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Speciation of arsenic and selenium by capillary electrophoresis

Baoguo Sun, Miroslav Macka, Paul R. Haddad*

Australian Centre for Research on Separation Science, School of Chemistry, University of Tasmania, G.P.O. Box 252-75, Hobart, Tasmania 7001, Australia

Abstract

Capillary electrophoresis (CE) with direct UV detection, both on-capillary and with a high-sensitivity detection cell (HSDC), were used for the simultaneous determination of arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), selenate [Se(VI)], selenite [Se(IV)], selenocystine (SeC), selenomethionine (SeM) and selenocystamine (SeCM). These anionic and cationic species were separated with negative separation voltage polarity in a capillary coated with poly(diallydimethylammonium chloride) (PDDAC). The background electrolyte (BGE) providing optimal separation was 15 mM phosphate buffer at pH 10.6. Arsenic and selenium species were detected at 195 and 200 nm, respectively. The limit of detection (LOD) values with on-capillary detection (75 μm i.d.) for the individual analytes were 1.02, 1.50, 1.08, 1.35, 19.5, 0.36, 0.32, 1.11 and 1.47 mg/L, respectively (expressed as arsenic or selenium). The method precision for peak area was from 2.1 to 3.4% relative standard deviation. HSDC was applied to increase the detection sensitivity and gave LOD improvement factors from 4.7 to 8.2, yielding LODs for the individual target analytes ranging from 0.049 to 2.38 mg/L. When the normal sample stacking mode was employed using a sample plug up to 4.6% of capillary volume, both the cationic and anionic analytes were stacked simultaneously with LOD improvement factors of 2.6–4.5 yielding LODs for the individual analytes ranging from 0.11 to 7.42 mg/L. The method was applied for the speciation of arsenic in sediment and determination of SeM in a selenium nutrition supplement. The achieved separation selectivity also gives the method a more general application potential for simultaneous arsenic and selenium speciation when hyphenated with inductively coupled plasma MS.

Keywords: Sediment; Food analysis; Arsenic; Selenium; Organoarsenic compounds; Organoselenium compounds

1. Introduction

Arsenic and selenium play important roles in the environment and in human health and therefore their speciation is of increasing concern. Among the arsenic species, inorganic arsenic compounds are highly toxic, whereas methylation is the most important pathway to transform inorganic arsenic into organic arsenic species of lower toxicity. Consequently, arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are among the most important arsenic species. It has been confirmed that these four arsenic compounds are major metabolic arsenic species in human urine [1]. Selenium is both a toxic element and an essential element. The toxicity of selenium again depends to a large extent on its chemical form, with organoselenium compounds being more toxic than inorganic selenium compounds. On the other hand, selenium(II), especially in the form of selenoamino acids, takes part in the biological selenium cycle, selenium is incorporated into proteins, and therefore selenium supplementation may aid in the prevention of some diseases [2]. The main selenoamino acid in plants is selenomethionine (SeM), which is used as a selenium supplement for humans and animals [2]. The target analytes in this study consist of the most important arsenic species and selenium species, and their formulae and abbreviations are summarized in Table 1.

In the past, high-performance liquid chromatography (HPLC) and gas chromatography (GC) have been the predominant methods for elemental speciation [3,4]. However, there has been an increasing interest in the application of CE for the separation and determination of arsenic and selenium species because CE has the advantages of short analysis time, high separation efficiency and low operating costs [5,6]. Simultaneous determination of some selenium and arsenic species with CE has been reported [7–12], but

* Corresponding author. Tel.: +61-3-62262179; fax: +61-3-62262858.
E-mail address: paul.haddad@utas.edu.au (P.R. Haddad).
URL: http://www.across.org.au/.

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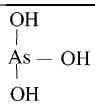
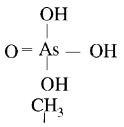
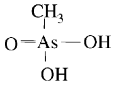
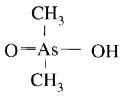
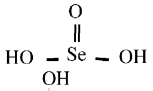
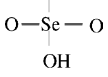
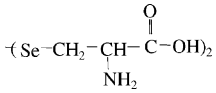
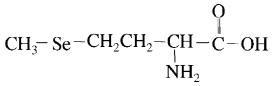
Table 1
Analytes in this study: chemical name, abbreviation, structure, and pK_a values [24]

