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Selective Separation of Tri- and Pentavalent Arsenic in Aqueous Matrix with a Macrocycle-Immobilized Solid Phase Extraction System

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Abstract

A simple flow-based method was developed for the selective separation of arsenic species (+3 and +5) using a macrocycle-immobilized solid phase extraction (SPE) system, commonly known as molecular recognition technology (MRT) gel. Arsenic species in solution or in the eluent were subsequently quantified with graphite furnace atomic absorption spectrometry. The separation behaviors of As(III) and As(V) on MRT-SPE were investigated. It was found that As(V) can be selectively collected on the SPE system within the range of pH 4 to 9, while As(III) was passed through the MRT-SPE. The retention capacity of the MRT-SPE material for As(V) was found to be $0.25 \pm 0.04 \text{ mmol g}^{-1}$. The detection limit of the method for As(V) was $0.06 \text{ } \mu\text{g L}^{-1}$, and the relative standard deviation was 2.9% ($n = 10$, $C = 1 \text{ } \mu\text{mol L}^{-1}$). Interference from the matrix ions was studied. In order to validate the developed method, certified reference materials of effluent wastewater and groundwater samples were analyzed and the determined values were in good agreement with the certified values. The proposed method was successfully applied to the speciation analysis of tri- and pentavalent arsenic in natural water samples showing satisfactory recoveries ($\geq 98.7\%$).

Keywords: Solid phase extraction; molecular recognition technology; arsenic (+3 and + 5); aqueous matrix; speciation

1.0 Introduction

Arsenic has raised a major public health concern because it has serious toxic effects even at low exposure levels and is widespread in the environment (WHO 2001). People exposed to high level of arsenic via drinking water and contaminated water-irrigated foods are at risk of both cancerous and non-cancerous health effects (Karim 2000, Rahman et al. 2008). The extent of exposure depends on the concentration levels, oxidation and binding states, ionic and molecular forms and metabolic pathways of arsenic, which vary strongly in different environmental compartments (Mandal & Suzuki 2002). Arsenite (oxidation state +3) and arsenate (oxidation state +5) are commonly found inorganic arsenic species in the natural aqueous matrix (Mandal & Suzuki 2002, Francesconi & Kuehnelt 2004). Information about the speciation of arsenic in the natural aqueous system is important because it indicates the bioavailability of arsenic from the source water (Liang & Liu 2007). Inorganic arsenic species are known to be more toxic than the organic counterparts, and As(III) is at least ten times more harmful than As(V) (Squibb & Fowler 1983). Selective and accurate measurement of arsenic species is also required for precise monitoring as imposed by increasingly stringent environmental regulations, *e.g.* 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).

In recent years, several researchers have been working for the quantification and speciation analysis of arsenic (Barra et al. 2000, Muñoz & Palmero 2005, Terlecka 2005, Kumar & Riyazuddin 2007, Mays & Hussam 2009). For the separation and detection of arsenic species, ion chromatography and high-performance liquid chromatography separation followed by sensitive detection such as inductively coupled plasma mass spectrometry (Lintschinger et al. 1998, Bissen & Frimmel 2000), atomic absorption spectrometry with hydride generation interface (Hasegawa et al. 1999, Kumar & Riyazuddin

2007) and electrospray/nanospray mass spectrometry (Pergantis et al. 1997, Ritsema et al. 1998) are widely used. 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). Since the 1980s, separation of analytes using solid-phase extraction (SPE) systems becomes popular. The technique is cost- and time-saving compared to the traditional extraction techniques with the facility to separate a wide range of metal ions, including specific selectivity to a particular ion (Nickson et al. 1995, Poole 2000, Rossi & Zhang 2000, Camel 2003). SPE techniques have been applied for the quantified analysis/speciation/separation of various trace elements, including arsenic (Liska 2000, Rossi & Zhang 2000, Yalcin & Le 2001, Camel 2003, Yu et al. 2003, Sanchez et al. 2009, Rahman et al. 2011a, 2011b). One group of SPE material includes the macrocyclic chelants, such as crown ethers, immobilized on a silica or polymer support (Hiraoka 1982, 1992), which possess the ion-selective behavior and are commonly known as molecular recognition technology (MRT) gel (Izatt et al. 1994, Hasegawa et al. 2010, Rahman et al. 2011a, 2011b, 2011c, 2011d, Hasegawa et al. 2013).

The separation of elements by macrocycles is managed by the accommodation of ions either within their circular cavity or in the three-dimensional cavity-like structures formed between the macro-ring and the sidearms. The retention behavior depends on the relative sizes and charges of analyte ions, the conformational flexibility of the macrocycle structure, and the interaction of the macrocycle with solvent. The selectivity behavior of the macrocycle can be modified by varying any of those factors (Tsukube 1993, Mahoney et al. 2001, 2004, Nabeshima et al. 2005). Macrocycles have been employed for the selective separation of metal ions from mixtures in bulk liquid membrane and/or solvent extraction systems (Izatt et al. 1986, Walkowiak et al. 2002, Walkowiak & Kozłowski 2009). However, separation of metal ions using extraction or membrane systems is not considered as a cost-

effective option due to the gradual loss of the expensive macrocyclic compounds from the organic membrane or layer (Bradshaw et al. 1989). The shortcoming was minimized by attaching the macrocyclic compounds to solid support using a stable hydrocarbon-ether linkage, which is capable of high selectivity and of use with very diluted solutions (Izatt et al. 1988, Bradshaw et al. 1989, Bruening et al. 1991, Izatt et al. 1994). Silica gel is used mostly among the solid support materials due to its high hydrophilic character, large number of binding sites and substantial inert nature. Other options are adopted only when the silica gel cannot be used as the support such as when the pH of solution is about 10 or when extreme purification of water is required, etc. (Biernat et al. 1994, Izatt et al. 1995).

