

Analytical Methods

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3 **A sequential solid phase microextraction system coupled with inductively**
4 **coupled plasma mass spectrometry for speciation of inorganic arsenic**
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34 **Abstract**
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39 A sequential solid phase microextraction (SPME) system consisting of two
40 monolithic capillary columns was developed for simultaneous separation and
41 preconcentration of inorganic arsenic, followed by inductively coupled plasma mass
42 spectrometry (ICP-MS) detection. The
43 N-(β -aminoethyl)- γ -aminopropyltriethoxysilane (AEAPTES) incorporated
44 organic-inorganic hybrid monolithic column was in situ prepared by sol-gel
45 technology in a fused capillary, and employed as the extraction medium for SPME in
46 this system, because the amino active sites on the synthesized monolith possess a high
47 adsorption selectivity for As(V). With the on-line design of dual columns and an
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3 oxidation coil, As(V) is quantitatively extracted by the first column, and As(III) in the
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5 effluent can be quantitatively extracted by the second column after oxidized to As(V)
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7 by a make-up KMnO_4 solution. The retained As(V) or As(III) is then sequentially
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9 eluted by diluted HNO_3 and introduced to ICP-MS for determination. In this work, the
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11 parameters effecting the retention and elution of As(V) and As(III) were optimized in
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13 detail. On-line SPME of 1 mL sample solution gave a signal enhancement factor of 60
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15 for both As(V) and As(III) by using the system. The precisions (RSDs) for six
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17 replicate measurements of $1 \mu\text{g L}^{-1}$ As(V) and As(III) were 3.8% and 3.2%,
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19 respectively. The limits of detection (LODs, defined as three times the signal-to-noise
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21 ratio) for As(V) and As(III) were $0.005 \mu\text{g L}^{-1}$. The developed method was
22
23 successfully applied to the speciation analysis of inorganic arsenic in drinking and
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25 environmental waters with satisfactory recoveries.
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32 **Key words:** Solid phase microextraction; Organic-inorganic hybrid monolithic
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34 capillary column; Inorganic arsenic speciation; Inductively coupled plasma mass
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36 spectrometry
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43 **1. Introduction**

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Speciation analysis of trace elements has become increasingly important due to the impact of a given element in an environmental or biological system depends critically on its chemical form [1]. Arsenic is an omnipresent toxic trace element and is mainly found in environmental water with its inorganic species, As(III) and As(V). It is well known that As(III) is the most toxic form of the water-soluble species while As(V) is

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3 also relatively toxic [2-5]. Thus, separation of As(III) and As(V) for speciation
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5 analysis of arsenic is very necessary. Over the past decades, commercial separation
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7 techniques, e.g. HPLC [6], GC [7] and CE [8] have been exploited for the separation
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9 of arsenic species, followed by element-specific detector determination. However,
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11 most of these hyphenated techniques with expensive separation modules consume
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13 greatly and cannot enrich the species of interest.
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16 Solid phase microextraction (SPME) was introduced by Pawliszyn in 1990 [9],
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18 typically using an immobilized extracting phase coating on a small fused silica fiber
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20 or inner wall of the tube. As a simple, solventless, easy-to-automate, and portable
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22 sample preparation technique, SPME has been applied to trace element speciation
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24 studies by selective preconcentration [10-14]. Monolithic capillary column which is
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26 comprised of a single piece of monolithic porous material formed in situ in capillary,
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28 offers uniform structure and convective mass transfer, making it a desirable medium
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30 for SPME [15]. According to the materials of monoliths, monolithic capillary columns
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32 can be divided into two major classes: the organic polymer-based monoliths that
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34 generally are prepared by polymerization of organic monomers and crosslinkers
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36 [16-17]; the inorganic silica-based monoliths that typically are prepared via a sol-gel
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38 process to form a silica skeleton followed by a chemical modification of the matrix
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40 with different silylation reagents [18]. Hu et al. has prepared a variety of monolithic
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42 capillary columns for SPME-ICP-MS determination of trace elements in recent years,
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44 including poly(glycidyl methacrylate-trimethylolpropane trimethacrylate) polymer
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46 monolith for trace rare earth elements analysis in human serum and urine samples
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48 [19], dual silica monoliths for sequential speciation of inorganic arsenic and selenium
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50 in natural waters [20].
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56 As an improved alternative, the organic-inorganic hybrid monolithic capillary
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3 columns have attracted great attentions in recent years. Since the organic functional
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5 moieties can be covalently linked into the inorganic silica monolithic matrixes via
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7 sol-gel process, the organic-inorganic hybrid monolithic capillary columns give
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9 advantages of both organic polymer- and silica-based monoliths, such as good
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11 mechanical stability and solvent resistance, and ease of preparation [21-22]. A series
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13 of organic functional silylation reagents with tetra-alkoxysilanes (either
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15 tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS)) have been employed as
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17 precursors to synthesize hybrid monolithic columns which have found favorable uses,
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19 for example, 3-aminopropyltriethoxysilane (APTES) for thrombin recognition [23],
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21 2-cyanoethyltriethoxysilane (CN-TEOS) for antidepressants preconcentration [24],
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23 N-(β -aminoethyl)- γ -aminopropyltriethoxysilane (AEAPTES) for DNA purification
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25 [25]. Although the application of organic-inorganic hybrid monolithic capillary
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27 columns shows a great success in the area of organic substances, it should be stressed
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29 that only a few applications have been reported on the analysis of trace elements and
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31 their speciation [26-27].
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37 In the present work, an organic-inorganic hybrid monolithic capillary column was
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39 synthesized in a single step by in situ polymerization of TEOS and AEAPTES. The
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41 resultant hybrid monolith exhibited specifically selective sorption toward As(V) in a
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43 certain pH range. Based on this column, an on-line sequential SPME system coupled
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45 with ICP-MS was designed for speciation of inorganic arsenic. The separation and
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47 preconcentration of As(V) and As(III) was performed by incorporating two monolithic
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49 capillary columns, the first one was to extract As(V), and the second one was to
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51 extract As(III) in the effluent after on-line oxidation of As(III) to As(V). The retained
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53 As(V) or As(III) was detected directly following the elution process, resulting a high
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55 enhancement factor of signal intensity at very less sample consumption.
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2. Experimental

