Available online at www.sciencedirect.com
ScienceDirect

Journal of Hazardous Materials 151 (2008) 58–64

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Simultaneous separation and speciation of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters utilizing capillary microextraction on ordered mesoporous Al_2O_3 prior to their on-line determination by ICP-MS

Wenling Hu, Fei Zheng, Bin Hu *

Department of Chemistry, Wuhan University, Wuhan 430072, PR China

Received 27 December 2006; received in revised form 15 May 2007; accepted 15 May 2007
Available online 18 May 2007

Abstract

In this paper, a system of flow injection (FI) capillary microextraction (CME) on line coupled with inductively plasma mass spectrometry (ICP-MS) was proposed for simultaneous separation and speciation of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters. Ordered mesoporous Al_2O_3 coating was prepared by sol-gel technology and used as CME coating material. Various experimental parameters affecting the capillary microextraction of inorganic arsenic and chromium species have been investigated and optimized. Under the optimized conditions, the limits of detection were 0.7 and 18 ng L^{-1} for As(V) and Cr(VI), 3.4 and 74 ng L^{-1} for As(III) and Cr(III), respectively, with an enrichment factor of 5 and a sampling frequency of 8 h^{-1}. The relative standard deviations (R.S.D.) were 3.1, 4.0, 2.8 and 3.9% ($C = 1$ ng mL^{-1}, $n = 7$) for As(V), As(III), Cr(VI) and Cr(III), respectively. The proposed method was successfully applied for the analysis of inorganic arsenic and chromium species in mineral water, tap water and lake water with the recovery of 94–105%. In order to verify the accuracy of the method, two certified reference of GSBZ50027-94 and GSBZ50004-88 water samples were analyzed and the results obtained were in good agreement with the certified values. The ordered mesoporous Al_2O_3 coated capillary showed an excellent solvent and thermal stability and could be re-used for more than 30 times without decreasing extraction efficiency.

Keywords: Capillary microextraction; Speciation of As(III)/As(V) and Cr(III)/Cr(VI); Ordered mesoporous Al_2O_3 coating; ICP-MS; Natural waters

1. Introduction

Arsenic is a toxic element for humans and it is commonly associated with serious health disruptions. It is well known that the toxicity of arsenic is highly dependent on its chemical forms. In fact, As(III) is more toxic than As(V) and methylated compounds that contain trivalent arsenic are more cytotoxic and genotoxic than arsenite [1,2]. The International Agency for Research on Cancer and US EPA have designated arsenic as a group of a ‘known’ human carcinogen, and the World Health Organization (WHO) guideline value for As in drinking water has been reduced from 50 to 10 ng mL^{-1} (daily intake) [3]. Chromium exists mainly in the hexavalent and trivalent states. In the environment Cr(III) occurs as $Cr(OH)_n^{(3-n)+}$, and Cr(VI) as CrO_4^{2-} or $HCrO_4^{-}$. The biological and chemical properties of the two species differ significantly, Cr(III) is an essential trace element in human body and it plays an important role in the metabolism of glucose and certain lipids such as cholesterol [4], whereas Cr(VI) compounds are approximately 100 times more toxic than Cr(III) [5], due to their high oxidation potentials and the ease with which they penetrate biological membranes. The most common form of massive and chronic exposure to As and Cr is by consumption of contaminated drinking water, but the concentration of organic forms of As and Cr are relatively low in natural waters [3,6]. Consequently, the speciation analysis of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters is of great importance.

The speciations of inorganic arsenic and chromium have been generally achieved by combining a very effective separation method with a sensitive detection technique. Several techniques, such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission

---

* Corresponding author. Tel.: +86 27 87218764; fax: +86 27 68754067.
E-mail address: binhu@whu.edu.cn (B. Hu).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.05.044

spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have been employed for the determination of arsenic and chromium species. Of all these methods, ICP-MS is especially suitable for elemental species determinations due to its excellent ability of detection of multi-elements and its possibility to perform isotope determination.

However, when ICP-MS is employed for trace elements speciation, an effective separation procedure for different species is often mandatory. Up to now, the most widely used separation techniques for the elemental speciation include high-performance liquid chromatography (HPLC) [7], gas chromatography (GC) [8], ion chromatography (IC) [9], capillary electrophoresis (CE) [10], solvent extraction [11], solid phase extraction [12], coprecipitation [13] and voltammetry method [14]. Solid phase microextraction (SPME), as a novel sample pretreatment technique for elemental speciation by GC–ICP-MS [15,16], was also directly coupled with ICP-MS for the speciation of various elemental species in biological and environmental samples [17,18].

