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Sensitive Arsenic Analysis by Carrier-Mediated Counter-Transport Single Drop Microextraction Coupled with Capillary Electrophoresis

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Abstract

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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 $CH_3(C_8H_{17})_3N^+Cl^-$ (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 were390, 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.

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

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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 [1,2], 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 [5-14].

Capillary electrophoresis (CE), having high separation performance through its opentubular capillary separation column, is suitable for the determination of arsenic species in real water samples but suffers from low sensitivity especially with absorbance detection due to the short optical pathlength of the capillary. One means of improving the sensitivity is to usea detection scheme of higher sensitivity. CE examples of arsenic compounds include a detection cell with a longer optical pathlength[15,16], indirect fluorescence detection[11,13], derivatization by molybdate[17], atomic

fluorescence spectrometric detection[18,19], and inductively coupled plasma-mass spectrometry[12,20]. Othersinclude various on-line sample preconcentration techniques such as field-enhanced sample stacking[12,16,21-23], field-enhanced sample injection [24],transient isotachophoresis[17],and dynamic pH junction[18,25]. To increase the sensitivity further, different schemes have been combined, such as sample stacking with a longer pathlength detection cell[16], sample stacking withinductively coupled plasma-mass spectrometry[12], or the use of dynamic pH junctions with atomic fluorescence spectrometric detection[18].Another obvious way is either liquid-phase or solid-phase extraction as a means of cleaning up and preconcentrating the sample. However, only limitedexamplesof off-line coupling of liquid-phase[19]and solid-phase extraction[25,26]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 [27-38]. 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 [31,32,39] 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 [33] 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 NANO pure 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 [15,25], 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 [33]. (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 of 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.

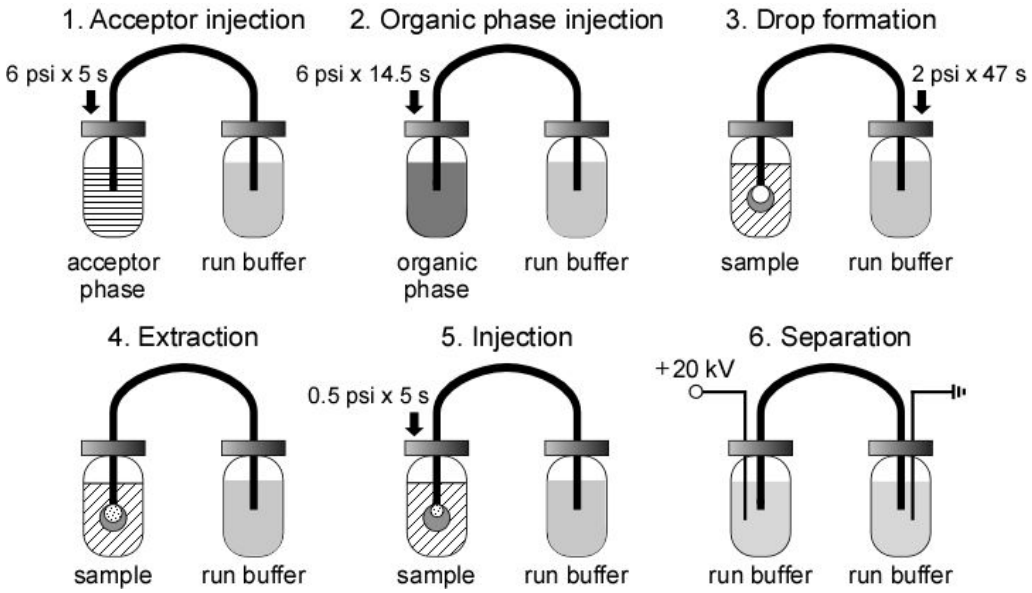

Fig. 1. SDME procedures: (1) acceptor injection, (2) organic injection (Aliquat 336 in octanol), (3) drop formation, (4) extraction, (5) sample injection, and (6) separation.

3 Results and discussion

3.1 Carrier-mediated counter-transport SDME

In 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 [40]:

$$\mathrm{EF}_{\mathrm{eq}} = \frac{C_{\mathrm{a2,eq}}}{C_{\mathrm{a1,initial}}} = \frac{1}{D_2/D_1 + D_2 V_{\mathrm{o}}/V_{\mathrm{a1}} + V_{\mathrm{a2}}/V_{\mathrm{a1}}} \qquad (1)$$

with the distribution coefficients D_1 and D_2 defined respectively as

$$D_1 = \frac{C_{\mathrm{o,eq}}}{C_{\mathrm{a1,eq}}} \quad \text{and} \quad D_2 = \frac{C_{\mathrm{o,eq}}}{C_{\mathrm{a2,eq}}} \qquad (2)$$

