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Received November 22, 2007
Revised February 4, 2008
Accepted February 5, 2008

Research Article

# A new interface used to couple capillary electrophoresis with inductively coupled plasma mass spectrometry for speciation analysis

In this work, a novel and high-efficiency interface has been developed in coupling CE with inductively coupled plasma MS (ICPMS). The interface completely avoids laminar flow in CE capillary caused by the suction of nebulizer, and can be easily and stably operated at room temperature with high analyte transport efficiency to ICPMS. The new interface has a liquid dead volume smaller than 5 nL, which was much smaller than those (65–2500 μL) reported previously for other interfaces. All above features led to a higher sensitivity and a better electrophoretic resolution for CE-ICPMS coupled with this new interface. With the help of this new interface, we have successfully separated and determined five species of arsenic, As(III), As(V), monomethylarsonic acid, dimethylarsinic acid and *p*-aminophenylarsonic acid using CE-ICPMS within 11 min with a detection limit of 0.046–0.075 ng/mL and an RSD of 2–6% ($n = 6$).

**Keywords:**
Arsenic / Capillary electrophoresis / Inductively coupled plasma mass spectrometry / Speciation analysis
DOI 10.1002/elps.200700849

## 1 Introduction

Many studies have shown that the toxicity, bioavailability, and transport property of an element are dependent not only on its total concentration but also on its speciation [1, 2]. For example, inorganic arsenic compounds are several orders of magnitude more toxic than organoarsenicals [3, 4]. Therefore, the speciation analysis of an element is very important in evaluation of its environmental and biological risks.

A variety of separation techniques have been used for elemental speciation analysis [5, 6], including HPLC, ion chromatography (IC), supercritical fluid chromatography (SFC) and GC. Element-selective detectors, such as MS, inductively coupled plasma emission spectrometry (ICP-ES), molecular UV-spectrometry, atomic absorption spectrometry (AAS) and so on have been used in combination with above separation techniques. However, currently available techniques for quantitative elemental speciation often suffer from one or more of the following deficiencies: long time of analysis, inadequate LOD, amenable to a limited range of sample types and inadequate stability [7].

In comparison with other chromatographic techniques, CE offers a higher separation efficiency and a relatively rapid separation [8]. On the other hand, inductively coupled plasma MS (ICPMS) is an element-specific multi-element detection method, providing extremely low LODs [9]. Therefore, the coupling of CE with ICPMS promises a powerful tool for elemental speciation [10, 11]. The coupling of CE with ICPMS for trace element speciation measurements was first reported in 1995 [7]. Since that time, this technique has received considerable attention because of the potential benefits offered by the combination of the two methodologies. However, the coupling of CE with ICPMS is not as straightforward as the coupling of chromatographic techniques with ICPMS because it requires an interface that should efficiently introduced trace analyte solution into ICPMS and not degrade the resolution of CE [12, 13].

Up to now, there are three kinds of interface reported in the literature to couple CE with ICP-MS on-line or off-line: no-sheath-flow interface, sheath-flow interface and hydride generation interface. Among these three interfaces, the hydride generation interface is expected to have higher sensitivities and lower LODs in principle [14], however, the reports on the application of this interface are scarce, because of the generation of $H_2$ gas in the hydride generation system and its need for derivation [15, 16]. In addition, the hydride

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**Abbreviations**: **DMA**, dimethylarsinic acid; **ICPMS**, inductively coupled plasma MS; **MMA**, monomethylarsonic acid; **pAs**, *p*-aminophenyl arsenic acid; **PEEK**, polyether ether ketone

generation interface just can be used for a limited amount of elements such as As, Se and Hg. Most interfaces with or without sheath-flow are based on pneumatic nebulization systems [8], which are typically used in common ICPMS configurations. Generally, CE coupled on-line with ICPMS through a no-sheath-flow interface offers higher sensitivity [7]., However, overcoming the suction effect from the ICPMS that will result in the degradation of electrophoretic resolution and maintaining a stable electrical connection to CE are two challengeable questions. To minimize the suction effect caused by ICPMS and maintain a stable electrical connection to CE, a sheath-flow interface, which balances ICPMS suction by introducing a makeup solution at the outlet of the CE capillary, was developed [8, 17–21]. However, the introduction of makeup solution at the outlet of the CE capillary dilutes the analyte excessively and eventually compromises the sensitivity and the LOD, as the flow rate of CE is much smaller than that of ICPMS.

