Speciation analysis of arsenic compounds by capillary electrophoresis on-line coupled with inductively coupled plasma mass spectrometry using a novel interface

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A B S T R A C T

In this work, a capillary electrophoresis (CE) coupled with inductively coupled plasma mass spectrometer (ICP-MS) system was developed for the simultaneous determination of ten arsenic compounds including arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, arsenocholine, 3-nitro-4-hydroxyphenylarsonic acid, o-Arsanilic acid, p-ureidophenylarsonic acid, and 4-nitrophenoxyarsinic acid. The CE-ICP-MS system was hyphenated by a novel and high efficient interface which was directly used as the nebulizer. The separation was achieved on a 100 cm length × 50 μm ID fused-silica capillary. Analytical conditions such as electrophoretic buffer composition, concentration and pH value, separation voltage, methanol concentration in the sheath flow liquid and sample injection time were optimized. Baseline separation of the ten arsenic species was achieved using an electrophoretic buffer consisting of 12 mM NaH2PO4 and 8 mM HBO3 at pH 9.20 with an applied voltage of +30 kV. The detection limits of the ten arsenic compounds ranged from 0.9 to 3.0 ng As g−1, corresponding to absolute detection limits in the range of 19–65 fg As and the relative standard deviations (RSD, n = 5) were below 1.5%, 5.7% and 4.8% for migration time, peak height and peak area, respectively. This method was successfully applied to determine various arsenicals in two certified reference materials (TORT-2 and DORM-3) and environmental samples such as ground water samples, herbal plants and chicken meat.

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1. Introduction

Arsenic speciation has become increasingly important and received considerable attention due to the ubiquitous presence in environment and the high toxicity and carcinogenicity to organism of the arsenic compounds [1]. The toxicity and carcinogenicity of arsenic compounds depend not only on the total concentration but also on the different arsenic species [2]. It is well-known that inorganic arsenic compounds, arsenite (As(III)) and arsenate (As(V)), are more toxic than the methylated species such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Besides, arsenobetaine (AsB), arsenocholine (AsC) and other arsensugars are considered to be non-toxic. In addition to these most prevalent species, some phenylarsonic acid compounds such as 3-nitro-4-hydroxyphenylarsonic acid (3-NHPAA, Roxarsone), p-ureidophenylarsonic acid (p-UHPAA, Carbarsone) and 4-nitrophenoxyarsinic acid (4-NPAA, Nitarsone) are now extensively used in the poultry industry due to their beneficial properties of controlling intestinal parasites, improving feed efficiency and promoting rapid growth [3,4]. For example, roxarsone has long been used in the production of cattle, pigs, and poultry in the United States, China and other countries [5], whereas nitarsone and carbarsone were used to control blackhead disease in turkeys in the United States [6]. Researches showed that toxic inorganic and methylated arsenic species have been found in composted litter samples [7] and therefore arsenic could be artificially introduced and released into the environment through this way. Due to the large differences of toxicity among arsenic species and their transformation in the environment, arsenic speciation analysis is of great significance to study the toxicity, transformation and bioavailability, and then to better understand the potential impacts of arsenic on the environment and human health. Therefore, it is very important to develop rapid, sensitive and simple analytical methods for arsenic speciation in different environmental samples.