Here $C_{i,\mathrm{eq}}$ 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 [41,42], 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 from the donor phase of pH 2 to the acceptor drop of pH 13, whereas fluoresceinamine was enriched by nearly 270-fold. One interesting finding was that DMA (p*K*a = 6.2) having two hydrophobic methyl groups, was extracted less than MMA (pK_{a1} = 4.1). We speculate that this occurred because DMA has more of a tendency toward protonation (at least partially) at pH 2 than MMA, as supported by quantum mechanical calculations using density functional theory. The Density Functional Theory (DFT) calculations using the restricted B3LYP method and the LANL2DZ basis set were performed to optimize the geometry and the total energy of molecules. All computations were carried out by applying the polarizable continuum model to consider the solvation effect in water. Although MMA and its protonated form are much more stable than DMA and its protonated form in water, it turned out that the energy difference between DMA and its protonated form is more stable by about 50 kJ/mol than that between MMA and its protonated form. This indicates that the protonated form of DMA is more highly populated than that of MMA at equilibrium in water

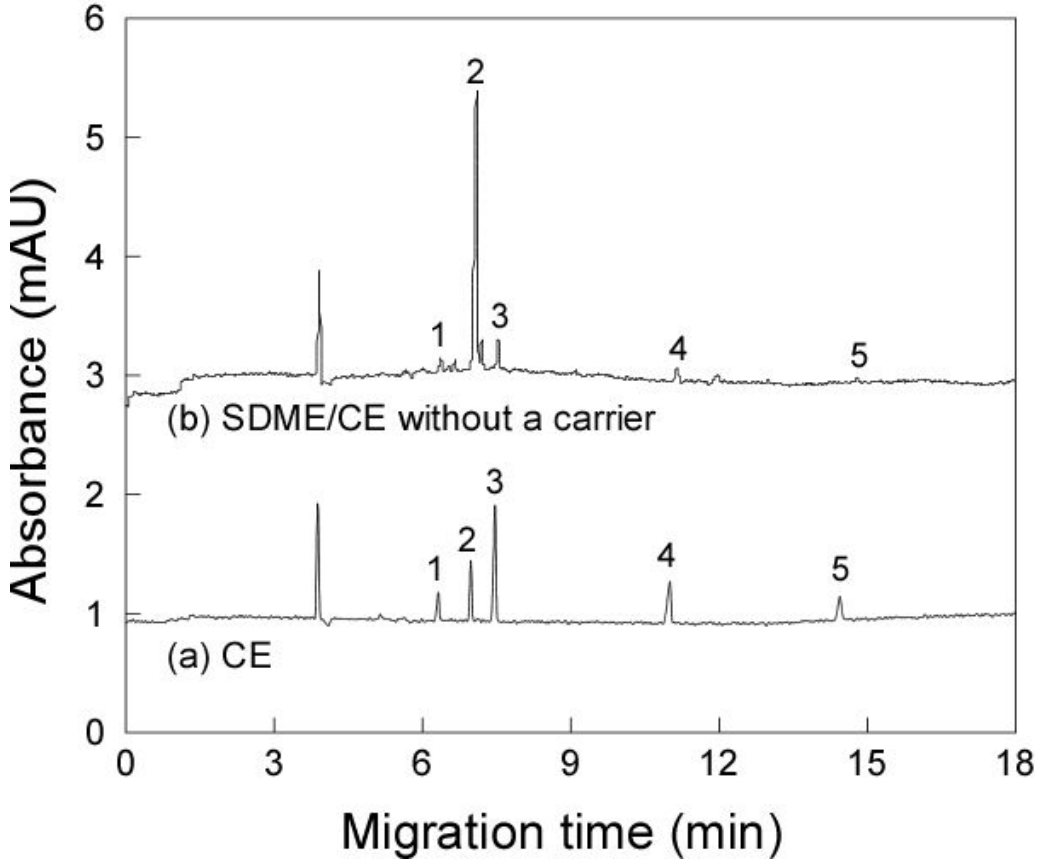

Fig. 2. Electropherograms of (a) CE of 1 mM of arsenic compounds and 100 μM of fluoresceinamine, and (b) SDME/CE using octanol as the organic phase without a carrier. Arsenic compounds: DMA (1), fluoresceinamine (2), As(III) (3), MMA (4), and As(V) (5). SDME conditions: 10 min extraction time, 1 mM of DMA, MMA and As(V), 50 μM of As(III) and 2 μM of fluoresceinamine in

phosphate buffer of pH 2 as the donor phase, and 0.1 M NaOH (pH 13) as the acceptor phase. CE conditions: 15 mM sodium phosphate buffer (pH 10.6), 20 kV, absorbance detection at 200 nm. Capillary: 60 cm (effective length 50 cm) × 25 μm id. Hydrodynamic injection for 5 s at 0.5 psi.