2.1 Reagents and solutions

Cetyltrimethylammonium bromide (CTAB, 98+%) was purchased from TCI (Tokyo, Japan). AEAPTES and TEOS (both 98%) were purchased from Ourchem (Shanghai, China) and Alfa Aesar (Tianjing, China), respectively. HNO₃ was of guarantee reagent, and all other chemicals were at least of analytical grade. Deionized water (DIW, 18.25 MΩ cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout the experiment.

Stock standard solutions of As(III) and As(V), 1000.0 mg L⁻¹, were prepared by respectively dissolving appropriate amounts of Na₃AsO₃ and As₂O₅ (Johnson Matthey, UK) in DIW. Lower concentration standard solutions were prepared daily by appropriate dilutions from their stock solutions.

2.2 Preparation of sample solutions

Tap water was collected in our laboratory in downtown campus located in Gulou District, Nanjing. Lake water was taken from Xuanwu Lake in Xuanwu District, Nanjing. Bottled purified water (Wahaha, Hangzhou, China) for drinking was purchased from a local supermarket. The certified reference material GSBZ 50004-88 (Standard environmental water sample) was obtained from the National Research Center for Certified Reference Materials (Beijing, China). Each water sample was filtered through a 0.45 μm cellulose acetate membrane before use.

2.3 Preparation of AEAPTES-silica hybrid monolithic capillary column

The fused-silica capillary (Reafine Chromatography Ltd., Heibei, China) with 530 μm i.d. and 690 μm o.d. was used to prepare the monolithic column. Prior to the preparation, the capillary was activated at ambient temperature by rinsing sequentially with 1.0 M sodium hydroxide for 4 h, water for 30 min, 1.0 M hydrochloric acid for 4 h, water for 30 min and methanol for 30 min, and dried at 160 $^{\circ}\text{C}$ while being purged with nitrogen for 3 h.

The AEAPTES-silica monolithic column was prepared by the following procedures based on the previously reported method [25] with minor modifications. Typically, 225 μL ethanol, 75 μL water and 22.2 mg CTAB were mixed together, and then 160 μL TEOS and 40 μL AEAPTES were added to the above mixture. The solution was vortexed at room temperature for 30 s and subsequently ultrasonicated at 0 $^{\circ}\text{C}$ for 30 s before being introduced into the above pre-treated capillary. With both ends sealed by silicon rubbers, the capillary was placed at 313 K for 20 h, and finally rinsed with HNO_3 /ethanol (v/v=1/200) and water, respectively.