So far, the most commonly used method for separation and quantification of arsenic compounds is the hyphenated technique based on the combination of a chromatographic separation technique and an element-selective/species detector. There are already some methods for the speciation of arsenic species by coupling high performance liquid chromatography (HPLC), gas chromatography (GC) and capillary electrophoresis (CE) with atomic fluorescence spectrometry (AFS), atomic absorption spectrometry (AAS) and
inductively coupled plasma mass spectrometry (ICP-MS) [3,7–15]. GC has a great separation capacity for volatile arsenicals, but its application is limited because most naturally occurring arsenic species are non-volatile and have to be derivatized before further analysis. This may cause the loss of analyte or species transformation [16]. HPLC is a very popular method in arsenic speciation including ion exchange [3], microbore HPLC [17], reversed phase [4] and reversed phase ion pair liquid chromatography [18]. However, the separation efficiency of HPLC is generally insufficient due to the low resolution, especially for biological samples [19]. Comparing to LC and GC, CE has several advantages such as high separation efficiency, relatively rapid analysis, small sample volume of sample requirement and low buffer consumption and it has been applied to the separation of arsenic species. For the determination and quantitation of arsenic, ICP-MS offers excellent sensitivity, wide linear dynamic range, high-speed analysis and isotope-specific detection capabilities, which facilitate accurate and fast detection. Therefore, the coupling of CE with ICP-MS promises a powerful tool for element speciation analysis and can provide a sensitive and highly efficient analytical technique for arsenic speciation in various matrices.

The interface is considered to be a key factor for successfully coupling of CE and ICP-MS [20]. It is required to maintain a stable electrical circuit from CE to nebulizer, introduce CE effluent into ICP-MS efficiently and keep a low dead volume [21,22]. Currently, typical sheath flow-based interfaces are commonly used, which combine a commercial nebulizer and commercially available tee or cross designed fittings to connect the CE capillary, the Pt electrode, the additional sheath flow liquid and the nebulizer of ICP-MS [23–26]. Generally, a sheath flow liquid (also called make-up solution) is needed in the interface in order to provide closed electrical circuit and increase the total liquid flow to match the nebulizer flow rate. There would be a variation in the flow rates of the sheath flow liquid by self-aspiration [27], so some studies used an extra equipment, such as peristaltic pump [15,28] or syringe pump [29] to maintain a steady and continuous sheath flow liquid. The presence of the dead volume is another factor affecting the CE separation. Peak broadening and low peak height could be observed due to the big dead volume, when the position of the end of the capillary in the nebulizer is not suitable [30]. In our work, a commercial sprayer kit was used as the nebulizer and the outlet of the CE capillary could be fixed on an exact position at the sprayer tip. The effluent from the capillary would be directly nebulized at the sprayer tip which ensures that no dead volume existed before nebulization. This interface has been reported for coupling CE-ESI-MS system [31] and CE-ESI-TOF-MS system [32], but to the best of our knowledge it has not yet been applied to couple CE with ICP-MS.

In this work, we endeavored to couple CE with ICP-MS using the commercial CE-ESI-MS sprayer kit as an interface. A simple and effective CE-ICP-MS hyphenated system was successfully established for the speciation and quantification of ten arsenic compounds: As (III), As (V), DMA, MMA, AsB, AsC, 3-NHPPA, 4-NPAA, o-ASA (o-arsanilic acid) and p-UPAA. The analytical conditions of the method, including the composition, concentration and pH of the electrophoretic buffer, the separation voltage, methanol concentration in the sheath flow liquid and sample injection time were optimized. The ten arsenic species were baseline separated under the optimized conditions and the proposed method was applied for arsenic speciation in several environmental samples.

2. Materials and methods

2.1. Materials, chemicals, and samples

Stock standard solutions of arsenic species (1000 mg L\(^{-1}\), concentration expressed as As) were prepared by dissolving an appropriate amount of the following compounds in de-ionized water: sodium arsenite (As(III)) (Chinese Reference Material Center, China), sodium arsenate (As(V)) (Beijing Chemical Regents Company, China), DMA (Sigma, USA), MMA (Sigma, USA), 3-NHPPA (Sigma, Germany), 4-NPAA (Dr. Ehrenstorfer GmbH, Germany), o-ASA (Sigma, USA), p-UPAA (Aldrich, USA) and AsB (Fluka, Italy). AsC standard solution (28.0 mg L\(^{-1}\)) was purchased from Chinese Reference Material Center. All stock solutions were stored in the dark at 4 °C. Working solutions were prepared by diluting above stock standard solutions to the desired concentrations with de-ionized water every day.

