Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1081 (2005) 232–237
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Speciation analysis of inorganic arsenic by microchip capillary electrophoresis coupled with hydride generation atomic fluorescence spectrometry

Feng Li [a], Dong-Dong Wang [a], Xiu-Ping Yan [a,*], Rong-Guo Su [b], Jin-Ming Lin [b,*]

[a] *Research Center for Analytical Sciences, College of Chemistry, Nankai University, 94 Weijin Road, Tianjin 300071, China*
[b] *Research Center for Eco-Environmental Sciences, Academic Sinica, P.O. Box 2871, Beijing, China*

Received 21 January 2005; received in revised form 29 April 2005; accepted 17 May 2005
Available online 13 June 2005

Abstract

A novel method for speciation analysis of inorganic arsenic was developed by on-line hyphenating microchip capillary electrophoresis (chip-CE) with hydride generation atomic fluorescence spectrometry (HG-AFS). Baseline separation of As(III) and As(V) was achieved within 54 s by the chip-CE in a 90 mm long channel at 2500 V using a mixture of 25 mmol l^{-1} H_3BO_3 and 0.4 mmol l^{-1} CTAB (pH 8.9) as electrolyte buffer. The precisions (RSD, $n = 5$) ranged from 1.9 to 1.4% for migration time, 2.1 to 2.7% for peak area, and 1.8 to 2.3% for peak height for the two arsenic species at 3.0 mg l^{-1} (as As) level. The detection limits (3σ) for As(III) and As(V) based on peak height measurement were 76 and 112 μg l^{-1} (as As), respectively. The recoveries of the spikes (1 mg l^{-1} (as As) of As(III) and As(V)) in four locally collected water samples ranged from 93.7 to 106%.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Speciation; Arsenic; Atomic fluorescence spectrometry; Microchip capillary electrophoresis; Miniaturization

1. Introduction

Arsenic is a ubiquitous trace element and it may be found in the atmosphere, water, food and in the soil. Many arsenic compounds are known to be highly toxic. Exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects [1]. However, the toxicity of arsenic depends strongly on its chemical forms [2]. The inorganic compounds are far more toxic than their organic metabolites [2]. Therefore, the speciation of arsenic is important for understanding both the biological and the geochemical behaviour of this element [1–5].

The methodologies currently used for arsenic speciation mainly involve a separation technique, capillary electrophoresis (CE) [6–12] or high performance liquid chromatography (HPLC) [5,13–23], coupled with a highly sensitive element-specific detector, such as atomic absorption spectrometry (AAS) [13–15], atomic fluorescence spectrometry (AFS) [9,10,16–19], inductively coupled plasma mass spectrometry (ICP-MS) [5–8,20–23]. Microfluidic chip technology has been undergoing rapid development in recent years. It can offer many attractive advantages, including short analysis time, minimal sample/reagent consumption, portability, and eventually reduced cost [24–26]. Little work on speciation analysis with chip-CE, however, has been previously reported [27–29]. Chip-CE with conductivity [27] and ICP-MS detection [28,29] has been employed for the determination of inorganic arsenic species. Integrated detection in chip-CE with conductivity electrodes for speciation analysis, however, possesses poor detection limits. Sensitive and element-specific detection techniques for chip-CE speciation would provide improved performance for this application. Chip-CE coupled with ICP-MS is becoming of growing importance in speciation analysis,

* Corresponding authors. Fax: +86 22 2350 6075.
E-mail address: xpyan@nankai.edu.cn (X.-P. Yan).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.05.037

and two excellent papers on this hyphenated technique for speciation have been published [28,29]. Although highly sensitive, element- and isotope-specific characteristic of ICP-MS makes it very attractive as an on-line detector for chip-CE, the high instrumental and running costs of the ICP-MS instrument as well as the strict requirement that the analyst be well-trained set a serious limitation on the wide application of such a hyphenated technique.