Analyte	Abbreviation	Molecular structure	pK_a
Arsenite	As(III)		9.23
Arsenate	As(V)		2.25, 6.77, 11.60
Monomethylarsonic acid	MMA		3.6, 8.2
Dimethylarsinic acid	DMA		1.3, 6.2
Selenite	Se(IV)		2.46, 7.31
Selenate	Se(VI)		<1, 1.92
Selenocystine	SeC		1–2.1, 8.71
Selenomethionine	SeM		2.28, 9.21
Selenocystamine	SeCM	$NH_2CH_2CH_2SeSeCH_2CH_2NH_2$	NA

none of the previously published studies has offered a single method that would include all of the target analytes. The electrophoretic mobility of Se(VI) is always higher than that of the electroosmotic flow (EOF) in fused silica capillaries in moderately alkaline background electrolytes (BGEs) and the electrophoretic mobility of Se(IV) is close to the usual magnitude of EOF, so that these species cannot be determined in a counter-EOF CE mode. To separate all the target analytes, it is necessary to suppress or reverse the EOF and to use a negative separation voltage polarity at the injection end. In principle, this could be achieved by adding cationic surfactants to the BGE, but previous studies [10–13] have indicated that this approach results in problems with separation efficiency and/or baseline stability. These problems could originate from the presence of the cationic surfactant in the electrolyte and the use of a low-UV detection wavelength. Moreover, the presence of surfactants in the BGE is likely to cause difficulties when the CE separation is coupled with MS or inductively coupled plasma (ICP) MS detectors. As an alternative to the dynamic coating with cationic surfactants, a capillary coated permanently or semi-permanently with a cationic polymer can be used to achieve EOF reversal [14,15]. In a similar approach using a suppressed EOF capillary, Vanifatova et al. [16] reported the use of a polyacrylamido-coated capillary for the separation of some arsenic and selenium compounds. In our previous work, a poly(diallydimethylammonium chloride) (PDDAC) coated capillary was used for the separation of nine arsenic compounds [14].

The low concentration sensitivity of on-capillary photometric detection and corresponding high limits of detection (LODs) often pose a serious limitation to the wider applicability of CE to real samples, especially in the area of environmental analysis. To improve the LOD of a CE met either more sample has to be introduced into the capillary and sample stacking techniques applied, or the detection path length has to be increased [5]. It is generally accepted that cationic and anionic analytes cannot be easily stacked simultaneously [17]. However, a new mode, co-electroosmotic normal stacking mode (co-EOF-NSM), was developed and its mechanism was investigated in our previous work [18]. Importantly, in this work we demonstrated that using this stacking mode, both cationic and anionic analytes could be stacked simultaneously. Once cationic and anionic analytes contained in a low conductivity sample matrix are introduced into a PDDAC-coated capillary and negative voltage is applied, cationic analytes can be stacked by the normal stacking mode (NSM) and anionic analytes can be stacked using co-EOF-NSM.

However, the conductivity of real sample matrices is often very high and sample stacking cannot be used to increase

the sensitivity. In this situation an increase in the path length of the detection cell is an alternative approach to achieve an improvement in the LOD values. When using direct absorbance detection, various technologies to produce a detection cell with an increased optical path length compared to that of a simple on-capillary detection have been reported and evaluated [19]. A high sensitivity detection cell (HSDC) provides a detection path length which more than an order of magnitude longer than conventional on-capillary detection. In the present study, sensitivity enhancement by both increased sample loading and through use of a HSDC have been utilized.

The aims of the present study were to develop a CE method for the simultaneous separation of all the arsenic and selenium species listed in Table 1, to improve the detection sensitivity by stacking and use of a HSDC, and to apply the developed method to the determination of arsenic species in a sediment sample and of SeM in a selenium nutrition sample. A further aim was to design the separation conditions to ensure that the developed method could potentially also be utilized with hyphenated detection methods such as CE–ICP-MS [20,21].

2. Experimental

2.1. Instrumentation

Experiments were performed on a HP^{3D} CE instrument (Agilent Technologies, Waldbronn, Germany) equipped with a diode-array detection (DAD) system operating in range 190–600 nm. Separations were performed in a PDDAC-coated capillary of dimensions 64.5 cm (56 cm to detector) × 50 μm i.d., which was produced by coating fused silica capillary (Polymicro Technologies, Phoenix, AZ, USA) using reported procedures [14]. High-sensitivity detection was performed with a high sensitivity detection cell (Agilent Technologies) connected by with inlet (56 cm) and outlet (8.5 cm) capillaries of 75 μm i.d. The capillary temperature was set to 20 °C. Hydrodynamic injection was used, with injection pressure and injection times being given in each of the figure captions. The centrifuge used was a Capsule HF-120 (Tomy Seiko, Tokyo, Japan).

