Published in final edited form as:

Phys Chem Earth (2002). 2011 ; 36(9-11): 436–441. doi:10.1016/j.pce.2010.03.027.

Field Deployable Method for Arsenic Speciation in Water

Thomas C. Voice¹, Lisveth V. Flores del Pino², Ivan Havezov³, and David T. Long¹

¹Michigan State University, East Lansing, MI, USA

²Universidad Nacional Agraria La Molina, Lima, Perú

³Bulgarian Academy of Sciences, Sofia, Bulgaria

Abstract

Contamination of drinking water supplies by arsenic is a world-wide problem. Total arsenic measurements are commonly used to investigate and regulate arsenic in water, but it is well understood that arsenic occurs in several chemical forms, and these exhibit different toxicities. It is problematic to use laboratory-based speciation techniques to assess exposure as it has been suggested that the distribution of species is not stable during transport in some types of samples. A method was developed in this study for the on-site speciation of the most toxic dissolved arsenic species: As (III), As (V), monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA). Development criteria included ease of use under field conditions, applicable at levels of concern for drinking water, and analytical performance.

The approach is based on selective retention of arsenic species on specific ion-exchange chromatography cartridges followed by selective elution and quantification using graphite furnace atomic absorption spectroscopy. Water samples can be delivered to a set of three cartridges using either syringes or peristaltic pumps. Species distribution is stable at this point, and the cartridges can be transported to the laboratory for elution and quantitative analysis. A set of ten replicate spiked samples of each compound, having concentrations between 1 and 60 µg/L, were analyzed. Arsenic recoveries ranged from 78–112 % and relative standard deviations were generally below 10%. Resolution between species was shown to be outstanding, with the only limitation being that the capacity for As (V) was limited to approximately 50 µg/L. This could be easily remedied by changes in either cartridge design, or the extraction procedure. Recoveries were similar for two spiked hard groundwater samples indicating that dissolved minerals are not likely to be problematic. These results suggest that this methodology can be used for analysis of the four primary arsenic species of concern in drinking water supplies.

Keywords

analysis; solid-phase extraction; speciation; As (III); As (V); monomethylarsonic acid (MMA); dimethylarsenic acid (DMA)

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Corresponding author: Thomas C. Voice, Michigan State University, A127 Research Complex, East Lansing, MI, 48824, USA. Phone: (517)353-1798; fax: (517)355-2050; voice@msu.edu.

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Introduction

Arsenic contamination in natural waters is a worldwide problem that has become the subject of considerable international attention. Long-term ingestion of drinking water contaminated with arsenic has been associated with health problems including skin, bladder and lung cancers, skin lesions, cardiovascular effects, and anemia (Tseng et al., 1968; Wu et al., 1989; Guo et al., 1997; Hopenhayn et al., 1998; Malik et al., 2009; WHO, 1996). Widespread health problems, including what is termed “blackfoot disease”, have been observed in Bangladesh following a program to replace contaminated surface water supplies with shallow wells. Arsenic levels as high as 1820 µg/L have been reported in some wells in Southwest, Taiwan (Tseng et al., 1968). Drinking water regulations for maximum allowable levels of arsenic vary by country across the range of 7 µg/L to 50 µg/L, the U.S. having recently lowered the standard to 10 µg/L (WHO, 1996). In most cases, the source of the arsenic is natural, resulting from the dissolution of arsenic-containing minerals in the aquifer (Kim et al., 2000; Simon et al., 1999).