Capillary microextraction (CME) [19,20] developed from SPME, as a new direction in the solventless sample preparation for the preconcentration of trace analytes, is a newly miniature extraction technique utilizing an open tubular capillary column as extraction device, and a sorptive coating on the inner surface of capillary as the extraction medium in which the analyte in aqueous sample is directly extracted and preconcentrated. This technology has become increasingly popular because of its simple, fast, solvent-free and inexpensive properties [21]. It also has the ability to combine with different detection techniques in on-line mode such as HPLC, GC and ICP-MS [22–24]. In-tube SPME on line coupled with LC–MS was first developed for speciation of trimethyllead and triethyllead in 1999 by Mester and Pawliszyn [25]. In the further study, they developed a method for the speciation of organoarsenic compounds by polypyrrole (PPY)-coated capillary in-tube SPME coupled with HPLC–ES-MS [26]. Garcia-Sanchea [27] reported a method for lead speciation in rainwater by modified fused silica capillary coupled to a direct injection nebulizer for sample introduction in ICP-MS.

It should be noted that the extraction coating plays a fundamentally important role in the CME technique, and the development of an extraction coating with high selectivity, stability and extraction efficiency is forever of interest to analysts. In our previous studies, we prepared ordered mesoporous Al_2O_3 coated capillary by using sol-gel technology and developed an on-line CME/ICP-MS system for the determination of trace Co, Ni and Cd in water, rice and urine samples [28]. The Al_2O_3 coating material showed high adsorption ability for target metal ions due to its ordered mesoporous structure with a pore size of about 10 nm.

The objective of this study was to realize simultaneous separation and speciation of inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters by ordered mesoporous alumina coated CME on line coupled with ICP-MS. Experimental parameters affecting the retention behaviors of As(III)/As(V) and Cr(III)/Cr(VI) on ordered mesoporous alumina coated capillary were discussed in detail. The proposed method was successfully applied to the speciation of inorganic As and Cr species in mineral water, tap water and lake water.

2. Experimental

2.1. Apparatus

An Agilent 7500a ICP-MS (Agilent, Japan) with a Babington nebulizer was used for detection. The optimum operation conditions are summarized in Table 1. The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A WX-3000 microwave accelerated digestion system (EU Chemical Instruments Co. Ltd., Shanghai, China) was used for sample digestion. An IFIS-C flow injection system (Ruimai Tech. Co. Ltd., Xi'an, China) was used for on line coupling CME with ICP-MS. A minimum length of PTFE tubing (i.d. 0.5 mm) was used for on-line connection. Fused silica capillary (320 μm i.d. × 450 μm o.d.) was obtained from Yongnian Optical Fiber Factory, Hebei, China.

2.2. Standard solutions and reagents

The stock standard solutions ($1\ \mathrm{mg\ mL^{-1}}$) of As(III), As(V), Cr(III) and Cr(VI) were obtained by dissolving appropriate amounts of Na_3AsO_3, Na_3AsO_4, $CrCl_3{\cdot}6H_2O$ and $K_2Cr_2O_7$ (A.R. The First Reagent Factory of Shanghai, Shanghai, China) in high purity deionized water, respectively. The standard stock solutions ($1\ \mathrm{mg\ mL^{-1}}$) of other elements were prepared from their salts by a conventional method. $AlCl_3$ was of analytical grade and purchased from the First Reagent Factory of Shanghai. The Poly (alkyleneoxide) blockpolymer $HO(CH_2CH_2O)_{73}(CH_2CH(CH_3)O)_{28}(CH_2–CH_2O)_{73}H(EO_{73}PO_{28}EO_{73}$; Pluronic PE6800) was obtained from BASF Performance Chemicals (Mount Olive, NJ, USA). HNO_3 and $NH_3{\cdot}H_2O$ were of high pure grade and purchased from The First Reagent Factory of Shanghai, China. All other reagents used were of specpure grade or analytical reagent grade. The high purity deionized water obtained by a Labconco system (18.2 MΩ) was used throughout this work.

Table 1
Equipment and operating parameters

ICP-MS plasma	
Rf power	1250 W
Outer gas flow rate	$15\ \mathrm{L\ min^{-1}}$
Intermediate gas flow rate	$0.9\ \mathrm{L\ min^{-1}}$
Nebulizer gas flow rate	$0.7\ \mathrm{L\ min^{-1}}$
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	50 ms
Integration mode	Peak area
Points per spectral peak	1
Mass number of element	^{75}As, ^{53}Cr

2.3. Contamination control

All laboratory wares were made of polyethylene or polypropylene material and thoroughly cleaned by soaking in nitric acid (1:1) for at least 24 h. Immediately prior to use, all acid-washed wares were rinsed with high purity deionized water.