To facilitate the first extraction of arsenic compounds into the organic layer, Aliquat 336, a water-insoluble quaternary ammonium chloride widely used as a phase transfer catalyst or as an extraction reagent for various metals [43,44], was added to the organic layer as a carrier. Aliquat 336 is known to form a hydrophobic complex in an organic phase with a negatively charged compound by ion pairing, or with an acid in the neutral form. In three-phase liquid extraction of an arsenic compound (HA), Aliquat 336 establishes the following equilibria at the interfacial regions [45]:

$$A^-(aq) + RX(o) \qquad X^-(aq) + RA(o) \qquad K_1 = \frac{[X^-(aq)][RA(o)]}{[A^-(aq)][RX(o)]} \qquad (3a)$$

$$HA(aq) + RX(o) \qquad RXHA(o) K_2 = \frac{[RXHA(o)]}{[HA(aq)][RX(o)]} \qquad (3b)$$

Here, "aq" denotes either the donor (a1) or acceptor (a2) phase, R^+ is the quaternary ammonium ion of Aliquat 336, and X^- is the counter-transporting anion which is usually Cl^- or OH^-. If the equilibrium constants on both sides of the organic layer are equal (ignoring any non-ideal behavior and osmosis through the organic phase) and if the concentrations of the complexes at both of the interfaces are identical, i.e., [RX(o1)] = [RX(o2)], [RA(o1)] = [RA(o2)], and [RXHA(o1)] = [RXHA(o2)], where "o1" and "o2" denote the interfacial regions of the organic phase in the donor and acceptor sides, respectively. The

concentration ratios of the arsenic compounds are then as follows [46]

$$\frac{[A^-(a2)]}{[A^-(a1)]} = \frac{[X^-(a2)]}{[X^-(a1)]} \quad (4a)$$

$$\frac{[HA(a2)]}{[HA(a1)]} = 1 \quad (4b)$$

Therefore, the extraction of anionic species can be driven by the difference in the concentrations of the counter-transporting anions. The concentrations of the neutral forms of HA in the donor and the acceptor phases are identical. Note, however, that by raising the pH of the acceptor, most of the HA can be ionized as A^-, resulting in the effective transport of HA from the donor to the acceptor phases. Although equilibria between the three phases could not be reached in our SDME with a relatively short extraction time, we discuss the trends in the EF values based on the equilibrium behaviors. A more detailed discussion of kinetically controlled three-phase liquid extraction can be found in Ref [47].

3.2.1 Chloride as a counter-transporting ion

Here, we first consider the case of Cl^- used as a counter-transporting ion. In the case, arsenic species were transported mainly through ion pairing with the carrier Aliquat 336. Fig. 3 shows that when adding 50 mM Aliquat 336 to the organic phase, three arsenic compounds, except As(III) of EF 2, were enriched well up to 230-fold from the donor phase ($[Cl^-(a1)]_{initial}$ = 0, unbuffered) to the acceptor phase ($[Cl^-(a2)]_{initial}$ = 100 mM, unbuffered) in 5 min. Since As(III), having a pK_{a1} value of 9.1, should be mostly in the neutral form in unbuffered water, the enrichment obtained by the difference in the

chloride concentrations was minimal. Fig. 4 shows the EF values as the NaCl concentration in the acceptor phase was increased to 500 mM. Up to $[Cl^-(a2)]_{initial}$ = 100 mM, the EF values increased. Past this point, however, there were little increase or even decrease in EF possibly due to the osmotic pressure effects [47]. When LiCl or NaBr was added to the acceptor phase as a counter-transporting ion, the EF values were smaller than those obtained with NaCl. When citrate [48] or phenolate [49] with a high affinity to Aliquat 336 was used, however, the arsenic compounds were not enriched. Analytes were not detected when 40 μM of DMA and As(III) and 20 μM of MMA and As(V) used. It seems to be from the complexes of phenolate and citrate with Aliquat 336 like organic phase more than aqueous solutions.