2.2. Reagents

All analyte concentrations were expressed in terms of the As or Se present. Standard solutions (1000 mg/L) of the As and Se species were prepared in water using the following reagents: $Na_2HAsO_4{\cdot}7H_2O$, selenocystine, selenomethionine, selenite, selenate, selenocystamine (Aldrich, Sydney, Australia); As_2O_3 (Merck, Victoria, Australia); DMA and MMA (purified in our laboratory by re-crystallization, purity >98%). Phosphate buffer solutions were prepared from analytical grade $Na_3PO_4{\cdot}H_2O$, NaH_2PO_4 and NaH_2PO_4 (Merck). 1.0 M NaOH solution was prepared from sodium hydroxide (Merck). An aqueous solution of PDDAC (0.5%, w/w) was prepared from material having a weight-average molecular mass M_w of ca. 100 000–200 000, 20% (w/w) (Aldrich, Sydney, Australia). All other chemicals were of analytical-reagent grade. All carrier electrolytes and standards were prepared in water treated with a Millipore (Bedford, MA, USA) Milli-Q water purification apparatus. These solutions were stored in the dark at 4 °C. Diluted solutions for daily use were prepared in pure water. Electrolytes were degassed using vacuum sonication and were filtered through a 0.45 μm syringe filter (Activon, Thornleigh, Australia) prior to use. A C_{18} cartridge (900 mg, Alltech, Australia) was used for sample treatment. Electrolyte replenishment was applied or fresh electrolyte was used for every separation.

2.3. Methods

2.3.1. CE method

The PDDAC-coated capillary was prepared by simply flushing fused silica capillary with PDDAC solution [14]. Sample was introduced by hydrodynamic injection, the injection pressure was 50 mbar and injection times are given in each of the figures. Signals at the wavelengths of 195 and 200 nm and the separation current were monitored simultaneously. Phosphate buffer (15 mM) pH 10.6 was used as BGE unless otherwise indicated. The applied voltage was −25 kV for the PDDAC-coated capillary and 25 kV for the bare fused silica capillary. The LODs were calculated for a signal/noise ratio = 3.

Individual electrophoretic mobilities of the analytes in the range of pH 5–11 were measured for Se(IV) and Se(VI) with a PDDAC-coated capillary operated in the co-EOF mode, and mobilities of all other analytes were determined using a fused silica capillary operated in the normal EOF mode, using 15 mM phosphate buffers at varying pH as BGEs.

To achieve co-EOF-NSM stacking, a maximum of 5% of capillary volume of sample of lower conductivity was injected, and then negative voltage was applied to stack and separate the analytes.

2.3.2. Sample treatment

A dried sediment sample (10 g), which had been spiked with arsenic species (1 mg/L stock solution used), was mixed with 50 mL water, agitated for 2 h, and then left standing for 10 min. A 3 mL aliquot of the supernatant was centrifuged for 10 min at 3000 rpm, and then passed through a C_{18} cartridge and a 0.45 μm membrane filter before injection into the CE system. The selenium nutrition sample (oral liquid) was diluted 10 times with pure water, a 3 mL aliquot of the diluted sample was centrifuged for 10 min at 3000 rpm, and then the supernatant was passed through a C_{18} cartridge and a 0.45 mm membrane filter before being injected into the CE system.

3. Results and discussion

3.1. Detection wavelength

Direct spectrophotometric detection is the method used most commonly in CE. In the literature, detection wavelengths of 192 and 195 nm have been used for arsenic species at pH 6–7. In our laboratory, it was confirmed that wavelengths in the 190–195 nm range were optimal by comparing the spectra of the arsenic analytes. As the noise at 195 nm was lower than that at 192 nm, lower LODs were achieved at the former wavelength. The baseline noise was further lowered at 200 nm, which was the optimum wavelength for the detection of selenium compounds, but the detection sensitivity for the arsenic species was reduced significantly compared to that at 195 nm. With the Agilent diode array detector, several wavelengths can be monitored simultaneously, so a wavelength of 195 nm was selected for the determination of arsenic species and 200 nm for the selenium species.