2.4 Apparatus

The scanning electron microscopy (SEM) images of the monolithic capillary column were obtained using a S-3400N scanning electron microscope (Hitachi, Tokyo, Japan). Fourier transform infrared (FT-IR) spectra (4000-400 cm^{-1}) in KBr were recorded on a NEXUS870 spectrometer (Nicolet, Madison, WI, USA). The pH values of solutions were controlled by a Mettler Toledo SevenMulti pH meter (Mettler-Toledo, Shanghai, China).

A PerkinElmer ELAN 9000 ICP-MS system equipped with a low flow rate micro concentric nebulizer (Glass Expansion, Switzerland) and a miniature cyclonic spray

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3 chamber was used for on-line detection. The instrument performance was optimized
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5 daily using standard sample introduction of tuning solution. The optimum operation
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7 conditions are summarized in Table 1.
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11 **Table 1.** Instrumental parameters for ICP-MS
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14 15 16 **2.5 On-line sequential SPME coupled to ICP-MS** 17

18 The schematic diagram of the sequential SPME system is shown in Fig. 1. The
19 device was consisted of three peristaltic pumps (Baoding Longer BT100, P1 and P2
20 and P3) and two six-port injection valves (Rheodyne 7725i, V1 and V2) connected
21 with a home-made needle adapter [16] for sample solution transfer. The sample loop
22 of each injection valve was replaced by a 5 cm monolithic capillary column (C1 and
23 C2). Capillary of 0.1 mm i.d. was adopted for all connections, which was kept as short
24 as possible to minimize dead volume of the SPME system.
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36 **Fig. 1.**
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40 The analytical procedures are presented in Table 2. Briefly, in the LOAD position,
41 DIW (pH=5, adjusted by HNO₃) was pumped through C1 and C2 by P2 to balance
42 column, then the sample solution was passed through the column and As(V) was
43 retained on C1. As(III) in the effluent of C1 was then mixed with KMnO₄ (5 μM,
44 pumped by P3), and oxidized to As(V) in the oxidation zone, and subsequently
45 extracted by C2. Then a certain amount of DIW (pH=5) was driven into the column to
46 remove the residual solution. Afterwards, V1 was switched to INJECT position, the
47 eluent (0.1 M HNO₃) pumped by P1 was passed through the column, and As(V)
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3 retained on C1 was desorbed and driven into ICP-MS for detection of As. After that,
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5 V2 was switched to INJECT position for eluting As(III), followed by ICP-MS
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7 detection.
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11 **Table 2.** Operation sequences of the on-line sequential SPME coupled with ICP-MS
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13 for speciation of inorganic arsenic
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20 21 **3. Results and discussion**

22 23 24 **3.1 Preparation and characterization of the organic-inorganic hybrid monolithic** 25 26 **capillary column** 27 28

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30 The whole procedure of the complete sol-gel reaction in the capillary and the SEM
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32 images of the formed monolith are shown in Fig. 2a. TEOS and AEAPTES were
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34 utilized as precursors, and CTAB was chosen as the template. Water and ethanol were
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36 used as co-solvents. From the SEM images, it can be seen that there were many
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38 macropores and flow-through channels in the network skeleton of the monolith, and
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40 the formed monolith attached well to the inner wall of the capillary. The uniform and
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42 small sizes of the particles could offer high surface area for extraction, and the
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44 macroporous structure would result in low back-pressure and high permeability, so
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46 such a monolithic structure enables an on-line SPME protocol.
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50 To confirm the existence of AEAPTES, FT-IR spectrum of the organic-inorganic
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52 hybrid monolithic column was examined as shown in Fig. 2b. Characteristic bands of
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54 the saturated C-H stretching vibrations at 2945 and 2890 cm^{-1} and the C-N stretching
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56 vibrations at 1470 cm^{-1} and the N-H stretching vibrations at 1620 cm^{-1} demonstrate
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3 the successful incorporation of AEAPTES in the matrix.
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8 **Fig. 2.**
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10 11 **3.2 Factors affecting the on-line SPME of As(V)** 12