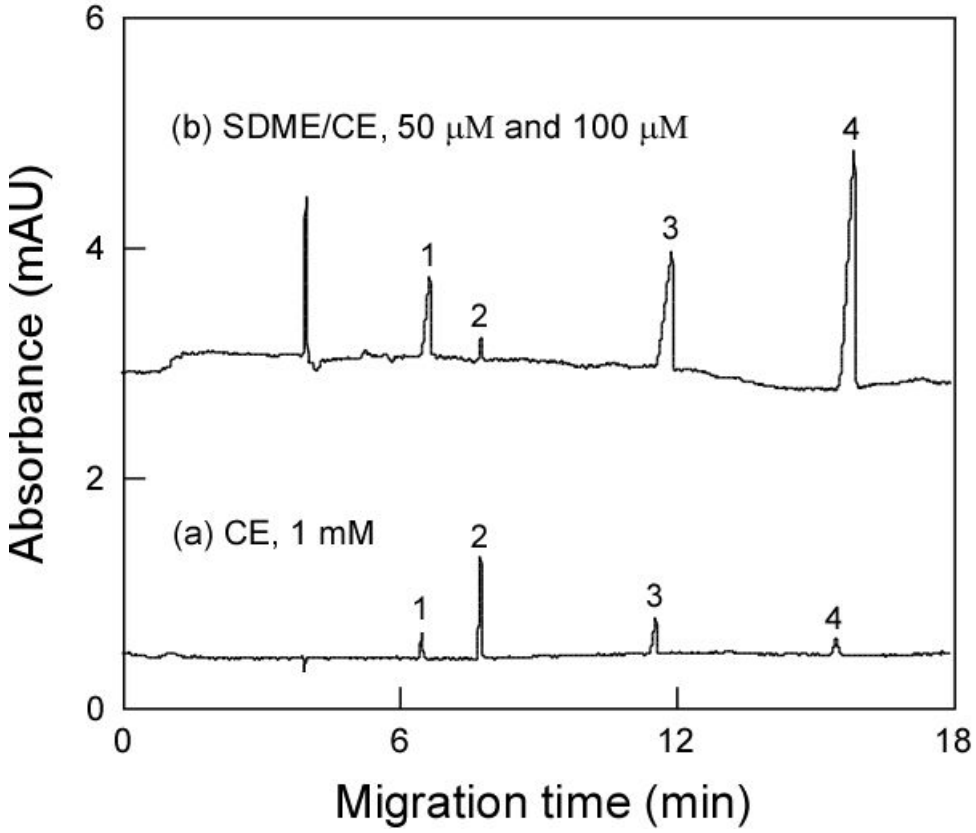

Fig. 3. (a) CZE of 1 mM arsenic compounds, (b) SDME/CE of 100 μM of DMA and As(III) and 50 μM MMA and As(V) in unbuffered water. Arsenic compounds: DMA (1), As(III) (2), As(V) (3), and As(V) (4). 100 mM NaCl as

the acceptor phase. 50 mM Aliquat 336 in octanol as the organic phase. 5-min SDME. Other conditions as in Fig. 2.

