Microchemical Journal 106 (2013) 220–225

Contents lists available at SciVerse ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Sensitive arsenic analysis by carrier-mediated counter-transport single drop microextraction coupled with capillary electrophoresis

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ARTICLE INFO

Article history:
Received 30 May 2012
Received in revised form 10 July 2012
Accepted 10 July 2012
Available online 17 July 2012

Keywords:
Capillary electrophoresis (CE)
Single drop microextraction (SDME)
Carrier
Aliquat 336
Arsenic

ABSTRACT

A sensitive analytical technique for arsenic compounds based on single drop microextraction (SDME) coupled in-line with capillary electrophoresis (CE) was developed. In SDME, a drop of an acceptor phase covered with an organic layer is hung at the inlet tip of a separation capillary. By adjusting the pH, analytes in the neutral form in an aqueous donor phase are first extracted into the organic layer, and then backextracted into the acceptor phase. However, the hydrophilic nature of the arsenic compounds, hampering the first extraction into the organic layer, lowers or even eradicates the efficiency of the SDME process. This problem can be solved by employing the scheme of carrier-mediated counter-transport using $CH_3(C_8H_{17})_3\ N^+Cl^-$ (Aliquat 336) as a carrier in the organic layer. Aliquat 336 enhances the transport of the arsenic compounds across the organic layer by forming hydrophobic complexes. The arsenic enrichment process is driven by the concentration gradient of hydroxide or chloride ion in conjunction with arsenic extraction from the donor phase to the acceptor phase of a high concentration of hydroxide or chloride. The gradient of hydroxide concentration yielded high enrichment factors for arsenic compounds, including As(III), which was not extracted well with the gradient of chloride only. After extraction, a portion of the enriched acceptor drop is injected and the arsenic compounds are separated by CE. Thus, the entire SDME and CE processes can be performed in an in-line mode using a commercial CE instrument. Using an acceptor phase at a pH of 13, the enrichment factors obtained for a sample in unbuffered water with extraction times of 15 min were 390, 340, 1100, and 1300 for As(III), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), and As(V), respectively. The limits of detection ($S/N=3$) with absorbance detection at 200 nm were 0.2, 0.7, 0.1, and 0.2 μM for As(III), DMA, MMA, and As(V), respectively. Tap water spiked with 5 μM of DMA and As(III), and 0.5 μM of MMA and As(V) was successfully analyzed by standard addition.

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1. Introduction

Arsenic compounds are toxic even at very low concentrations and the World Health Organization provisional guideline for arsenic in drinking water is 10 ppb currently [1]. Among more than twenty arsenic compounds known in biological systems and environments [2], inorganic As(III) species such as arsenite are considered to be most toxic, followed by inorganic As(V) species as arsenate and then organic forms such as dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) [3]. On the other hand, some arsenic compounds, including arsenobetaine and arsenocholine, are non-toxic [4]. Consequently, the health risk of drinking water contaminated with arsenic may vary depending on the actual arsenic species present. Therefore, it is desirable to determine the composition of the various arsenic species in addition to the total arsenic levels. To this end, numerous chromatographic and electrophoretic separation studies have been conducted [5–9].

Capillary electrophoresis (CE), having high separation performance through its open tubular capillary separation column, is suitable for the determination of arsenic species in real water samples but suffers from the low sensitivity especially with absorbance detection due to the short optical pathlength of the capillary. One means of improving the sensitivity is to use a detection scheme of higher sensitivity. CE examples of arsenic compounds include a detection cell with a longer optical pathlength [10], indirect fluorescence detection [5,11], derivatization by molybdate [12], atomic fluorescence spectrometric detection [13,14], and inductively coupled plasma-mass spectrometry [6,15]. Others include various on-line sample preconcentration techniques such as field-enhanced sample stacking [6,10,16–18], field-enhanced sample injection [19], transient isotachophoresis [12], and dynamic pH junction [14,20]. To increase the sensitivity further, different schemes have been combined, such as sample stacking with a longer pathlength detection cell [10], sample stacking with inductively coupled plasma-mass spectrometry [6], or the use of dynamic pH junctions with atomic fluorescence spectrometric detection [14]. Another obvious way is either liquid-phase or solid-phase extraction as a means of cleaning up and preconcentrating the sample. However,

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doi:10.1016/j.microc.2012.07.005

only limited examples of off-line coupling of liquid-phase [13] and solid-phase extraction [20,21] with CE have been reported for an analysis of arsenic compounds.