Investigations to date have focused largely on total arsenic levels in water supplies, but it is now understood that toxicity varies with the chemical form of the arsenic (NRC, 2001; Jain and Ali, 2000). In waters with relatively low levels of organic carbon (including most ground waters), the inorganic arsenic species predominate, with higher levels of As (V) (H_3AsO_4 , H_2AsO_4^- , HASO_4^{2-} , AsO_4^{3-}) found under oxidizing conditions and more greater amounts of As (III) (H_3AsO_3 , H_2AsO_3^- , HASO_3^{2-}) under reducing conditions (Bose and Sharma, 2002). Under strongly reducing conditions, biological methylation of inorganic arsenic can occur. Concentrations of methylarsenicals can be significant: Anderson and Bruland (1991) reported them to constitute 59% of the total As in a lake water. Monomethylarsonic acid/monomethylarsonate ($(\text{CH}_3)\text{AsO}(\text{OH})_2$) (MMAA/MMA) and dimethylarsinic acid/dimethylarsinate ($(\text{CH}_3)_2\text{AsO}(\text{OH})$) (DMAA/DMA) are the most commonly observed forms. As (III) is reported to be 25 to 60 times as toxic as As (V) and several hundred times as toxic as the methylated arsenicals (Korte, 1991). A number of other organic forms can be found, but these are generally considered to be non-toxic (Shiomi, 1994; Philips, 1990).

Total arsenic measurement in environmental matrices is relatively straightforward, with the principal methodologies based on flame (FAAS), hydride generation (HGAAS) or graphite furnace atomic absorption (GFAAS). Arsenic speciation has been more problematic, however, and a number of separation techniques have been employed to resolve the various species. Separation approaches reported in the literature include methods based on sequential volatilization (Braman et al., 1977; Carvalho and Hercules, 1978; Heinrichs and Keltsch, 1982; Tesfalidet and Agrium, 1988; Galban et al., 1993; Moller and Scholz, 1995; Frankenberger, 1998; Anderson et al., 1986; Lopez-Molinero et al., 2001; Lopez-Molinero et al., 1999), liquid-liquid extraction (Kalyanaraman and Khopkar, 1977; Chakraborti et al., 1980; Puttemans et al., 1983; Rohr and Meckel, 1992), arsine generation (Narsito and Agterdenbos, 1987; Masscheleyn et al., 1991(20,25); Michel et al., 1992; Howard and Comber, 1992; Cabredo et al., 1995; Burguera and Burguera, 1997), ion exchange (Henry and Thorpe, 1980; Pacey and Ford, 1981; Ficklin, 1983; Aggett and Kadwani, 1983; Gomez et al., 1997; Edwards et al., 1998; Miller et al., 2000; Le et al., 2000; Kim, 2001), ion-pair high-performance liquid chromatography (Grabinski, 1981; Ding et al., 1995; Yalcin and Le, 1998; Le and Ma, 1998; Mattusch and Wennrich, 1998; Szpunar et al., 2000), and reverse-phase high-performance liquid chromatography (Brinckman et al., 1980; Tye et al., 1985; Ebdon et al., 1988; Bohari et al., 2001; Martin et al., 1995; Le et al., 1996; Larsen, 1998; Londesborough et al., 1999).

The problem with using most of the above techniques to assess exposure to various arsenic species is that they are laboratory-based and the distribution of species in a collected sample is not necessarily stable. For example, it has been shown that As (III) can be oxidized to As (V) during storage even when water samples preserved with hydrochloric acid and other chemicals (Orho and Wilderer, 1997; Volke and Merkel, 1999). The arsenic separation methods reported in the literature that might be carried out on-site are limited to separation of As (III) and As (V) (Ficklin, 1983; Edwards et al., 1998; Kim, 2001; Russeva et al., 1993). Thus, there remains a need for a method capable of determining the distribution of the most toxic arsenic species (As (III), As (V), MMA and DMA) at the point of exposure, at concentration levels of interest in drinking water.

The aim of this study was to develop a simple, field-deployable, As-species separation technique that could be easily coupled to laboratory analysis methods for the four species of primary interest. Such a method would be useful in both routine monitoring and exposure assessment studies. Our approach was to utilize or develop solid-phase extraction materials to selectively retain As species, develop a sequential extraction approach based on these materials to isolate all four species, implement this approach in a simple cartridge system that can be used in the field, optimize a methodology for field extraction, laboratory elution and GFAAS analysis of the extracts, to produce accurate and precise As species concentration data.