In this work, we developed a new interface for coupling CE with ICPMS. The new interface completely avoids laminar flow in CE capillary, caused by the suction from ICPMS, makes electric supply easier in CE, and transports analyte solution to ICPMS more efficiently. Using this interface, we have successfully coupled CE with ICPMS and determined five species of arsenics, including As(III), As(V), dimethylarsinic acid (DMA), *p*-aminophenyl arsenic acid (pAs) and monomethylarsonic acid (MMA) in water sample.

## 2 Materials and methods

### 2.1 Reagents

The analytical grade of five species of arsenics including $As_2O_3$, dimethylarsinic acid (DMA), *p*-aminophenyl arsenic acid (pAs), monomethylarsonic acid sesquihydrate (MMA) and $Na_2HAsO_4$ were purchased from Shenzhen Meryer Chemical Technology (Shenzhen, China). The 1000-μg/mL stock standard solution of As(III) was prepared by dissolving above $As_2O_3$ in 0.2% NaOH solution, and the 1000-μg/mL stock standard solutions of DMA, pAs, MMA and As(V) were prepared by dissolving above standard matters in Milli-Q water. All the stock standard solutions were stored at 4°C, and the running standard solutions were prepared by diluting stock standard solutions to the desired concentration with running buffer solution. The running buffer solution of 20 mmol/L of $NaH_2PO_4$ −5.0 mmol/L of $Na_2B_4O_7$ (pH 6.25) was prepared by dissolving analytical grade sodium dihydrogenphosphate ($NaH_2PO_4 \cdot 2H_2O$) and sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), which were purchased from Shanghai Reagents (Shanghai, China), in Milli-Q water. All solutions were treated by ultrasonic agitation and filtered through a 0.22-μm polypropylene filter before use. All experiments were performed at room temperature (25°C). Water used in this experiment was Milli-Q water, and nitric acid and NaOH used in this experiment were super-pure $HNO_3$ and NaOH purchased from Shanghai Reagents.

### 2.2 CE

The CE system used in this experiment was fabricated in-house. As illustrated in Fig. 1, a 60-cm length × 75-μm id × 375-μm od fused-silica capillary (Hebei Yongnian Optic Fiber Factory, Hebei, China) was used. The total volume of the capillary was 2.65 μL. The two ends of the capillary were positioned on an identical level to eliminate siphonic effect, and the electrophoresis through the capillary was driven by a high-voltage DC-power supply, which can be operated in a voltage range of −30 to +30 kV (Shanghai Institute of Atomic Nuclear Science Research, Chinese Academy of Science, Shanghai, China). The inlet end of the electrophoretic capillary was connected at a positive potential and the outlet end of the electrophoretic capillary was directly connected to the earth through interface (see Fig. 1). Sample solution was injected into CE by electromigration injection. No separate cooling measures were taken on the CE system, but the temperature of the laboratory was regulated in 25–27°C by an air conditioning system during all experiments. The CE capillary was conditioned daily by purging with Milli-Q water for 10 min, 0.1 mol/L NaOH solution for 10 min, Milli-Q water for 10 min, and running buffer solution for 10 min. Between each run, the CE capillary was flushed with Milli-Q water and running buffer solution for 2 min, respectively.

### 2.3 ICPMS

An Agilent 7500ce ICPMS (Agilent Technologies, USA) equipped with a microconcentric nebulizer (MCN, Agilent Technologies, optimum flow 50–200 μL/min) was used for the element-specific detection of $^{75}As$. Signals at $m/z$ of 75 and 77 were both monitored in order to observe the chlorine interference on the arsenic signal ($^{40}Ar^{35}Cl^+$ and $^{40}Ar^{37}Cl^+$). No detectable chlorine interference was observed during the determination.

### 2.4 Interface

The schematic diagram of our interface is shown in Fig. 1. It was composed from a stainless-steel capillary (1.5 cm length × 600 μm id × 800 μm od), some tygon tubes, two peristaltic pumps, a pulse controller and a three-way polyether ether ketone (PEEK) union. As shown in Fig. 1, the outlet end of the CE capillary was directly inserted into stainless steel capillary with a gap between the outlet end of CE capillary and stainless-steel capillary, and the end of stainless-steel capillary was connected to peristaltic pump 1 through tygon tube. The cathode of CE power supply was directly connected to stainless-steel capillary. The pulse controller was used to control the driving of peristaltic pump 1 and peristaltic pump 2, where the pump 2 was used to send Milli-Q water to clean ICPMS and the pump 1 was used to segregate CE and ICPMS and send the effluent from the CE to ICPMS for the determination.