2.4. Preparation of Al_2O_3 coated capillary

Mesoporous ordered Al_2O_3 coating was prepared on the inner surface of a pre-activated capillary (40 cm × 320 μm i.d.) by sol–gel method as described previously [28]. Finally, the Al_2O_3 coated capillary was calcined by heating at a rate of 1 °C min^{-1} to 380 °C and holding for 8 h to remove PE6800 species and increase cross-linking of the inorganic framework, leading to the formation of Al_2O_3 coating.

2.5. Analytical procedure

The FI-CME–ICP-MS system and its operation sequence of the on-line preconcentration and determination were the same as our previous report [28]. A 10 mL portion of aqueous sample solution containing As(III), As(V), Cr(III) and Cr(VI) was prepared, and the pH value was adjusted to 4.0 with 0.01 mol L^{-1} $NH_3 \cdot H_2O$ and 0.1 mol L^{-1} HNO_3. After mesoporous Al_2O_3 coated capillary was conditioned with 0.01 mol L^{-1} $NH_3 \cdot H_2O$ for 1 min, the sample solution (0.5 mL) was passed through Al_2O_3 coated capillary at a flow rate of 0.1 mL min^{-1} by using a peristaltic pump, and the effluent was directly introduced into the ICP-MS for determination of As(III) and Cr(III). Afterwards, high purity deionized water was sucked through the mesoporous alumina coated capillary to rinse the capillary column for 1 min. The analytes retained on the capillary were then on line eluted with 0.1 mL of 0.01 mol L^{-1} NaOH at the flow rate of 0.1 mL min^{-1} for ICP-MS determination of As(V) and Cr(VI). The blank solution and the series of standard solution were prepared and subjected to the same procedure of FI-CME–ICP-MS.

A 0.5 mL solution (pH 4.0) of 0.01 mol L^{-1} $NH_3 \cdot H_2O$ and 0.1 mol L^{-1} HNO_3, chosen as the blank solution, was passed through the microextraction capillary. And then the microextraction capillary was eluted by using 0.1 mL of 0.01 mol L^{-1} NaOH. The blank values of analytes were obtained by determining the elution.

2.6. Sample preparation

A 5 mL of mineral water (purchased from local supermarket), tap water (Wuhan, China) and Lake water (East Lake, Wuhan, China, was filtered through a 0.45 μm membrane filter) were collected and acidified to pH of about 1 with concentrated HNO_3, respectively. Before use, the pH value was adjusted to 4.0 with 0.01 mol L^{-1} $NH_3 \cdot H_2O$ and diluted to 10 mL. The blank sample with the same amount of acid was prepared with the same procedure except for adding no analytes.

A 5 mL aliquot of GSBZ50027-94 and GSBZ50004-88 water samples was also prepared according to the above procedure. Again, the blank sample with the same amount of acid was prepared with the same procedure except for adding no analytes.

3. Results and discussion

3.1. The effect of pH

The pH value plays an essential role with respect to the adsorption of different species of arsenic and chromium on ordered mesoporous Al_2O_3 coating surfaces. In this work, the effect of pH on the adsorption rate of the studied inorganic species on the capillary was investigated, and the result was shown in Fig. 1. It was obvious that in the pH range of 2.0–5.0, As(V) and Cr(VI) were retained on the Al_2O_3 coated capillary with an adsorption percentage above 90%, while As(III) and Cr(III) were not retained by the coating material in the pH range of 3.0–4.0, and they just passed directly through the capillary. Thus, it was possible that by selection of a proper pH, As(V) and Cr(VI) could be effectively separated from As(III) and Cr(III) on Al_2O_3 coated capillary. In this work, a pH of 4.0 was selected for simultaneous separation of As(V) and Cr(VI) from As(III) and Cr(III).

The mechanisms for the adsorption of As(V) and Cr(VI) on Al_2O_3 coating could be attributed to the electrostatic charge. In the acidic medium, the surface of Al_2O_3 coating was positive charged (Al–OH^+), which posessed its preference to As(V) and Cr(VI) because they existed as anions in the form of negatively charged $AsO_4{}^{3-}$ and $Cr_2O_7{}^{2-}/CrO_4{}^{-}$ while As(III) and Cr(III) existed as cations in the form of positively charged as $As(OH)_3$ and Cr^{3+}. For the same reason, the different adsorption behaviors of arsenic and chromium species in the basic medium could be explained.