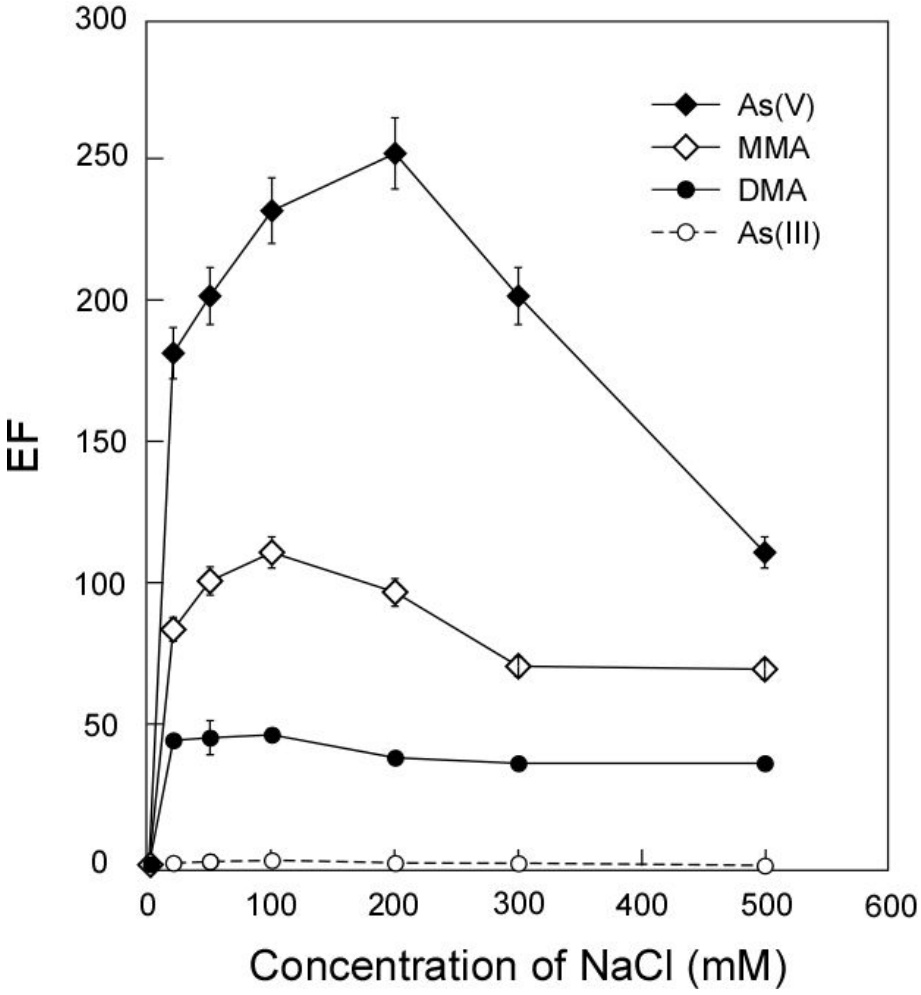

Fig. 4. Effect of the concentration of NaCl in the acceptor phase. SDME/CE of 40 μM DMA and As(III), and 20 μM MMA and As(V) in unbuffered water. 5-min SDME. Other conditions as in Fig. 2. Bars represent standard deviations (*n*

= 4).

3.2.2 Hydroxide as a counter-transporting ion

At this point, we consider the case when OH^- is used as a counter-transporting ion. In this case, As(III) existing mainly in a neutral form in the donor phase, either unbuffered or at a low pH, can also be enriched into the acceptor of high pH due to the deprotonation of As(III). Fig. 5 shows that all the four arsenic compounds including As(III) were well enriched with 5 min SDME from a donor phase of unbuffered water to an acceptor phase containing OH^- from 0 to 500 mM. For 5 min SDME, EF values of 100, 140, 320, and 400, respectively, for As(III), DMA, MMA and As(V) were obtained for the acceptor phase of 100 mM OH^-. When anions of Cl^- or Br^- of up to 100 mM were added to the acceptor phase of pH 13, the EF values were always smaller than those obtained without the additional anions. When 100 mM LiCl was added to the acceptor 100 mM NaOH, the EFs were 23, 29, 200 and 270 for DMA, As(III), MMA and As(V) respectively. When 100 mM NaBr was added in the acceptor with 100 mM NaOH, the EFs were 26, 28, 210, and 300 for DMA, As(III), MMA, and As(V), respectively. When the ionic strength of the donor phase was increased by adding chloride, the EF values decreased, as shown in Fig. 6, as the anions in the donor phase compete with the arsenic compounds for complexing with Aliquat 336 in the organic phase.