 

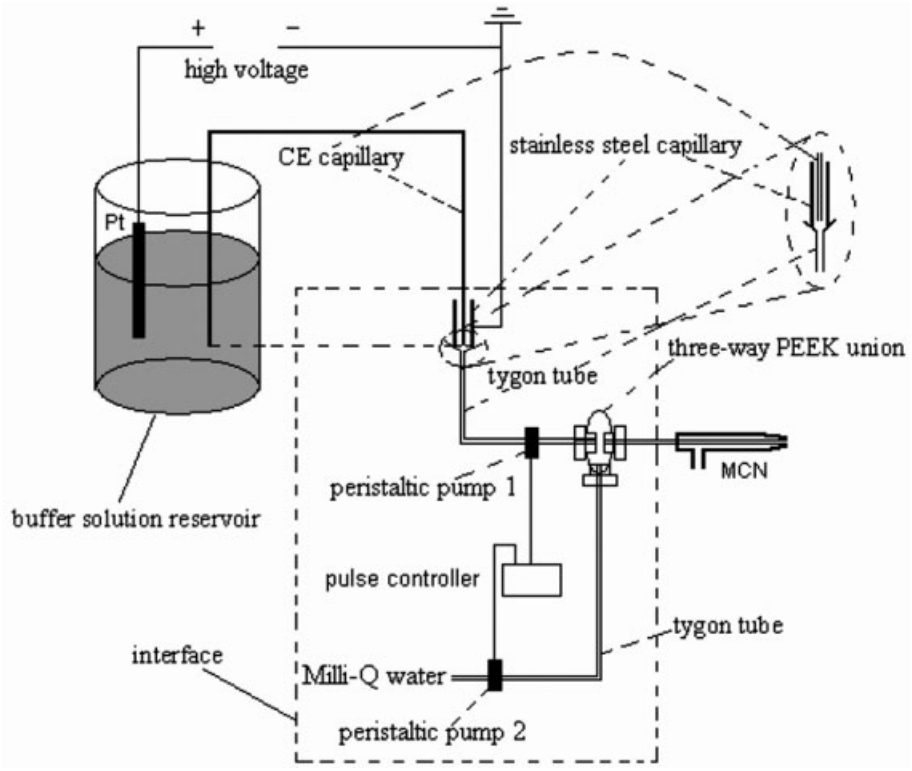


**Figure 1.** Schematic diagram of the new interface.

CE capillary dimensions have an effect on CE separation in several respects such as migration time, sensitivity, and separation efficiency. When ICPMS is used as a detector, the capillary with a smaller inside diameter offers higher separation efficiencies, but gives poorer LODs than that with a larger id [20]. In the present study, a 75-μm id × 60-cm-length capillary was selected for the evaluation of our new interface in the CE-ICPMS system because these dimensions are typical in CE. If a capillary with a larger id is used, the length of capillary must be much longer in order to keep enough electrophoretic resolution, and the longer capillary will result in a much longer analytical time.

As mentioned above, most interfaces reported previously connected the CE capillary to the pneumatic nebulizer of ICPMS directly. In such case, it is very difficult to maintain the CE electrical circuit without a sheath-flow at outlet end of the capillary, and to completely overcome the peaks broadening caused by the suction of pneumatic nebulizer even if makeup solution is pumped to interface to minimize the suction of nebulizer [22, 23]. In the present study, peristaltic pump 1 was used to segregate the CE and nebulizer and send the effluent from the CE to ICPMS. Therefore, the suction caused by the nebulizer was eliminated when peristaltic pump 1 was stopped during CE separation. In addition, an open gap between the outlet end of CE capillary and stainless steel capillary (see Fig. 1) caused the air to be inhaled through the gap when pump 1 was driven to transport the analyte solution to ICPMS. The inhalation of air not only greatly minimizes the suction of nebulizer, but also makes solution transport easier. Therefore, the suction caused by the pneumatic nebulizer was almost eliminated, too, when pump 1 was driven for short time to transport the analyte solution to ICPMS. All the above features of our new interface make CE maintaining its intrinsic separation-efficiency and resolution.