The running buffer was prepared from appropriate amounts of sodium dihydrogen phosphate dehydrate (Beijing Chemical Reagents Company, China) and boric acid (Sigma, France). Sodium hydroxide solutions (1.0 mol L\(^{-1}\) and 0.1 mol L\(^{-1}\)) were prepared by dissolving sodium hydroxide (Sigma, Sweden) in de-ionized water. Rhodium solution in the sheath flow liquid was prepared by diluting rhodium internal standard solution for ICP-MS (10 μg g\(^{-1}\); Fluka, Switzerland) in the 5% (v/v) methanol (J.T. Baker, USA) and was used to maintain the electrical circuit and monitor the stability of CE-ICP-MS system. All other chemicals were analytical grade or better.

De-ionized water (18.2 MΩ CM) was used throughout the experiment and was prepared by Milli-Q Advanced A10 system (Millipore, Bedford, USA).

2.2. CE operating condition

For the separation of the ten arsenic compounds, a HP3D CE system (Agilent, Germany) was used in this experiment. Fused-silica capillaries of 100 cm length with an inner diameter of 50 μm and an outer diameter of 365 μm were obtained from Yongnian Optical Fiber Company (Hebei, China). For initialization, the new CE capillary was conditioned by flushing with 1 mol L\(^{-1}\) NaOH for 60 min, then 0.1 mol L\(^{-1}\) NaOH for 60 min, de-ionized water for 30 min and finally the running buffer solution for 60 min. Between each run, the capillary was flushed with 0.1 mol L\(^{-1}\) NaOH and de-ionized water for 2 min followed by running buffer solution for 4 min. Electrolyte solution was also replenished by new solution after each run. For recycling, the operating capillary was conditioned daily by successively purging with 0.1 mol L\(^{-1}\) NaOH and de-ionized water for 10 min. Sample was injected into the capillary by hydrodynamic method under a gas pressure of 50 mbar for 25 s, which produced an injection volume of about 21.5 μL. The applied voltage and capillary temperature were set at 30 kV and 25 °C, respectively (Table 1).

2.3. ICP-MS system

An Agilent 7500ce ICP-MS (Agilent Technologies, USA) coupled with the HP3D CE system was used for the element quantification of As. The ICP-MS instrument was tuned and optimized for m/z 75 at the beginning of the experiment every day. A standard torch was used with a plasma gas flow rate of 15 L min\(^{-1}\), carrier gas flow rate of 1.1 L min\(^{-1}\) and the makeup gas flow rate of 0.1 L min\(^{-1}\). The plasma RF power was 1500 W in the experiment. Signals of m/z 75 for arsenic and m/z 103 for rhodium were monitored in time-resolved analysis mode in order to determine the arsenic and also to monitor the stability and sensitivity of CE-ICP-MS system between each run. The integration time for arsenic and rhodium was 0.7 s and 0.05 s, respectively.

2.4. CE-ICP-MS interface

For the coupling of CE with ICP-MS, the interface used in this study was fabricated by a CE-ESI-MS sprayer kit (G1607A, Agilent, USA), which has previously been used to couple CE with ESI-MS
Table 1
Table 1. Equipment and operation conditions.