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14 Sample pH is critical for the separation of As(III) and As(V) because it influences
15 the distribution of arsenic species and the surface property of sorbents. The effect of
16 the pH of sample solution on the adsorption percentages of As(III) and As(V) was
17 investigated and the results are shown in Fig. 3. It can be seen that in the pH range of
18 3.5-8.0, As(V) was quantitatively adsorbed by AEAPTES monolithic column, while
19 As(III) was not retained in the whole tested pH range. The different affinity between
20 column and arsenic can be explained by their successive acid dissociation constants
21 (pK_a). As(V), having pK_a values of 2.3, 7.0 and 11.5, is mainly in the form of
22 $H_2AsO_3^-$ and $HAsO_3^{2-}$ at pH 3.5-8.0, while As(III), having pK_a values of 9.2, 12.1
23 and 13.4, is mainly present as uncharged species. Therefore, AEAPTES monolith,
24 possessing positively charged surface (protonated) under pH range of 3.5-8.0, tends to
25 attract the anionic species of As(V), and shows no favor of As(III). Because the pH
26 values of the most natural water are around 7.0, we finally selected pH value of 5.0
27 for the subsequent experiments to avoid violent change of sample solution.
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47 **Fig. 3.**
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52 As(V) is not extracted under lower pH region and diluted HNO_3 is often used as the
53 carrier solution for ICP-MS detection without any interference for As, so we selected
54 diluted HNO_3 as the eluent for desorbing As(V) from the column. The concentration
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3 of HNO₃ and the desorption time were also investigated. Finally, eluting with 0.1 M
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5 HNO₃ at a 150 μL min⁻¹ flow rate for 1 min was found to be sufficient for the
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7 complete desorption of As(V) with better elution curve and less balance time for next
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9 analysis.

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11 The influence of sample flow rate on As(V) retention was investigated by passing 1
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13 mL sample solution through the monolithic column with the flow rate varying in the
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15 range of 50-500 μL min⁻¹. The experiments indicated that the retention efficiency was
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17 higher than 95% in the whole tested flow rate range. However, high flow rates are
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19 prone to destroy the hybrid skeleton, thus a sample loading rate of 150 μL min⁻¹ was
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21 adopted, which is an enough safe flow rate for the monolithic capillary column.
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23 Accordingly, an eluting flow rate of 150 μL min⁻¹ which was compatible with the
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25 micro concentric nebulizer was used to obtain better precision.
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3.3 Factors affecting the on-line SPME of As(III)

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33 Since As(III) was not extracted on the prepared monolithic capillary column, As(III)
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35 in the effluent of Column 1 was designed to be oxidized by KMnO₄ to As(V), which
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37 was subsequently extracted on the Column 2 for SPME. Therefore, the oxidation
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39 process is crucial to the SPME of As(III). Under the optimized SPME condition of
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41 As(V), a high concentration of 100 μg L⁻¹ As(III) was employed to examine the
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43 on-line oxidation conditions. Fixing the length of oxidation coil of 1 m (0.1 mm i.d.),
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45 the effect of concentration and the flow rate of KMnO₄ were investigated. The
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47 experiments showed that when KMnO₄ solution was added at a fixed flow rate of 20
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49 μL min⁻¹, no As signal was observed in the effluent of Column 2 as the concentration
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51 of KMnO₄ was increased to 5 μM, which indicating As(III) was completely oxidized
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53 to As(V) in the oxidation zone. Then, fixing the concentration of KMnO₄ at 5 μM and
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3 varying its flow rate, an insufficient oxidation of As(III) to As(V) along with a less
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5 stable result was found when the flow rate of KMnO_4 was lowered to $10 \mu\text{L min}^{-1}$.
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7 Moreover, no further improvement of As signal intensity in the elution solution was
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9 observed when the flow rate of KMnO_4 was increased from $20 \mu\text{L min}^{-1}$ to $50 \mu\text{L}$
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11 min^{-1} . Therefore, $5 \mu\text{M KMnO}_4$ at the flow rate of $20 \mu\text{L min}^{-1}$ was sufficient for
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13 complete oxidation of As(III) to As(V).
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16 The effect of oxidation coil size was also examined, the results showed that the
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18 complete oxidation process of As(III) could be finished in nearly ten seconds,
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20 indicating a short coil was satisfied well for oxidation zone. Finally, we used 1 m
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22 length capillary (0.1 mm i.d.) as the oxidation coil for further study.
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25 Besides, another oxidation reagent KIO_3 was also tested. However, no obvious
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27 oxidation of As(III) to As(V) occurred under the same condition.
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30 31 32 **3.4 Effect of the loading time on the on-line SPME**