In this work, a simple process is developed for the separation of tri- and pentavalent arsenic species in the aqueous matrix with the subsequent graphite furnace atomic absorption spectrometric (GF-AAS) determination using a single MRT-SPE cartridge namely AnaLig AN-02. The proposed technique is rapid and is suitable for routine speciation analysis of inorganic arsenic in aqueous matrix to comply with the legislative recommendations in countries where the extent of contamination is severe, and a large number of samples are required to be monitored.

2.0 Experimental

2.1 Instruments

The AAnalyst 600 GF-AAS (PerkinElmer, Waltham, MA, USA) equipped with an AS 800 autosampler and a dedicated transversely-heated graphite atomizer system with Zeeman background correction facility was used as detector. The light source was an electrodeless discharge lamp (EDL) powered by EDL System II operated at 380 mA. The wavelength was set at 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 at the pre-set flow rate of 250 mL min⁻¹. A temperature program has been performed as follows: first and second dry at 110 and 130°C, ashing at 1200°C and atomization at 2000°C with hold times of 30, 30, 20 and 5 s, respectively. The system was calibrated with five-standards of As(III) or As(V) (0.5–2.5 µmol L⁻¹). Sample (20 µL) and Pd-Mg matrix modifier (10 µL) solutions were introduced in the graphite furnace with three replicates of each measurement.

A GL-SPE vacuum manifold kit (for 12 samples) (GL Sciences, Tokyo, Japan) combined with an air pump (CAS-1, AS ONE, Osaka, Japan) was used for SPE. A Navi F-52 pH meter (Horiba, Kyoto, Japan) and a combination electrode were used for pH measurement. A four-housing E-Pure water purification system (Barnstead/Thermolyne, Dubuque, IA, USA) was used for deionized water preparation, and the deionized water is referred to as EPW hereafter.

2.2 Materials

As(III) and As(V) stock solutions (10 mmol L⁻¹) were prepared from sodium arsenite (Kanto Chemical, Tokyo, Japan) and sodium arsenate heptahydrate (Nacalai Tesque, Kyoto Japan). All chemicals were analytical-grade commercial products and used as received. Weight basis dilution with EPW was used to prepare the working standards.

MRT-SPE: AnaLig AN-02 (AN-02) (base support: silica gel, functional group: crown ether) was supplied from GL Sciences (Tokyo, Japan) and manufactured commercially by IBC Advanced Technologies (American Fork, UT, USA). Other SPE materials were (a) Chelex-100 (base support, styrene divinylbenzene; functional group, iminodiacetic acid), (b) NOBIAS Chelate PA-1 (base support, hydrophilic methacrylate; functional group, polyamino-polycarboxylic acid), (c) NOBIAS Chelate PB-1 (base support, divinylbenzene/methacrylate polymer; functional group, polyamino-polycarboxylic acid), (d) NOBIAS Ion SA-1 (base support, hydrophilic methacrylate; functional group, quaternized

amine), and (e) NOBIAS Ion SC-1 (base support, hydrophilic methacrylate; functional group, sulfonic acid). Chelex 100 was supplied by Bio-Rad Laboratories (Hercules, CA, USA), while the other SPEs are from Hitachi High-Technologies (Tokyo, Japan). Chelex-100, NOBIAS Chelate PA-1, and NOBIAS Chelate PB-1 were the chelating resin-type SPE systems, while the NOBIAS Ion SA-1 and NOBIAS Ion SC-1 were the ion-exchange resin types. All the SPE systems were available as 3 or 5 mL mini-columns.

The experimental pH was adjusted within the range of 4 to 10 using either HCl or NaOH of 1 mol L⁻¹ concentration. 2-(*N*-morpholino)ethanesulfonic acid (pH 4–6) (Sigma–Aldrich, St. Louis, MO, USA), 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (pH 7–8) (Nacalai Tesque, Kyoto, Japan), or TAPS (N-Tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid) (pH 9–10) (MP Biomedicals, Solon, OH, USA) were used as the buffer reagent to maintain the desired pH as indicated in the parentheses.

To study the probable interference from coexisting ions, NaCl, KCl, CaCl₂, and MgCl₂ were used as source of cations, while NaCl, NaNO₃, and Na₂SO₄ were used as source of anions as purchased from Nacalai Tesque (Kyoto, Japan). Working solutions of 1 mmol L⁻¹ concentration with pH maintained to 7 were prepared in H₂O matrix followed by an equilibration period of 24 h.

Certified reference materials (CRMs) of effluent wastewater (BCR-713) (Segura et al. 2004) and groundwater (BCR-610) (Quevauviller et al. 1998) from EC-JRC-IRMM (certified reference materials from European Commission Joint Research Centre, Institute of Reference Materials and Measurements), and spiked-samples of “real” waters: tap water (*source*: Kakuma campus, Kanazawa University, Kanazawa, Japan), lake water (*source*: Lake Biwa, Shiga, Japan), and river water (*source*: Asano River, Kanazawa, Japan) were analyzed using the proposed separation process. Cellulose membrane filter (0.45 µm) (Advantec, Tokyo, Japan) was used to treat each of the real water samples before the analysis.

2.3 Cleaning

Low-density polyethylene bottles (Nalge Nunc, Rochester, NY, USA), perfluoroalkoxy tubes and micropipette tips (Nichiryo, Tokyo, Japan) were used throughout. For cleaning, the laboratory wares were soaked in Scat 20X-PF alkaline detergent (Nacalai Tesque, Kyoto, Japan) overnight followed by rinsing with EPW, and then soaked in 4 mol L⁻¹ HCl overnight with subsequent rinsing using EPW.