The liquid dead volume of an interface contributes to band broadening and peak asymmetry, and finally degradation of the electrophoretic resolution. Therefore, the reduction in the dead volumes should be taken into consideration. In this study, analyte solution was collectively transported to ICPMS, which greatly reduced the liquid dead volume. We clearly observed that even only one droplet (about 5 nL) eluted out CE capillary, the solution was completely transported to ICPMS during qualitative analysis. Therefore, we estimated that the liquid dead volume of our interface was smaller than 5 nL. To keep a stable atomization to aid in keeping a higher sensitivity and a good reproducibility, peristaltic pump 2 was designed to send a proper makeup solution to the nebulizer.

### 2.5 Measuring procedure

The measurement of CE-ICPMS was divided into two steps. (i) The first step is qualitative analysis, namely, determination of CE migration time of each analyte. In this step, the running standard solution of each analyte was measured by

 

CE-ICPMS under the continuous driving of both of peristaltic pump 1 and peristaltic pump 2. (ii) The second step is the quantitative determination of each analyte. This step is a practical process, in which calibration curve and sample were measured. In this step, the standard solution or sample was injected into CE for separation under the stop of peristaltic pump 1 and the driving of peristaltic pump 2 in order to avoid the suction effect caused by ICPMS. When one analyte was completely separated and eluted out of the CE capillary (according to the migration time obtained in first step), the pump 1 was driven to transport the analyte solution to three-way PEEK union, and then the analyte solution was introduced into ICPMS by makeup solution for determination. After the first analyte was transported to three-way PEEK union, the peristaltic pump 1 was stopped again until the second analyte was completely separated and eluted out of the CE capillary according to the migration time obtained in first step, and then, the pump 1 was driven to transport the solution of second analyte to three-way PEEK union again. The above process was repeated until all analytes were determined. Considering the reproducibility of CE and that the stop/start of pump 1 consumed some time, in the case of two analytes, which have close migration times, it is difficult to precisely control the stop/start of pump 1 for the transfer of each analyte, respectively. In general, a better reproducibility of CE and a more rapid response of pump 1 allow to stop/start pump1 for separating and transferring two close analytes. In our experiment, the interface could smoothly transfer each analyte solution to ICPMS, if the difference between the migration times of the analytes was bigger than 20 s.

## 3 Results and discussion

### 3.1 Optimal conditions of CE separation for five species of arsenic

Three kinds of buffer solution including phosphate, borate, and the mixture of phosphate and borate, were used as running buffer solution for separating As(III), DMA, pAs, MMA and As(V). The experimental results showed that five species of arsenic could not be completely separated when borate was used as running buffer solution. When phosphate was used as running buffer solution, five species of arsenic could be completely separated within 10 min; however, the reproducibility of CE was inferior. The mixture of phosphate and borate (phosphate/borate = 4:1, mole concentration) gave the most acceptable separation efficiency and reproducibility, therefore, the mixed solution of phosphate and borate (4:1, mole concentration) was chosen as running buffer solution in this study.

The pH and concentration of the running buffer solution strongly affect the electrophoretic resolution. The relationship between migration times/resolution and pH was studied in detail with a phosphate-borate buffer solution in the pH range of 5.50–7.50. We found that DMA and As(III) were not completely separated when pH was lower than 6.10, and that DMA and pAs were not completely separated when pH was higher than 6.50. Five species of arsenic were clearly separated with pH in the range of 6.10 to 6.50. Thus, we chose pH 6.25 as the optimum pH value for the separation of As(III), DMA, pAs, MMA and As(V).

The effect of concentration of running buffer solution on the separation was studied using different concentrations of phosphate-borate buffer solution (phosphate/borate =10:2.5, 20:5, 30:7.5, 40:10 and 50:12.5 mmol/L) at pH 6.25 with an applied voltage of +18 kV. The results showed that the peak shapes of all five species of arsenic were improved and the migration times increased with the increase of the concentration of running buffer solution. Considering both the analytical time and the electrophoretic resolution, 20 mmol/L of $NaH_2PO_4$–5.0 mmol/L of $Na_2B_4O_7$ (pH 6.25) was selected as the running buffer solution.

