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ARTICLE *in* ANALYTICAL CHEMISTRY · JANUARY 2005

Impact Factor: 5.64 · DOI: 10.1021/ac049066t · Source: PubMed

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Hydride Generation Interface for Speciation Analysis Coupling Capillary Electrophoresis to Inductively Coupled Plasma Mass Spectrometry

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A novel hydride generation (HG) interface for coupling capillary electrophoresis (CE) with inductively coupled plasma mass spectrometry (ICPMS) is presented in this work. The CE-HG-ICPMS interface was applied to the separation and quantitation of common arsenic species. Lack of a commercially available HG interface for CE-ICPMS led to a three concentric tube design allowing alleviation of back pressure commonly observed in CE-HG-ICPMS. Due to the high sensitivity and element-specific detection of ICPMS, quantitative analysis of As(III), As(V), monomethylarsonic acid, and dimethylarsinic acid was achieved. Optimization of CE separation conditions resulted in the use of 20 mmol L^{-1} sodium borate with 2% osmotic flow modifier (pH 9.0) and −20 kV applied potential for baseline resolution of each arsenic species in the shortest time. Hydride generation conditions were optimized through multiple electrophoretic separation analyses with 5% HCl and 3% $NaBH_4$ (in 0.2% NaOH) determined to be the optimum conditions. After completion of system optimization, detection limits obtained for the arsenic species were less than 40 ng L^{-1} with electromigration time precision less than 1% within a total analysis time of 9.0 min. Finally, the interface was used for speciation analysis of arsenic in river and tap water samples.

Elemental speciation is defined as determination of the distribution of a specific element in different chemical species in a sample.[1−4] Information obtained from speciation analysis of trace elements allows better understanding of the chemical/biochemical processes, environmental availability, and toxicological risks associated with different species.[1,5] However, speciation analysis is a difficult task considering the various steps involved in finding the distribution of species without altering the original chemical form of such. Most speciation analyses are affected by complex sample matrixes, low natural occurrence, and the usually extensive sample preparation required.[1−3] Sample preparation methods such as solid-phase microextraction[6] and solid-phase extraction[7] have been commonly used to overcome some of these difficulties. On the other hand, improved sample collection, extraction, and purification techniques can help to overcome the problems associated with complex sample matrixes. Sample introduction systems such as electrothermal vaporization,[8] laser ablation,[9] and hydride generation (HG)[10−14] have also been used to compensate for the low natural occurrence of species studied. These methods have resulted in improved detection limits due to their higher sample transport efficiency, selective sample preconcentration, and better separation from complex sample matrixes.

Hydride generation has been recognized for more than 35 years as a valuable sample derivatization technique for the analysis of trace elements such as As, Se, Sn, Sb, Te, Bi, and Ge, whose hydrides are readily volatile. Typical HG techniques include metal−acid reduction, thermochemical generation, electrochemical generation, photoinduced generation, and sodium borohydride reduction.[12,13,15,16] Reduction of an acid with aqueous sodium borohydride is the most commonly used technique due to its ability to reduce multiple hydride-forming elements and for the production of volatile analyte products from complex matrixes.[12,13] The use of HG as a sample introduction method has improved detection limits by a factor of 10 or more with inductively coupled plasma mass spectrometric detection (ICPMS). Due to the

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10.1021/ac049066t CCC: $27.50
Published on Web 00/00/0000

Table 1. Summary of As(III), As(V), MMA and DMA Detection Limits by Various Analysis Techniques

analysis technique	detection limit (μg L^{-1})	ref
HPLC-ICPMS	1.0−3.0	27
HPLC-HG-ICPMS	0.011−0.051	15
CE-ICPMS	1.0−2.0	26
CE-HG-AFS	9.0−18.0	18
CE-HG-ICPMS	0.027−0.039	this study