<table>
<thead>
<tr>
<th>Equipment and operation conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CE parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Fused silica capillary</td>
<td>50 μm id = 100 cm length</td>
</tr>
<tr>
<td>Buffer</td>
<td>NaH₂PO₄ 12 mM, H₂BO₃ 8 mM, pH = 9.20</td>
</tr>
<tr>
<td>Voltage</td>
<td>30 kV</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Sample injection</td>
<td>Hydrodynamic 25 s</td>
</tr>
<tr>
<td>Pre-analysis rinse</td>
<td>0.1 M sodium hydroxide (2 min) De-ionized water (2 min) Running buffer (4 min)</td>
</tr>
<tr>
<td>Post-analysis rinse</td>
<td>0.1 M sodium hydroxide (2 min) De-ionized water (2 min)</td>
</tr>
<tr>
<td><strong>ICP-MS parameters</strong></td>
<td></td>
</tr>
<tr>
<td>RF POWER</td>
<td>1500 W</td>
</tr>
<tr>
<td>Sample depth</td>
<td>8.0 mm</td>
</tr>
<tr>
<td>Plasma gas</td>
<td>15.0 L min⁻¹</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>1.10 L min⁻¹</td>
</tr>
<tr>
<td>Makeup gas</td>
<td>0.10 L min⁻¹</td>
</tr>
<tr>
<td>Monitored isotope (m/z)</td>
<td>75</td>
</tr>
<tr>
<td><strong>Interface</strong></td>
<td></td>
</tr>
<tr>
<td>Nebulizer</td>
<td>CE-ESI-MS Sprayer</td>
</tr>
<tr>
<td>Sheath flow liquid</td>
<td>100 ng mL⁻¹ Rh, 5% methanol</td>
</tr>
<tr>
<td>Sheath flow rate</td>
<td>5 μL min⁻¹</td>
</tr>
</tbody>
</table>

The sprayer consists of a concentrically shaped stainless steel capillary surrounded by an outer stainless steel tube and was used as the nebulizer of the ICP-MS. As shown in Fig. 1, the CE capillary passed through the inner stainless steel capillary of the sprayer with a gap between them and protruded approximately 0.1 mm out of the sprayer tip. Sheath flow liquid was added into the inner stainless steel capillary to close the electric circuit and deliver a suitable flow rate to produce a stable electrospray. The carrier gas was added at the outer stainless steel tube. The sheath flow liquid is mixed with the CE effluent at the sprayer tip and the mixture is then nebulized by the carrier gas from the outer tube. To maintain a steady separation voltage, the stainless-steel shell of the sprayer was grounded. The sprayer was then installed at the base of the spray chamber to ensure that the liquid from the capillary can be directly introduced into the ICP-MS after nebulization.

A mixture of water and methanol (95:5, v/v) with 100 ng mL⁻¹ Rh solution was used as the sheath flow liquid and was introduced into ICP-MS by an Agilent 1200 series quaternary pump (Agilent, Germany) in conjunction with a built-in active 1:100 flow-splitter (Agilent, USA), which provided a constant flow rate of 5 μL min⁻¹. Using the proposed interface, solution at the sprayer tip was collectively nebulized by the carrier gas with high nebulization efficiency. As the outlet of the CE capillary was directly inserted into the sprayer chamber of ICP-MS, the dead volume was also significantly reduced and the analytes could be effectively transported to the ICP-MS after nebulization. The advantages of the sprayer make it very suitable as an interface for coupling CE with ICP-MS.

2.5. Sample analytical procedure

The species of water-soluble arsenic in ground water, TORT-2 (lobster hepatopancreas), DORM-3 (fish protein), two herbal plants (flower of Chrysanthemum morifolium Ramat which is also called Flos Chrysanthemi and root of Rehmannia glutinosa Libosch) and chicken meat purchased from local market were determined by the CE-ICP-MS system after pretreatment. The ground water sample used in the experiment was obtained from Shanyin town (Shanxi, China) and stored at −20 °C after sampled.

The herbal plants and chicken meat were lyophilized and homogenized before the following extraction procedure: (1) 0.5 g of freeze-dried samples or the dried TORT-2 and DORM-3 were weighed into a 15 mL centrifuge tube and 10 mL de-ionized water was added. (2) The tube was vortexed for 1 min, sonicated for 30 min and then centrifuged at 4000 rpm for 10 min. (3) The supernatant was collected and another 5 mL de-ionized water was added into the precipitate. Thereafter, the procedure (2) was repeated. (4) The supernatant in the procedure (2) and (3) was mixed together. The extracted solution and water samples were filtrated through 0.22 μm nylon filter membranes and then analyzed by CE-ICP-MS.