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34 The effect of loading time on the on-line SPME was investigated using a sample
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36 flow rate of $150 \mu\text{L min}^{-1}$ and a solution concentration of $10 \mu\text{g L}^{-1}$. The experiments
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38 showed an increasing signal intensity trend in a wide range of loading time. The
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40 obtained results could be attributed to the sufficient capacity for the complete
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42 adsorption of the large amount of As(V). To investigate the maximum adsorption
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44 capacity, frontal analysis of the monolithic capillary column was carried out by
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46 pumping $500 \mu\text{g L}^{-1}$ As(V) (pH=5) through the column at $150 \mu\text{L min}^{-1}$. Fig. 4 is the
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48 obtained breakthrough curve. According to 5% breakthrough volume, the adsorption
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50 capacity of the 5 cm monolithic column was found to be $5.2 \mu\text{g}$, indicating longer
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52 loading time and larger sample volume could be suitable for this system.
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56 Although a high enhancement factor of signal intensity can be achieved by a large
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3 sample volume, it will take much longer time for loading sample, which is
4 unfavorable for analytical efficiency and utilization of ICP-MS. To complete an
5 analysis cycle in 10 min, 1 mL sample solution was employed for the further
6 experiments, giving an enhancement factor of 60.
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14 **Fig. 4.**
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18 **3.5 Interference study**

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20 Generally, the coexisting ions in the solution may compete with analyte for the
21 active sites of monolith. Therefore, interferences from coexisting ions should be
22 considered. The effects of cations and anions on the determination of arsenic were
23 investigated under the optimized conditions. The recovery of $1 \mu\text{g L}^{-1}$ of As(V) was
24 tested with individual interfering ion added. Taking the deviation of the recovery out
25 of 90%-110% as the criterion for interference, it was found that cations such as Ca^{2+} ,
26 Mg^{2+} , Al^{3+} , Fe^{3+} and Zn^{2+} could be tolerated up to at least $1000 \mu\text{g L}^{-1}$, especially, the
27 Na^{+} and K^{+} can reach up to $10,000 \mu\text{g L}^{-1}$. Anions such as SO_4^{2-} , NO_3^{-} and PO_4^{3-} with
28 concentrations of $1000 \mu\text{g L}^{-1}$ and Cl^{-} of $10,000 \mu\text{g L}^{-1}$ did not cause any significant
29 change to results. Therefore, the potential coexisting ions in real samples have minor
30 interferences with the determination of inorganic arsenic.
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48 **3.6 Analytical performance**

49 Under the above developed conditions, the analytical performance of the method
50 was evaluated. Fig. 5 shows a complete elution chromatogram under the optimized
51 elution conditions. As can be seen, the signal of two species was clearly enhanced
52 after sequential SPME. Comparing the peak height with conventional direct
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3 introduction, an enhancement factor of 60 was obtained after preconcentration.
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5 However, the EF could be further enhanced by increasing the loading time if the
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7 analysis time is not important. The precision (RSD) for six replicate measurements of
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9 $1 \mu\text{g L}^{-1}$ As(V) and As(III) was 3.8% and 3.2%, respectively. The limits of detection
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11 (LODs, defined as three times the signal-to-noise ratio) for As(V) and As(III) were
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13 $0.005 \mu\text{g L}^{-1}$. Good linearity was obtained in the concentration range from their limit
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15 of quantification to $10.00 \mu\text{g L}^{-1}$ for As(V) and As(III), with both linear correlation
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17 coefficients above 0.999. In addition, 0.1 M HNO_3 was pumped into ICP-MS all the
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19 time, and all data was collected under this background, which was conducive to the
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21 stability of plasma and the precision of the result, respectively.
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27 **Fig. 5.**
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32 **3.7 Applications**

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34 The proposed method was validated by determining the As content in the certified
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36 reference material GSBZ 50004-88 (Standard environmental water sample). As can be
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38 seen in Table 3, both kinds of the inorganic arsenic were found in the sample and
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40 As(III) was the main species, As(Total) was in good agreement with the certified
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42 value, whereas no certified value for As(V) and As(III) was available.
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45 The method was applied in the analysis of inorganic arsenic in bottled purified
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47 water, tap water and lake water. The results are listed in Table 4. The recoveries of
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49 inorganic arsenic for four spiked samples were also evaluated. The results showed that
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51 the recoveries in all spiked samples were in the range from 88% to 108%,
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53 demonstrating that the proposed method is suitable for the determination of inorganic
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55 arsenic in drinking and environmental samples.
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5 **Table 3.** Analytical results of inorganic arsenic species in certified reference material
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7 by the present method (mean±SD, n=3)
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11 **Table 4.** Determination of inorganic arsenic species in drinking and environmental
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13 water samples (mean±SD, n=3)
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20 21 **4. Conclusions** 22 23 24