The effect of the separation voltage on the migration time and electrophoretic resolution was investigated in the range of 14 to 24 kV. The results showed that higher voltage was favorable to shorten migration time, however, high voltage led to the broadening of peak due to Joule heating effect. Considering both the analytical time and separation efficiency, +18 kV was selected as the separation voltage.

In this study, pump 1 was designed to collectively transport the analyte solution eluted out the outlet of CE capillary to ICPMS; pump 1 was intermittently driven corresponding to the migration time of each species of arsenic. The flow rate of pump 1 influences the peak shapes and the sensitivity. Changing the rate of pump 1 from 5.0 rpm (10 μL/min) to 15.0 rpm (30 μL/min), we found that 10.0 rpm of pump 1 (20 μL/min) provided a better peak shapes and sensitivity. The peristaltic pump 2 was used to pump makeup solution (Milli-Q water) to nebulizer in order to introduce analyte solution into ICPMS and achieve stable atomization and ionization efficiency; pump 2 keeps driving during total analytical process. The higher flow rate of makeup solution will excessively dilute the analyte and result in the degradation of sensitivity, whereas the lower flow rate of makeup solution will influence the atomization efficiency of analyte and result in the degradation of sensitivity, too. The optimum rate of pump 2 was selected by changing the rate from 2.5 rpm (100 μL/min) to 15.0 rpm (600 μL/min), and the results showed that the flow rate of pump 2 at 5.0 rpm (200 μL/min) is an optimum rate.

Different injection times (10, 20, 30, 40 and 50 s) were tested in this experiment, and results showed that the signal of ICPMS becomes higher with the increase of injection time. However, longer injection time will degrade electrophoretic resolution. In our instrument, DMA and pAs could not been completely separated when injection time was longer than 40 s. Considering both the sensitivity and the separation efficiency, we selected 30 s as sample's injection time. At above optimal conditions, the RSD of

 

migration times is less than 5% ($n$ = 6) and the RSD of analytical results is less than 6% ($n$ = 6) for all five species of arsenic.

### 3.2 Quantitative determination of five species of arsenic

Under the optimum conditions (see Table 1), quantitative analysis of five species of arsenic was performed according to the process mentioned in the Section 2.5.

**Table 1.** Operating parameters of CE-ICPMS

| Parameter | Value |
|---|---|
| CE voltage | 18 kV |
| Sampling time | 30 s |
| CE capillary | id 75 μm; od 365 μm; 60 cm long |
| Stainless-steel capillary | id 600 μm; od 800 μm; 1.5 cm long |
| Temperature | 25 °C |
| Running buffer solution | 20 mmol/L $NaH_2PO_4$-5 mmol/L $Na_2B_4O_7$, pH 6.25 |
| Velocity of pump 1 | 20 μL/min |
| Velocity of pump 2 | 200 μL/min |
| RF power | 1300 W |
| Outer plasma gas | 12 L/min |
| Intermediate plasma gas | 1.0 L/min |
| Carrier gas | 0.75 L/min |
| Nebulizer type | MCN (optimum flow, 50–200 μL/min) |

First, 100 μg/L standard solution of each species of arsenic was measured by CE-ICPMS with a continuous driving of both of pump 1 and 2 to get the approximate migration time of each species of arsenic. From the approximate migration times of five species of arsenic shown in Fig. 2, we found that the about CE migration time of As(III), DMA, pAs, MMA and As(V) was 270–300 s, 340–375 s, 405–440 s, 470–510 s and 560–605 s, respectively.

Second, the standard solution and sample solution were injected into CE-ICPMS for quantitative determination with the stop of pump 1 and the driving of pump 2. The pulse controller was adjusted to control pump 1 at 300 s (the time when As(III) was completely separated and flowed out of CE), 375 s (DMA), 440 s (pAs), 510 s (MMA) and 605 s (As(V)) for 10 s, to transport each species of arsenic to ICPMS for determination. The real electrograms (see Fig. 3A) and the counts of peak area of each species of arsenic were automatically recorded by a computer, and the counts of peak area were used to calculate the concentration of each analyte.