Hydride generation atomic fluorescence spectrometry (HG-AFS) has been shown to offer similar sensitivity to ICP-MS for hydride-forming elements [30]. Compared with ICP-MS, AFS also presents the advantages of much lower instrument and running costs, shorter warm-up times prior to analysis, and easy handling [30]. The use of HG-AFS as an on-line detector of chip-CE is expected to be attractive for the speciation analysis of arsenic compounds owing to the low cost, easy operation, high selectivity, and sensitivity.

The objective of this work was to evaluate a new hybrid technique, chip-CE coupled with HG-AFS [31] for rapid speciation analysis of inorganic arsenic. The optimization of the chip-CE system for the separation of inorganic arsenic species, the conditions for hydride generation, and analytical performance of the developed CE–HG-AFS technique for the speciation of inorganic arsenic were described and discussed.

2. Experimental

2.1. The chip-CE–AFS system [31]

Fig. 1 shows the schematic setup of the chip-CE–AFS system, which includes a microchip, a homemade interface and AFS. The borosilicate glass microchip was fabricated through standard photolithography, wet chemical etching, and heat bonding technology. Reservoir 1, 2, and 3 were solution container and reservoir 4 was designed as the inlet for the makeup solution (20%, v/v HCl), which met the sample from separation channel at junction 6 and carried the sample through the chip exit port 7 to the chip-CE–HG-AFS interface. Reservoir 4 was epoxy sealed with a silicone pad, into which a Teflon tube and a platinum electrode were inserted for the makeup solution and electrical contact, respectively. The double tee injection cross was 200 μm long. A concentric "tube-in-tube" interface was adopted to couple the chip to the AFS (see Section 3.2).

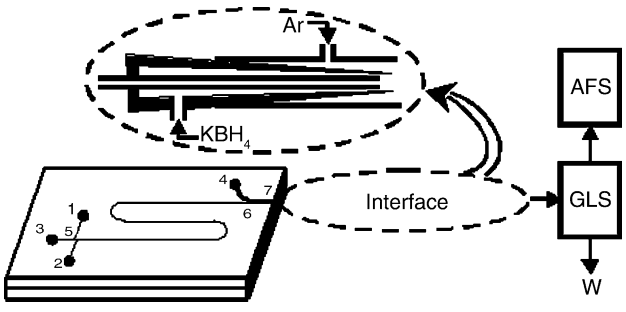

Fig. 1. Schematic diagram of the chip-CE–AFS system (not to scale): 1, sample reservoir; 2, sample waste reservoir; 3, buffer reservoir; 4, makeup solution reservoir; 5, injection cross; 6, junction of separation channel and makeup solution channel; 7, chip exit port; The length of channels 1–5, 2–5, 3–5: 10 mm, 5–6: 90 mm, 6–7: 5 mm. The dimension of channels 1–5, 2–5, 3–5, 5–6: 39 μm deep and 118 μm wide, 4–7: 350 μm deep and 900 μm wide.

2.2. Instrumentation

A model XCDY high-voltage power supply (Shandong Chemical Engineering Institute, Jinan, China) and a Model XGY-1011A nondispersive atomic fluorescence spectrometer (Institute of Geophysical and Geochemical Exploration, Langfang, China) were employed throughout. A high-intensity arsenic hollow cathode lamp (Ningqiang Light Sources, Hengshui, China) was used as radiation source. A laboratory-made gas-liquid separator (GLS) as described in a previous work [9] was used to isolate the gas from liquid. A quartz tube (4 mm i.d. × 14 cm) was used as atomizer, into which the volatile species and the hydrogen evolved from the reactor were swept by an argon flow. The argon flow was controlled by a rotameter. The gas mixture is self-ignited at the outlet of the furnace, and a hydrogen-argon-air entrained flame is maintained without the addition of any auxiliary hydrogen. A Chromatographic Workstation (Nanjing Qianpu Software Co. Ltd., Nanjing, China) was used for data acquisition and data treatment.