25 AEAPTES incorporated organic-inorganic hybrid monolithic capillary column was
26 prepared and used as the extraction medium for speciation of inorganic arsenic by
27 using an on-line sequential SPME system coupled with ICP-MS. The amino active
28 sites on the macroporous structure of the monolith show good adsorption selectivity
29 for As(V). Interestingly, the designed sequential SPME system provides a
30 simultaneous preconcentration/determination of As(V) and As(III) at very less
31 sample consumption in a single analysis run, which avoids the error arisen from
32 off-line oxidation or reduction mode. In addition, satisfactory recoveries and
33 reproducibility were acquired for drinking and environmental waters, indicating that
34 the proposed method has the potential ability for the determination of trace amount of
35 arsenic species in complex matrix.
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54 **Acknowledgments** 55 56 57 58 59 60

This work was supported by National Basic Research Program of China (973 program, 2009CB421601, 2011CB911003), National Natural Science Foundation of China (21275069, 90913012), National Science Funds for Creative Research Groups (21121091), and Analysis & Test Fund of Nanjing University.

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Tables**Table 1.** Instrumental parameters for ICP-MS

Parameter	Settings
Rf power	1000 W
Carrier gas flow rate	0.85 L min ⁻¹
Auxiliary gas flow rate	1.20 L min ⁻¹
Plasma gas flow rate	15 L min ⁻¹
Sampling cone	Ni/1.1 mm
Skimmer cone	Ni/0.9 mm
Acquisition mode	Time-resolved data acquisition
Scanning mode	Peak-hopping
Dwell mode	250 ms
Integration mode	Peak area
Isotope monitored	⁷⁵ As

Table 2. Operation sequences of the on-line sequential SPME coupled with ICP-MS for the speciation analysis of inorganic arsenic

Step	Valve position		Solution	Flow rate ($\mu\text{L min}^{-1}$)	Time (min)	Function
	V1	V2				
	LOAD	LOAD	DIW	150	1	Balance column
1			Sample	150	6.7	Load sample
			DIW	150	1	Wash and clean
2*	INJECT	LOAD	Eluent	150	1	Elute As(V)
3*	LOAD	INJECT	Eluent	150	1	Elute As(III)

* ^{75}As signal was collected by ICP-MS.

Table 3. Analytical results of inorganic arsenic species in certified reference material by the present method (mean±SD, n=3)

Sample	Species	Certified ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
GSBZ 5004-88	As(V)	--	1.1±0.1	--
	As(III)	--	130.5±7.6	--
	As(Total)	124±8	131.6±7.7	106

Table 4. Determination of inorganic arsenic species in environmental water samples
(mean±SD, n=3)

Sample	Spiked level ($\mu\text{g L}^{-1}$)		Found ($\mu\text{g L}^{-1}$)		Recovery (%)	
	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)
Purified Water	0	0	--	--	--	--
	1.00	1.00	1.01±0.05	0.98±0.04	101	98
Tap water	0	0	1.71±0.10	0.30±0.08	--	--
	1.00	1.00	2.70±0.12	1.18±0.04	99	88
Lake water	0	0	1.31±0.05	0.87±0.07	--	--
	1.00	1.00	2.26±0.09	1.96±0.19	95	108

Figure captions

Fig. 1. Construction of on-line sequential SPME-ICP-MS system. V1 and V2 are in the extraction state. Detail operation sequences as shown in Table 2.