advantages of this technique, it has been successfully applied when analytical separation methods such as high-performance liquid chromatography (HPLC)[17] or capillary electrophoresis (CE)[18] are coupled to element-specific detectors such as atomic fluorescence spectroscopy (AFS)[18] and ICPMS[19−21] (Table 1). As a result of the ease of usage, HPLC is reported to be the most popular analytical separation technique used in conjunction with hydride generation for elemental speciation.[17,22−24] Although, the HG technique is relatively easy to adapt for HPLC separations, it is also susceptible to various problems associated with the HG interface. Mester et al.[22] reported an improvement in detection limit of 1 order of magnitude with an HPLC-HG-AFS system using an ultrasonic nebulizer. In this work, the use of several homemade gas−liquid separators was also attempted; however, higher noise was observed due to pulsation caused by the hydride generation reactions.[22] Story and Caruso in their review of hydride generation techniques reported a decrease in detection limits of 1−3 orders of magnitude for hydride-forming elements compared to conventional nebulization techniques.[25]

CE is the other separation technique that is effectively coupled to element-specific detectors. However, little is available in the literature for the coupling of CE to element-specific detectors with a hydride generation interface. Recently, Yin et al.[18] proposed a novel CE-HG interface for arsenic speciation with AFS, which resulted in improved detection limits compared to conventional CE-ICPMS. Magnuson et al.[19,20] reported two similar CE-HG-ICPMS interfaces for selenium and arsenic speciation. Both interface designs utilized multiple peristaltic pumps, which isolated the CE from the HG system in order to overcome the back pressure and capillary suction induced from the excess hydrogen generated from the acid−borohydride reaction.[19,20] Despite the improvement in sensitivity that HG provides to element-specific detectors, the lack of a simple HG interface and the complexity of the available interfaces have slowed the application of CE-HG-ICPMS for speciation analyses.

In this work, a simple CE-HG interface coupled to ICPMS is proposed and successfully applied for arsenic speciation in tap and river water samples. A detailed description of the HG interface design is given. CE separation and HG conditions are carefully optimized to obtain the best resolution and signal-to-noise ratio. Analytical figures of merit for each of the four species studied, As(III), arsenate (As(V)), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) are presented.

Table 2. CE-HG-ICPMS Instrumental Parameters

ICPMS Parameters	
forward power	1400 W (with shielded torch)
plasma gas flow rate	15.6 L min^{-1}
auxiliary gas flow rate	1.0 L min^{-1}
make up gas flow rate	0.66 L min^{-1}
carrier gas flow rate	0.1 L min^{-1}
nebulizer	none
spray chamber	cyclonic (∼0 °C)
sampling depth	6 mm
sampling and skimmer cones	nickel
dwell time	0.1 s
isotopes monitored (m/z)	75 (As^+), 77 ($ArCl^+$, Se^+)
octopole reaction system	not used in this study
CE and Hydride Generation Operating Conditions	
CE instrument	Waters Quanta 4000 capillary ion analyzer
power supply	−20 kV
injection	30-s electromigration: −15 kV
capillary	i.d. 75 μm; o.d. 365 μm; 75 cm long
temperature	25 °C
electrolyte solution	20 mmol L^{-1} sodium borate 2% OFM, pH 9.0
hydride generation conditions	5% HCl and 3% $NaBH_4$ (in 0.2% NaOH)

EXPERIMENTAL SECTION

Reagents. A 20 mmol L^{-1} sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) solution (Fisher Scientific, Fair Lawn, NJ) with 2% CIA-Pak OFM Anion Bt (Waters, Milford, MA) was used as the electrolyte buffer. The buffer was prepared fresh from the stock solution before starting the experiment. A 0.1 mol L^{-1} NaOH (Fisher Scientific) solution was used to adjust the pH of the electrolyte buffer solution. Analytical reagent grade HCl (12 mol L^{-1}) (J. T. Baker, Phillipsburg, NJ) and sodium borohydride (Fluka, Buchs, Switzerland) were used for preparing hydride generation solutions. The optimum hydride generation conditions required the following: 5% HCl and 3% sodium borohydride (0.2% NaOH) and were prepared by diluting/dissolving calculated quantities of the reagent in doubly deionized (DDI) water (Table 2).