2.4 Separation process

The work-flow sequence for the separation of As(III) and As(V) with AN-02 column followed by GF-AAS determination is shown schematically in Fig. 1. HNO₃ (1 mol L⁻¹, 8 mL) and EPW (6 mL) were used for SPE column cleaning, and the desired pH condition (4–10) was maintained by allowing an appropriate buffer solution (5 mL) to follow through the column. After the cleaning step, pH-adjusted sample solution (4 mL) was introduced into the SPE column at the pre-set flow rate of 0.2 mL min⁻¹, and the column effluent was collected. The analyte that is not captured in the SPE column is then removed by EPW washing. The unretained concentration of analyte in the SPE system can be calculated from the total analyte concentration in the column effluent and EPW wash solution. The “captured” analyte is then eluted with HNO₃ (1 and 6 mol L⁻¹). The arsenic concentrations in the sample solution, in the effluents and in the eluent were measured with GF-AAS.

3.0 Results and Discussion

3.1 Optimization of variables

3.1.1 Sample loading flow rate

Effect of sample loading flow rates, which has a reasonable impact on metal retention in SPE columns (Bag et al. 1998), adjusted in the range of 0.2 to 2 mL min⁻¹ was checked (Fig. 2a). The retention patterns up to the flow rate of 0.25 mL min⁻¹ were quantitative while it

decreased with an increase of flow rates. Therefore, for the next experiments, a flow rate of 0.2 mL min^{-1} was selected as optimum.

3.1.2 Eluent concentration

Selection of analyte is important to maintain the high enrichment factor without affecting the precise determination of analyte. The effect of eluent concentration on the elution of analyte from the MRT gel SPE column (MRT-SPE) was studied using HNO_3 (4 mL) of varying concentrations ($0.1\text{--}6 \text{ mol L}^{-1}$). The recovery was quantitative up to the concentration of $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ and then remained constant (Fig. 2b). Hence, a combination of $1 \text{ mol L}^{-1} \text{ HNO}_3$ (2 mL)+ $6 \text{ mol L}^{-1} \text{ HNO}_3$ (1 mL)+EPW (1 mL) was selected as eluent for the subsequent experiments.

3.2 Separation behavior of MRT-SPE

The separation behavior of the AN-02 column with As(III) and As(V) is illustrated in Fig. 3 in terms of pH. The terms extraction and recovery were used to associate the retention performance of the SPE system with that of the elution. The number of moles of analyte in the elution effluent with the cumulative number of moles of the analyte present in the total effluents was compared to calculate the extraction rate. The recovery rate was calculated by comparing the number of moles of analyte recovered in all fractions with that of the number of moles of analyte in the solution loaded to the column.

Sample solutions (4 mL) spiked with $100 \text{ }\mu\text{mol L}^{-1}$ of As(III) and As(V) were loaded to the AN-02 MRT-SPE system at a flow rate of 0.2 mL min^{-1} . At pH 4 to 10, insignificant extraction was observed with As(III), while an average extraction of 97.4 ± 4.0 was observed for As(V) until pH 9. Factors such as pK_a values, ionic characters of the arsenic species, and hydrophobic interaction between the arsenic species and the SPE materials may have a significant effect on the retention efficiency of the SPE columns (Yu et al. 2003). The

distribution of different arsenic species in terms of pH in the aqueous medium can be determined from the respective pK_a values of As(III) ($pK_{a1}=9.2$, $pK_{a2}=12.2$, $pK_{a3}=13.4$) and As(V) ($pK_{a1}=2.2$, $pK_{a2}=6.9$, $pK_{a3}=11.5$), and it has been confirmed that As(III) exists mostly as a neutral species (H_3AsO_3) and As(V) as an anionic species ($H_2AsO_4^{4-}$, $HAsO_4^{2-}$) within the studied pH range (Chen et al. 2009). The macrocycle immobilized in AN-02 MRT-SPE system is designed for anion separation (Anonymous 2005), and therefore the observed behavior was expected.

The extraction and recovery behavior shows that AN-02 MRT-SPE system can selectively separate As(III) and As(V) at varying pH conditions (pH 4–9), *i.e.*, the separation process is almost pH independent and is useful for the quantitative determination of As(III) and As(V) content in the sample water. The recovery rate with AN-02 SPE column for all the arsenic species at the entire studied pH range was quantitative while a certain decrease in the extraction rate was observed above pH 9. The deviation is attributable to the increasing dissolving tendency of the silica gel base support with increasing pH (Vogelsberger et al. 1992).

3.3 Effect of matrix ions

The likely interfering effect from the matrix co-component ions on the As(V) separation efficiency with the AN-02 MRT-SPE system was examined at the following conditions: matrix– H_2O , pH–7, sample volume–4 mL, flow rate– 0.2 mL min^{-1} , elution– $1\text{ mol L}^{-1} HNO_3$ (2 mL)+ $6\text{ mol L}^{-1} HNO_3$ (1 mL)+EPW (1 mL). The binary mixtures containing the 1 mmol L^{-1} of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , or SO_4^{2-} and $10\text{ }\mu\text{mol L}^{-1}$ of As(V) were individually loaded to the MRT-SPE system. The rate of recovery was in the range of 92.1 ± 1.8 to $96.2\pm3.7\%$, which can be termed as quantitative. Therefore, it can be assumed that the deterring impact due to the ions commonly found in natural water on the separation of As(V) with the AN-02 MRT-SPE is negligible.

3.4 Retention capacity of the MRT-SPE

Retention capacity of the MRT-SPE system, an important property for determining the stability of the SPE column during the separation process, was computed from the analyte concentration and breakthrough volume—the volume of sample that causes the target analyte to be eluted from the SPE columns (Yu et al. 2003). As(V)-fortified sample solution prepared in H₂O matrix was fed to the SPE column at a flow rate of 0.2 mL min⁻¹ and then eluted with 2 mL of 1 mol L⁻¹ HNO₃+1 mL of 6 mol L⁻¹ HNO₃+1 mL of EPW. The retention capacity of the AN-02 column at pH 7 was calculated as 0.25±0.04 mmol g⁻¹.