2.3. Chemicals

All of the reagents employed were at least of analytical grade. Doubly deionized water (DDW, 18.2 MΩ cm^{-1}) obtained from a WaterPro water purification system (Labconco Corporation, Kansas City, MO, USA) was used throughout. A standard stock As(III) solution of 1000 mg l^{-1} (as As) was prepared by dissolving arsenic trioxide (As_2O_3, Beijing Chemicals, Beijing, China) in dilute NaOH and neutralizing with dilute HCl solution. The As(V) stock solution of 1000 mg l^{-1} (as As) was prepared by dissolving $Na_2HAsO_4{\cdot}7H_2O$ (Beijing Chemicals) in DDW directly. The stock solutions were stored at 4 °C. Working standard solutions and their mixtures were prepared daily by step-wise diluting the stock solutions just before use.

Boric acid (H_3BO_3, Beijing Chemicals Co., Beijing, China) and cetyltrimethylammonium bromide (CTAB, Shanghai Chemicals Co., Shanghai, China) were used to prepare the electrolyte buffer solution. The pH of the buffer solution was adjusted with 0.5 mol l^{-1} NaOH (Tianjin Taixing Chemicals). The buffer was filtered through a 0.45 μm filter prior to use.

A 3.0% (m/v) KBH_4 solution was prepared by dissolving KBH_4 (Tianjin Institute of Chemical Reagents, Tianjin,

China) in 0.2% (m/v) KOH (Beijing Chemicals) solution as the reductant. A 20% (v/v) solution of HCl (Tianjin Taixing Chemicals) was used as the carrier of the chip-CE effluent and also as the medium of subsequent hydride generation.

River water and lake water samples were collected locally. Immediately after sampling, the samples were filtered through 0.45 μm Supor filters (Gelman Sciences) and analysed.

2.4. Electrophoresis conditions

The electrophoresis buffer consisted of 25 mmol l^{-1} boric acid and 0.4 mmol l^{-1} CTAB (pH 8.9). The channels were dynamically coated with the cationic surfactant CTAB to reverse the EOF. Before separation, the channels were flushed with 0.1 mol l^{-1} NaOH for 30 min, with DDW for 10 min and finally with the buffer for 40 min. No recondition was necessary between runs.

Injection was performed by electrokinetic injection for 40 s. One thousand volts was applied to the sample waste reservoir and 200 V was applied to the buffer reservoir, with the sample reservoir grounded and the makeup solution reservoir floated. To fill the intersection of the channel with the sample solution, sufficient time (>30 s) is required [32]. For chip-CE separation, 2500 V was applied to the makeup solution reservoir whereas the buffer reservoir grounded. Meanwhile, 750 V (30% of the separation voltage, pull back voltage) was applied to both the sample and waste reservoirs to avoid the leakage of analytes from the sample channel to the separation channel. The experimental conditions for the chip-CE and HG-AFS are summarized in Table 1.

Table 1
Operating parameters of chip-CE and HG-AFS

Parameter	Setting
Microchip capillary electrophoresis	
Separation length	90 mm
Electrolyte buffer	25 mmol l^{-1} H_3BO_3 + 0.4 mmol l^{-1} CTAB (pH 8.9)
Injection voltage	Reservoir 1, 2, 3, 4: 0 V, 1000 V, 200 V, floated
Injection time	40 s
Separation voltage	Reservoir 1, 2, 3, 4: 750 V, 750 V, 0 V, 2500 V
Atomic fluorescence spectrometer	
Arsenic hollow cathode lamp	60 mA (primary current) 60 mA (boost current)
Quartz furnace temperature	200 °C
Quartz furnace height	6 mm
Negative high voltage of photomultiplier	−280 V
Hydride generation system	
Flow rate of 20% (v/v) HCl	0.5 ml min^{-1}
Flow rate of 3.0% (m/v) KBH_4	1.0 ml min^{-1}
Carrier gas (argon) flow rate	190 ml min^{-1}