3.2. The effect of sample flow rate

The sample flow rate will influence the retention of analytes on Al_2O_3 coated capillary. Its effect was studied by passing

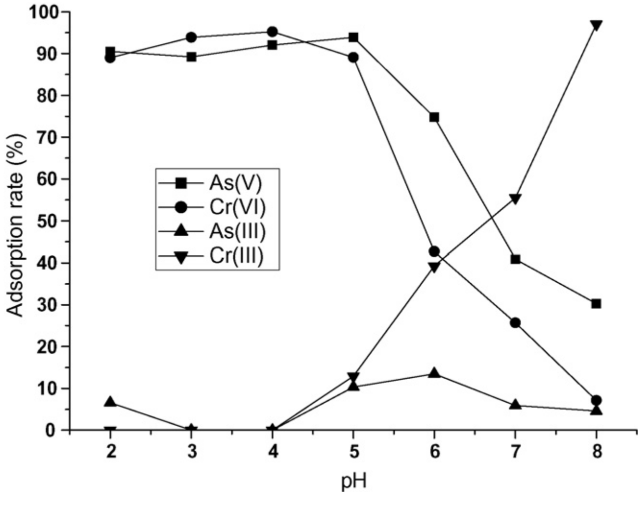

Fig. 1. Effect of pH on the adsorption rate (%) of different inorganic arsenic and chromium species. Sample volume: 0.5 mL; As(V), As(III), Cr(VI) and Cr(III) concentration: 20 ng mL^{-1}.

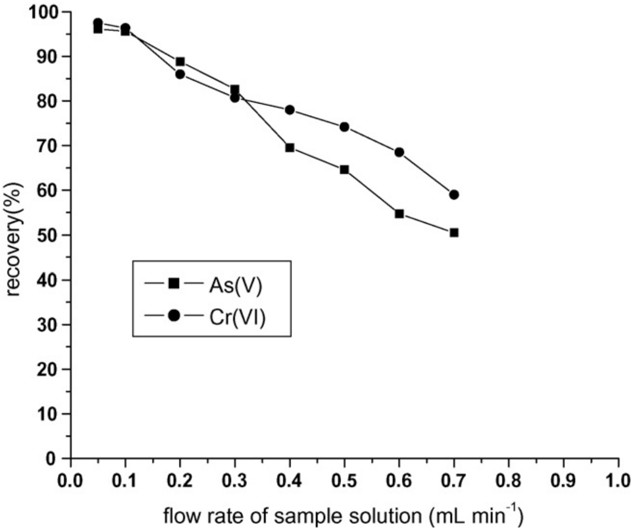

Fig. 2. Effect of sample flow rate on recovery of different inorganic arsenic and chromium species. Sample volume: 0.5 mL; As(V), As(III), Cr(VI) and Cr(III) concentration: 20 ng mL^{-1}; eluent: 0.1 mL of 0.01 mol l^{-1} NaOH at flow rate of 0.1 mL min^{-1}.

0.5 mL of sample solution through the capillary with the sample flow rates ranging in 0.05–0.7 mL min^{-1}. As shown in Fig. 2, quantitative recoveries of As(V) and Cr(VI) (>90%) were obtained at flow rates less than 0.1 mL min^{-1}. However, the recoveries of these species would decrease with the further increasing flow rate beyond 0.1 mL min^{-1}, due to decrease in the adsorption kinetics at a high flow rate. Thus, a flow rate of 0.1 mL min^{-1} was employed in this work.

3.3. Elution effect

From the evidence given by Fig. 1, As(V) and Cr(VI) were not retained on the ordered mesoporous alumina coated capillary in basic condition (pH >8), hence, NaOH was used as eluent reagent to elute the retained As(V) and Cr(VI) on the coated capillary. The effect of eluent concentration on the recovery of the analytes was evaluated. The results given in Table 2 indicated that the retained species could be eluted quantitatively with the concentration of NaOH higher than 0.01 mol L^{-1}.

The effect of eluent flow rate and volume was also explored in this study with the concentration of eluent reagent NaOH fixing at 0.01 mol L^{-1}. For study the effect of the elution volume, six aliquot of 0.05 mL (c = 0.01 mol L^{-1}) NaOH were used as eluent to continuously elute the analytes adsorbed on the capillary, and the analytes in the six effluents (each 0.05 mL) were determined by ICP-MS. The experimental results in Fig. 3 demonstrated that the analytes could be eluted quantitatively after second 0.05 mL elution (corresponding to a total elution volume of 0.1 mL). Finally, 0.1 mL of 0.01 mol L^{-1} NaOH with the flow rate of 0.1 mL min^{-1} was sufficient for quantitative elution.