The basic strategy involves three columns and a selective elution procedure. The first cartridge uses a cation exchange resin to remove interfering cations. The pH of the sample is then reduced to less than 1.5, which results in formation of the protonated cation of DMA. This can then be extracted with a second cation exchange resin, and later eluted with acid. The pH of the effluent is increased to the range 2.5 to 3.5. The third column is silanized diatomaceous earth that has been treated with dioctyltin dichloride to retain As (V) and MMA. These are later eluted with different strength acids. The mechanism for these separations has not been verified, but it is thought that As (V) is retained as H_2AsO_4^- by a combination of anion exchange, the formation of tin-oxygen bonds, while MMA is held by the diatomaceous earth (Davies, 1997; Shkinev et al., 1985; Spivakov et al., 1983). As (III) is found in the effluent from the third cartridge as it remains in the neutral form and is not retained.

Materials and Methods

Cartridges were prepared using a slurry method. A small plug of glass wool was placed in the bottom of the cartridges to provide a support for the media. A small volume of an appropriate solvent was mixed with the extraction media to form a homogeneous paste that would flow. This paste was poured into the cartridges, taking care to prevent cracks, channels and air bubbles. Glass wool was placed on the top to hold the media in place. Three cartridges were used, the first removes interferences; the second one retained DMA and the third retains As (V) and MMA. Cartridge 1 was packed with 0.6g Chelex 100 in sodium form, as purchased, using deionized water as a solvent. It was then converted to the ammonia form by passing 20 mL of 1.0 M NH_4OH through the cartridge. The cartridge was then flushed with about 50 mL deionized water to remove the residual NH_4OH . A plastic cartridge was used. Cartridge 2 was packed with 0.3 g Dowex 50w (50–100 mesh, 8% crosslinkage) in the hydrogen form as purchased using 0.1 M HCl as a solvent. A plastic cartridge was used. Cartridge 3 was packed with a custom sorbent prepared as follows. Dioctyltin dichloride was dissolved in n-decanol and mixed with chloroform as a carrier solvent. This solution was shaken with Chromosorb W for 2 hours and dried at room temperature. The suspension was dried using a rotary evaporator at room temperature, and

the dry material is used to pack glass cartridges using 0.001 M hydrochloric acid as a solvent.

After initial development of the procedure, optimization studies were performed to evaluate the effects of variations in pH adjustment between cartridges, and flow rates for both extraction and elution. The capacities of cartridges 2 and 3 were evaluated for the three species retained. The optimized extraction/elution procedure is shown schematically in Figure 1. A water sample was first passed through cartridge 1 using either a syringe or peristaltic pump. The effluent was adjusted to pH 1–1.5 with 1M HCl and passed through Cartridge 2 at a rate of 3–4 mL/min. The effluent was adjusted to pH 2.5–3.5 using NH₄OH and passed through Cartridge 3 at a rate of 0.5–1 mL/min. Cartridge 2 was eluted with 5 mL 1 M HCl to produce the DMA fraction. Cartridge 3 was first eluted with 8 mL 0.2 M HCl and then with 5 mL of 1.0 M HCl to produce As(V) and MMA fractions, respectively. The effluent of Cartridge 3 contained the As(III) fraction.

An arsenate standard solution (Inorganic Ventures, Inc.) containing 100.00 µg as As /mL in 0.7 % perchloric acid was used as the As(V) stock solution and as an analytical standard. An As(III) stock solution was prepared by dissolving high purity arsenious oxide (GFS Chemical) in a minimal volume of 1M NaOH, neutralizing with 1M HCl using a methyl orange indicator, and diluting with dionized water to achieve a concentration of 1,000 mg as As/L. Stock solutions containing 1,000 mg as As/L of monomethyl arsonate (Chem Service) and dimethyl arsinatate (GFS Chemical) were prepared by direct dissolution in dionized water. Standard solutions, which were used for the calibration and spiked samples were prepared daily by dilution of the stock solutions. All chemicals were trace analysis grade.