The reagents utilized throughout this experiment were of analytical grade and prepared fresh daily through dilution of stock standards with DDI water. All water was prepared by passing through a NanoPure (18 MΩ·cm) treatment system (Barnstead, Boston, MA).

Individual arsenic stock solutions of 1000 μg mL^{-1} As were kindly provided by the U.S. Food and Drug Administration. Inorganic arsenic standards, As_2O_3 in 2% (v/v) HCl and $H_3AsO_4 \cdot {}^1/_2H_2O$ in 2% (v/v) HNO_3 were purchased from Spex Industries (Metuchen, NJ) whereas DMA and disodium methylarsenate (MMA) were from Chem Service (West Chester, PA). The stock solutions were stored at 4 °C, and further standards of lower concentrations were prepared by serial dilution of the stock solution with DDI water.

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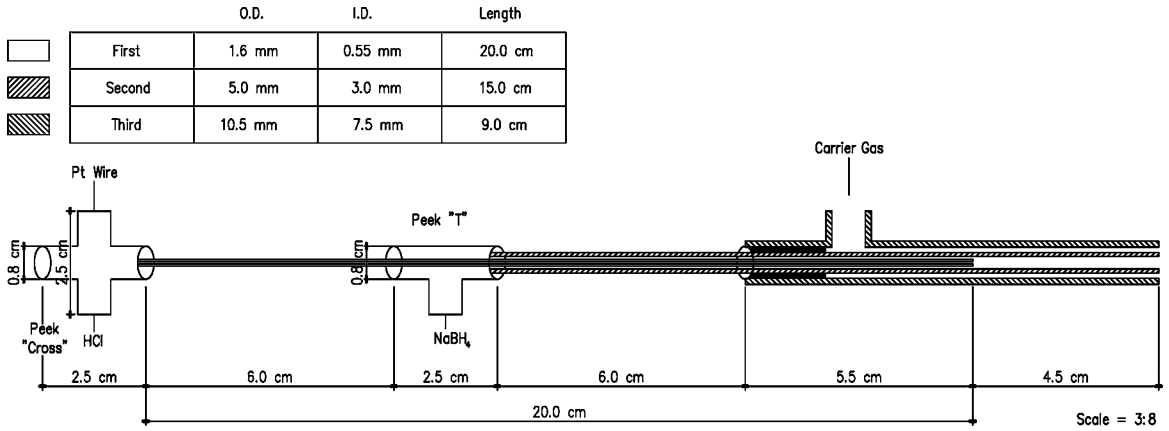

Figure 1. Computer-aided drawing (CAD) of CE-HG-ICPMS interface.

Instrumentation. An Agilent 7500c ICPMS (Agilent Technologies, Tokyo, Japan) equipped with shielded torch technology was used for the element-specific detection of ^{75}As. Signals at m/z 75 and 77 were both monitored in order to study the chlorine interference on the arsenic signal ($^{40}Ar^{35}Cl^+$ and $^{40}Ar^{37}Cl^+$). No detectable chlorine interference was observed during the separation. The octopole reaction cell was not used in this study. The instrumental parameters are presented in Table 2.

CE separations were performed on a Waters Quanta 4000 capillary ion analysis system (Waters Corp., Milford, MA). CE operating conditions are presented in Table 2. A 75-cm fused-silica capillary (75-μm i.d., 365-μm o.d.) purchased from Polymicro Technologies (Phoenix, AZ) was used for the separation. The capillary was conditioned through purging with 0.1 mol L^{-1} NaOH solution for 10 min followed by washing with DDI water for 10 min. Finally, the electrolyte buffer solution was passed through the capillary for a minimum of 30 min before starting the electrophoretic separation.

