Application of Capillary Electrophoresis (CE) coupled with Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) for Simultaneous Speciation Analysis of Arsenic and Selenium

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NMEC 2015

Agilent Technologies

Introduction

The presence of arsenic, selenium in the environment raises concern about their potentially toxic properties. This work describes the coupling of CE with ICP-MS for the simultaneous separation and determination of arsenic and selenium in environmental matrices. Using a direct-injection high-efficiency nebulizer (DIHEN) interface allowed for the baseline separation an determination of six arsenic species, including arsenite (As(III), arsenate (As(V)), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and arsenocholine (AsC), and five selenium species such as sodium selenite (Se(IV)), sodium selenate (Se(VI)), selenocysteine (SeCys), selenomethionine (SeMet), and Se-methylselenocysteine (MeSeCys) in a single run. Detection limits were ranged between 0.11–0.37 µg/L for the six arsenic compounds and 1.33–2.31 µg/L for the five selenium species. Repeatability (RSD, n = 6) of both migration time and peak area were better than 2.68% for arsenic compounds and 3.28% for selenium compounds. The method has been successfully applied to the determination of arsenic and selenium species in the certified reference materials DORM-3, water, urine, and fish samples.

Experimental

CE-ICP-MS System

The CE-ICP-MS System configuration consisted of a HP3D CE (Agilent Technologies, Germany) and an Agilent 7500ce ICP-MS (Agilent Technologies, USA). Table 1 summarizes the operating parameters.

System Optimization

A standard solution of 10 µg L–1 Li, Y, Ce and Tl, was used to optimize the torch position and argon flow rate prior to hyphenation. Detection of 75As and 82Se used time resolved analysis mode for signals collected at m/z of 75 and 82, respectively.

Separation Conditions

CE Separation used a 60cm×75µm id×365µm od fused-silica capillaries. New capillaries were conditioned by flushing with 1 mol L–1 NaOH for 60 min, 0.1 mol L–1 NaOH for 60 min, H2O for 30 min, and running buffer solution for 60 min, sequentially.

Experimental

ICP-MS Parameters	
RF power	1500 W
sample depth	8.0 mm
plasma gas flow rate	15 L/min
carrier gas flow rate	1.05 L/min
makeup gas flow rate	0.10 L/min
dynamic reaction cell	off
monitored isotope(m/z)	^{75}As, ^{82}Se
CE Parameters	
fused silica capillary	75 µm id × 60 cm length
buffer	NaH_2PO_4 (6 mM), H_3BO_3 (9 mM), pH 9.0
voltage	+25 kV
temperature	25 °C
sample injection	hydrodynamic 10 s (50 mbar), 72.6 nL
preanalysis rinse	0.1 M sodium hydroxide (2 min)
deionized (DI) water (2 min)	
running buffer (2 min)	
Interface	
nebulizer	CE-ESI-MS sprayer
sheath liquid	100 µg L^{-1} $Rh(NO_3)_3$, 6% methanol
sheath flow rate	4 µL/min

Table 1. Equipment and Operating Conditions of CE-ICPM

Separation Conditions (Continued)

Between runs the capillary was flushed with 0.1 mol/L NaOH, H2O and buffer for 2 min, respectively. The capillary was reconditioned by purging with 0.1 mol/L NaOH and H2O for 10 min, daily. Samples were injected into the capillary at 50 mbar for 10 sec. The applied voltage and cassette temperature were set at 25 kV and 25 °C.

CE to ICP Interface

The interface used in this research work was configured per Figure 1.

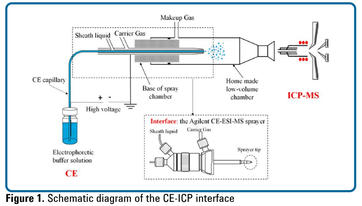

Figure 1. Schematic diagram of the CE-ICP interface

CE-ESIMS sprayer (Agilent Technologies, USA) was used for the CE-ICP-MS nebulizer interface. The CE capillary passed through the inner stainless steel capillary of the sprayer. A liquid sheath flow was added in the gap between the CE capillary and the inner stainless steel capillary,

Experimental

Analytes were separated under the high voltage in the CE capillary. Capillary effluent was mixed with the sheath flow and directly nebulized by the carrier gas, Nebulized analytes were carried to the ICP-MS torch for ionization/detection. Analytes were separated under the high voltage in the CE capillary. Capillary effluent was mixed with the sheath flow and directly nebulized by the carrier gas, Nebulized analytes were carried to the ICP-MS torch for ionization/detection.