3.2. Optimum separation conditions

Preliminary investigations of electrophoretic mobilities of the analytes confirmed that the mobilities of selenate and selenite (see Fig. 1) were too large to achieve separation under counter-EOF conditions. As shown in Fig. 1, the pH of the BGE significantly influenced the electrophoretic mobilities and corresponding migration times of the analytes.

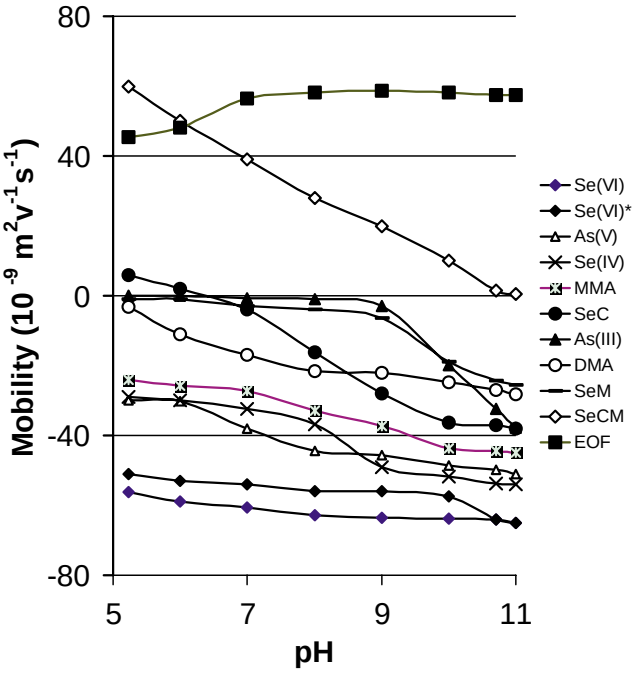


Fig. 1. Plot of electrophoretic mobilities vs. electrolyte pH for the target arsenic and selenium compounds (data for arsenic compounds taken from [14]). Conditions: BGE, 15 mM phosphate buffer; temperature, 20 °C, for other conditions, see Section 2.

For arsenic and inorganic selenium analytes, the degree of deprotonation depends on the pH of the BGE and the pK_a values of each analyte, and a steep change in the magnitude of their electrophoretic mobilities with increasing pH occurred in the pH region close to their pK_a value. For selenoamino acids, which are zwitterionic substances, both the magnitude and direction of their electrophoretic mobility can be changed with pH. For example, SeC is positively charged at low pH and negatively charged at high pH. In the case of SeCM, the direction of the electrophoretic mobility was the same as that of the EOF over a wide pH region because it is positively charged, but the magnitude of the electrophoretic mobility decreased with increasing pH because of deprotonation of SeCM. It should be noted that selenate produced two broadened peaks over a wide pH region between 5 and 10.0, possibly because an interaction between the doubly negatively charged selenate ion and the positively charged PDDAC capillary surface. This problem could be eliminated by using a high pH buffer (pH > 10.5). Finally, pH 10.6 was selected as the optimum pH of the BGE since at this pH value, all analytes could be separated (Fig. 1).

Choice of an appropriate buffer for the BGE presented some problems. Although carbonate buffer had a high buffer capacity at pH 10, it absorbed strongly in the low−UV region and this background absorbance would be substantially increased if the HSDC was used. Borate buffer was a good buffer at the desired pH, but suffered from a higher level of baseline noise compared to phosphate. Although the buffering capacity of phosphate buffer was relatively low at pH 10.6, it provided very good separation efficiency, a stable baseline during separation and low UV absorbance. Phosphate buffer pH10.6 was easily made up by mixing Na_3PO_4 and Na_2HPO_4 in a ratio of 1:10.