Table 2
Recoveries (%, average ± S.D., n = 3) with different concentration of NaOH elution

Eluent (NaOH, mol L^{-1})	Cr(VI)	As(V)
0.0005	88.4 ± 3.1	76.5 ± 2.9
0.001	95.2 ± 2.2	72.8 ± 3.0
0.005	93.4 ± 2.3	88.9 ± 1.9
0.01	96.8 ± 1.8	93.6 ± 1.7
0.02	92.9 ± 2.0	94.4 ± 1.9

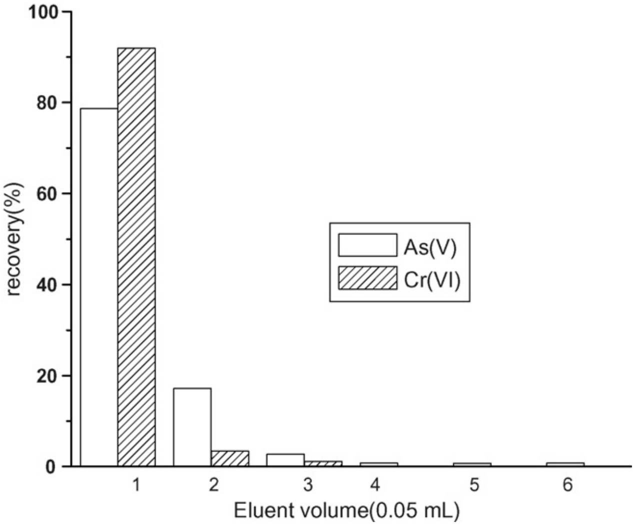

Fig. 3. Effect of eluent volume on recovery of different inorganic arsenic and chromium species. Sample volume: 0.5 mL; sample flow rate: 0.1 mL min^{-1}; As(V), As(III), Cr(VI) and Cr(III) concentration: 20 ng mL^{-1}; eluent: 0.01 mol l^{-1} NaOH at flow rate of 0.1 mL min^{-1}; 1–6 stand for continuous elution with 0.05 mL of 0.01 mol l^{-1} NaOH.

3.4. Effect of sample volume

The sensitivity of the procedure when determining very low concentration of analytes was investigated. For this purpose, various volumes of sample containing 1 ng of target analytes were passed through the capillary under the selected conditions. As shown in Fig. 4, quantitative recoveries were obtained for

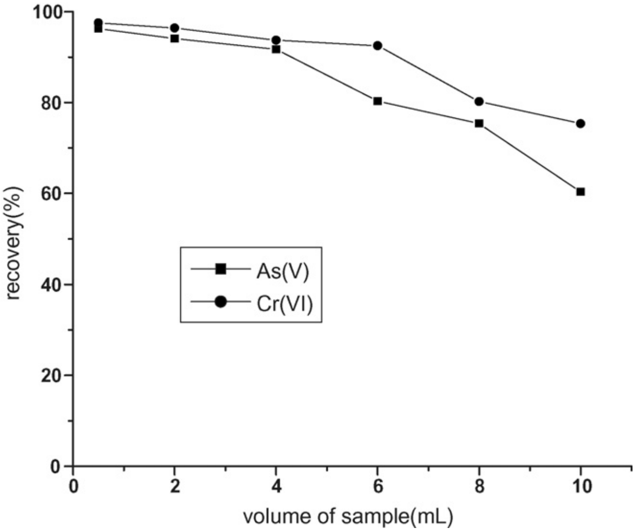

Fig. 4. Effect of sample volume on the recovery of different inorganic arsenic and chromium species (1 ng). Sample flow rate: 0.1 mL min^{-1}; As(V), As(III), Cr(VI) and Cr(III) concentration: 20 ng mL^{-1}; eluent: 0.1 mL of 0.01 mol l^{-1} NaOH at flow rate of 0.1 mL min^{-1}.

Table 3
Tolerant fold of coexisting ions to the studied species with the concentration of 20 ng mL^{-1}

Coexisting	Tolerance times	Recovery (%, average ± S.D., $n = 3$)			
		As(V)	As(III)	Cr(VI)	Cr(III)
K^+, Na^+	10000	96.6 ± 2.2	97.8 ± 1.9	97.3 ± 2.0	95.1 ± 1.6
Mg^{2+} Ca^{2+}	5000	97.4 ± 1.7	96.0 ± 2.0	96.6 ± 1.7	94.8 ± 1.5
Fe^{3+}	100	94.7 ± 1.6	97.3 ± 1.1	94.8 ± 2.3	95.4 ± 2.0
$SiO_4{}^{2-}$, $SO_4{}^{2-}$, $PO_4{}^{3-}$	2000	95.7 ± 2.0	96.3 ± 2.2	95.7 ± 1.8	96.1 ± 2.3
Cl^-	3000	95.1 ± 2.4	96.4 ± 1.9	95.2 ± 2.3	94.8 ± 1.8

sample volumes less than 4 mL for As(V) and 6 mL for Cr(VI) with 0.1 mL 0.01 mol L^{-1} NaOH elution. Thus the enrichment factor of 40 and 60 could be achieved for As(V) and Cr(VI), respectively. To trade off the enrichment factor and analytical speed, 0.5 mL sample volume and 0.1 mL eluent were used for real sample analysis; therefore, an enrichment factor of 5 was obtained with a sampling frequency of 8 h^{-1}.