3.5 Reusability of the MRT-SPE

The reusability of the AN-02 MRT-SPE was investigated with the sample solution spiked with 100 µmol L⁻¹ of As(V) ions in the aqueous matrix (flow rate—0.2 mL min⁻¹, elution—2 mL of 1 mol L⁻¹ HNO₃+1 mL of 6 mol L⁻¹ HNO₃+1 mL of EPW; *n*=3). As(V) extraction rate (%) of the fresh SPE column at pH 7 was 100±3.4, while it was 98.3±4.2 after 100 cycles. Hence, AN-02 column can be regenerated for more than 100 loading and elution cycles without the loss of analytical performance. The regeneration process for MRT-SPE is also simple because As(III) remain in the column effluent while As(V) eluted completely. SPE systems with macrocycles attached onto solid supports offer the option of selective separation of analytes from the matrix with the advantage of repeated use of the macrocycles (Bradshaw et al. 1988, Horwitz et al. 1992, Izatt 1997). Such opportunity of regeneration could facilitate the amortization of the initial high cost of material synthesis.

3.6 Analytical characteristics

The calibration graphs obtained at the optimized conditions showed linear patterns up to at least 2.5 µmol L⁻¹ with the respective correlation coefficients of 0.9981 and 0.9914. The precision at 1 µmol L⁻¹ of As(III) and As(V) concentrations were 0.7 and 2.9 % relative

standard deviations ($n=10$). The value of the limit of detection, calculated by three times the standard deviation of the blank ($n=15$), were $0.06 \mu\text{g L}^{-1}$ for As(III) and As(V).

3.7 Comparative performance of MRT-SPE and other commercial SPE materials

Aqueous solutions containing $100 \mu\text{mol L}^{-1}$ of As(V) were treated with AN-02 MRT-SPE and other commercial SPE materials (Chelex-100, NOBIAS Chelate PA-1, NOBIAS Chelate PB-1, NOBIAS Ion SA-1, NOBIAS Ion SC-1) to compare the separation efficiencies at optimized conditions. As shown in Fig. 4, MRT-SPE demonstrates quantitative separation efficiency from fortified aqueous solutions, while the recovery rate achieved for other SPE systems is $\leq 80\%$. The MRT-SPE types contain macrocyclic chelants, such as crown ethers, immobilized on the solid-phase (Izatt et al. 1994, Bradshaw & Izatt 1997). The crown ethers possess excellent structural diversity and superior selectivity properties among all the parent macrocycles (Tsukube 1993), and this might be associated to the greater retention performance with the MRT-SPE than the traditional ion-exchange or chelating resin-type SPE systems.

A comparison of the proposed technique for the selective separation of As(III) and As(V) in aqueous matrix using MRT-SPE with the other SPE-coupled options, as reported in the literature, is listed in Table 1. The recovery rate (%) of the target analyte, method detection limit (D_L , $\mu\text{g L}^{-1}$), and maximum reuse cycles were the terms for evaluation irrespective of the instrumental method used for analysis. The As(V) recovery rate (%) from the AN-02 MRT-SPE was analogous to the other appraised techniques. A better D_L was reported for LC-SAX (Yalcin & Le 2001) or silica/AAPTS (Chen et al. 2009) coupled separation techniques, while the reuse sustainability of those SPE systems was either lower or not available for comparison. The technique with the ion-exchange resin Dowex 1-X8 (Cl^- form) (Smichowski et al. 2002) has better method detection limit and can sustain for the same number of reuse cycles as compared to the proposed AN-02 MRT-SPE option. The advantage of the MRT-

SPE types than the ion-exchange resin types is the selectivity in the separation via “host-guest” complexation, which occur only when the host (usually a macrocycle that is tailored to the target based on charge, size, and shape) recognizes the specific electronic and spatial features of the guest (Izatt et al. 1995). The MRT-SPE materials have a greater concentration of active sites compared to the conventional option for separation of ions in solid phase due to the attachment of the enmeshed small microporous particles into the microfibrinous matrix. The aforesaid approach also eliminates the channeling effect that recurrently appeared with packed bed SPE processes (Goken et al. 1994, Izatt et al. 1995).

3.8 Accuracy and applications

3.8.1 Evaluation using certified reference materials

The accuracy of the proposed method was evaluated by analyzing two EC-JRC-IRMM CRMs: effluent wastewater (BCR-713) and groundwater (BCR-610). Total arsenic contents in the CRMs were in good agreement with the certified values (Table 2).

3.8.2 Analysis of natural water samples

The proposed separation process was applied to the analysis of natural water samples (tap water, lake water, and river water) collected from local sources. The samples were spiked with known amounts of As(III) and As(V). Analytical results for the natural waters are given in Table 3, and almost quantitative recoveries were obtained in all cases.

4.0 Conclusion

Selective determination with GF-AAS after selective separation of As(III) and As(V) with a single MRT-SPE column: AnaLig AN-02 was achieved. As(V) was completely retained and recovered from the MRT-SPE system within the pH of 4 to 9, while As(III) remained in the column effluent. At a flow rate of 0.2 mL min^{-1} , the following elution combination was used: $1 \text{ mol L}^{-1} \text{ HNO}_3$ (2 mL)+ $6 \text{ mol L}^{-1} \text{ HNO}_3$ (1 mL)+EPW (1 mL) to

recover the “captured” species from the MRT gel structure. The process offers a single-step separation option of trivalent and pentavalent arsenic species that commonly exist in the natural aqueous matrix. Easy operation, rapid separation performance, and reusability for more than 100 cycles without loss of the analytical performance of the MRT-SPE are some additional characteristics of the proposed process which make it a suitable and economic option for, particularly, the arsenic-prone nations suffering from natural arsenic contamination.