When voltage is applied, hydronium ions and hydroxyl ions are produced in the inlet and the outlet vials. The electrolyte buffering capacity should be sufficient to maintain a stable pH in both vials. When phosphate buffer at pH 10.6 was used as BGE with a 75 μm capillary, the baseline was very stable for at least 9 min during which all anion analytes could be separated (see Fig. 2a), then the baseline started to drift because the pH in both vials was changing. These separation conditions were suitable for the anionic analytes, but not for the cation analyte SeCM, which passed through the detection window after the EOF at a migration time around 10 min. When a 50 μm capillary used, the working current was much lower and as a result the pH change in the vials could be eliminated and a very stable baseline obtained for more than 20 min. Additionally, the reproducibility in both peak area and migration time of most analytes was improved. As a result, the anionic and cationic analytes could be determined in one run with a 50 μm capillary (see Fig. 3a) but with poorer detection sensitivity compared to a 75 μm capillary because of the shorter optical path length (see Tables 2 and 3). As a compromise, all anion analytes were determined using a 75 μm capillary, while the cationic

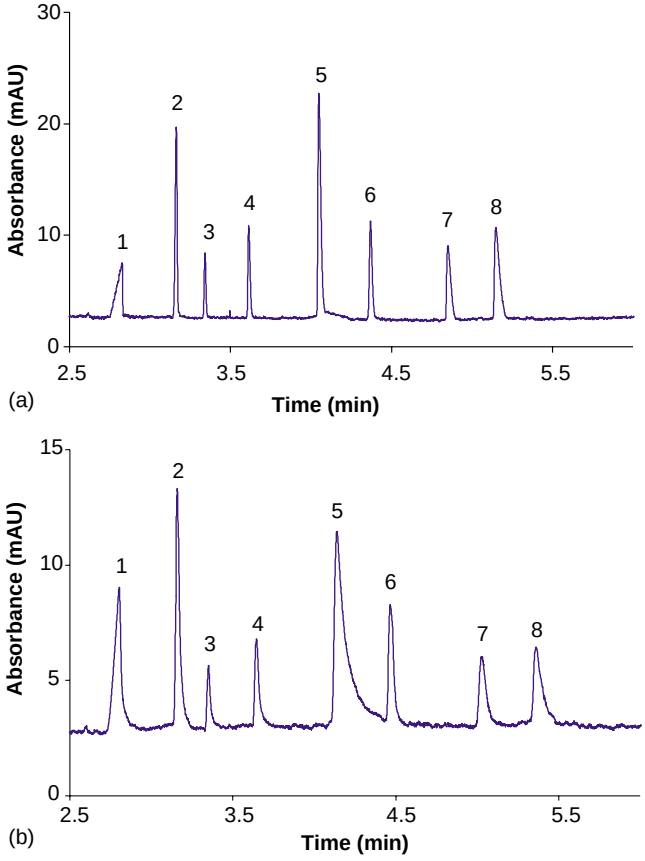


Fig. 2. Electropherograms for separations of a standard mixture of arsenic and selenium compounds using (a) on-capillary detection and (b) detection with a HSDC. Conditions: 64.5 cm × 75 μm PDDAC-coated capillary, −25 kV, 15 mM phosphate buffer pH 10.6, detection wavelength, 195 nm, injection, 4 s at 50 mbar. Concentration (as As or Se): (a) Se(VI) 150 mg/L and others 10 mg/L each, (b) Se(VI) 7.5 mg/L and others 0.5 mg/L each. Peaks: (1) Se(VI), (2) Se(IV), (3) As(V), (4) MMA, (5) SeC, (6) As(III), (7) DMA and (8) SeM.

SeCM was determined in a 50 μm capillary. In both cases an applied voltage of −25 kV was used.

It should be noted that the difference between the conditions used in this method and those in our previously published results [14,18] is the use of phosphate instead of carbonate as the BGE. This lowered the background absorptivity of the BGE and increased the optimal separation pH from 10.0 to 10.6, which provided the separation selectivity necessary for a wider range of analytes. The only disadvantage of the phosphate BGE compared to carbonate was the somewhat lower buffering capacity of phosphate at the given pH. This may necessitate the use of a 50 μm i.d. capillary to lower the separation current and the resultant rate of pH changes in the BGE due to electrolysis, in cases where the cationic analyte SeCM is present.

3.3. Analytical method performance parameters

3.3.1. On-capillary detection

The analytical method performance parameters for on-capillary detection with a 75 mm capillary under optimum condition are listed in the second column of Table 2. Compared to our previous work [14], the LOD values for arsenic compounds had been improved greatly, especial for arsenate. LOD values for the 50 μm capillary are shown in the second column of Table 3 and are higher than those in Table 2 due to the shorter optical path length of this capillary. The precision of the migration time of SeCM was affected by the water plug from the injection, which migrated with the EOF and for this reason precision for this analyte was somewhat poorer than for the other analytes.