Interface Design. The interface used in this experiment was based upon a three concentric tube design illustrated in Figure 1. The interface components were made of PEEK material; finger tight fittings, three-way tee, and four-way tee (Upchurch Scientific, Oak Harbor, WA). The design consists of two tees, one four-way followed by a three-way union. In the four-way tee union, a platinum electrode connected at one of the sidearms served as a ground connection and its opposite end was connected to a Teflon tubing 30.0 cm in length for the purpose of introducing hydrochloric acid. The other end of the Teflon tubing was connected to a Tygon tube (3.0-mm o.d., 1.02-mm i.d.) attached to a Gilson Miniplus 3 (Gilson, Villiers Le Bel, France) peristaltic pump. The flow rate through this tube was calibrated at different rpm values of the peristaltic pump. A flow rate of 0.285 mL min^{-1} for both acid and reducing agent was found to be the optimum for the introduction into the HG system. The remaining two ends of the four-way tee were used for the introduction of the capillary into the interface. PEEK tubing (0.50-mm i.d., 1.6-mm o.d.) was used as a sleeve around the CE capillary allowing an airtight seal during its insertion into the four-way tee union. The final connection to the four-way tee consisted of a 20-cm-long Teflon tube (1.6-mm o.d., 0.55-mm i.d.). This Teflon tube served as the innermost tube in the interface design and allowed HCl sheath flow around the CE capillary providing a constant current during the eletrophoretic separation. This Teflon tube was then passed through the three-way tee as shown in the Figure 1. The length of the Teflon tube between the two tee connections was 6.0 cm. The sidearm of the three-way tee was connected to a Teflon tubing 30.0 cm in length for the purpose of introducing the $NaBH_4$ flow. The remainder of the connection used was similar to the one for introducing HCl in the four-way tee. The flow of $NaBH_4$ through this tubing was found to be lower compared to HCl. This difference is due to slight differences in the tubing internal diameters and the presence of bubbles generated in a fresh solution of $NaBH_4$. The final connection to the three-way tee consisted of a 15.0-cm glass tube (5.0-mm o.d., 3.0-mm i.d.), which concentrically covered the internal Teflon tube allowing sheath flow of the sodium borohydride around the internal Teflon tube carrying HCl. The final stage of the interface had a 9.0-cm glass tube (10.5-mm o.d., 7.5-mm i.d.) placed 6.0 cm from the three-way tee and consisted of a sidearm (1.0 cm) for the introduction of argon carrier gas spaced 2.0 cm from the beginning of the tube. This tube was attached to the internal glass tube through the use of a rubber fitting and Teflon tape to ensure a proper seal and complete the interface design. Figure 1, drawn to scale, shows the complete design of this interface.

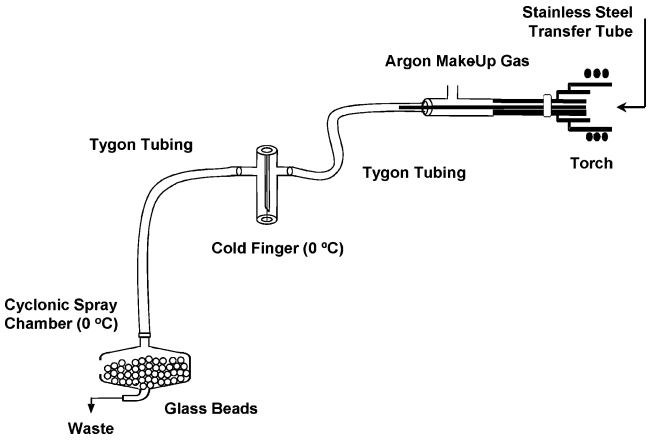

Figure 2. CE-HG interface transfer line utilized for removal of hydride condensation and more efficient analyte transport to ICPMS.