Samples and Sample Preparation.

Two groundwater samples and one tap water sample were collected from wells in Shanyin (Shanxi province, China), Tap water was collected from the laboratory (Beijing, China). A urine sample was collected from a volunteer living in Shanyin and fish samples were collected from *Paralichthys olivaceus* in Dalian (Liaoning province, China), and *Racoma biddulphi Gunther* from Tibetan plateau (Tibet, China). Water and urine samples were filtrated through 0.22 µm nylon filter to remove particulates. Fish samples were lyophilized and homogenized prior to extraction,

Sample Extraction

For extraction 0.3–0.5 g DORM-3 and/or fish power was placed to the centrifuge tubes with of 5 mL deionized water. Following 2 min vortex mixing samples were sonicated for 120 min. Resulting suspensions were centrifuged at 4000 rpm for 10 min. Supernatant was collected and filtered, 0.22 µm nylon filter. All extracted solutions were diluted to volume with buffer solution prior to injection.

Results and Discussion

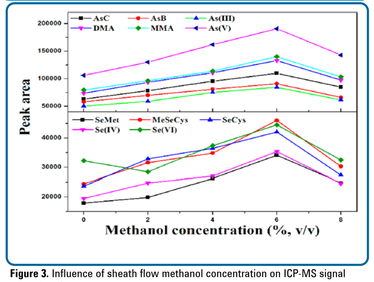

Figure 3. Influence of sheath flow methanol concentration on ICP-MS signal intensities for arsenic and selenium compounds.

Results and Discussion

Optimizing CE Interfaces Sheath Flow

Response of arsenic and selenium species increased with increasing concentrations of methanol between 0% to 6%. Response decreased at a methanol concentration 8% as depicted in Figure 3. Therefore, 6% was chosen as the methanol concentration for the sheath flow liquid.

Optimization of CE Conditions

Figure 4 depicts the effect of buffer concentration (phosphate–borate buffer solution at (10, 15, 20, 25, 30 mmol/L, phosphate:borate ratio =2:3) on CE separation. Increasing of the buffer concentration increased migration time of the species in the capillary resulting in improved separation efficiency.

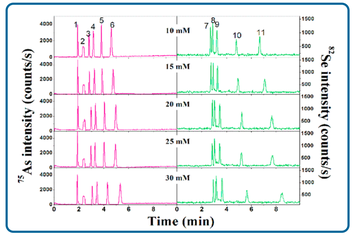

Figure 4. Effect of buffer concentration on the CE separation of arsenic (6) and selenium (5) cntaining mopounds at 100 µg/L and 200 µg/L respectively. Peak identity: 1, AsC; 2, AsB; 3, As(III); 4, DMA; 5, MMA; 6, As(V); 7, SeMet; 8, MeSeCys; 9, SeCys2; 10, Se(IV); and 11, Se(VI).

Analytical Performance.

Using the optimized conditions for CE separation,, AsB, AsC, As(III), DMA, MMA, As(V), SeMet, MeSeCys, SeCys, Se(IV), and Se(VI) were baseline-separated within 10 min. Table 2 summarizes the analytical performance. Calibration curves (As: 5–200 µg/L, SE: 10–400 µg L) were linear with correlation coefficients r^2 >0.998. Precision for analysis of mixed species (As: 100 µg/L and Se: 200 µg L–1, n=6) yielded RSD 0.72% to 2.68% for migration and RSD 0.71%–3.28% for peak area.

Results and Discussion

analyte	linear range (µg L^{-1})	correlation coefficient	Limit of Detection, LOD (µg L^{-1})[a]	(fg)[b]	RSD[c] (%) retention time	peak area
AsC	5–200	0.9997	0.21	15.6	0.74	0.88
AsB	5–200	0.9995	0.37	26.5	0.72	0.72
As(III)	5–200	0.9995	0.25	17.8	1.01	1.22
DMA	5–200	0.9999	0.21	15.5	0.76	3.28
MMA	5–200	0.9996	0.11	7.8	1.04	1.71
As(V)	5–200	0.9989	0.22	15.9	1.23	0.91
SeMet	10–400	0.9999	1.48	107.5	1.07	2.59
MeSeCys	10–400	0.9998	1.33	96.4	1.49	1.39
SeCys	10–400	0.9992	1.27	91.9	1.48	1.72
Se(IV)	10–400	0.9999	2.31	167.8	2.68	0.71
Se(VI)	10–400	0.9999	2.23	161.6	1.87	0.89

[a]Calculated using 3σ/S based on the peak height measurement. [b]Absolute detection limits (fg) based on a 72.6 nL sample injection. [c]Standard concentration, 100 µg L^{-1} (As) and 200 µg L^{-1} (Se), n = 6.

