



## Selective separation of arsenic species from aqueous solutions with immobilized macrocyclic material containing solid phase extraction columns

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### ABSTRACT

A combination of solid phase extraction (SPE) columns was used for selective separation of water-soluble arsenic species: arsenite, arsenate, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). The SPE columns, namely AnaLig TE-01 (TE-01), AnaLig AN-01 Si (AN-01) and AnaLig As-01 PA (As-01), contain immobilized macrocyclic material as the sorbent and commonly known as molecular recognition technology (MRT) gel. The retention, extraction and recovery behavior of the MRT gel SPE columns were studied at pH 4–10. Fortified deionized water spiked with 100  $\mu\text{M}$  of arsenic species were treated at the flow rate of 0.2  $\text{mL min}^{-1}$ .  $\text{HNO}_3$  (1.0 and 6.0 M) was used as eluent to recover the retained arsenic species from TE-01 and AN-01 SPE columns. Arsenic species retained in the As-01 column were eluted with  $\text{HNO}_3$  (0.1 M) followed by  $\text{NaOH}$  (2.0 M). Likely interference from the various coexisting ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ ) (10 mM) were negligible. Quantitative separation of As(III), As(V), MMA and DMA was achieved based on the differences in extraction and recovery behavior of the MRT gel SPE columns with pH for different arsenic species. Complexation between arsenic species and MRT gel is the core phenomenon of the proposed technique as the complexation of MRT gels is expected to be stronger than the resin-based separation processes. MRT gel SPE columns are advantageous as compared with other reported SPE columns in terms of its performance with As(III). Effortless regeneration and unaltered separation performance of the sorbent materials for more than 100 loading and elution cycles are other sturdy characteristics to consider the MRT gel SPE columns for sensitive and selective arsenic species separation.

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### 1. Introduction

Arsenic, a ubiquitous toxic trace element, has raised a major toxicological and environmental concerns (WHO, 2001). The concentration levels, oxidation and binding states, ionic and molecular forms and metabolic pathways of As vary strongly in different environmental compartments, food chains and ultimately in humans (Mandal and Suzuki, 2002). Widespread human exposure to high levels of As is reported to occur via drinking water and contaminated water irrigated food causing both cancerous and non-cancerous health effects (Karim, 2000; Rahman et al., 2008).

Arsenite (oxidation state +III), arsenate (oxidation state +V), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are common water-soluble arsenic species existing in natural water

systems—a major pathway of arsenic ingestion to humans (Smedley and Kinniburgh, 2002). Arsenic toxicity in human depends strongly on its chemical form. As(III) is 10 times more toxic than As(V) while almost 70 times more toxic than the methylated forms, MMA and DMA (Squibb and Fowler, 1983). As(III), having successive acid dissociation constants ( $\text{pK}_a$ ) of 9.2, 12.2 and 13.4, is not dissociated at neutral pH and is present as a neutral species. As(V) and MMA has a wide range of  $\text{pK}_a$  values [As(V): 2.2, 6.9, 11.5; MMA: 4.1, 8.7], and exist mainly as anionic species at almost all pH. DMA with a  $\text{pK}_a$  value of 6.2 subsists as a cation in acidic medium (Committee on Medical and Biologic Effects of Environmental Pollutants, 1977). The United States Environmental Protection Agency proposed a maximum contaminant level of 10  $\mu\text{g L}^{-1}$  arsenic for the community water systems (USEPA, 2002). Because of increasingly stringent environmental regulations, selective and accurate measurement of arsenic species is required for precise monitoring and understanding the extent of arsenic contamination.

In natural waters, As usually exists at trace levels and several techniques are proposed for selective quantification and speciation analysis of arsenic species at trace levels (Barra et al., 2000; Munoz

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and Palmero, 2005; Terlecka, 2005; Kumar and Riyazuddin, 2007; Mays and Hussam, 2009). Ion chromatography and high performance liquid chromatography separation followed by sensitive detection such as inductively coupled plasma mass spectrometry (Lintschinger et al., 1998; Bissen and Frimmel, 2000), atomic absorption spectrometry (AAS) with hydride generation interface (Hasegawa et al., 1999; Kumar and Riyazuddin, 2007) and electro-spray/nanospray mass spectrometry (Pergantis et al., 1997; Ritsema et al., 1998) are some potential techniques. However, concerns related to the use of element-selective detectors to interface the chromatographic methods limit the efficiency of these techniques (Yu et al., 2003).

Separation and preconcentration of contaminant ions using solid sorbent materials, known as solid phase extraction (SPE) systems, have increased in popularity since the 1980s (Hosten and Welz, 1999). The technique has been developed as a cost- and time-saving alternative to the traditional extraction techniques featuring the capability to interact with a variety of metal ions including the fairly specific selectivity to a particular ion (Nickson et al., 1995; Ghaedi et al., 2008). Ion exchange resins (Leal et al., 2004; Jitmanee et al., 2005), silica gel bonded with octadecyl functional groups (Pozebon et al., 1998), yeast immobilized on controlled pore glass (Koh et al., 2005), activated alumina (Karthikeyan et al., 1999), open tubes knotted reactors (Yan et al., 2002; Herbelo-Hermelo et al., 2005), polytetrafluoroethylene turnings-packed micro-columns (Anthemidis et al., 2010) have been employed as SPE sorbent material. One group of SPE materials includes the macrocyclic chelants, such as crown ethers, immobilized on a silica or polymer support (Hosten and Welz, 1999). Ion-selective behavior of SPE-type systems with immobilized macrocyclic materials has been mentioned for preconcentration and separation of metals (Bradshaw et al., 1988; Izatt et al., 1994; Hasegawa et al., 2010). SPE techniques have been applied for the quantitative analysis/speciation/separation of various trace elements including arsenic (Yalcin and Le, 2001; Yu et al., 2003; Liang et al., 2004; Long et al., 2006; Sanchez et al., 2009). Reports on the retention behavior of different arsenic species with some SPE systems (silica-based or resin-based) at pH 5.5 (Yalcin and Le, 2001) and pH 5.6 (Yu et al., 2003) were available. It was observed that the hydrophobic interaction of the arsenic species with the SPE materials,  $pK_a$  values and ionic characters are important factors which may control the retention efficiency of the SPE columns (Yu et al., 2003). Though quantitative retention was achieved with the SPE columns for the water-soluble arsenic species (As(III), As(V), MMA and DMA), elution of the retained species was quiet difficult or sometimes unachievable for some species particularly with As(III) (Yalcin and Le, 2001; Yu et al., 2003).