3. Results and discussion

3.1. Optimization of CE-ICP-MS conditions

CE-ICP-MS system was successfully developed using the interface of sprayer for the speciation of various arsenic species. In CE separation technique, several conditions such as the composition, concentration and pH of the electrolyte and the separation voltage could affect the migration time of each analyte and finally affect the separation. These separation parameters were optimized in this study. The detector response of arsenic can significantly be affected by the sample injection volume which is linearly associated with the injection time and the addition of methanol in the sheath flow liquid. Therefore, the injection time and the methanol concentration were also optimized to obtain better detector response and lower detection limits.

3.1.1. Optimization of electrolyte composition

Three kinds of buffer solution including sodium dihydrogen phosphate, borate and mixture of sodium dihydrogen phosphate and borate were used as the running buffer solution for separating the ten arsenic compounds. The results showed that the ten arsenic species could not be separated completely using borate as the running buffer solution, but could be separated within 35 min when the 20 mM phosphate was used as running buffer solution and the migration time reduced with the addition of borate in the electrolyte. Therefore, the mixture of sodium dihydrogen phosphate and borate solution was used as the electrophoretic buffer solution. The ratios of NaH₂PO₄ and HBO₃ (15 mM:5 mM, 12 mM:8 mM,
The data was obtained by determining 200 ng g⁻¹ mixed arsenic standard solution under optimized conditions: running buffer solution of pH 5.2, 30 kV, 25 °C, 50 mbar × 25 s injection, 5% methanol in the sheath flow liquid. Arsenic compounds: 1, AsC; 2, AsB; 3, As(III); 4, DMA; 5, p-UPAA; 6, o-ASA; 7, 4-NPAA; 8, MMA; 9, 3-NHPAA; 10, As(V). Electrolyte buffer composition: (A) 15 mM HBO₂ and 5 mM NaH₂PO₄; (B) 12 mM HBO₂ and 8 mM NaH₂PO₄; (C) 10 mM HBO₂ and 10 mM NaH₂PO₄; (D) 8 mM HBO₂ and 12 mM NaH₂PO₄; (E) 5 mM HBO₂ and 15 mM NaH₂PO₄.

10 mM:10 mM, 8 mM:12 mM and 5 mM:15 mM) were studied to obtain a better electrophoretic resolution with other conditions at constant values. The results in Fig. 2 showed that when the ratio of phosphate and borate were less than 1:1, 4-NPAA and MMA could not be well separated. The mixture of phosphate and borate at the ratio of 12 mM:8 mM achieved baseline separation and gave the best acceptable migration time. Therefore, the proportion of NaH₂PO₄ and HBO₂ solution was chosen as 12 mM:8 mM.

3.1.2. Effect of buffer concentration

The electrophoretic resolution and the migration time of analytes can be strongly affected by the concentration of the running buffer solution. In general, the migration times of the analytes would be prolonged at higher buffer concentrations because of the increase of the buffer ionic strength which finally improve the separation efficiency. However, if the concentration of the buffer solution is too high, the conductivity of the electrolyte will increase and Joule heating will be large enough to increase the temperature, which leads to the broadening of the peaks and degradation of resolution. In this work, the effect of the buffer concentration on the separation was studied using different concentrations of phosphate–borate buffer solution in the range of 10–30 mM at the same ratio of phosphate and borate (3:2) at the pH 9.20 with an applied voltage of +30 kV. The results shown in Fig. 3 indicated that the migration times of arsenic compounds were prolonged with the increase of buffer concentration, especially 3-NHPAA and As(V). It was also found that a better separation and lower retention time was achieved when the phosphate–borate solution was 20 mM. Thus the concentration of running buffer solution was selected as 20 mmoL⁻¹ in all experiments.

