg of C18 immobilized silica beads (100 μm) or 11 mg of 717 anion exchange resin (150 μm) into a piece of PTFE tubing (1.8 mm i.d./2.3 mm o.d.) and blocked at both ends with glass wool.

2.2. Reagents

All the reagents used were at least of analytical reagent grade, and deionized water of 18 MΩ cm as carrier solution was used throughout. Working standard solutions of As(III) and As(V) were prepared by stepwise dilution of 1000 mg L^{-1} stock solutions. A 0.06% (m/v) ammonium pyrrolidine dithiocarbamate (APDC) (Sinopharm Chemical Reagent Co., China) solution as complexing reagent was prepared daily by dissolving appropriate amount of APDC in deionized water. A $NaBH_4$ solution of 1.0% (m/v) in 0.5% NaOH (m/v) solution was prepared daily with sodium tetrahydroborate (Sinopharm Chemical Reagent Co., China). Other chemicals used include suprapur hydrochloric acid (Sinopharm Chemical Reagent Co., China), octadecyl immobilized silica beads (nominal bead size: 100 μm, Tianjin Di-er Chemicals Co., Tianjin, China), 717 anion exchange resin (300–1200 μm in diameter, Sinopharm Chemical Reagent Co., China) was grounded and sieved to control the diameter at ca. 150 μm for mini-column packing.

2.3. Samples and sample pretreatment

A certified reference material of SLRS-4 (Riverine Water, National Research Council, Canada) is used for demonstrating the practical applicability of the proposed procedure. The pH value of the water sample is adjusted to pH 3 before undergoing the preconcentration process.

A lake water sample from Nan-Hu Lake outside the campus of Northeastern University is used for spiking recovery test. Appropriate amount of the lake water is filtered through a qualitative filter paper with aperture of 30–50 μm, the acidity of which is afterwards adjusted to pH 3 before preconcentration on the mini-columns.

2.4. Operating procedures

The flow manifold of the sequential injection system was illustrated in Fig. 1. The procedure includes the sorption of As(III)–PDC complex onto the C18 micro-column and the retention of As(V) by the 717 anion exchange resin column, followed by mini-columns rinsing, elution and hydride generation.

2.4.1. Preconcentration and determination of As(III)

Syringe pump SP1 was set to successively aspirate 800 μL air from port 2 and 1000 μL of sample solution from port 3 into holding coil HC1 at a flow rate of 100 μL s^{-1}. In the meantime, 1000 μL of APDC solution was aspirated into SP2 at a same flow rate. The sample solution was thereafter dispensed via port 4 at 15 μL s^{-1} to meet the APDC solution zone delivered by P2 at a same flow rate, and the formed As(III)–PDC complex was adsorbed onto the C18 mini-column. The mini-column was then evacuated by the stored air zone, followed by a prewashing procedure with 600 μL of deionized water, and the mini-column was finally evacuated.

100 μL of hydrochloric acid (3 mol L^{-1}) solution was aspirated into holding coil HC1 via port 6 which was thereafter directed via port 4 at 10 μL s^{-1} to collect the retained As(III)–PDC complex and the eluate was stored in holding coil HC2. Afterwards, the eluate and a sodium tetrahydroborate solution zone were directed by syringe pumps of the AFS system to confluence downstream and trigger the hydride generation process. The hydride was isolated in the gas–liquid separator and swept by an argon stream to flow through the atomic fluorescence spectrometer for quantification.

2.4.2. Preconcentration and determination of As(V)

1000 μL of sample solution was aspirated via port 3 into holding coil HC1, which was thereafter dispensed via port 5 at a flow rate of 15 μL s^{-1} to flow through the 717 anion exchange resin mini-column for facilitating the sorption of As(V). Afterwards, the mini-column was thoroughly rinsed with 400 μL of deionized

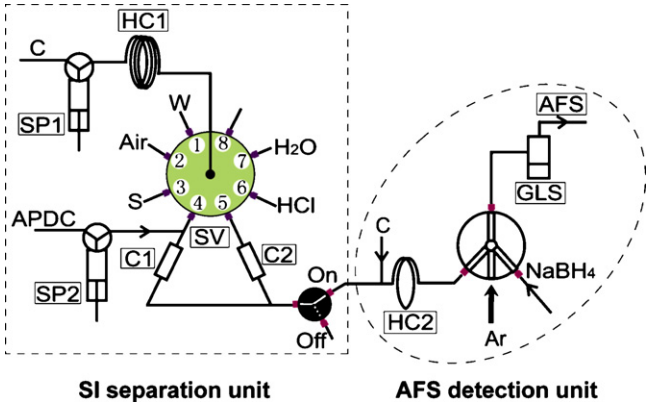

Fig. 1. The flow manifold for separation and preconcentration of As(III)–PDC complex and As(V) respectively onto C18 and 717 anion exchange resin mini-columns in a sequential injection system, followed by their speciation with detection by hydride generation atomic fluorescence spectrometry. SP1, SP2: syringe pumps; HC1, HC2: holding coils; SV: 8-port selection valve; C1: C18 packed mini-column; C2: a mini-column packed with 717 anion exchange resin; GLS: gas–liquid separator; AFS-920: atomic fluorescence spectrometer; S: sample; W: waste; C: carrier solution (deionized water).