Coupling the Hydride Generation Interface with ICPMS. The experimental setup used for coupling the interface to ICPMS is shown in Figure 2. A cyclonic spray chamber was used as a gas−liquid separator for the HG interface. To decrease the dead volume in the gas−liquid separator, the spray chamber was filled

with glass beads. Two separate flows of argon gas were used to carry the hydrides formed in the interface to the ICPMS instrument. Initial experimental observations of the interface coupled with ICPMS showed high back pressure due to the hydrogen gas generated during the reaction. To overcome the back pressure in the HG interface, the carrier and makeup gas flow rates were first optimized through continuous introduction of 10 μg L^{-1} As(III) in 5% (v/v) HCl solution followed by optimization of the interface parameters. Optimum values for the carrier and makeup gases were found to be 0.10 and 0.66 L min^{-1}, respectively (Table 2). Thus, a low carrier gas flow of 0.10 L min^{-1} was used to carry the hydrides formed during the derivatization reaction. Higher carrier gas flow decreased the dispersion of the peaks but at the same time increased the back pressure in the gas−liquid separator. On the other hand, lower carrier gas flow rates increased the dispersion of the transient signals and thereby affected peak separation. A stainless steel transfer tube, which was passed through the central channel of the torch, along with a glass makeup gas connector surrounding it up to the beginning of the torch was an integral part in connecting the interface to the ICPMS (Figure 2). The stainless steel transfer tube was grounded securely to avoid rf problems in lighting the plasma; however, this design was affected by the condensation of water in the transfer line due to the lack of a proper system to remove the moisture. Efforts to remove condensation led to the use of a coldfinger between the gas−liquid separator and the metal transfer tube that was used for the introduction of the hydrides into the plasma. Thus, the transfer line consisted of two pieces of Tygon tubing, one running from the cyclonic spray chamber to a coldfinger and the second running from the coldfinger to a stainless steel transfer tube (Figure 2). Finally, improved hydride transport resulting from the removal of condensation was achieved through cooling both the cyclonic spray chamber and coldfinger in an ice−water bath. The use of a small gas−liquid separator with minimum dead volume allowed the use of lower flow for both HCl and $NaBH_4$, which in turn lowered the production of the hydrogen gas. Having lower hydrogen gas generation during the derivatization reaction aided in a more efficient stabilization of the plasma. Also, the use of lower carrier gas flow not only decreased the back pressure but improved the signal by lowering the dilution factor. Through the reduction in back pressure and removal of condensation, optimum CE-HG interface conditions were achieved and applied for all additional experiments.

RESULTS AND DISCUSSION

Optimization of Hydride Generation Conditions. The optimization of the HG conditions consisted of determining the optimum HCl and $NaBH_4$ concentrations for maximum formation of hydride species without affecting the normal instrumental run parameters. The use of high $NaBH_4$ concentrations is typically limited by plasma extinguishing due to the excess formation of hydrogen during the HG reaction. Due to the difference in the instrumental conditions for continuous sample introduction and transient injection, all the optimizations were performed by injecting the arsenic standards in the CE-HG-ICPMS system. The optimization of HCl consisted of multiple CE separations of the standard arsenic mixture with 1, 2, 4, and 5% (v/v) HCl reacted with 2% $NaBH_4$ (in 0.2% NaOH). Figure 3 shows resulting peak areas of each arsenic species plotted versus HCl concentration