3.5. Stability/interconversion of inorganic arsenic and chromium during the analysis

Meanwhile, the stability/interconversion of inorganic arsenic and chromium species was also explored during the extraction and desorption process in our experiment. In this work, no interconversion of As(III)/As(V) and Cr(III)/Cr(VI) was observed. Under the optimized conditions of extraction (pH 4, 0.01 mol/L NaOH), the analytes can be kept stable within 2 days.

3.6. Effects of co-existing ions

The effect of some coexisting ions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, $SiO_4{}^{2-}$, $SO_4{}^{2-}$, $PO_4{}^{3-}$ and Cl^- on the speciation of the studied analytes was investigated. In the study, an aqueous solution (0.5 mL) containing 20 ng of As(V) and Cr(VI) and 100–10,000 folds of other ions was taken and operated according to the proposed procedure. The results in Table 3 revealed that in the presence of these interfering ions, the recoveries of analytes were still above 90%. From the experiment results obtained, it could be concluded that the Al_2O_3 coating material had a good selectivity towards As(V) and Cr(VI) under optimized conditions.

Table 4
Adsorption rate (%, average ± S.D., $n = 3$) of As(V) and Cr(VI) in ordered mesoporous alumina capillary column with times of use

Times	Cr(VI)	As(V)
1	94.8 ± 2.8	97.6 ± 1.7
10	90.3 ± 3.5	94.2 ± 2.5
20	97.6 ± 3.1	92.1 ± 2.3
30	92.0 ± 2.8	95.2 ± 3.0

3.7. Analytical performance

The capillary regeneration is another important factor in evaluating the adsorption material. The Al_2O_3 coated capillary could be re-used for more than 30 times under the optimized conditions while the recovery was kept above 90% as shown in Table 4.

According to the IUPAC definition, the limits of detection were calculated as the concentration of an analyte yielding a signal equivalent to three times of the standard deviation of the blank value ($n = 7$). The detection limits (3σ) of the method were 0.7 and 18 ng L^{-1} for As(V) and Cr(VI), and 3.4 and 74 ng L^{-1} for As(III) and Cr(III), respectively, with an enrichment factor of 5. The relative standard deviations (R.S.D.) were 3.1, 4.0, 2.8

Table 5
Analytical results of As(V), As(III), Cr(VI) and Cr(III) in natural waters (average ± S.D., $n = 3$)

Sample	Species	Contents (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Mineral water	As(V)	n.d.	2.0	1.94 ± 0.04	97 ± 2
	As(III)	n.d.	2.0	2.04 ± 0.10	102 ± 5
	Cr(VI)	n.d.	2.0	1.91 ± 0.04	96 ± 2
	Cr(III)	n.d.	2.0	1.88 ± 0.07	94 ± 4
Tap water	As(V)	1.20 ± 0.04	2.0	3.15 ± 0.07	99 ± 2
	As(III)	0.89 ± 0.06	2.0	3.0 ± 0.10	102 ± 3
	Cr(VI)	n.d.	2.0	1.94 ± 0.05	97 ± 3
	Cr(III)	2.86 ± 0.07	2.0	4.92 ± 0.08	101 ± 2
Lake water	As(V)	2.84 ± 0.09	2.0	4.65 ± 0.14	100 ± 3
	As(III)	1.22 ± 0.07	2.0	3.37 ± 0.06	105 ± 2
	Cr(VI)	1.75 ± 0.04	2.0	3.64 ± 0.09	97 ± 2
	Cr(III)	0.84 ± 0.12	2.0	2.75 ± 0.11	96 ± 4

Table 6
Analytical results of As(V), As(III), Cr(VI) and Cr(III) in certified materials of GSBZ50027-94 water and GSBZ50004-88 water (average ± S.D., $n = 3$)

Sample	Element	Certified (ng mL^{-1})	Determined (ng mL^{-1})	*t*-test[a]
GSB Z50004-88	Total As	47.9 ± 2.5	49.2 ± 3.2	0.6
	As(V)	–	45.7 ± 3.0	
	As(III)	–	3.5 ± 0.2	
GBS Z50027-94	Cr(VI)	0.299 ± 0.011	0.294 ± 0.020	0.38

[a] $t_{0.05,2} = 4.30$.

and 3.9% ($C = 1$ ng mL^{-1}, $n = 7$) for As(V), As(III), Cr(VI) and Cr(III), respectively.