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References

- Anonymous (2005). AnaLig® Data Sheet: AN-02. IBC Advanced Technologies, Inc., American Fork, UT.
- Bag, H., Lale, M. & Türker, A. R. (1998). Determination of iron and nickel by flame atomic absorption spectrophotometry after preconcentration on *Saccharomyces cerevisiae* immobilized sepiolite. *Talanta*, 47, 689–696.
- Barra, C. M., Santelli, R. E., Abrão, J. J. & Guardia, M. d. I. (2000). Arsenic speciation – A review. *Quimica Nova*, 23, 58–70.
- Biernat, J. F., Konieczka, P., Tarbet, B. J., Bradshaw, J. S. & Izatt, R. M. (1994). Complexing and chelating agents immobilized on silica gel and related materials and their application for sorption of inorganic species. *Separation and Purification Methods*, 23, 77–348.
- Bissen, M. & Frimmel, F. H. (2000). Speciation of As(III), As(V), MMA and DMA in contaminated soil extracts by HPLC-ICP/MS. *Fresenius Journal of Analytical Chemistry*, 367, 51–55.
- Bradshaw, J. S., Bruening, R. L., Krakowiak, K. E., Tarbet, B. J., Bruening, M. L., Izatt, R. M. & Christensen, J. J. (1988). Preparation of silica gel-bound macrocycles and their cation-binding properties. *Journal of the Chemical Society-Chemical Communications*, 812–814.
- Bradshaw, J. S. & Izatt, R. M. (1997). Crown ethers: The search for selective ion ligating agents. *Accounts of Chemical Research*, 30, 338–345.
- Bradshaw, J. S., Izatt, R. M., Christensen, J. J., Krakowiak, K. E., Tarbet, B. J., Bruening, R. L. & Lifson, S. (1989). Stable silica gel-bound crown ethers. Selective separation of metal ions and a potential for separations of amine enantiomers. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 7, 127–136.
- Bruening, M. L., Mitchell, D. M., Bradshaw, J. S., Izatt, R. M. & Bruening, R. L. (1991). Effect of organic solvent and anion type on cation binding constants with silica gel bound macrocycles and their use in designing selective concentrator columns. *Analytical Chemistry*, 63, 21–24.
- Camel, V. (2003). Solid phase extraction of trace elements. *Spectrochimica Acta Part B-Atomic Spectroscopy*, 58, 1177–1233.
- Chen, D., Huang, C., He, M. & Hu, B. (2009). Separation and preconcentration of inorganic arsenic species in natural water samples with 3-(2-aminoethylamino)

- propyltrimethoxysilane modified ordered mesoporous silica micro-column and their determination by inductively coupled plasma optical emission spectrometry. *Journal of Hazardous Materials*, 164, 1146–1151.
- Francesconi, K. A. & Kuehnelt, D. (2004). Determination of arsenic species: A critical review of methods and applications, 2000-2003. *Analyst*, 129, 373-395.
- Goken, G., Bruening, R. & Bray, L. (1994) Solid phase extraction membranes for selective radionuclide separation. *AIChE Summer National Meeting*. Denver, CO.
- Hasegawa, H., Matsui, M., Okamura, S., Hojo, M., Iwasaki, N. & Sohrin, Y. (1999). Arsenic speciation including 'hidden' arsenic in natural waters. *Applied Organometallic Chemistry*, 13, 113–119.
- Hasegawa, H., Rahman, I. M. M., Begum, Z. A., Umehara, Y., Maki, T., Furusho, Y. & Mizutani, S. (2013). A silica gel-bound macrocycle system for the selective separation of toxic cadmium from metal-affluent aqueous matrix. *Central European Journal of Chemistry*, 11, 341–347.
- Hasegawa, H., Rahman, I. M. M., Kinoshita, S., Maki, T. & Furusho, Y. (2010). Non-destructive separation of metal ions from wastewater containing excess aminopolycarboxylate chelant in solution with an ion-selective immobilized macrocyclic material. *Chemosphere*, 79, 193–198.
- Hiraoka, M. (1982). *Crown Compounds: Their Characteristics and Applications*. Amsterdam: Elsevier.
- Hiraoka, M. (1992). *Crown Ethers and Analogous Compounds*. Amsterdam: Elsevier.
- Horwitz, E., Dietz, M. & Chiarizia, R. (1992). The application of novel extraction chromatographic materials to the characterization of radioactive waste solutions. *Journal of Radioanalytical and Nuclear Chemistry*, 161, 575–583.
- Izatt, R. M. (1997). Review of selective ion separations at BYU using liquid membrane and solid phase extraction procedures. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 29, 197–220.
- Izatt, R. M., Bradshaw, J. S., Bruening, R. L. & Bruening, M. L. (1994). Solid phase extraction of ions of analytical interest using molecular recognition technology. *American Laboratory*, 26, 28C–28M.
- Izatt, R. M., Bradshaw, J. S., Bruening, R. L., Tarbet, B. J. & Bruening, M. L. (1995). Solid phase extraction of ions using molecular recognition technology. *Pure and Applied Chemistry*, 67, 1069–1074.