The objective of the work is to investigate the feasibility of an ion-selective immobilized macrocyclic material attached to a solid phase, commonly known as a molecular recognition technology (MRT) gel, for the selective separation of As(III), As(V), MMA and DMA from aqueous solutions followed by graphite furnace AAS determination. We used following MRT gel SPE columns: AnaLig TE-01, AnaLig AN-01 Si and AnaLig As-01 PA. Specific MRT gel SPE columns have the advantage of the selective retention of the mentioned arsenic species followed by quantitative recovery. Most importantly, As(III) was quantitatively retained and recovered with the AnaLig As-01 PA SPE column.

## 2. Experimental

### 2.1. Instruments

A PerkinElmer model AAnalyst 600 AAS (PerkinElmer, Massachusetts, USA) including the AS-800 autosampler equipped with

a transverse-heated graphite atomizer with integrated, pyrolytic graphite coated platform (THGA) and longitudinal Zeeman-effect background corrector was used. End-capped THGA tubes were used for better sensitivity and improved precision. An electrodeless discharge lamp (EDL) powered by EDL System II operated at 380 mA was employed as light source. The wavelength was set at the 193.7 nm resonance line and the monochromator spectral bandpass at 0.7 nm. Baseline offset correction time was set to 2.0 s and the read delay at 0.0 s. Argon was used as purge gas and the flow rate was set to 250 mL min<sup>-1</sup>. A temperature program was performed and the different steps were: first and second dry at 110 and 130 °C, ashing at 1200 °C and atomization at 2000 °C held at 30, 30, 20 and 5 s respectively. After a calibration with 5 standards (0.5–2.5 µM), 20 µL of sample and 10 µL of Pd–Mg matrix modifier were introduced in the graphite furnace with three replicates of each measurement. The pH of the sample solutions was measured with a Navi F-52 pH meter (Horiba Instruments, Japan) and a combination electrode.

### 2.2. Reagents and materials

Analytical grade commercial products were used. Stock solutions (10 mM) of As(III), As(V), MMA and DMA were prepared from sodium arsenite (NaAsO<sub>2</sub>) (Kanto Chemical, Japan), sodium arsenate heptahydrate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O), monomethylarsonic acid (CH<sub>3</sub>AsO(OH)<sub>2</sub>), dimethylarsinic acid sodium salt trihydrate (C<sub>2</sub>H<sub>6</sub>AsNaO<sub>2</sub>·3H<sub>2</sub>O) (Nacali Tesque, Japan). Working standards of metal solutions in the range of µM to mM were prepared by dilution on a weight basis. Deionized water prepared with a Barnstead four housing E-Pure systems was used to prepare all solutions and is referred to as EPW hereafter.

The experimental pH range was 4–10, and adjusted using either 1 M HCl or 1 M NaOH. MES (2-(*N*-morpholino) ethanesulfonic acid monohydrate, C<sub>6</sub>H<sub>13</sub>NO<sub>4</sub>S·H<sub>2</sub>O) (Sigma–Aldrich, USA), HEPES (N-2-Hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid, C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S) (Nacali Tesque, Japan), and TAPS (N-Tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid, C<sub>7</sub>H<sub>17</sub>NO<sub>6</sub>S) (MP Biomedicals, USA) were used as buffer reagents for pH 4–6, 7–8 and 9–10, respectively.

NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> were used as a source of cations while the Na-salt of anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>) (Nacali Tesque, Japan) were used to study the effect of coexisting ions. Working solutions of 10 mM concentration were prepared in H<sub>2</sub>O matrix and pH was maintained to 7.0. The final solutions were allowed to equilibrate for 24 h before use. The interference study were carried out in a non-competitive environment by applying 4 mL of fortified deionized water at the optimized flow rate with subsequent collection using appropriate eluent.

Experimental variables, e.g. sample loading flow rate, selection of eluent and eluent concentration were optimized using As(V) spiked solutions (100 µM) in H<sub>2</sub>O matrix with pH maintained at 5.0. The MRT gel SPE columns were fed with 4 mL of sample solutions at varying flow rates, and the retention percentage of the As-species into the columns was determined. Different eluent (individual or combinations), 0.1–6.0 M HNO<sub>3</sub> and 0.1–4.0 M NaOH, was checked to select the most appropriate eluent or eluent combinations that were suitable for optimum recovery of the 'captured' species.

Certified reference materials (CRMs): BCR-713 (effluent wastewater) and BCR-610 (groundwater) from EC-JRC-IRMM (European Commission Joint Research Centre, Institute of Reference Materials and Measurements), fortified samples of 'real' waters: tap water sample from our laboratory in Kakuma campus, Kanazawa University (Kanazawa, Japan) and river water sample from Asano River (Kanazawa, Japan) were analyzed to validate the proposed separation process. Each of the real water samples was filtered through

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