3.3.2. Stacking

Stacking by co-EOF-NSM was achieved by introducing the analytes in a low conductivity matrix. When negative voltage was applied, the anionic arsenic species were stacked at the boundary between the sample and the BGE. At the same time sample cations moved in the opposite direction towards the inlet and were stacked at the boundary between the sample and the BGE. As a result, both anionic and cationic analytes were stacked (see Fig. 3b). To achieve good separation efficiency, a 50 μm capillary was used in combination with a 40 mM phosphate buffer as BGE to increase the electric field enhancement factor. The LOD improvement factors

Table 2
Analytical method parameters for on-capillary and HSDC detection

Analytes	LOD[a] on-capillary (mg/L)[b]	Correlation coefficient for calibration[c]	R.S.D.[d] (%)		LOD HSDC[a] (mg/L)[b]	LOD improvement factor
			Migration time (min)	Peak area		
Se(VI)	19.5	0.9904	1.63	3.4	2.38	8.19
Se(IV)	0.36	0.9927	0.91	3.2	0.049	7.34
As(V)	1.50	0.9926	0.83	2.4	0.27	5.56
MMA	1.08	0.9952	0.85	2.3	0.23	4.70
SeC	0.32	0.9915	0.86	2.9	0.065	4.92
As(III)	1.02	0.9982	0.74	2.8	0.20	5.10
DMA	1.32	0.9960	0.61	2.3	0.23	5.74
SeM	1.11	0.9944	0.63	2.1	0.19	5.84

[a] Conditions: 75 mm capillary, injection: 4 s at 50 mbar (0.9% capillary to window). Other conditions: see Section 2.
[b] Expressed as As or Se.
[c] Concentration arrange of analytes (as As or Se): Se(VI) 30–300 mg/L and others 2–20 mg/L.
[d] Seven continuous runs. Concentration (as As or Se): Se(VI) 150 mg/L and others 10 mg/L.

Table 3
Analytical method parameters using stacking

Analytes	LOD[a] on-capillary (mg/L)[b]	Correlation coefficient for calibration[c]	R.S.D.[d] (%)		LOD stacking[d] (mg/L)[b]	LOD improvement factor
			Migration time (min)	Peak area		
Se(VI)	28.8	0.9944	1.63	3.1	7.42	3.88
Se(IV)	0.37	0.9937	0.83	2.8	0.14	2.64
As(V)	1.17	0.9913	0.77	2.3	0.31	4.02
MMA	1.33	0.9962	0.70	2.0	0.32	4.16
SeC	0.42	0.9905	0.87	2.4	0.11	3.82
As(III)	2.05	0.9971	0.85	2.3	0.46	4.45
DMA	2.25	0.9910	0.57	2.0	0.75	3.13
SeM	1.07	0.9956	0.66	2.4	0.40	3.6
SeCM	1.47	0.9814	1.92	4.3	0.29	3.68

[a] Conditions: 50 mm capillary, injection: 8 s at 50 mbar. Other conditions: see Section 2.
[b] Expressed as As or Se.
[c] Concentration arrange (as As or Se): Se(VI) 30–300 mg/L and others 2–20 mg/L.
[d] Injection: 40 s at 50 mbar.