- Izatt, R. M., Bruening, R. L., Bruening, M. L., Tarbet, B. J., Krakowiak, K. E., Bradshaw, J. S. & Christensen, J. J. (1988). Removal and separation of metal ions from aqueous solutions using a silica-gel-bonded macrocycle system. *Analytical Chemistry*, 60, 1825–1826.
- Izatt, R. M., Clark, G. A., Bradshaw, J. S., Lamb, J. D. & Christensen, J. J. (1986). Macrocycle-facilitated transport of ions in liquid membrane systems. *Separation and Purification Methods*, 15, 21–72.
- Karim, M. (2000). Arsenic in groundwater and health problems in Bangladesh. *Water Research*, 34, 304–310.
- Kumar, A. R. & Riyazuddin, P. (2007). Non-chromatographic hydride generation atomic spectrometric techniques for the speciation analysis of arsenic, antimony, selenium, and tellurium in water samples – A review. *International Journal of Environmental Analytical Chemistry*, 87, 469–500.
- Liang, P. & Liu, R. (2007). Speciation analysis of inorganic arsenic in water samples by immobilized nanometer titanium dioxide separation and graphite furnace atomic absorption spectrometric determination. *Analytica Chimica Acta*, 602, 32–36.
- Lintschinger, J., Schramel, P., Hatalak-Rauscher, A., Wendler, I. & Michalke, B. (1998). A new method for the analysis of arsenic species in urine by using HPLC-ICP-MS. *Fresenius Journal of Analytical Chemistry*, 362, 313–318.
- Liska, I. (2000). Fifty years of solid-phase extraction in water analysis – Historical development and overview. *Journal of Chromatography A*, 885, 3–16.
- Mahoney, J. M., Beatty, A. M. & Smith, B. D. (2001). Selective recognition of an alkali halide contact ion-pair. *Journal of the American Chemical Society*, 123, 5847–5848.
- Mahoney, J. M., Beatty, A. M. & Smith, B. D. (2004). Selective solid-liquid extraction of lithium halide salts using a ditopic macrobicyclic receptor. *Inorganic Chemistry*, 43, 7617–7621.
- Mandal, B. K. & Suzuki, K. T. (2002). Arsenic round the world: A review. *Talanta*, 58, 201–235.
- Mays, D. E. & Hussam, A. (2009). Voltammetric methods for determination and speciation of inorganic arsenic in the environment – A review. *Analytica Chimica Acta*, 646, 6–16.
- Muñoz, E. & Palmero, S. (2005). Analysis and speciation of arsenic by stripping potentiometry: A review. *Talanta*, 65, 613–620.

- Nabeshima, T., Saiki, T., Iwabuchi, J. & Akine, S. (2005). Stepwise and dramatic enhancement of anion recognition with a triple-site receptor based on the calix[4]arene framework using two different cationic effectors. *Journal of the American Chemical Society*, 127, 5507–5511.
- Nickson, R. A., Hill, S. J. & Worsfold, P. J. (1995). Analytical perspective. Solid phase techniques for the preconcentration of trace metals from natural waters. *Analytical Proceedings including Analytical Communications*, 32, 387–395.
- Pergantis, S. A., Winnik, W. & Betowski, D. (1997). Determination of ten organoarsenic compounds using microbore high-performance liquid chromatography coupled with electrospray mass spectrometry mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 12, 531–536.
- Poole, C. F. (2000). Solid-phase extraction. In D. W. Ian (ed.), *Encyclopedia of Separation Science*. Oxford: Academic Press.
- Quevauviller, P., Andersen, K., Merry, J. & Jagt, H. V. D. (1998). The Certification of the Contents (Mass Fractions) of Aluminium, Arsenic, Cadmium, Copper and Lead in Groundwater (Low Content CRM 609; High Content CRM 610). Luxembourg: Institute for Reference Materials and Measurements, European Commission.
- Rahman, I. M. M., Begum, Z. A. & Hasegawa, H. (2011a). Application of Molecular Recognition Technology: For Selective Solid Phase Extraction of Ions. Saarbrücken, Germany: LAP LAMBERT Academic Publishing.
- Rahman, I. M. M., Begum, Z. A., Nakano, M., Furusho, Y., Maki, T. & Hasegawa, H. (2011b). Selective separation of arsenic species from aqueous solutions with immobilized macrocyclic material containing solid phase extraction columns. *Chemosphere*, 82, 549–556.
- Rahman, I. M. M., Furusho, Y., Begum, Z. A., Izatt, N., Bruening, R., Sabarudin, A. & Hasegawa, H. (2011c). Separation of lead from high matrix electroless nickel plating waste solution using an ion-selective immobilized macrocycle system. *Microchemical Journal*, 98, 103–108.
- Rahman, I. M. M., Furusho, Y., Begum, Z. A., Sabarudin, A., Motomizu, S., Maki, T. & Hasegawa, H. (2011d). Selective separation of some ecotoxic transition metal ions from aqueous solutions using immobilized macrocyclic material containing solid phase extraction system. *Central European Journal of Chemistry*, 9, 1019–1026.