3.1.3. Effect of buffer pH on the separation

As the ionic arsenic species are separated based on their charges and sizes in CE, the pH of buffer solution significantly influences the migration time and finally affects the separation. It had been reported that separation of weak acids was optimized at the vicinity of their corresponding pKₐ values [33]. Considering the pKₐ values of the analytes and the fact that the silica capillary wall could not be completely ionized when the pH value was lower than 7, the pH was selected around 9 [23]. The relationship between the pH and the resolution was investigated with a 12 mM:8 mM phosphate–borate buffer solution in the pH range of 8.50–9.80. As shown in Fig. 4, the migration time of several arsenic compounds significantly changed at different pH, especially for As(III), p-UPAA, o-ASA and 3-NHPAA. In detail, peaks of DMA and p-UPAA at pH 8.50, 4-NPAA and MMA at pH 9.00, o-ASA and 4-NPAA at pH 9.80 were partly or even completely overlapped. In short, the ten arsenic species were completely separated within 27 min when the pH of the buffer solution was adjusted to 9.20. Therefore, pH 9.20 was finally chosen as the optimum pH value for the separation in the experiments.

3.1.4. Effect of voltage on the separation

The effect of electrophoretic voltage on the CE separation and resolution was studied with 12 mM NaH₂PO₄ and 8 mM HBO₂ at pH 9.20 as buffer solution. The highest voltage was set at +30 kV because of the limitation of the maximum voltage of the instrument. The results showed that the ten arsenic species were baseline separated in the range of +20 kV to +30 kV while the migration times of arsenic species decreased with the increase of the electrophoretic voltage. Therefore, +30 kV was selected as the separation voltage due to its less time consumption.
3.1.5. Effect of sample injection time

Hydrodynamic injection was chosen as the sample injection mode in this experiment. The injection volume, which is proportional to the injection time and the applied pressure, has a significant effect on the resolution and the sensitivity. The injection volume of CE (nl level) is much smaller than the conventional injection volume of HPLC (μL level), which would limit the detector response. In order to increase the sample injection volume and obtain better sensitivity, a series of injection time of 10 s, 15 s, 20 s, 25 s and 30 s were investigated at the hydrodynamic injection pressure of 50 mbar. The results in Fig. 5 showed that each peak height and the peak area were increased linearly with the increase of the injection time from 10 s to 25 s. However, the peak areas of AsC, As(III) and 4-NPAA decreased when the injection time was prolonged to 30 s, while the peak areas of the other compounds, such as AsB, DMA, p-UPAA, o-ASA, MMA, 3-NHPAA and As(V) remained increased. Degradation of electrophoretic resolution was also observed and the widths of several peaks were severely broadened when the injection time up to 30 s. Thus an injection time of 25 s was chosen in order to obtain sufficient resolution and also high sensitivity.

3.1.6. Effect of methanol concentration in the sheath flow liquid

It is well known that methanol increases the signal intensity of arsenic [34,35], so the influence of methanol in the sheath liquid on the intensity of ICP-MS signals was investigated. As shown in Fig. 6, it was obvious that the peak areas of arsenicals were raised with the increase of the methanol concentration from 0% to 5%. However, the plasma of the ICP-MS became unstable when the concentration of methanol in the sheath liquid was more than 5%. Considering both the intensity and separation of arsenic compounds, 5% methanol was used as the sheath flow liquid.

In summary, a 20 mM mixture solution of 12 mM NaH2PO4 and 8 mM HBO2 at pH 9.20 was selected to be the optimum running buffer solution when the voltage was set at 30 kV in the CE system for the separation of ten arsenic species. The best signal of arsenic in the ICP-MS system at m/z 75 was obtained when the sample injection time in CE was 25 s and the methanol concentration in the sheath flow was 5%. The final optimum operating conditions of the CE-ICP-MS is shown in Table 1.