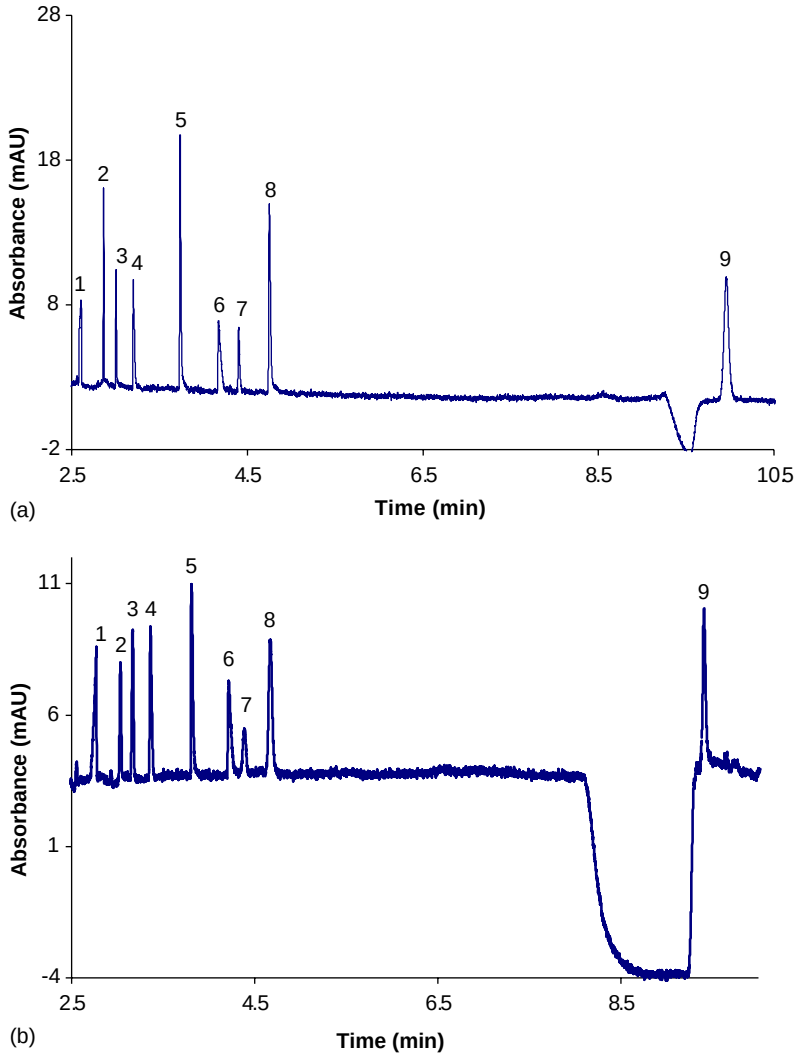


Fig. 3. Electropherogram of separations of a standard mixture of arsenic and selenium target analytes without (a) and with (b) sample stacking. Conditions: 64.5 cm × 50 μm PDDAC-coated capillary, −25 kV, on-capillary detection at 200 nm. BGE: (a) 15 mM phosphate buffer at pH 10.6 and (b) 40 mM phosphate buffer at pH 10.6. Injection: (a) 8 s at 50 mbar and (b) 40 s at 50 mbar. Concentration (as As or Se): (a) Se(VI) 15 mg/L and others 10 mg/L each, and (b) Se(VI) 15 mg/L and others 1 mg/L each. Peaks: (1) Se(VI), (2) Se(IV), (3) As(V), (4) MMA, (5) SeC, (6) As(III), (7) DMA, (8) SeM and (9) SeCM.

(see Table 3) ranged from 2.64 to 4.45. The injection volume could be as large as 4.6% of the total capillary volume, but larger injection volumes were not possible as the cationic SeCM was not resolved from the large EOF peak under these conditions.

3.3.3. High-sensitivity detection

The use of a HSDC can improve the detection sensitivity around 10 times compared to on-capillary detection in a 75 μm capillary. However, the PDDAC-coated capillary wall was positively charged while the uncoated inner wall of the HSDC was negatively charged, leading to loss of separation efficiency because of the different EOF values between the capillary and the cell. As can be seen in Fig. 2b, the peaks were tailed, especially SeC. This effect could be eliminated by coating the HSDC wall with PDDAC, but since such a coating would be irreversible this option was not investigated. Nevertheless, LOD values were improved by four to eight times (see Table 2). Attempts to combine both stacking and the HSDC for further improvement in LODs were unsuccessful because no HSDC was available for 50 μm i.d. capillaries. When a 75 μm capillary was combined with the HSDC and stacking, broad peaks were produced and the resolution was so poor that SeC and As(III) could not be separated.

3.4. Applications

Australian and New Zealand Guidelines for Fresh and Marine Water Quality [22] stipulate a recommended guideline value (ISQG-low, Interim Sediment Quality Guideline) of 20 mg/kg for total arsenic in sediment samples. Four arsenic compounds were spiked into a marine sediment sample which contained no detectable arsenic compounds and the sample was extracted and analyzed using the developed CE method. As shown in Fig. 4, the extraction and clean up processes were effective, and the sample matrix did not interfere with the determination of the arsenic compounds. In this work, the blank sample was spiked at two concentration levels with the arsenic analytes, leading to recoveries in the range 92–101% and reproducibilities in the range 6.0–8.4% R.S.D. (Table 4).