Table 2:. Analytical Performance for CE-ICP-MS Analytical Method

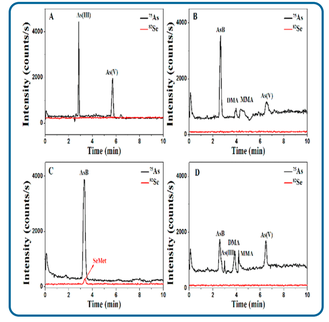

Figure 5:. Electropherogram of arsenic and selenium species in (A) Ground Water-1, (B) DORM-3, (C) Fish-2, and (D) Urine sample.

compound	Water Samples (µg L^{-1}) Ground water-1	Ground water-2	tap water	recovery[a] (%)	Fish Samples (µg g^{-1}) DORM-3[b]	Fish-1	Fish-2	recovery[c] (%)	Urine Sample (µg L^{-1}) Urine	recovery (%)
AsC	nd		nd	93.0	nd	nd	nd	97.9	nd	94.9
AsB	nd		nd	99.0	5.11 ± 0.09	4.87 ± 0.23	0.61 ± 0.04	106.3	314.3 ± 24.5	110.2
As(III)	357.7 ± 4.3	85.5 ± 1.4	nd	99.7	nd	nd	nd	100.4	50.5 ± 5.7	106.6
DMA	nd		nd	99.3	0.43 ± 0.01	0.21 ± 0.01	nd	96.4	150.4 ± 8.7	95.9
MMA	nd		nd	97.1	0.45 ± 0.06	nd	0.16 ± 0.01	101.1	85.1 ± 1.1	100.6
As(V)	126.3 ± 1.3	201.1 ± 2.9	2.04 ± 0.02	99.4	0.32 ± 0.02	nd	0.13 ± 0.01	96.2	19.0 ± 1.2	98.4
SeMet	nd	nd	nd	99.8	nd	1.56 ± 0.02	nd	102.7	nd	103.4
MeSeCys	nd	nd	nd	96.2	nd	nd	nd	105.8	nd	100.8
SeCys	nd	nd	nd	88.9	nd	nd	nd	93.7	nd	110.1
Se(IV)	nd	nd	nd	97.5	nd	nd	nd	102.0	nd	97.5
Se(VI)	nd	nd	nd	98.3	nd	nd	nd	103.0	nd	93.3
total As	499.1 ± 2.3	310.8 ± 3.7	3.3 ± 0.06		6.73 ± 0.13	5.90 ± 0.06	1.04 ± 0.02		637.0 ± 10.2	
total Se	nd	nd	nd		2.98 ± 0.17	2.38 ± 0.05	0.01 ± 0.001		nd	

[a]Spiked 100 µg L^{-1} arsenic and 200 µg L^{-1} selenium species on groundwater-1. [b]Certified value of the total arsenic (6.88 ± 0.3 µg g^{-1}). [c]Spiked 50 µg L^{-1} arsenic and 100 µg L^{-1} selenium species on DORM-3.

Table 3:. Concentrations and Recoveries of Arsenic and Selenium Species in Water, Fish and Urine Samples Quantified by CE-ICP-MS

Conclusions

CE-ICP-MS analysis was applied successfully to the quantification of arsenic and selenium species in real world samples producing linear calibration response and precise and reproducible quantitative results. Analysis in all matrices yielded excellent recovery. The sensitivity of the ICP-MS allows for the analysis of low sample volumes making hyphenated CE-ICP-MS analysis system a viable tool for determining concentration, distribution, and toxicity of trace arsenic and selenium in aqueous and biological samples.

Collaborator Reference: Liu, L.; Yun, Z.; He, B.; and Jiang, G. *Anal Chem* **2014**, 86, 8167–8175