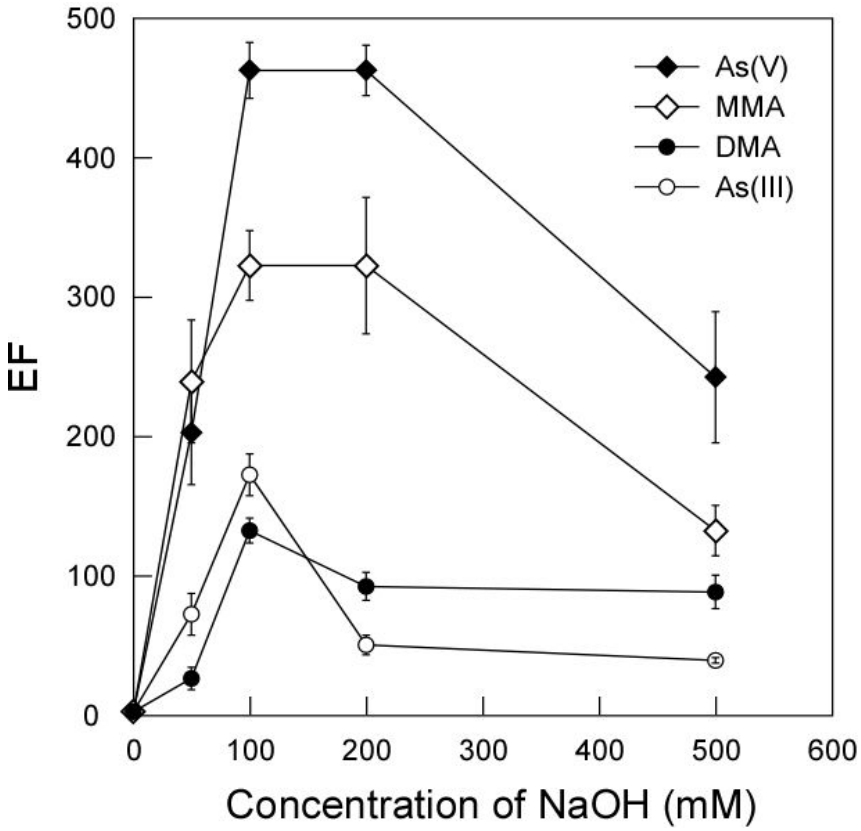

Fig. 5. Effect of the concentration of NaOH in the acceptor phase. SDME/CE of 10 μM DMA and As(III), and 2 μM MMA and As(V) in unbuffered water. 5-min SDME. Other conditions as in Fig. 2. Bars represent standard deviations

(n = 4).

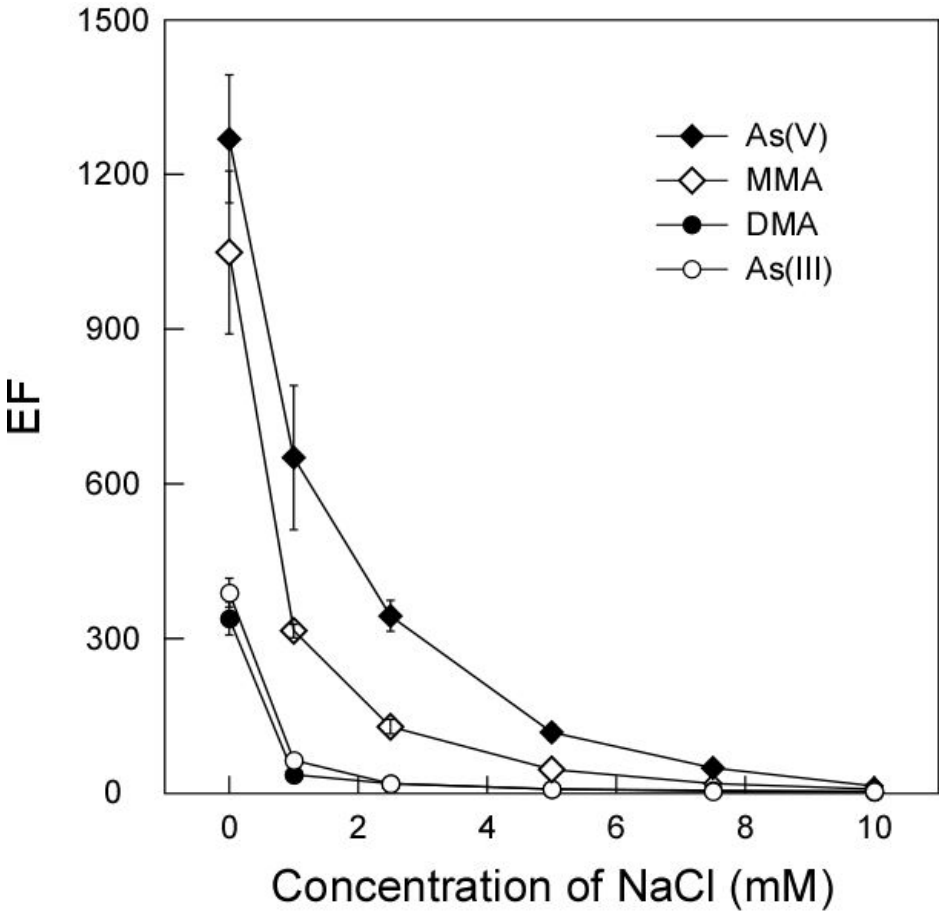

Fig. 6. Effect of the addition of NaCl to the sample. SDME/CE of 50 μM DMA

and As(III), and 20 μM MMA and As(V) in unbuffered water. 100 mM NaOH as the acceptor phase. 15-min SDME. Other conditions as in Fig. 2. Bars represent standard deviations (n = 4).

From the observations above obtained with various configurations, we concluded that OH^- was much more effective than Cl^- or other anions in driving the extraction of not only anionic arsenic species but also neutral As(III) species. Therefore, 100 mM NaOH (pH 13) was chosen as the optimal acceptor phase for the enrichment of arsenic species using Aliquat 336 as a carrier in the organic phase.

3.3 Optimization of other extraction conditions

When the concentration of Aliquat 336 in the organic layer was increased, the EF values were increased but the drop became unstable due to the amphiphilic nature of Aliquat 336. We chose 50 mM of Aliquat 336 in octanol as optimal. In addition, a capillary of 25 μm id was chosen to improve the drop stability by increasing the end surface area for the drop attachment, as compared to the most widely used one of 50 μm id. Another advantage of a capillary with a smaller id combined with a longer length was the increased level of precision in controlling the drop geometry with a given pressure control precision level via a commercial CE instrument. However, one drawback was the relatively low detection sensitivity.