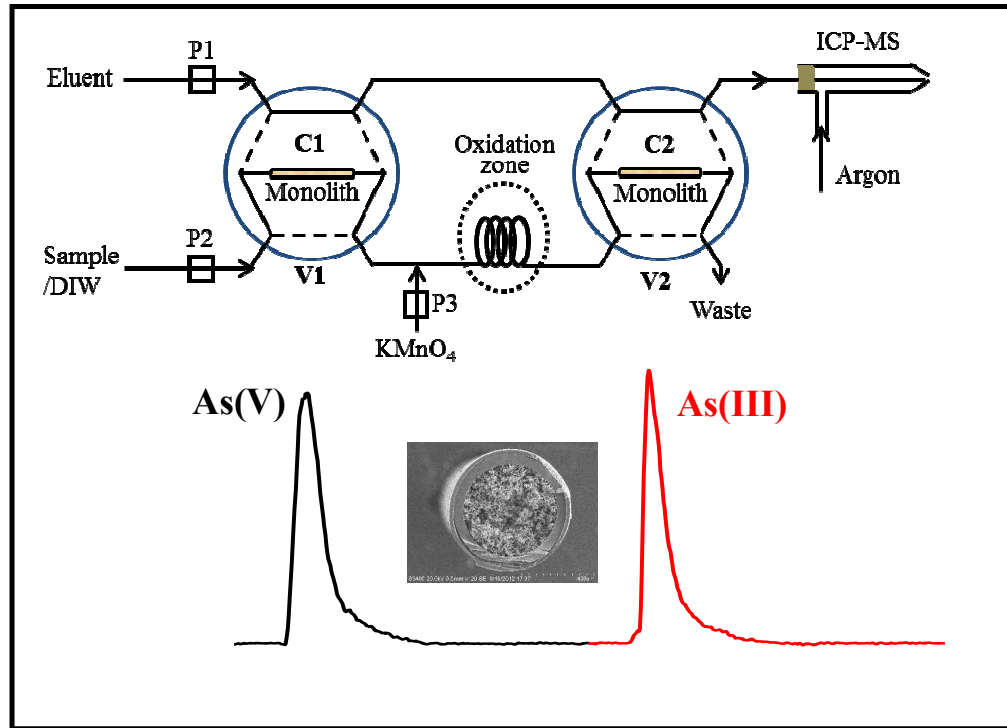
Fig. 2. Characterization of the organic-inorganic hybrid monolithic capillary column. (a) Scheme of the preparation and the SEM images (I×120; II×1000; III×5000); (b) FTIR spectra.

Fig. 3. Effect of the pH of the sample solution on the adsorption percentage of $1 \mu\text{g L}^{-1}$ As(III) and As(V) on the monolith.

Fig. 4. Breakthrough curve of the monolithic capillary column at pH 5.0. Concentration: $500 \mu\text{g L}^{-1}$. Flow rate: $150 \mu\text{L min}^{-1}$.

Fig. 5. Complete elution chromatogram of As(V) and As(III) after preconcentration. Sample solution consists of $1 \mu\text{g L}^{-1}$ As(V) and As(III).

Graphic abstract



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Figures

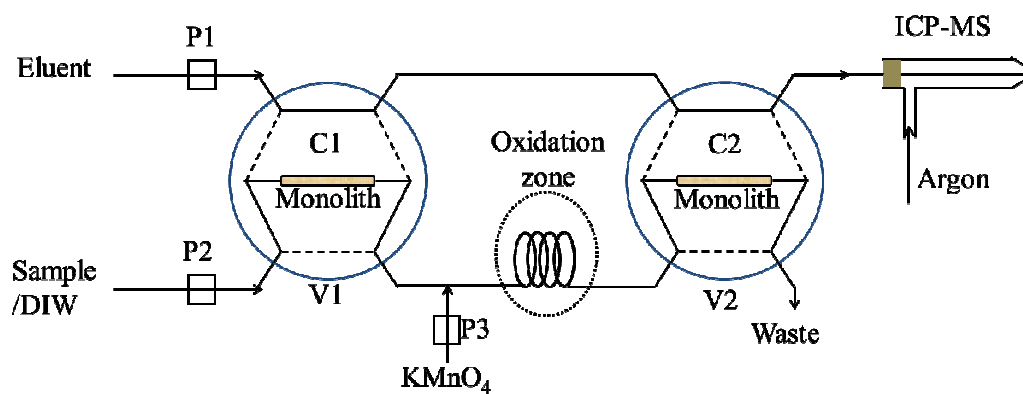
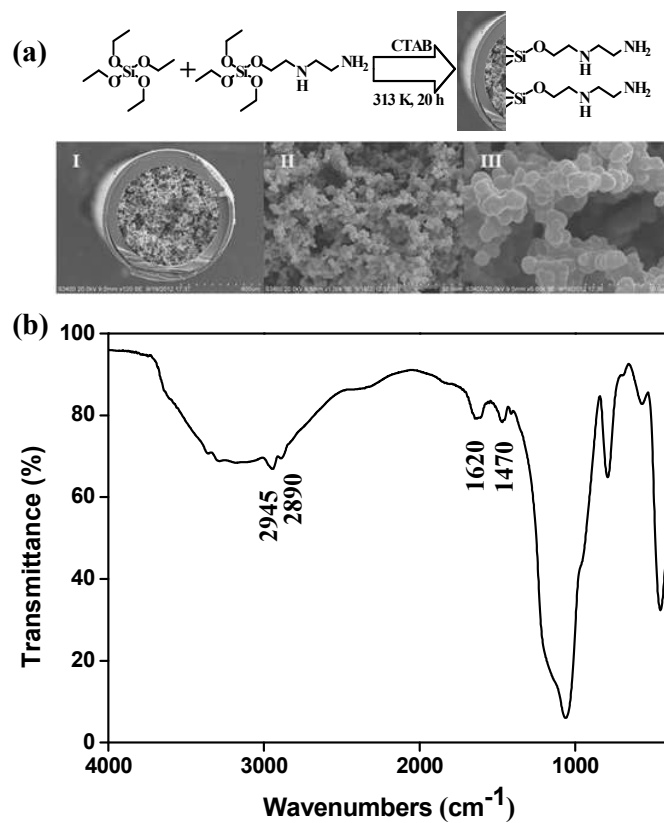