3. Results and discussion

3.1. Design of the microchip

To overcome the flow incompatibility between the chip-CE and the HG-AFS, a makeup solution was needed to facilitate the sample transportation. Makeup solution has been widely used in the chip-MS, in which the makeup solution channel is usually a straight line, forming a sharp angle at the junction with the separation channel [33,34]. This chip design can satisfy the needs of the chip-MS system, but cannot be directly adopted in the chip-AFS system. In the chip-MS system, the makeup solution can be steered to the expected direction under high-voltage's control, while in the chip-AFS system, the makeup solution was delivered with the peristaltic pump and a backpressure at the junction with the separation channel would be produced. For this reason, another type of makeup solution channel, one quarter of a circle (5.0 mm diameter) was directly etched on the chip and the makeup solution channel was tangent to the separation channel, so that the flow of the makeup solution was in the same direction as that of the EOF in the separation channel and the hydrodynamic effect of the makeup solution flow on the EOF was decreased. The channel dimension between junctions 6 and 7 was purposely enlarged to have significantly lower resistance to flow than the separation channel and also to reduce the negative effect of makeup solution on EOF.

3.2. Consideration of the chip-CE–AFS interface

The efficiency of the chip-CE separation should not be impaired by the interface. The sample must be transported to the detector as efficiently as possible in a form that can be read by the AFS. As can be seen in Fig. 1, a concentric "tube-in-tube" design was employed to couple the chip-based separation system with the AFS [31]. A 100 μL of Eppendorf pipette (intermediate tube) was cut into an appropriate length (25 mm), into which a piece of Teflon tubing (i.d. 0.5 mm, inner tube) was inserted. One end of the Teflon tubing was inserted into the chip exit port 7, which was manually enlarged to accommodate the Teflon tubing, and epoxy-sealed on the side wall of the chip. The big end of the pipette was plugged with an appropriate silicone gasket, into which the other end of the Teflon tubing was inserted until the end of the Teflon tubing reached a position approximately 0.1–0.2 mm to the small end of the pipette. The small end of the pipette was inserted into a thicker wall silicone tube (outer tube) tightly. Two holes were opened at appropriate places on the walls of the intermediate tube and the outer tube to introduce the KBH_4 solution and argon flow into the interface, respectively. The chip effluent (the mixture of separation channel effluent and the makeup solution HCl) merged with KBH_4 solution at the exit of the inner tube. The reaction mixture was swept by an argon flow into the GLS, where the volatile arsenic species were separated from the

mixture and detected by the AFS. A 20% (v/v) solution of HCl and 3.0% (m/v) KBH_4 were supplied separately by the two peristaltic pumps of a model FIA-3100 flow injection analyser (Vital Instrumental Co. Ltd., Beijing, China). Obviously, the KBH_4 solution and argon flow forced the chip effluent into the GLS, so the effect of the backpressure due to hydrodynamic effect on the separation was minimized.

The position of the outlet of the inner tube was found to be critical for the chip-CE–AFS interface. When the outlet of the inner tube was placed beyond the intermediate tube, poor peak shape and repeatability were observed. The optimum position of the outlet of the inner tube located just 0.1–0.2 mm inside of the intermediate tube. In this place, the effluent from the inner tube can react with the KBH_4 efficiently and the generated hydrogen is easy to release forward.

The hydrostatic pressure resulting from the elevation difference between the liquid surface in the reservoirs and the chip exit would also exert an effect on the separation. The liquid surface in the reservoirs was higher (∼3 mm) than that in the chip exit, so that the sample had a potential to flow to the chip exit even when there was no electrical field. This hydrostatic pressure would shorten the analysis time, but might impair the separation efficiency. To offset the effect of the hydrostatic pressure, the elevation of the GLS was adjusted to where the liquid surface in the sidearm of the GLS was level with that in the reservoirs. Compared with other chip-based system [28,29], the reservoirs in this work were not made airtight so that the liquid surface was easy to adjust, and this was vital for good repeatability.

3.3. Factors affecting chip-CE separation

The migrations of ions in chip-CE generally occur under the combined action of electrophoretic and electroosmotic flow. Applying positive high voltage on the buffer reservoir 3, EOF is oriented toward the makeup solution reservoir 4, while the electrophoretic mobility of the anions, such as As(III) and As(V), is in opposite direction. If the magnitude of the EOF is higher than electrophoretic mobilities, arsenic species will consequently move towards the makeup solution reservoir 4. This is usually the case for As(III). However, As(V) was not detected at all even under high EOF conditions because of its high electrophoretic mobility. Thus, it is necessary to suppress or reverse the direction of EOF.