From Fig. 3A, it was found that the peak shapes and the sensitivity of five arsenic species were greatly improved under quantitative determination mode. As mentioned above, all interfaces reported previously transported analyte solution to ICPMS continuously. However, the continuous

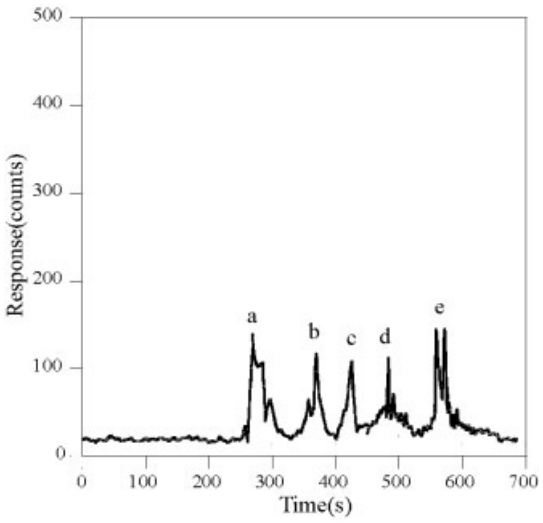


**Figure 2.** Qualitative separation of As(III) (a), DMA (b), pAs (c), MMA (d) and As(V) (e). The data was obtained by determining 100 μg/L mixed standard solution of five species of arsenic with CE-ICPMS under the conditions of continuous driving of pump 1 (10 rpm, 20 μL/min) and pump 2 (5 rpm, 200 μL/min), 20.0 mmol/L $NaH_2PO_4$-5.0 mmol/L $Na_2B_4O_7$ buffer solution (pH 6.25), 18 kV separation voltage, injection time 30 s, 25°C. Peak a is As(III), b is DMA, c is pAs, d is MMA and e is As(V).

transport suffers from the following deficiencies: a greater dilution of analyte, a relatively wider peak width and a relatively bigger liquid dead volume, because the flow rate of CE is much smaller than that of makeup solution and the CE effluent of one analyte lasts some time. In this study, the CE effluent of one analyte was collectively transported to ICPMS. The collective transport decreased the dilution times of analyte, narrowed the peak width, reduced the dead volume, and eventually resulted in a higher sensitivity and better electrophoretic resolution. The dead volume of our interface is smaller than 5 nL, and the peak widths and the LOD of five species of arsenic are 7–10 s and 0.046–0.075 ng/mL, respectively, in this study, which is much smaller than 65–2500 μL, 14–28 s and 0.3–0.5 ng/mL reported previously for other interfaces [8, 21].

A series of different concentrations of standard solution have been determined in order to obtain a calibration curve, and the relationship between peak area and concentration is shown in Fig. 4. A good linear fit and no intercept were observed in Fig. 4 for all of As(III), DMA, pAs, MMA and As(V), indicating that five species of arsenic have been completely separated. The LOD ($3\sigma/S$, the concentration necessary to yield a net signal equal to three times the SD of the background) calculated with peak area is 0.050, 0.046, 0.048, 0.053 and 0.075 ng/mL for As(III), DMA, pAs, MMA and As(V), respectively.

An artificial water sample was composed by adding 25 μg/L of As(III), DMA, pAs, MMA and As(V) into natural water collected from water supply in our laboratory, and the

 