3.8. Sample analysis

The proposed method was applied to the determination of As(V), As(III), Cr(VI) and Cr(III) in mineral water (purchased in local supermarket), tap water (Wuhan, China) and lake water (East Lake, Wuhan, China, which was filtered through a 0.45 μm membrane filter), and the analytical results along with the recoveries for the spiked samples were given in Table 5. As could be seen, the recoveries for different inorganic species of arsenic and chromium were 94–105%. It should be noted that the mineral water sample analyzed in this work is a kind of drinking water purchased from local supermarket. Maybe this was why the chromium and arsenic could not be detected in such drinking mineral water.

In order to establish the validity of the proposed procedure, the method had been applied to the determination of As(V), As(III), Cr(VI) and Cr(III) in certified reference materials of GSBZ50027-94 and GSBZ50004-88 water samples and the results were given in Table 6. Applying the *t*-test, the $t_{0.05,2}$ values for both certified reference materials of GSBZ50027-94 and GSBZ50004-88 were calculated (Table 6). As could be seen, there did not exist statistical differences between determined value and certified ones, which means that the determined values obtained by the proposed method coincided very well with the certified values.

4. Conclusion

In the present paper, a novel method using capillary microextraction (CME) on line coupled with ICP-MS, utilizing ordered mesoporous Al_2O_3 as the coating material has been proposed for simultaneous separation and speciation of inorganic As (III)/As (V) and Cr (III)/Cr (VI) in natural waters. The speciation scheme is based on electrostatic action between the Al_2O_3 coating material and the retained analytes (As(V) and Cr(VI)). The ordered mesoporous structure and chemical bonding to the inner walls of the capillary are favorable to the high extraction efficiency and the high chemistry stability. This extraction approach of CME is made possible by the extremely low detection limits associated with ICP-MS. The data presented in our study have demonstrated the capability and advantages of the automated sequential continuous flow extraction system of CME–ICP-MS for determination of As(III)/As(V) and Cr(III)/Cr(VI) in natural waters. In addition, CME is simple, efficient and integrated in sample extraction, preconcentration and introduction. It is expected that developing new CME coating materials will extend its application in ultratrace elements and their species analysis in various samples with complicated matrix.

Acknowledgments

Financial supports from the Science Fund for Creative Research Groups of NSFC (no. 20621502), National Nature Science Foundation of China (grant no. 20575048) and NCET-04-0658, MOE of China are gratefully acknowledged.

References

[1] D.J. Thomas, M. Styblo, S. Lin, The cellular metabolism and systemic toxicity of arsenic, Toxicol. Appl. Pharmacol. 176 (2001) 127–144.

[2] J. Yanez, V. Fierro, H. Mansilla, L. Figueroa, L. Cornejo, R.M. Barnes, Arsenic speciation in human hair: a new perspective for epidemiological assessment in chronic arsenicism, J. Environ. Monit. 7 (2005) 1335–1341.

[3] E. Terlecka, Arsenic speciation analysis in water samples: A review of the hyphenated techniques, Environ. Monit. Assess. 107 (2005) 259–284.

[4] S. Scaccia, S. Frangini, Sensitive assay for oxygen solubility in molten alkali metal carbonates by indirect flame atomic absorption spectrometric Cr(VI) determination, Talanta 64 (2004) 791–797.

[5] H. Gurleyuk, D. Wallschlager, Determination of chromium(III) and chromium(VI) using suppressed ion chromatography inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 16 (2001) 926–930.

[6] M.T. Siles Cordero, E.I.V. Alonso, A.G. Torres, J.M.C. Pavon, Development of a new system for the speciation of chromium in natural waters and human urine samples by combining ion exchange and ETA-AAS, J. Anal. At. Spectrom. 19 (2004) 398–403.

[7] S. Hirata, H. Toshimitsu, Determination of arsenic species and arsenosugars in marine samples by HPLC–ICP-MS, Anal. Bioanal. Chem. 383 (2005) 454–460.

[8] D. Kremer, G. Ilgen, J. Feldmann, GC-ICP-MS determination of dimethylselenide in human breath after ingestion of Se-77-enriched selenite: monitoring of in-vivo methylation of selenium, Anal. Bioanal. Chem. 383 (2005) 509–515.

[9] K. Tirez, W. Brusten, A. Cluyts, J. Patyn, N. De Brucker, Determination of hexavalent chromium by species specific isotope dilution mass spectrometry and ion chromatography 1,5-diphenylcarbazide spectrophotometry, J. Anal. At. Spectrom. 18 (2003) 922–932.