- Rahman, I. M. M., Nazim Uddin, M., Hasan, M. T. & Hossain, M. M. (2008). Assimilation of arsenic into edible plants grown in soil irrigated with contaminated groundwater. In J. Bundschuh, M. A. Armienta, P. Birkle, P. Bhattacharya, J. Matschullat & A. B. Mukherjee (eds.), *Natural Arsenic in Groundwaters of Latin America*. Leiden, The Netherlands: CRC Press/Balkema.
- Ritsema, R., Dukan, L., Navarro, T. R. I., van Leeuwen, W., Oliveira, N., Wolfs, P. & Lebre, E. (1998). Speciation of arsenic compounds in urine by LC-ICP MS. *Applied Organometallic Chemistry*, 12, 591–599.
- Rossi, D. T. & Zhang, N. (2000). Automating solid-phase extraction: Current aspects and future prospects. *Journal of Chromatography A*, 885, 97–113.
- Sanchez, W. M., Zwicker, B. & Chatt, A. (2009). Determination of As(III), As(V), MMA and DMA in drinking water by solid phase extraction and neutron activation. *Journal of Radioanalytical and Nuclear Chemistry*, 282, 133–138.
- Segura, M., Madrid, Y., Cámara, C., Rebollo, C., Azcarate, J., Kramer, G. N., Gawlik, B. M., Lamberty, A., Quevauviller, P. & Bowadt, S. (2004). The Certification of the Mass Concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn in Wastewater, BCR-713 (Effluent Wastewater), BCR-714 (Influent Wastewater) BCR-715 (Industrial Effluent Wastewater). Luxembourg: Institute for Reference Materials and Measurements, European Commission.
- Smichowski, P., Valiente, L. & Ledesma, A. (2002). Simple method for the selective determination of As(III) and As(V) by ETAAS after separation with anion exchange mini-column. *Atomic Spectroscopy*, 23, 92–97.
- Squibb, K. S. & Fowler, B. A. (1983). The toxicity of arsenic and its compounds. In B. A. Fowler (ed.), *Biological and Environmental Effects of Arsenic*. New York: Elsevier Science Publishers B.V.
- Terlecka, E. (2005). Arsenic speciation analysis in water samples: A review of the hyphenated techniques. *Environmental Monitoring and Assessment*, 107, 259–284.
- Tsukube, H. (1993). Double armed crown ethers and armed macrocycles as a new series of metal-selective reagents: A review. *Talanta*, 40, 1313–1324.
- USEPA (2002). Implementation Guidance for the Arsenic Rule – Drinking Water Regulations for Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring (EPA-816-K-02-018). Washington, DC: United States Environmental Protection Agency (USEPA).

- Vogelsberger, W., Seidel, A. & Rudakoff, G. (1992). Solubility of silica gel in water. *Journal of the Chemical Society-Faraday Transactions*, 88, 473–476.
- Walkowiak, W. & Kozłowski, C. A. (2009). Macrocyclic carriers for separation of metal ions in liquid membrane processes – A review. *Desalination*, 240, 186–197.
- Walkowiak, W., Ulewicz, M. & Kozłowski, C. (2002). Application of macrocyclic compounds for metal ions separation and removal – A review. *Ars Separatoria Acta*, 1, 87–98.
- WHO (2001). Environmental Health Criteria 224: Arsenic and Arsenic Compounds Geneva: World Health Organization (WHO).
- Xiong, C., He, M. & Hu, B. (2008). On-line separation and preconcentration of inorganic arsenic and selenium species in natural water samples with CTAB-modified alkyl silica microcolumn and determination by inductively coupled plasma-optical emission spectrometry. *Talanta*, 76, 772–779.
- Yalcin, S. & Le, X. C. (2001). Speciation of arsenic using solid phase extraction cartridges. *Journal of Environmental Monitoring*, 3, 81–85.
- Yu, C. H., Cai, Q. T., Guo, Z. X., Yang, Z. G. & Khoo, S. B. (2003). Inductively coupled plasma mass spectrometry study of the retention behavior of arsenic species on various solid phase extraction cartridges and its application in arsenic speciation. *Spectrochimica Acta Part B-Atomic Spectroscopy*, 58, 1335–1349.

Table 1. Comparison of the proposed technique with the AN-02 MRT-SPE for selective separation of tri- and pentavalent arsenic, and the other SPE-coupled options

SPE-system	Sample	pH	Eluent	Detector	R	D_L	R_c	Ref.
AnaLig AN-02 ^a	Tap, lake, and river water, CRM BCR-713 and BCR-610 ^b	4–9	1 and 6 mol L ⁻¹ HNO ₃	GF-AAS	98.7–101	0.06	100	This work
Silica/AAPTS ^a	Lake and well water, GSBZ50004-88 ^b	3–9	1 mol L ⁻¹ HCl	ICP-OES	91–108	0.05	50	Chen et al. (2009)
Extract–Clean SPE SAX ^a	CRM EP-H-1 and EP-L-1 ^b	6.5	1 mol L ⁻¹ HNO ₃	NAA	–	1.7	–	Sanchez et al. (2009)
CTAB/Silica ^a	River, lake, well, rain, pool and tap water, ERM BW3209 (0602) and BW3210 (0602) ^b	6.5	1 mol L ⁻¹ HNO ₃	ICP-OES	93–106	0.15	15	Xiong et al. (2008)
Dowex 1-X8 ^a	Tap, lake, and well water	7	0.8 mol L ⁻¹ HCl	GF-AAS	92–106	0.004	100	Smichowski et al. (2002)
LC-SAX ^a	River and tap water; Urine; NIST-SRM 2670 ^b	Acidic	1 mol L ⁻¹ HCl	FI-HGAFS	~100	0.05	–	Yalcin and Le (2001)

* R Recovery (%), D_L Detection limit ($\mu\text{g L}^{-1}$), R_c Maximum reuse cycle, FI-HGAFS flow injection - hydride generation atomic fluorescence spectrometry, GF-AAS graphite furnace atomic absorption spectrometry, ICP-OES inductively coupled plasma optical emission spectrometry, NAA neutron activation analysis.

^a LC-SAX, silica-based quaternary amine-bonded SPE system, commercial product from Supelco, Bellefonte, PA, USA; Extract–Clean SPE SAX, resin-based strong anion exchange column, commercial product from Alltech, Ontario, Canada; Dowex 1-X8, anion exchange resin, commercial product from Bio-Rad Labs, Richmond, CA, USA; CTAB/Silica, cetyltrimethylammonium bromide (CTAB)-modified alkyl silica sorbent; silica/AAPTS, 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) modified ordered mesoporous silica; AnaLig AN-02, Immobilized macrocyclic material containing SPE system, commercial product from IBC Advanced Technologies, Inc., Utah, USA;