It is well known that some surfactants could reverse the EOF [35,36]. So, a cationic surfactant, CTAB was added into the electrolyte buffer to modify the channels surface, which led to the appearance of the positive fixed charges and reversed EOF. Separation of As(III) and As(V) was achieved by reversing the polarity of the electric field in this system.

The effect of the concentration of CTAB on the separation was examined in the concentration range from 0.2 to 0.8 mmol l^{-1}. It was shown that no apparent difference was observed on the separation with the variety of CTAB concentration. In this work, 0.4 mmol l^{-1} CTAB was included in the buffer solution.

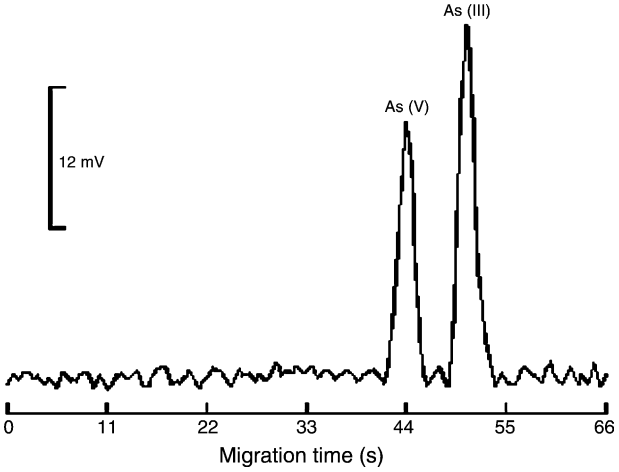

Fig. 2. Electropherogram of 3.0 mg l^{-1} (as As) As(V) and As(III). All other conditions as shown in Table 1.

The pH of the electrolyte buffer is one of the keys controlling chip-CE separation. It influences the separation characteristic by affecting the electrophoretic mobility of the arsenic anions as well as the EOF. A pH range of 8.2–9.8 for the buffer solution (25 mmol l^{-1} H_3BO_3 and 0.4 mmol l^{-1} CTAB) was investigated. It was found that As(III) and As(V) could be baseline separated in a pH range of 8.7–9.5, while best separation efficiency was achieved at a pH of 8.9.

The effect of the concentration of boric acid on the separation was tested in the concentration range of 10–40 mmol l^{-1} with 0.4 mmol l^{-1} CTAB in the buffer solution (pH 8.9). Over the concentration range, the two arsenic species were baseline separated. But the migration time of each individual species increased with increase of the buffer concentration. In addition, the repeatability was somewhat poor at lower boric acid concentrations (<20 mmol l^{-1}). Therefore, a concentration of 25 mmol l^{-1} boric acid was used to ensure a reasonable electric current and good repeatability.

The influence of the applied voltage on the separation of As(III) and As(V) was investigated from 1000 to 4000 V. As expected, by increasing the applied voltage, the migration time and half-peak width dramatically decrease. Both species were baseline separated between 1500 and 3000 V. To ensure a good resolution, an applied voltage of 2500 V was chosen for the separation. A typical electropherogram under 2500 V is shown in Fig. 2.

3.4. Concentration and flow rate of the makeup liquid

Choice of a proper makeup liquid is important for the successful coupling of chip-CE to HG-AFS. A makeup liquid should be employed not only to complete the electrophoresis circuit and to facilitate the transportation of the chip-CE effluent, but also to provide a favorable medium for the ensuing hydride generation reaction. To this end, diluted HCl solution was employed as the makeup liquid.

The influence of HCl concentration on the signals of the two arsenic species was investigated at a flow rate of 0.5 ml min^{-1}. As HCl concentration increased from 5 to 20% (v/v), the signal intensities of the two arsenic species increased. Further increase in HCl concentration from 20 to 35% (v/v) resulted in a slight increase in the signal intensity of As(V) but a decline in the signal intensity of As(III). For further experiments, a 20% (v/v) HCl solution was employed as the makeup liquid.