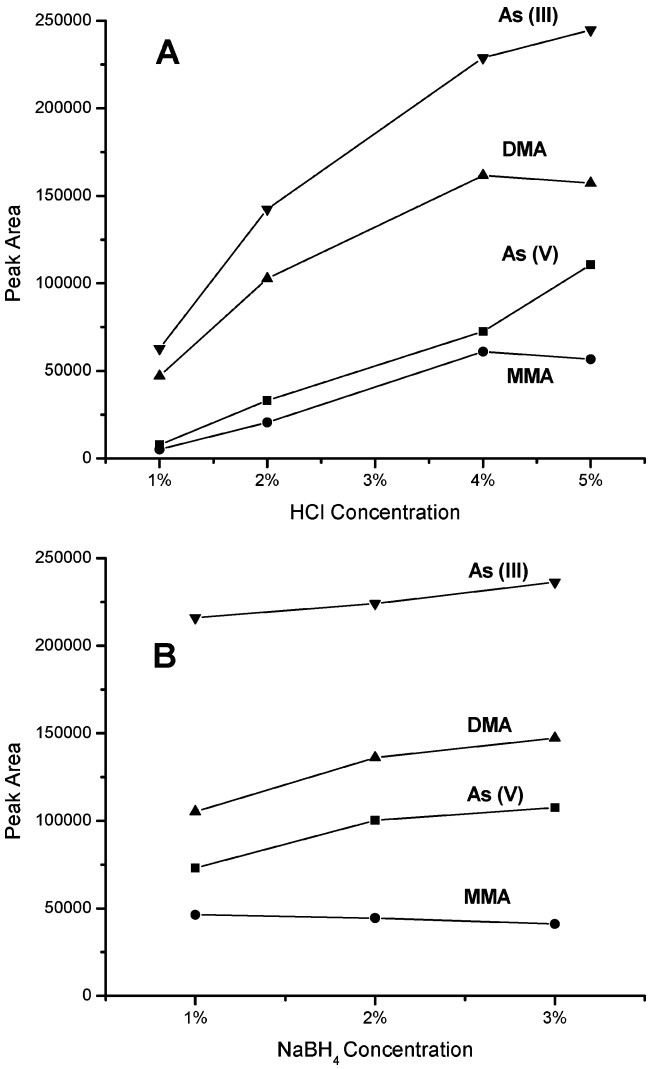

Figure 3. Optimization of hydrochloric acid (A) and sodium borohydride (B) for standard arsenic mixture based upon peak area during CE separation. Instrumental parameters are presented in Table 2.

with 5% HCl established as the optimum concentration. The plot shows a consistent increase in peak area for each arsenic species over concentrations of 1, 2, and 4% HCl (Figure 3). Minimal peak area increases were seen for MMA and DMA between 4 and 5% HCl; however, significant increases were observed for As(III) and As(V) resulting in 5% HCl as the optimum concentration. Once the optimum concentration of HCl (5%) was obtained, optimization of $NaBH_4$ was performed with multiple CE separations of the standard arsenic mixture over concentrations of 1, 2, and 3% $NaBH_4$ (in 0.2% NaOH). Plots obtained for the resulting peak areas of each arsenic species versus the concentration of $NaBH_4$ showed a consistent increase in peak area for As(III), As(V), and DMA with 3% chosen as the optimum concentration (Figure 3). All hydride generation optimization trials utilized a Gilson Minipuls 3 peristaltic pump with a flow rate of 0.285 mL min^{-1} for both HCl and $NaBH_4$. Flow rate values higher than 0.285 mL min^{-1} produced a significant back pressure, whereas lower flow rates lead to suction at the interface, which often resulted in loss of current. Therefore, a mobile-phase flow rate of 0.285 mL min^{-1} was used for the remaining experiments. In previous publications involving the use of HG interface for CE-ICPMS systems,[19,20] a

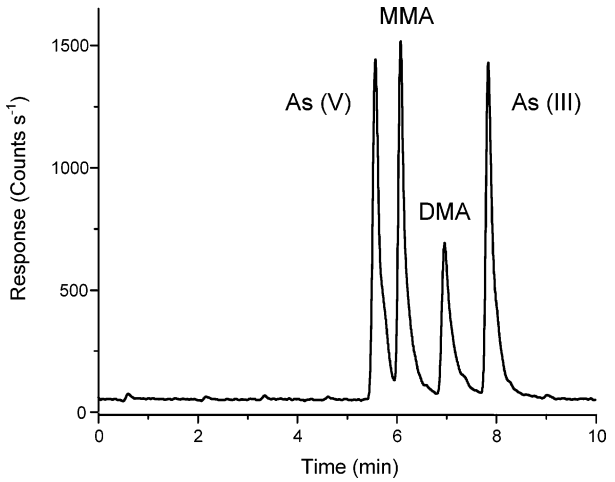

Figure 4. Separation of standard arsenic mixture (500 μg L^{-1}) under optimum CE and HG conditions.