^b NIST-SRM 2670, toxic metals in urine [NIST-SRM: standard reference material from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA)]; CRM EP-H-1 (high-level concentrate) and EP-L-1 (low-level concentrate), drinking water certified reference materials (SCP Science, Canada); ERM BW3209 (0602) and ERM BW3210 (0602), environmental water samples complying National standard of the People's Republic of China [ERM: Environmental reference materials from Institute of Reference Materials, SEPA Beijing, P.R. China]; GSBZ50004-88, certified reference material of environmental water [Institute for Environmental Reference Materials, Ministry of Environmental Protection of China, Beijing, China]; CRM BCR-713 (effluent wastewater) and BCR-610 (groundwater), certified reference materials from EC-JRC-IRMM (European Commission Joint Research Centre, Institute of Reference Materials and Measurements)

Table 2. Evaluation of the tri- and pentavalent arsenic separation performance of the AN-02 MRT-SPE with the EC-JRC-IRMM CRMs

Arsenic species	Effluent wastewater CRM		Groundwater CRM	
	BCR-713 ($\mu\text{g L}^{-1}$) ^a		BCR-610 ($\mu\text{g L}^{-1}$) ^b	
	This work	Certified value ^c	This work	Certified value ^c
As(III)	1.9 ± 0.3	NR	3.3 ± 0.6	NR
As(V)	7.1 ± 1.2	NR	6.9 ± 1.1	NR
Σ (As-species)	9.0 ± 1.4	9.7 ± 1.1	10.2 ± 1.6	10.8 ± 0.4

^a BCR-713 is an effluent wastewater reference material certified by BCR (Community Bureau of Reference, the former reference materials programme of the European Commission) and available from the EC-JRC-IRMM (European Commission Joint Research Centre, Institute of Reference Materials and Measurements) (Segura et al. 2004).

^b BCR-610 is a groundwater reference material certified by BCR (Community Bureau of Reference, the former reference materials programme of the European Commission) and available from the EC-JRC-IRMM (European Commission Joint Research Centre, Institute of Reference Materials and Measurements) (Quevauviller et al. 1998).

^c BCR-713 and BCR-610 are certified for total contents of different metal ions in the samples following collaboratively tested and harmonized procedures (Quevauviller et al. 1998, Segura et al. 2004). The mentioned certified value is for total arsenic contents in the samples while the term “NR” stands for “Not reported”

Table 3. The tri- and pentavalent arsenic content analysis in the natural water samples after the AN-02 MRT-SPE separation

Sample	As(III)			As(V)		
Tap water	Added ($\mu\text{g L}^{-1}$)	0	19.5	Added ($\mu\text{g L}^{-1}$)	0	31.2
	Found ($\mu\text{g L}^{-1}$)	BDL ^a	19.4 $\pm$ 0.1	Found ($\mu\text{g L}^{-1}$)	BDL ^a	31.5 $\pm$ 0.3
	Recovery (%)	–	99.5 $\pm$ 0.6	Recovery (%)	–	100.9 $\pm$ 1.0
Lake water	Added ($\mu\text{g L}^{-1}$)	0	19.5	Added ($\mu\text{g L}^{-1}$)	0	31.2
	Found ($\mu\text{g L}^{-1}$)	BDL ^a	19.7 $\pm$ 0.3	Found ($\mu\text{g L}^{-1}$)	5.24 $\pm$ 0.67	31.3 $\pm$ 0.2
	Recovery (%)	–	100.9 $\pm$ 1.4	Recovery (%)	–	100.3 $\pm$ 0.7
River water	Added ($\mu\text{g L}^{-1}$)	0	19.5	Added ($\mu\text{g L}^{-1}$)	0	31.2
	Found ($\mu\text{g L}^{-1}$)	0.71 $\pm$ 0.12	19.6 $\pm$ 0.2	Found ($\mu\text{g L}^{-1}$)	1.34 $\pm$ 0.15	30.8 $\pm$ 0.2
	Recovery (%)	–	100.3 $\pm$ 0.9	Recovery (%)	–	98.7 $\pm$ 0.7

^a ‘BDL’ – Below Detectable Limit

Fig. 1. Schematic diagram of the experimental setup

Fig. 2. Effect of (a) sample loading flow rate and (b) eluent concentration on the separation performance of the AN-02 MRT-SPE system. Sample solution–As(V) (100 $\mu\text{mol L}^{-1}$), matrix–H₂O, pH–7, sample volume–4 mL, loading flow rate–(a) 0.2 to 2 mL min⁻¹ (b) 0.2 mL min⁻¹, elution–(a) 1 mol L⁻¹ HNO₃ (2 mL)+6 mol L⁻¹ HNO₃ (1 mL)+EPW (1 mL) (b) 0.1 to 6 mol L⁻¹ HNO₃ (4 mL) ($n=3$)

Fig. 3. The behavior of the AN-02 MRT-SPE system for the separation of tri- and pentavalent arsenic species. Sample solution–As(III) and As(V) ($100 \mu\text{mol L}^{-1}$), matrix– H_2O , pH–4 to 10, sample volume–4 mL, flow rate– 0.2 mL min^{-1} , elution– $1 \text{ mol L}^{-1} \text{ HNO}_3$ (2 mL)+ $6 \text{ mol L}^{-1} \text{ HNO}_3$ (1 mL)+EPW (1 mL) ($n=3$)

Fig. 4. Comparative separation performance of different SPE systems (AN-02: AnaLig AN-02, C-100: Chelex-100, PA-1: NOBIAS Chelate PA-1, PB-1: NOBIAS Chelate PB-1, SA-1: NOBIAS Ion SA-1, SC-1: NOBIAS Ion SC-1). Sample solution–As(V) ($100 \mu\text{mol L}^{-1}$), matrix– H_2O , pH–7, sample volume–4 mL, flow rate– 0.2 mL min^{-1} , elution– $1 \text{ mol L}^{-1} \text{ HNO}_3$ (2 mL)+ $6 \text{ mol L}^{-1} \text{ HNO}_3$ (1 mL)+EPW (1 mL) ($n=3$)