The influence of the flow rate of the makeup solution on the response of As(III) was examined with 3.0% (m/v) KBH_4 at a flow rate of 1.0 ml min^{-1}. It was found that the argon-hydrogen flame was difficult to maintain below 0.2 ml min^{-1} of 20% (v/v) HCl. However, the signal intensity increased with increase in the flow rate of the HCl solution from 0.3 to 0.5 ml min^{-1} and then leveled off from 0.5 to 0.9 ml min^{-1}. In addition, no detrimental effect on the separation caused by the makeup solution flow was observed due to no variation in the migration time with the makeup solution flow in the range of 0.3–0.9 ml min^{-1}. These results could be understood in terms of atomization efficiency and dilution of the chip-CE effluent. Below a flow rate of 0.5 ml min^{-1}, atomization efficiency might dominate the signal intensity, whereas over the flow rate of 0.5 ml min^{-1}, the dilution of the chip-CE effluent probably controlled the signal. Accordingly, a flow rate of 0.5 ml min^{-1} was selected for the makeup solution.

3.5. Concentration and flow rate of KBH_4 solution

The KBH_4 solution acts not only as the reducing agent for the generation of volatile arsenic hydrides but also as the source of hydrogen for maintaining the argon–hydrogen flame to atomize the volatile arsenic species. The influence of KBH_4 concentration was investigated at a flow rate of 1.0 ml min^{-1}. KBH_4 concentrations below 1.3% (m/v) were found to be insufficient to maintain the flame. The responses of the two arsenic species increased up to 3.0% (m/v) KBH_4 and then decreased gradually with further increase in the concentration of KBH_4. Higher concentrations of KBH_4 (>3.0%, m/v) would cause serious effervescence and splashing of solution droplets on the GLS walls due to the fast reaction. As a result, water vapor or a mist of reagents might condense on the transfer line and consequently trap the volatile arsine, resulting in a decrease of the signal intensity. Low KBH_4 concentrations (<3.0%, m/v) probably gave incomplete reduction of the analyte or provided insufficient hydrogen to maintain the argon–hydrogen flame, leading to low signal intensity.

The influence of the flow rate of 3.0% (m/v) KBH_4 solution was investigated with the makeup solution of 20% (v/v) HCl at a flow rate of 0.5 ml min^{-1}. When the flow rate of 3.0% (m/v) KBH_4 solution was less than 0.5 ml min^{-1}, the argon–hydrogen flame was unstable and difficult to maintain. The signal intensity increased with increase in the flow rate of 3.0% (m/v) KBH_4 from 0.5 to 1.0 ml min^{-1} and then dropped rapidly from 1.0 to 1.8 ml min^{-1}. According to the above results, a 3.0% (m/v) KBH_4 solution at a flow rate of 1.0 ml min^{-1} was used for further work.

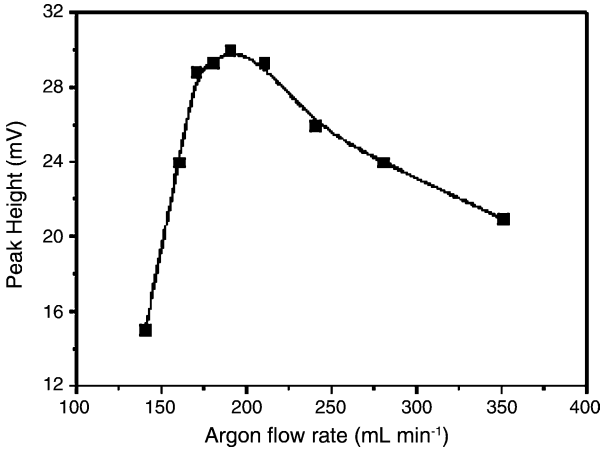

Fig. 3. Influence of argon flow rate on fluorescent intensities of arsenite (3.0 mg l^{-1} (as As)). All other conditions as shown in Table 1.