Table 4
Recovery of arsenic species from spiked marine sediment samples

Spiked concentration (mg As/kg)	Recovery (%)[a]			
	As(V)	MMA	As(III)	DMA
10	101.0 ± 6.4	93.3 ± 6.9	95.9 ± 7.3	91.8 ± 8.4
20	100.4 ± 6.0	94.2 ± 6.4	96.7 ± 6.9	93.1 ± 8.0

[a] Standard deviation values were determined for number of parallel measurements $n = 7$. For conditions: see Section 2.

The method was also applied to the determination of SeM in a Se nutrition supplement product containing high concentrations of inorganic ions, proteins, amino acids, food additives and sugar. Gomez et al. [23] have reported that a C_{18} cartridge can effectively remove organic sample matrix components while SeM is not retained, but when applied to the Se nutrition supplement sample, some interfering matrix components persisted. A 10-fold dilution of the original sample was therefore necessary before the clean-up step. The conductivity of the diluted sample was similar to that of the BGE, so stacking could not be used effectively. However, the HSDC provided sufficient detection sensitivity for analysis of the sample, as shown in Fig. 5. The identity of the SeM peak was confirmed by spiking the sample. The SeM concentration in this product was determined as 1.81 ± 0.57 mg/L ($n = 5$) as Se (compared to the label value of 2 mg/kg Se) and the relatively large R.S.D. was due to the fact that the concentration of SeM in the diluted sample was close to the LOD. A more powerful detection technique, such as ICP-MS or MS would have to be used when a more sensitive analysis is required.

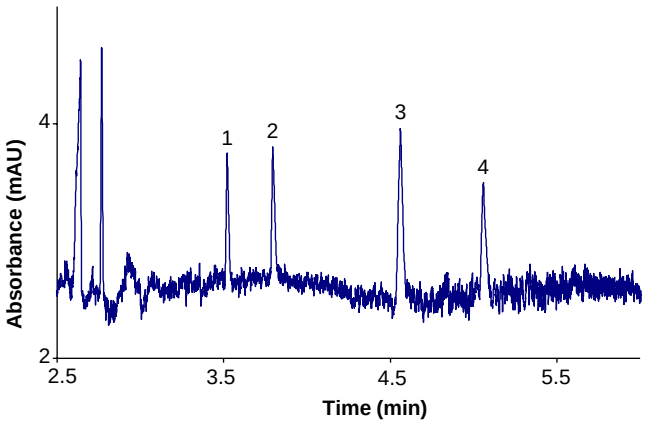


Fig. 4. Determination of arsenic species in a spiked marine sediment sample. Spiked concentration: 10 mg/kg each. Conditions: as for Fig. 2a. Peaks: (1) As(V), (2) MMA, (3) As(III) and (4) DMA.

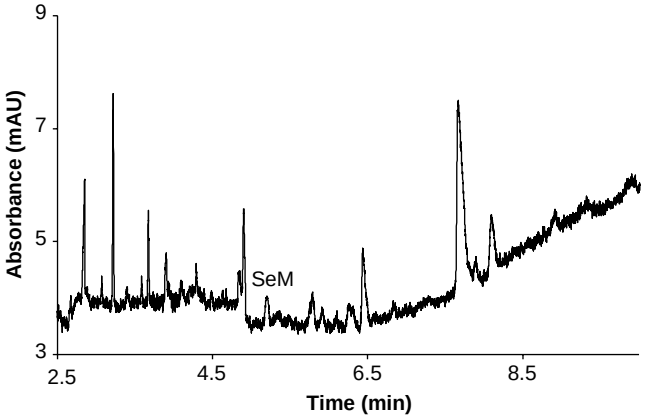


Fig. 5. Determination of selenomethionine (SeM) in a food supplement sample. Conditions: as for Fig. 2b.

4. Conclusions

A range of common arsenic and selenium species can be separated simultaneously by CE using alkaline electrolytes with direct photometric detection in the low-UV region. A HSDC or stacking can be used to enhance the detection sensitivity by factors ranging approximately between 3 to 8. For most analytes, the HSDC can improve the LOD values by five to eight times, which was somewhat less than the expected improvement because of the different EOF existing between the PDDAC-coated capillary wall and the uncoated HSDC wall. This work also demonstrated that cationic and anionic analytes can be stacked and separated simultaneously leading to enhancements of sensitivity up to 4.5 times. The developed method was applied to the speciation of As in a marine sediment and of SeM in a nutritional supplement product. Finally, it should be noted that the developed separation system could potentially be capable of simple hyphenation with inductively coupled plasma mass spectrometry.

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