Recently, single drop microextraction (SDME) coupled with CE was shown to be effective in preconcentrating analytes before injection into a separation capillary [22–27]. In three-phase SDME, the analytes are extracted from an aqueous donor phase to an aqueous acceptor drop covered with an organic layer. Due to the large volume ratio between the sample donor phase and the acceptor drop as well as the thin organic layer, high enrichment factors (EFs) can be obtained with SDME in a short time. The convenience and efficiency of in-line coupling with CE are additional advantages of SDME. Most acidic or basic analytes can be enriched by SDME, adjusting the pH to promote neutral forms of the analytes in the donor phase and their charged forms in the acceptor phase. However, when analytes are very hydrophilic or when they contain charges such as zwitterionic amino acids and arsenic compounds, either blocking an ionizable group [25,28,29] or ion pairing with a carrier is needed to facilitate SDME.

There are two ways to use a carrier for SDME. The first is to add a carrier to the donor phase [26] and the second is to add a carrier to the organic phase. In this report, we present a scheme of SDME for arsenic compounds based on carrier-mediated counter-transport using $CH_3(C_8H_{17})_3N^+Cl^-$ (Aliquat 336) as an ion pairing carrier in the organic phase. The arsenic enrichment process is driven by the concentration gradient of the hydroxide or chloride ion in counter with the arsenic extraction. The entire process of SDME and CE can be performed in an in-line mode using a commercial CE instrument. After optimizing the SDME condition, the EFs obtained for a sample in unbuffered water after 15 min of extraction were 390, 340, 1100, and 1300 for As(III), DMA, MMA, and As(V), respectively. The limits of detection (LODs; $S/N=3$) with absorbance detection at 200 nm were 0.2, 0.7, 0.1, and 0.2 μM for As(III), DMA, MMA, and As(V), respectively.

2. Experimental

2.1. Reagents

Sodium phosphate dibasic, sodium arsenate dibasic heptahydrate (As(V)), sodium (meta)arsenite (AS(III)), ethanol, 1-octanol, octadecyl thrimethoxysilane (ODTS), NaCl, NaOH, fluoresceinamine, and Aliquat 336 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium phosphate tribasic was from Wako Pure Chemical (Osaka, Japan). Disodium methyl arsonate (sodium salt of MMA) and DMA were from Chem-Serivce (Bellefonte, PA, USA). Acetic acid was from Merck (Darmstadt, Germany). Water was treated using a Nanopure II System (Barnstead, Dubuque, IA, USA).

20 mM stock solutions of arsenic compounds were prepared in water. Sample solutions were prepared by diluting the stock solutions with water. A stock buffer solution of pH 10.6 was prepared by adjusting the pH of 100 mM sodium phosphate dibasic with 100 mM sodium phosphate tribasic. Each day, by diluting 3 mL of the stock buffer solution with 17 mL water and ultrasonic degassing, a 15 mM sodium phosphate of pH 10.6 was used as a run buffer for CE.