3.6. Argon flow rate

The flow rate of argon should be optimized because the argon was used not only to transfer the volatile arsine to the atomizer, but also to support the argon–hydrogen flame for the atomization of arsine. No suction effect on the separation due to the argon flow was observed because the migration time did not vary as the argon flow rate increased from 140 to 350 ml min^{-1}. As shown in Fig. 3, the optimal argon flow rate ranged from 170 to 210 ml min^{-1}. Lower signal intensity below the flow rate of 170 ml min^{-1} likely resulted from incomplete release of the volatile arsine from the reaction mixture, incomplete atomization, of both. At higher flow rates (>210 ml min^{-1}), the dilution of the evolved volatile species and short residue of the analyte species in the atomizer would be dominant, leading to the decrease of the signal intensities. Thus, an argon flow rate of 190 ml min^{-1} was used to maintain the maximum signal with good precision.

3.7. Figures of merit

The analytical figures of merit of the present chip-CE–HG-AFS technique for the speciation of inorganic arsenic are summarized in Table 2. One of the most significant advantages of the present chip-CE–HG-AFS hybrid technique is the remarkable reduction in separation time (54 s) for As(III) and As(V) in comparison with the HPLC- and conventional CE–HG-AFS techniques (usually >10 min) [9,16]. The detection limits (3σ) for As(III) and As(V) based on peak height measurement were 76 and 112 μg l^{-1} (as As), respectively. The detection limits of the developed chip-CE–HG-AFS system are lower than those obtained by a chip-CE with conductivity detection system [27] but higher than those obtained by a chip-CE–ICP-MS system [28]. The recoveries of the spikes (1.0 mg l^{-1} (as As) of As(III) and As(V)) from

Table 2
Characteristic performance date of the chip-CE–HG-AFS for arsenic speciation

	As(III)	As(V)
Precision[a] (RSD, $n = 5$) (%)		
Migration time	1.9	1.4
Peak area	2.1	2.7
Peak height	1.8	2.3
Detection limits ($\mu g\,l^{-1}$)	76	112
Calibration function[b]	$A = 9.79C + 0.67$	$A = 7.10C + 0.49$
Correlation coefficient	0.9990	0.9983
Recovery[c] (%)		
River water 1	103	94.9
River water 2	95.4	98.5
Lake water 1	106	101
Lake water 2	93.7	97.1

[a] For $3.0\,mg\,l^{-1}$ (as As) As(V) and As(III).
[b] A, peak height (mV); C, concentration ($mg\,l^{-1}$) (as As).
[c] Recovery for spiking with $1.0\,mg\,l^{-1}$ (as As) of each species.

the natural water samples ranged from 93.7 to 106%. To demonstrate the repeatability of the developed chip-CE–HG-AFS system for arsenic speciation, the electropherograms of the two arsenic species with five consecutive injections were recorded. The liquid surface in the reservoirs was adjusted about every two runs. No recondition of the channels was needed between runs. Excellent repeatability for $3.0\,mg\,l^{-1}$ (as As) As(V) and As(III) was obtained with the precisions (RSD, $n = 5$) of the migration time, peak area and peak height in the range of 1.9–1.4, 2.1–2.7, 1.8–2.3%, respectively.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 20475028, 20437020, 50273046), and Specialized Research Fund for the Doctoral Program of Higher Education (No. 20040055038).