As the extraction time was increased from 5 to 15 min, the EF values increased linearly with the extraction time as shown in Fig. 7. When the time exceeded 15 min, however, the extraction results became unreliable due to the

instability of the drop. We chose 15 min as the optimal extraction time.

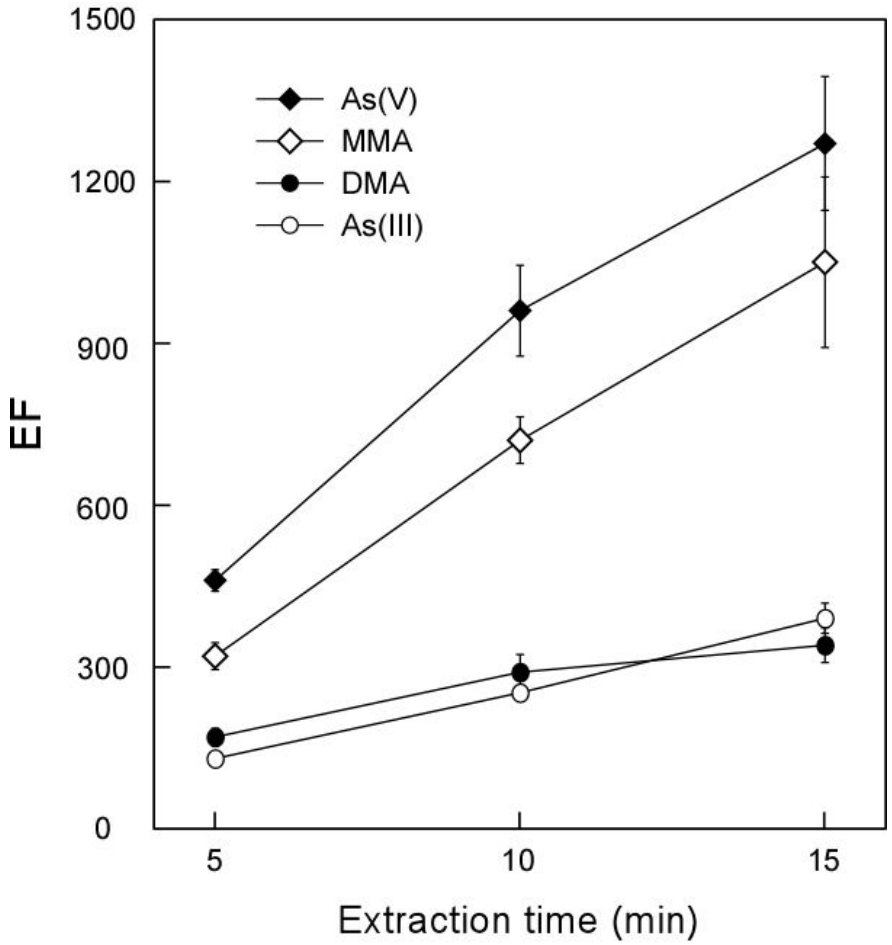

Fig. 7. Effect of the extraction time. Other conditions as in Fig. 5 except the extraction time. Bars represent standard deviations (n = 4).

3.4 Reproducibility and detection limits

With the optimal conditions of 15 min SDME from an unbuffered donor to the acceptor phase of 100 mM OH^- through the octanol layer containing 50 mM Aliquat 336 as a carrier, the relative standard deviations (n = 4) of migration times and peak heights for samples containing 2 μM of As(III), 4 μM of DMA, 0.5 μM of MMA, and 0.5 μM of As(V) were 1-2% and 7-15%, respectively. The LODs (S/N = 3) for As(III), DMA, MMA, and As(V) were 0.2, 0.7, 0.1, and 0.2 μM, respectively, in the range of 14~97 ppb. In countries such as Cambodia, the groundwater contains arsenic compounds at a level of several hundred ppb [50,51]. In some areas of India and Bangladesh, the arsenic levels in the groundwater are as high as 1000 ppb [52,53]. When people have no other options but to drink groundwater contaminated with arsenic available, our carrier mediated SDME-CE scheme can be used to secure groundwater sources containing less toxic arsenic species.

3.5 Application

The applicability of carrier-mediated counter transport SDME was evaluated by analyzing tap water samples spiked with arsenic compounds. As shown in Fig. 6, the EF values of carrier-mediated SDME depended significantly on the chloride concentration in the sample donor solution. In order to take care of such donor matrix effects, standard additions were used.