2.2. SDME and CE

We adopted the optimal CE conditions of a 15 mM sodium phosphate buffer (pH 10.6) for arsenic compounds in the literature [20,30], after checking with our system. CE was performed with an MDQ CE system (Beckman, Fullerton, CA, USA) monitoring at 200 nm. A new fused silica capillary of 60 cm (50 cm to the detector) × 25 μm id × 363 μm od from Polymicro Technologies (Phoenix, AZ, USA) was conditioned by rinsing with 1 M NaOH, water, and then run buffer for 10 min each at 80 psi. Between runs, the capillary was conditioned by rinsing with 0.1 M NaOH and water each for 1 min at 80 psi and then with a run buffer for 3 min at 80 psi. Samples were injected hydrodynamically for 5 s at 0.5 psi. Electrophoresis was carried out at a constant voltage of 20 kV across the capillary held at 25 °C.

As the first step for SDME each day, the end surface of the capillary tip was treated with a hydrophobic coating to improve the attachment of the drop covered with an octanol layer. The capillary inlet tip was dipped into a vial containing 5 vol% ODTS and 0.1 vol% acetic acid in ethanol for 6 s. After waiting for 7 min, the coating process was repeated. The capillary was then conditioned in the same way as for normal CE as described above. SDME was carried out as shown in Fig. 1, similarly to the process in a previous report [26]. (1) The capillary was filled with a run buffer and the acceptor phase was then injected at 6 psi for 5 s (~4 nL estimated using Poiseuille's equation). (2) The organic phase of Aliquat 336 in octanol was injected at 6 psi for 14.5 s (~7 nL estimated from the dimension of a drop formed afterwards). As the viscosity of the organic phase depends on the Aliquat 336 concentration, the injection time was adjusted accordingly to keep the organic phase volume constant. It was necessary to clean the outside of the capillary inlet by dipping in a vial of ethanol for 1 s after injecting the organic phase, in order to prevent the drop from creeping up along the side wall of the capillary. (3) The capillary inlet was inserted into the sample vial and a backpressure of 2 psi was applied for 47 s to form a drop of the acceptor phase (~3 nL) covered with a thin layer of the organic phase. About 1 nL of the acceptor phase remained inside the capillary. (4) During extraction for a desired time, a backpressure of 0.3 psi was applied for 0.18 min at an interval of 0.96 min to keep the drop in shape. Stirring of the donor phase was not applied. (5) After extraction, the enriched acceptor phase was injected at 0.5 psi for 5 s. (6) The capillary inlet was transferred to a run buffer vial and electrophoresis was performed at 20 kV. The EFs were calculated by comparing the peak heights of SDME/CE and CE. Given that the CE instrument did not have the capability of controlling the temperature of the inlet and outlet vials, we held the ambient temperature at 25 °C.

3. Results and discussion

3.1. Carrier-mediated counter-transport SDME

In the three-phase SDME, an analyte is first extracted from an aqueous donor phase (a1) into an organic layer (o) and then backextracted into an aqueous acceptor drop (a2). The EF at equilibrium is expressed as follows [31]:

$$EF_{eq} = \frac{C_{a2,eq}}{C_{a1,initial}} = \frac{1}{D_2/D_1 + D_2 V_o/V_{a1} + V_{a2}/V_{a1}} \tag{1}$$

with the distribution coefficients D_1 and D_2 defined respectively as

$$D_1 = \frac{C_{o,eq}}{C_{a1,eq}} \text{ and } D_2 = \frac{C_{o,eq}}{C_{a2,eq}} \tag{2}$$

Here $C_{i,eq}$ is the equilibrium analytical concentration of the analyte in phase i of volume V_i, as denoted by the subscript i. These two steps of extraction/backextraction are usually driven by controlling the pH of the two aqueous phases. For example, an acidic compound in a neutral form in a donor with a low pH can be enriched into a basic acceptor at a high pH, where it takes a negatively charged form. However, when analytes such as arsenic compounds are very hydrophilic or they have charges [32,33], the first step of extraction into the organic layer from the aqueous donor phase becomes difficult. Thus, the effectiveness of SDME can be significantly hampered. Fig. 2 shows that, without a carrier, very little extraction of the arsenic compounds occurred with 10-min SDME

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