References

[1] D.-Q. Hung, O. Nekrassova, R.G. Compton, Talanta 64 (2004) 269–277.
[2] R.M. Harrison, S. Rapsomanikis, Environmental Analysis Using Chromatography Interfaced with Atomic Spectroscopy, Wiley, Chichester, 1989.
[3] B.K. Mandal, K.T. Suzuki, Talanta 58 (2002) 201–235.
[4] K.A. Francesconi, D. Kuehnelt, Analyst 129 (2004) 373–395.
[5] C. B'Hymer, J.A. Caruso, J. Chromatogr. A 1045 (2004) 1–13.
[6] M.V. Holderbeke, Y.-N. Zhao, F. Vanhaecke, L. Moens, R. Dams, P. Sandra, J. Anal. At. Spectrom. 14 (1999) 229–234.
[7] Y. Liu, V. Lopez-Avila, J.J. Zhu, D.R. Wiederin, W.F. Beckert, Anal. Chem. 67 (1995) 2020–2025.
[8] C. Vandecasteele, K. Van den Broeck, V. Dutré, Waste Manage. 20 (2000) 211–216.
[9] X.-B. Yin, X.-P. Yan, Y. Jiang, X.-W. He, Anal. Chem. 74 (2002) 3720–3725.
[10] X.-B. Yin, Electrophoresis 25 (2004) 1837–1842.
[11] A.R. Timerbaev, Talanta 52 (2000) 573–606.
[12] E. Dabek-Zlotorzynska, E.P.C. Lai, A.R. Timerbaev, Anal. Chim. Acta 359 (1998) 1–26.
[13] M.C. Villa-Lojo, E. Alonso-Rodríguez, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, Talanta 57 (2002) 741–750.
[14] B.A. Manning, D.A. Martens, Environ. Sci. Technol. 31 (1997) 171–177.
[15] O. Munoz, D. Velez, M.L. Cervera, R. Montoro, J. Anal. At. Spectrom. 14 (1999) 1607–1613.
[16] N.M. Melo Coelho, C. Parrilla, M.L. Cervera, A. Pastor, M. de la Guardia, Anal. Chim. Acta 482 (2003) 73–80.
[17] B. He, Y. Fang, G.-B. Jiang, Z.-M. Ni, Spectrochim. Acta B 57 (2002) 1705–1711.
[18] Z. Šlejkovec, J.T. van Elteren, A.R. Byrne, Anal. Chim. Acta 358 (1998) 51–60.
[19] W.-H. Zhang, Y. Cai, K.R. Downum, L.Q. Ma, J. Chromatogr. A 1043 (2004) 249–254.
[20] K. Wrobel, K. Wrobel, B. Parker, S.S. Kannamkumarath, J.A. Caruso, Talanta 58 (2002) 899–907.
[21] K. Van den Broeck, C. Vandecasteele, J.M.C. Geuns, Anal. Chim. Acta 361 (1998) 101–111.
[22] H. Helgesen, E.H. Larsen, Analyst 123 (1998) 791–796.
[23] Q.-L. Xie, R. Kerrich, E. Irving, K. Liberb, F. Abou-Shakra, J. Anal. At. Spectrom. 17 (2002) 1037–1041.
[24] D.R. Reyes, D. Iossifidis, P.A. Auroux, A. Manz, Anal. Chem. 74 (2002) 2623–2636.
[25] P.A. Auroux, D. Iossifidis, D.R. Reyes, A. Manz, Anal. Chem. 74 (2002) 2637–2652.
[26] T. Vilkner, D. Janasek, A. Manz, Anal. Chem. 76 (2004) 3373–3386.
[27] J.E. Prest, S.J. Baldock, P.R. Fielden, N.J. Goddard, B.J. Treves Brown, J. Chromatogr. A 990 (2003) 325–334.
[28] Q.-J. Song, G.M. Greenway, T. McCreedy, J. Anal. At. Spectrom. 19 (2004) 883–887.
[29] Q.-J. Song, G.M. Greenway, T. McCreedy, J. Anal. At. Spectrom. 18 (2003) 1–3.
[30] J.L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, Talanta 51 (2000) 257–268.
[31] F. Li, D.-D. Wang, X.-P. Yan, J.-M. Lin, R.-G. Su, Electrophoresis 26 (2005) 2261.
[32] Y. Zeng, H. Chen, D.-W. Pang, Z.-L. Wang, J.-K. Cheng, Anal. Chem. 74 (2002) 2441–2445.
[33] B. Zhang, H. Liu, B.L. Karger, F. Foret, Anal. Chem. 71 (1999) 3258–3264.
[34] J.J. Li, P. Thibault, N.H. Bings, C.D. Skinner, C. Wang, C. Colyer, J. Harrison, Anal. Chem. 71 (1999) 3036–3045.
[35] C.Y. Tsai, Y.R. Chen, G.R. Her, J. Chromatogr. A 813 (1998) 379–386.
[36] A.G. Diress, C.A. Lucy, J. Chromatogr. A 1027 (2004) 185–191.