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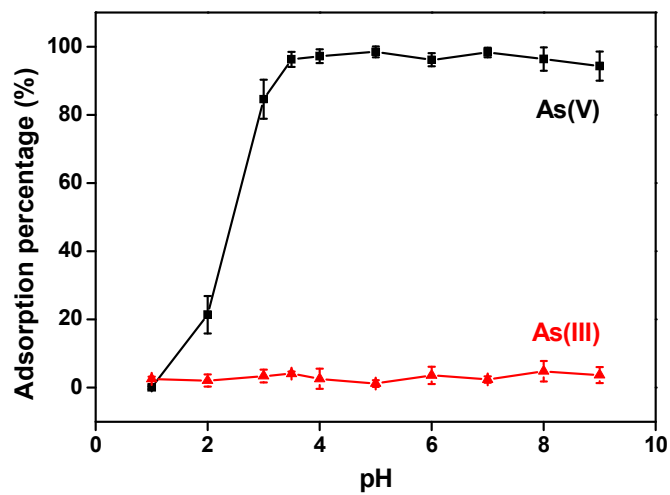


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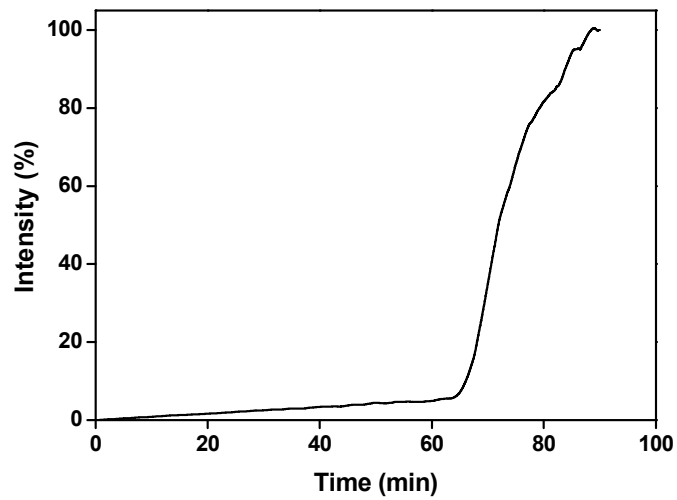


Fig. 4. Breakthrough curve of the monolithic capillary column at pH 5.0.

Concentration: $500 \mu\text{g L}^{-1}$. Flow rate: $150 \mu\text{L min}^{-1}$.

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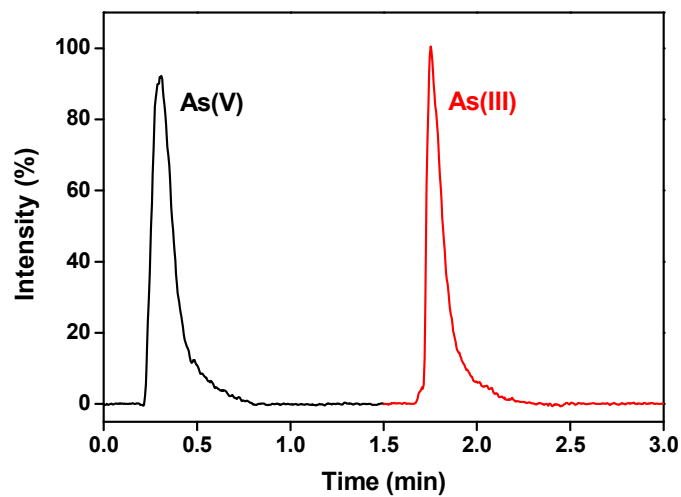


Fig. 5. Complete elution chromatogram of As(V) and As(III) after preconcentration.

Sample solution consists of $1 \mu\text{g L}^{-1}$ As(V) and As(III).