3.2. Analytical performance

Under the optimized conditions, ten arsenic compounds including As(III), As(V), DMA, MMA, AsB, AsC, p-UPAA, o-ASA, 4-NPAA, 3-NHPAA were all baseline separated within 30 min. The typical electropherogram of the ten arsenic species at 100 ng g⁻¹ level obtained by the CE-ICP-MS method was shown in Fig. 7. Good linearity (r² ≥ 0.9970) was obtained for all the analytes in the range of 20–250 ng g⁻¹. The relative standard deviations (RSD, n = 5) for migration time, peak height and peak areas were in the range of 0.3–1.5%, 0.8–5.7% and 0.2–4.8%, respectively (Table 2), which indicated a good reproducibility and reliability of this method. The detection limits (LODs) of the method were calculated using 3σ/S based on the peak height. The LODs for various arsenic species were in the range of 0.9–3.0 ng g⁻¹, corresponding to absolute detection limits in the range of 19–65 fg of As based on a 21.5 nl sample injection (Table 2). Compared to the other CE-ICP-MS methods [10,23,26,32,36], our method could simultaneously separate more arsenic compounds with higher separation efficiency than other methods. The detection limits were comparable or even better than those of the reported methods.

3.3. Determination of arsenic species in different samples

The proposed method was used to determine various arsenic compounds in different matrix samples in order to verify the
Table 2
Analytical performance data of ten arsenic compounds under optimized conditions by CE-ICP-MS.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Linear range (ng·g⁻¹)</th>
<th>r²</th>
<th>LOD* (ng·g⁻¹)</th>
<th>LOD⁺ (fg)</th>
<th>RSD⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsC</td>
<td>20–250</td>
<td>0.9987</td>
<td>0.9</td>
<td>19</td>
<td>1.0</td>
</tr>
<tr>
<td>AsS</td>
<td>20–250</td>
<td>0.9994</td>
<td>3.0</td>
<td>65</td>
<td>0.8</td>
</tr>
<tr>
<td>As(III)</td>
<td>20–250</td>
<td>0.9974</td>
<td>1.4</td>
<td>30</td>
<td>0.9</td>
</tr>
<tr>
<td>DMA</td>
<td>20–250</td>
<td>0.9975</td>
<td>1.1</td>
<td>24</td>
<td>0.4</td>
</tr>
<tr>
<td>3-UPAA</td>
<td>20–250</td>
<td>0.9984</td>
<td>1.6</td>
<td>34</td>
<td>0.3</td>
</tr>
<tr>
<td>o-ASA</td>
<td>20–250</td>
<td>0.9976</td>
<td>0.9</td>
<td>19</td>
<td>0.8</td>
</tr>
<tr>
<td>4NPAA</td>
<td>20–250</td>
<td>0.9949</td>
<td>1.3</td>
<td>28</td>
<td>0.7</td>
</tr>
<tr>
<td>MMA</td>
<td>20–250</td>
<td>0.9994</td>
<td>1.1</td>
<td>24</td>
<td>1.5</td>
</tr>
<tr>
<td>3NHPPA</td>
<td>20–250</td>
<td>0.9974</td>
<td>1.6</td>
<td>34</td>
<td>1.0</td>
</tr>
<tr>
<td>As(V)</td>
<td>20–250</td>
<td>0.9970</td>
<td>1.6</td>
<td>34</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* Calculated using 3σ/5 based on the peak height measurement.
⁺ Absolute detection limits of As based on a 21.5 nl sample injection.
⁻ Sample concentration: 250 ng·g⁻¹, n = 5.

applicability for practical analysis. Solid samples used for determination were extracted by the processes described previously.