[10] Q.J. Song, G.M. Greenway, T. McCreedy, Interfacing microchip capillary electrophoresis with inductively coupled plasma mass spectrometry for chromium speciation, J. Anal. At. Spectrom. 18 (2003) 1–3.

[11] M. Yaman, G. Kaya, Speciation of iron(II) and (III) by using solvent extraction and flame atomic absorption spectrometry, Anal. Chim. Acta 540 (2005) 77–81.

[12] C.H. Yu, Q.T. Cai, Z.X. Guo, Z.G. Yang, S.B. Khoo, Simultaneous speciation of inorganic selenium and tellurium by inductively coupled plasma mass spectrometry following selective solid-phase extraction separation, J. Anal. At. Spectrom. 19 (2004) 410–413.

[13] R. Murata, T. Shimizu, N. Uehara, Speciation arsenic(III) and arsenic(V) in natural water by graphite furnace AAS after coprecipitation with a copper–pyrrolidinedithiocarbamate complex, Bunseki Kagaku 54 (2005) 831–836.

[14] J.H. Pei, M.L. Tercier-Waeber, J. Buffle, Simultaneous determination and speciation of zinc, cadmium, lead, and copper in natural water with minimum handling and artifacts by voltammetry on a gel-integrated microelectrode array, Anal. Chem. 72 (2000) 161–171.

[15] C. Dietz, J.S. Landaluze, P.X. Embun, Y. Madrid-Albarran, C. Camara, SPME-multicapillary GC coupled to different detection systems and applied to volatile organo-selenium speciation in yeast, J. Anal. At. Spectrom. 19 (2004) 260–266.

[16] X.M. Yu, J. Pawliszyn, Speciation of alkyllead and inorganic lead by derivatization with deuterium-labeled sodium tetraethylborate and SPME-GC/MS, Anal. Chem. 72 (2000) 1788–1792.

[17] C. Dietz, T. Perez-Corona, Y. Madrid-Albarran, C. Camara, SPME for on-line volatile organo-selenium speciation, J. Anal. At. Spectrom. 18 (2003) 467–473.

[18] P. Jitaru, H.G. Infante, F.C. Adams, Simultaneous multi-elemental speciation analysis of organometallic compounds by solid-phase microextraction and multicapillary gas chromatography hyphenated to inductively coupled plasma-time-of-flight-mass spectrometry, J. Anal. At. Spectrom. 19 (2004) 867–875.

[19] R. Eisert, J. Pawliszyn, Automated in-tube solid phase microextraction coupled to high-performance liquid chromatography, Anal. Chem. 69 (1997) 3140–3147.

[20] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Sol–gel capillary microextraction, Anal. Chem. 74 (2002) 752–761.

[21] H. Kataoka, Automated sample preparation using in-tube solid-phase microextraction and its application, a review, Anal. Bioanal. Chem. 373 (2002) 31–45.

[22] H. Kataoka, S. Narimatsu, H.L. Lord, J. Pawliszyn, Automated in-tube solid-phase microextraction coupled with liquid chromatography/electrospray ionization mass spectrometry for the determination of β-blockers and metabolites in riune and serum samples, Anal. Chem. 71 (1999) 4237–4244.

[23] H.W. Wang, W.M. Liu, Y.F. Guan, In-tube solid-phase microextraction and on-line coupling with high-resolution GC, LC–GC (North America) 22 (2004), 16-+.

[24] A.K. Malik, M. Gomez, C. Camara, H.G. Riepe, J. Bettmer, On-line chloride interference removal for arsenic determination in waste water and urine by ICP-MS using a modified capillary, Int. J. Environ. Anal. Chem. 82 (2002) 795–804.

[25] Z. Mester, J. Pawliszyn, Electrospray mass spectrometry of trimethyllead and triethyllead with in-tube solid phase microextraction sample introduction, Rapid Commun. Mass Spectrom. 13 (1999) 1999–2003.

[26] J.C. Wu, Z. Mester, J. Pawliszyn, Speciation of organoarsenic compounds by polypyrrole- coated capillary in-tube solid phase microextraction coupled with liquid chromatography/electrospray ionization mass spectrometry, Anal. Chim. Acta 424 (2000) 211–222.

[27] R. Garcia-Sanchea, R. Feldhaus, J. Bettmer, L. Ebdon, Lead speciation in rainwater by modified fused silica capillary coupled to a direct injection nebulizer for sample introduction in ICP-MS, J. Anal. At. Spectrom. 16 (2001) 1028–1034.

[28] W.L. Hu, B. Hu, Z.C. Jiang, On-line preconcentration and separation of Co, Ni and Cd via capillary microextraction on ordered mesoporous alumina coating and determination by ICP-MS, Anal. Chim. Acta 572 (2006) 55–62.