After adding proper amounts of 1 mM arsenic standard solutions to 10-mL samples of tap water spiked with 5 μM of DMA and As(III), and 0.5 μM of MMA and As(V), the total volumes were adjusted to 20 mL with distilled water. The concentrations of DMA and As(III) were increased by 5, 10, 15, and 20 μM while the concentrations of MMA and As(VI) were increased by 0.5, 1, 1.5, and 2 μM. The linearity (r^2) of the standard addition curves constructed with average peak heights obtained with the optimal SDME conditions (n = 4) for DMA, As(III), MMA, and As(V) were 0.9889, 0.9946, 0.9954, and 0.9830, respectively. The concentrations of DMA, As(III), MMA, and As(V) in the spiked tap water samples were 6.7 ± 2.8, 5.0 ± 1.7, 0.4 ± 0.1, and 0.6 ± 0.3 μM with 95% confidence, respectively. These results show that the proposed method is suitable for the analysis of arsenic compounds in a real sample as tap water.

4 Conclusions

Arsenic compounds were studied with SDME-CE and were successfully extracted from water. Aliquat 336 was added to the organic phase as a carrier to form ion pairs with negatively charged arsenic compounds. The use of an acceptor phase containing NaCl or NaOH can promote the transfer of arsenic species through the organic phase. The optimal EFs were 390, 340, 1100, and 1300 for As(III), DMA, MMA, and As(V) respectively, with 15 min SDME. In spite of the low absorbance of arsenic compounds, the proposed method provides the LODs in the low ppb range for direct monitoring of arsenics by

absorbance detection. Moreover, this method can help people choose less toxic types of groundwater to drink by determining the contamination levels of more toxic inorganic As(III) and As(V) and less toxic organic DMA and MMA.

Acknowledgement

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국문초록

비소 화합물의 분석감도 개선을 위한 모세관 전기영동 미세방울 추출법이 개발되었다. 미세방울 추출법은 모세관 끝에 유기용매 층으로 쌓여진 받개 용액 방울을 만듦으로써 이루어진다. 용액의 pH를 조절함으로써, 수용성 주개 용액에서 중성형태로 존재하는 분석물질은 제일 먼저 유기용매 층으로 추출되고 다시 받개 용액으로 추출된다. 그러나 비소 화합물이 가지는 친수성으로 인하여 유기용매로 이동하는 첫 번째 추출이 방해되고 결과적으로는 미세방울 추출법의 효율이 저하되는 문제점이 생기는데 이러한 문제는 유기용매 층 안에 Aliquat 336 ($CH_3(C_8H_{17})_3N^+Cl^-$)을 운반체로 도입, 운반체 매개 미세방울 추출법을 이용함으로써 해결될 수 있다. Aliquat 336이 소수성의 화합물을 형성시킴으로써 비소화합물을 유기용매를 거쳐 받개 용액으로 이동할 수 있도록 돕기 때문이다. 주개 용액에서 고농도의 수산화물이나 염화물이 포함된 받개 용액으로의 비소화합물의 농축과정은 pH 차에 따른 추출과 함께 수산화이온과 염화이온의 농도 기울기에 의해서 유도된다. 수산화물 농도 기울기는 염화물 농도 기울기로만은 잘 추출되지 않는 비소 (III)를 포함하여 비소 화합물의 고농축 효과를 준다. 추출이 끝난 농축된 받개 용액 방울은 모세관 안으로 주입된 다음 모세관 전기영동으로 분리되므로 모세관 전기영동 미세방울 추출법은 상용화된 CE장비를 사용할 수 있다. 전기영동 미세방울 추출법을 통해 비소 화합물을 분석하여 받개 용액의 pH가 13일 때 15분 추출하여 pH가 보정되지 않은 물에 녹여진 시료의 농축지수를 비소 (III) 390, dimethylarsinic acid (DMA) 340, monomethylarsonic acid (MMA) 1100, 비소(V) 1300으로 얻을 수 있었고, 검출한계는 200 nm UV 흡광분석법을 사용하였을 때, 비소(III) 0.2 μM, DMA 0.7 μM, MMA 0.1 μM, 비소(V) 0.2 μM 수준이었다. 또한 수돗물에 5 μM DMA, 비소(III)와 0.5 μM MMA, 비소(V) 표준용액을 첨가하여 수돗물에서의 비소화합물을 분석해 낼 수 있었다.

관련어: 모세관 전기영동, 미세방울 추출법, 운반체, Aliquat 336, 비소(Arsenic)

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