Speciation of arsenic in two certified reference materials of TORT-2 (lobster hepatopancreas) and DORM-3 (fish protein), was performed in order to validate the proposed method. Because there were no certified values of arsenic species in the reference materials, the sum values of arsenic species were compared with the certified values of total arsenic to validate the proposed method. AsB (13.38 ± 0.06 µg·g⁻¹), DMA (2.14 ± 0.10 µg·g⁻¹) and As(V) (4.46 ± 0.03 µg·g⁻¹) were detected in TORT-2. The sum of the quantified species in TORT-2 (19.98 ± 0.10 µg·g⁻¹) of this work achieved good agreement with the certified value (21.6 ± 1.8 µg·g⁻¹). AsB (3.51 ± 0.2 µg·g⁻¹), DMA (0.54 ± 0.02 µg·g⁻¹), MMA (0.40 ± 0.01 µg·g⁻¹) and As(V) (1.40 ± 0.04 µg·g⁻¹) were found in DORM-3. It was also reported in another literature [37] and the sum of quantified species in DORM-3 (5.85 ± 0.4 µg·g⁻¹) indicated 85% extraction efficiency (certified value of 6.88 ± 0.3 µg·g⁻¹). This result demonstrated that arsenic was satisfactorily extracted and detected using our method. Recovery test of TORT-2 was performed by spiking a standard mixture (100 ng·g⁻¹) to TORT-2 before extraction and acceptable recoveries for all ten arsenic compounds were achieved (89–107%). This indicated that each arsenic species remained unchanged during the extraction procedure and analysis process. Therefore, this method was efficient and suitable for arsenic speciation in environmental samples.

Two ground water samples (collected from Shanyin, Shanxi province), two herbal plants (Flos Chrysanthemi and root of Rehmannia glutinosa Libosch) and chicken meat were also analyzed by the CE-ICP-MS method under optimized conditions. Organic arsenic compounds were not detectable in all of the water samples and only As(V) was detected, which was 279.9 and 22.7 ng·g⁻¹ for ground water samples A and B, respectively. AsB, As(III) and As(V) were detected in the two herbal plants, which were 0.90, 1.31, 1.09 µg·g⁻¹ for Flos Chrysanthemi and 1.08, 3.97, 3.65 µg·g⁻¹ for Rehmannia glutinosa Libosch root, respectively. As(III) (457.5 ng·g⁻¹) was the only arsenic compound detected in the chicken sample. Acceptable recoveries in ground water sample (94–110%) and Flos Chrysanthermi (86–118%) for the ten arsenic compounds were achieved by spiking suitable amounts of mixed standard solution to the samples prior to extraction.

The electropherograms of arsenic speciation in various samples are shown in Fig. 8. Four arsenic species were detected in the samples and ten arsenic species in the spiked samples were baseline separated under the optimized conditions. Good agreements between the sum values of arsenic species with the certified total values demonstrated an effective extraction procedure and detection method. Very good recovery for all the arsenic compounds was observed which implied that the species were not transformed during extraction and analytical process. These results therefore clearly indicated that the developed CE-ICP-MS method is valid for arsenic speciation in different environmental matrices.

4. Conclusions

In this study, a CE-ESI-MS sprayer kit was used as a novel and effective interface to couple CE and ICP-MS. The analytes were directly transported into the ICP-MS through the interface and then nebulized. The use of this interface reduced the dead volume, narrowed the peak width and led to a higher sensitivity and better electrophoretic resolution. Experimental conditions of the hyphenated system were optimized for the speciation of ten arsenic species and the baseline separation was successfully accomplished within 30 min, and the detection limits were in the range of 0.9–3 ng·g⁻¹. The optimized method was successfully applied to the analysis of As in ground water, herbal plant, chicken meat and two standard reference materials (TORT-2 and DORM-3). Good recoveries were achieved for the different samples, which indicated a broad application range for this hyphenated system to analyze various matrices. It is hoped that this CE-ICP-MS system will be used in the future to determine arsenic species in various environmental and biological samples to investigate their toxicity, transformation and bioavailability, and to help assessing their potential impacts on the environment and human health.
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References