The four fractions were analyzed using graphite furnace atomic absorption spectroscopy (GFAAS). A matrix modifier solution containing palladium chloride, bidistilled hydrochloric acid, ammonium paratungstate, and citric acid was employed. An electrodeless discharge lamp (EDL) was used with Zeeman-effect background correction. Ultra-clean graphite tubes with integrated platforms tube were used with the furnace temperature program shown in Table 1.

To evaluate the method, water samples were spiked with various concentrations and combinations of the four arsenic species by adding the appropriate stock solution to water and immediately passing the solution through the series of cartridges. Solutions containing the four compounds individually were analyzed over the concentration range 10 – 100 µg as As/L. Ten replicates of twelve different combinations of the four species at levels up to 100 µg as total As were also analyzed. Finally, a comparison between spiked samples using deionized water and very hard groundwater was performed.

Results and Discussion

Seven-point calibration curves for the each of the four arsenic species were established for the concentration range of 1 to 10 µg/L and 5–100 µg/L using peak areas. Correlation coefficients were higher than 0.998 for all species and the relative standard deviations for the points of the calibration graphs were between 5–10 % for 1–10 ppb and 1–6% from 5–100 µg/L. Previous studies have reported different response factors, or slopes of the calibration curves, for different As species (Masscheleyn, 1991(20); Ochsenuhn-Petropolu et al., 1995). We found no significant differences. Three replicates of the calibration procedure were performed on each of three different days. The relative standard deviation did not exceed 8 % for 1–10 µg/L and 5 % for the concentration range of 5–100 µg/L. A detection limit of 0.37 µg/L was determined using the criterion $3 \times \sigma / S$, where σ is the

standard deviation of the ten replicates of background signal and S is the slope of the calibration curve (IUPAC, 1995; Jaganathan, 2001).

Optimization studies for extraction pH indicated that complete retention of DMA occurred in the pH range 1.0–1.5. Similarly, complete retention of As (V) and MMA was achieved in the pH range 2.5–3.5. The effect of the flow rate for extraction by cartridges 2 and 3 was evaluated over the range 0.5–4 mL/min using peristaltic pumps in place of syringes that would normally be employed under field conditions. The best results were obtained in the range 3–4 mL/min for cartridge 2 and 0.5–1 mL/min for cartridge 3. Elution flow rate was evaluated over the same range with the result that 0.5–1 mL/min was best for cartridge 2 and 1 mL/min for cartridge 3. The elution curve for cartridge 3 shown in Figure 2 demonstrates excellent resolution of As (V) and MMA.

Table 2 shows the results obtained using deionized water spiked with each of the four arsenic species individually at concentrations from 10 to 100 $\mu\text{g/L}$. It can be seen that in all cases except for the higher levels of As (V), recovery is essentially complete (98 – 102%).

Recovery of As (V) drops to 82% and 67% in the 80 and 100 $\mu\text{g/L}$ samples, respectively. An amount of As similar to that not recovered appears as a “false positive” amount of As (III). This suggests that the capacity of cartridge 3 for As (V) is between 50 and 80 $\mu\text{g/L}$ (1.25–2 μg) such that the As (V) introduced to the column above this amount is not retained, and appears in the column effluent, which is where we would expect to find As (III). This could be easily addressed by using a smaller volume of sample, or in future designs, by either using more sorbent material or higher loading of dioctyltin dichloride on the sorbent.

It was of interest to evaluate whether the cartridges could be reused after elution. Cartridges 1 and 2 utilize commercial materials that are designed to be regenerated so this was not tested further. Cartridge 3 was subjected to 50 extraction/elution cycles. Analytical performance remained constant over this period of use. The stability of extracted materials on the cartridge 3 was also evaluated by comparison of cartridges eluted immediately and after one month of storage at room temperature covered with aluminum foil. No differences were found.