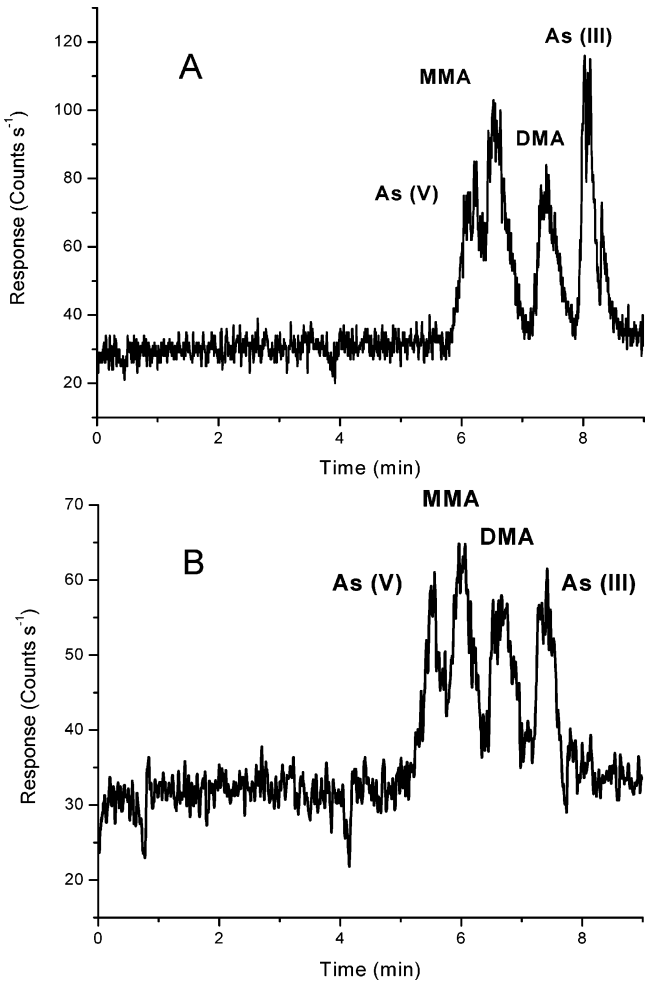

Figure 5. Arsenic mixture (100 μg L^{-1}) spiked (A) tap water sample and (B) Miami River water sample.

higher flow was used for both HCl and $NaBH_4$ leading to a major dilution of the transient signals generated in the CE separation and significantly lowering the sensitivity. On the other hand, the use of a lower flow rate for the HG reagents in this work was found to improve the signal-to-noise ratio. Additionally, the low flow rate of the HG reagents alleviated the back pressure by diminishing the excess H_2 gas in the CE-HG-ICPMS experiments performed. The reduction of the H_2 gas produced not only reduced the noise but also increased the signal by lowering the dilution of the hydrides formed.

Arsenic Species Separation by Capillary Electrophoresis. The electrophoretic buffer used in this work has previously been reported for the separation of four anionic arsenic species; As(III), As(V), MMA, and DMA by Van Holderbeck et al.[26] This work utilized co-electroosmotic flow as the mode of separation through the use of an osmotic flow modifier for the analysis of the previously mentioned arsenic species by CE-ICPMS.[26] It was also reported that 20 mmol L^{-1} sodium borate buffer over an optimum buffer pH range of 8−10, with 9.3 the optimum value, allowed complete baseline CE separation of these four anionic arsenic species.[26] The current experiment confirmed the previously reported CE separation conditions after optimization experiments with 20 mmol L^{-1} sodium borate buffer at pH 9.0 utilized for the CE separation of As(III), As(V), MMA, and DMA (Table 2). The charges on these different arsenic species over various buffer pH values were calculated from the previously reported pK_a values.[26] At pH 9.0, all the arsenic species are negatively charged and therefore the maximum resolution is obtained. The resolution achieved was sufficient to compensate for the dispersion of the peaks due to the dead volume in the CE-HG interface and the transfer line from the CE-HG interface to the ICPMS instrument (Figure 2).