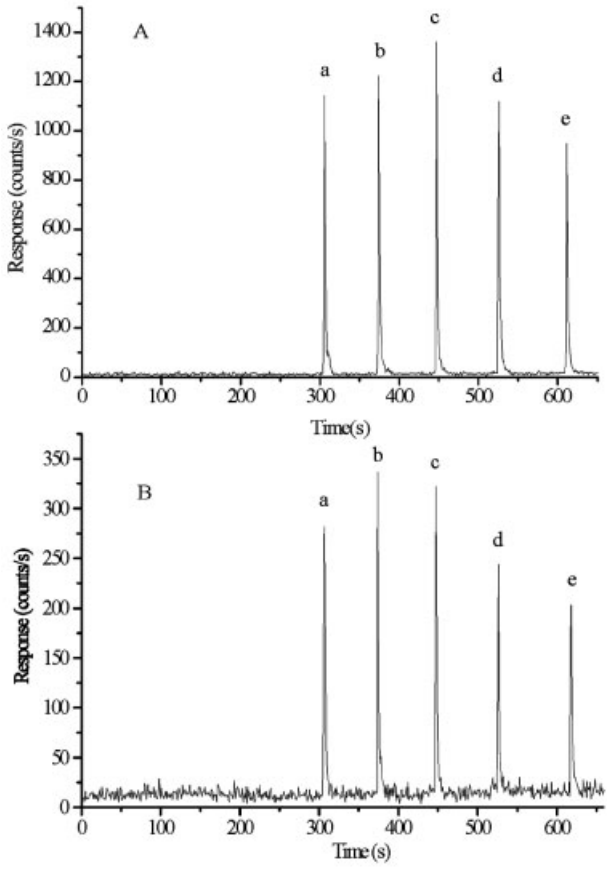


**Figure 3.** Electrograms of five species of arsenic. (A) Data was obtained by analyzing a 100 μg/L mixed standard solution of five species of arsenic with CE-ICPMS according to quantitative method mentioned in text under conditions shown in Table 1. (B) Quantitative determination of five species of arsenic in artificial water sample with the same method as above. Peak a is As(III), b is DMA, c is pAs, d is MMA and e is As(V).

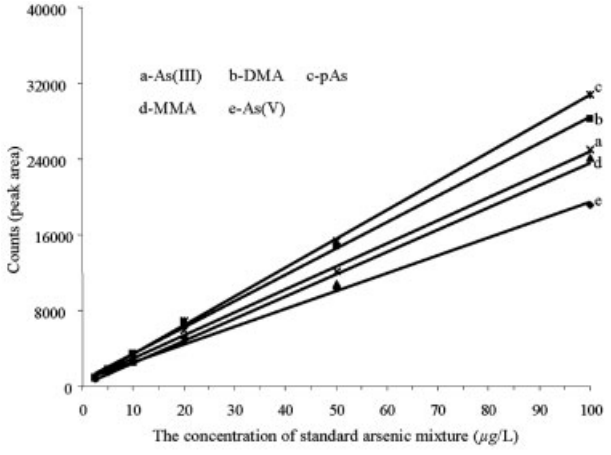


**Figure 4.** Calibration curves of five species of arsenic. Data was obtained by determining 2.5–100 μg/L standard solution of five species of arsenic with CE-ICPMS according to quantitative method mentioned in the text under conditions shown in Table 1.

concentration of each species of arsenic in it was determined using the above method. The electrograms of samples shown in Fig. 3B indicate a good reproducibility on the migration time between sample and standard. A satisfactory recovery (92–106%) and reproducibility of migration time (RSD <5%, $n = 6$) and concentration (RSD < 6%, $n = 6$) were obtained for each of As(III), DMA, pAs, MMA and As(V) despite of the presence of various matrix components (see Table 2).

**Table 2.** Analytical results of artificial water sample together with recovery and detection limit

| | As (III) | DMA | pAs | MMA | As (V) |
|---|---|---|---|---|---|
| Added concentration (μg/L) | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
| Recovered concentration (μg/L) | 26.5 | 23.4 | 24.0 | 23.1 | 23.9 |
| Recovery (%) | 106 | 94 | 96 | 92 | 96 |
| Detection limit (ng/L, 3σ/S) | 50 | 46 | 48 | 53 | 75 |
| RSD ($n = 6$) | 4% | 3% | 2% | 3% | 6% |

## 4 Concluding remarks

The new interface developed in this study completely avoided laminar flow in CE capillary caused by the suction from ICPMS. In addition, the new interface can be easily and stably operated at room temperature with high analyte transport efficiency to the plasma and has been successfully used to analyze five species of arsenic. The liquid dead volume of the new interface is smaller than 5 nL, much smaller than those (65–2500 μL) reported previously for other interfaces [8]. The near zero liquid dead volume together with no nebulizer suction effect and collective solution transport can considerably reduce the in- and post-capillary dispersion and led to much lower LODs (0.046–0.075 ng/mL) for five species of arsenic. This was demonstrated by the better symmetry and narrow peak widths (7–10 s) of five species of arsenic obtained in this study (see Fig. 3). All the above features of the new interface suggest a good potential for routine usage of this interface in coupling CE with ICPMS for real sample speciation analysis.

*This work was supported by Fujian Provincial Department of Science and Technology(2005HZ1009) and National Nature Sciences Funding of China (NSFC, 20735002). We also thank Agilent Technologies for supplying our convenient utilization of ICPMS.*

*The authors declare no conflict of interest.*

 

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