The performance of the method for samples containing multiple As species is shown in Table 3. Ten replicated of various combinations and concentrations of the four species ranging from 1 to 60 $\mu\text{g/L}$ were prepared in deionized water. It can be seen that recoveries were all greater than 80%. Precision is seen to be very good, with relative standard deviations generally less than 5% except for when concentrations were less than 10 $\mu\text{g/L}$, where slightly higher values were found. These results show that there are no interferences amongst the As species.

Two groundwater samples with different hardness levels were spiked with different concentrations of the four arsenic species to evaluate whether the presence of other ions that would normally be present affect recovery. The results from 5 replicates of each water sample are shown in Table 4. It can be seen that acceptable recoveries and comparable precision was found for the groundwater samples.

Conclusions

The separation technique reported in this study provides a means to analyze the four arsenic species of primary human health interest: inorganic As (III), inorganic As (V), monomethylarsonic acid (MMA), dimethylarsenic acid (DMA). The approach is field-deployable, and can be easily coupled to laboratory analysis methods having detection limits

useful for drinking water analysis. Recovery was high for all analytes, with the exception of an apparent capacity limitation for As (V) that could likely be addressed with a larger cartridge design. Precision was very good, with relative standard deviations generally less than 5% except when concentrations were less than 10 µg/L, where slightly higher values were found. False positive results and “cross-talk” between species were low.

Acknowledgments

This study was supported in part by grant 5D43 TW00641-03 from the Fogarty International Center, National Institutes of Health, USA, the Michigan State University Food Safety and Toxicology Center, the Fulbright Program and American Association of University Women Educational Foundation (AAUW)

References

- Anderson K, Thompson M, Culbard E. Selective reduction of arsenic species by continuous hydride generation 1, reaction media. *Analyst*. 1986; 111:1143–1152.
- Anderson LC, Bruland KW. Biogeochemistry of Arsenic in natural-waters the importance of methylated species. *Environ. Sci. Tech.* 1991; 25:420–427.
- Aggett J, Kadwani R. Anion-exchange method for speciation of arsenic and its application to some environmental-analyses. *Analyst*. 1983; 108:1495–1499.
- Braman R, Johnson D, Foreback C, Ammons J, Bricker J. Separation and determination of monogram amounts of inorganic arsenic and methylarsenic compounds. *Anal. Chem.* 1977; 49:621–625. [PubMed: 848769]
- Burguera M, Burguera J. Analytical methodology for speciation of arsenic in environmental and biological samples. *Talanta*. 1997; 44(4):1581–1604. [PubMed: 18966898]
- Bohari Y, Astruc AM, Astruc M, Cloud JJ. Improvements of hydride generation for the speciation of arsenic in natural freshwater samples by HPLC-HG-AFS. *Anal. Atomic Spec.* 2001; 16(7):774–778.
- Borho M, Wilderer P. A reliable method for preservation and determination of arsenate (III) concentrations in groundwater and water works samples. *J. Water Supply Research and Technology-Aqua*. 1997; 46(3):138–143.
- Bose PB, Sharma A. Role of iron in controlling speciation and mobilization of arsenic in subsurface environment. *Water Research*. 2002; 36:4916–4926. [PubMed: 12448536]
- Brinckman F, Jewett K, Iverson W, Irgolic K, Ehrhardt K, Stockton R. Graphite-furnace atomic-absorption spectrophotometers as automated element-specific detectors for high-pressure liquid-chromatography - the determination of arsenite, arsenate, methylarsonic acid and dimethylarsinic acid. *J. Chrom.* 1980; 191:31–46.
- Carvalho M, Hercules D. Trace arsenic determination by volatilization and x-ray photoelectron-spectroscopy. *Anal. Chem.* 1978; 50:2030–2034.
- Cabredo S, Sanz AJ, Galban J. Simultaneous determination of arsenic, antimony and selenium by gas-phase diode array molecular absorption spectrometry, after preconcentration in a cryogenic trap. *Anal. Chim. Acta*. 1995; 300(1–3):321–327.
- Chen CJ. Ecological correlation between arsenic level in well water and age-adjusted mortality from malignant neoplasms. Wang, C.J. *Cancer Research*. 1990; 5:5470–5474.
- Chakraborti D, De Jonche W, Adams F. The determination of arsenic by electrothermal atomic-absorption spectrometry with a graphite-furnace .2. determination of arsenic (III) and arsenic(V) after extraction. *Anal. Chim. Acta*. 1980; 120:121–127.
- Currie LA. Nomenclature in evaluation of analytical methods, including detection and quantification capabilities. *Pure and Applied Chemistry*. 1995; 67(10):1699–1723.
- Davies, A. *Organotin Chemistry*. 1st ed.. New York: Weinheim-VCH;
- Ding H, Wang J, Dorsey J, Caruso J. Arsenic speciation by micellar liquid-chromatography with inductively-coupled plasma-mass spectrometric detection *J. Chromat. A*. 1995; 1997; 694:425–432.
- Ebdon L, Hill S, Walton A, Ward R. Coupled chromatography-atomic spectrometry for arsenic speciation - a comparative-study *Analyst*. 1988; 113:1159–1165.