Both hydrodynamic and electrostatic injections of the samples were performed to obtain the maximum sample transfer into the capillary without affecting the resolution of the peaks. Electrostatic injection was found to be better when compared with hydrodynamic injection, which seemed to be affected more by the back pressure resulting in an unreliable sample injection. An injection time of 30 s at −20 kV gave the best results for the given capillary dimensions (Table 2, Figure 4).

Analytical Performance of the CE-HG-ICPMS. The detection limits (3σ) based on peak area for the analysis of As(III), As(V), MMA, and DMA by CE-HG-ICPMS were found to be 35.0, 35.0, 27.0, and 39.0 ng L^{-1}, respectively. The detection limits of the four As species obtained by this novel CE-HG-ICPMS system are comparable to those previously reported for CE-HG-ICPMS.[20] The complexity of the earlier interfaces was overcome in this work through the application of the concentric tube interface. The use of reduced reagent flow rates allowed lower consumption of chemicals and decreased the generation of hydrogen gas resulting in higher hydride transport efficiency and plasma stability. The precision for repeated injections of a 100 μg L^{-1} standard mixture were within the range of 0.3−0.9% for migration times and 3−9% for peak areas.

Speciation Analysis in Water Samples. Demonstration of the application of the CE-HG-ICPMS interface was accomplished through the analysis of tap and Little Miami River (Ohio) water samples. Little Miami River water samples were collected in 1000-mL borosilicate glass bottles. Immediately after sampling, the samples were analyzed for arsenic. None of the samples analyzed showed detectable amounts of arsenic. Lack of any detectable arsenic species in the samples led to spiking of both the tap and

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river water samples with a 100 μg L^{-1} mixture of As(III), As(V), MMA, and DMA (Figure 5). When spiked samples were stored at 4 °C, conversion between the various arsenic species over a period of time was observed. In the case of tap water samples there was nearly 80% conversion from As(III) to As(V), whereas in the Little Miami River water samples no conversion was observed over the same period of time. The remaining two arsenic species MMA and DMA were found to be the same in both samples. This conversion can be attributed to matrix differences between the two samples. In the river water samples, the matrix stabilized the arsenic species and prevented them from converting. In the case of tap water sample (Figure 5), baseline resolution was not achieved between As(V) and MMA. Unfortunately, the presence of various matrix components is the most likely cause of the lack of complete baseline separation between these two species. However, this lack of resolution could be effectively solved by changing the electrophoretic separation conditions while the generation of hydrides is assured with the proposed HG system. Species oxidation-state changes are most likely due to oxidizing cations. However, this would naturally happen in drinking water as As(III) was introduced.

CONCLUSION

In this work, an HG interface was designed and successfully coupled to CE-ICPMS for the analysis of As(III), As(V), MMA, and DMA species. Coupling CE with ICPMS using the HG interface was demonstrated as an efficient separation technique with short analysis time while considerably increasing the efficiency of analyte introduction into the plasma resulting in improved signal-to-noise ratio. Electrophoretic separation of the four species was achieved in less than 9.0 min with detection limits less than 40 ng L^{-1} for each species. This novel interface design, when compared with previous HG interfaces, simplified the coupling process, while at the same time problems such as high back pressure associated with the previous interfaces were overcome to a large extent. Application of the novel interface to the analysis of arsenic species in real sample matrixes demonstrated the proposed HG interface to be a capable technique for speciation analysis by CE-HG-ICPMS.

ACKNOWLEDGMENT

We give special thanks to Gregory J. De Nicola for providing the CAD drawing of the interface. Also the authors thank Agilent Technologies for continuing support of our work. We also acknowledge NIEHS Grant ES04908 for partial funding of this research.

Received for review June 25, 2004. Accepted September 7, 2004.

AC049066T