- Edwards M, Patel S, McNeill L, Chen H, Frey M, Eaton A, Antweller R, Taylor H. Considerations in As analysis and speciation. *J.A.W.W.A.* 1998; 90:104–113.
- Ficklin W. Separation of arsenic (III) and arsenic (V) in ground waters by ion-exchange. *Talanta.* 1983; 30:371–373. [PubMed: 18963377]
- Frankenberger W. Short communication effects of trace elements on arsenic volatilization. *Soil Biol. Biochem.* 1998; 30:269–274.
- Galban J, Marcos E, Lamana J, Castillo J. Evaluation of a method for arsenic (III) and antimony (III) determination by vapor-phase molecular absorption spectrometry using graphite-furnace volatilization. *Spectr. Acta Part B-Atomic. Spectr.* 1993; 48:53–63.
- Gomez M, Camara C, Palacios M. Anionic cartridge preconcentrators for inorganic arsenic, monomethylarsonate and dimethylarsinate determination by on-line HPLC-HG-AAS. *Fres. J. Anal.Chem.* 1997; 357:844–849.
- Grabinski A. Determination of arsenic (III), arsenic(V), monomethylarsonate, and dimethylarsinate by ion-exchange chromatography with flameless atomic-absorption spectrometric detection *Anal. Chem.* 1981; 53:966–968.
- Guo HR, Chiang HS, Hu H, Lipsitz SR, Monson RR. Arsenic in drinking water and incidence of urinary cancers. *Epidemiology.* 1997; 8:545–550. [PubMed: 9270957]
- Heinrichs H, Keltsch H. Determination of arsenic, bismuth, cadmium, selenium, and thallium by atomic-absorption spectrometry with a volatilization techniques. *Anal. Chem.* 1982; 54:1211–1214.
- Henry F, Thorpe T. Determination of arsenic (III), arsenic (V), monomethylarsonate, and dimethylarsinate by differential pulse polarography after separation by ion-exchange chromatography. *Anal. Chem.* 1980; 52:80–83.
- Hopenhayn-Rich C, Biggs ML, Smith AH. Lung and kidney cancer mortality associated with arsenic in drinking water in Cordoba, Argentina. *International Journal of Epidemiology.* 1998; 27:561–569. [PubMed: 9758107]
- Howard A, Comber S. Hydride-trapping techniques for the speciation of arsenic. *Mikrochimica Acta.* 1992; 109:27–33.
- Jaganathan J. A random testing of table wines for arsenic using electrothermal atomic absorption spectrometry. *Atom. Spectr.* 2001; 22:280–283.
- Jain C, Ali I. Arsenic: Occurrence, toxicity and speciation techniques. *Water Research.* 2000; 34:4304–4312.
- Jeckel, M. Arsenic in the Environment Part I. Nriagu, J., editor. New York: John Wiley & Sons; 1994. p. 119-132.
- Kalyanaraman S, Khopkar S. Liquid-liquid-extraction of arsenic (III) with diluted tributyl-phosphate. *Talanta.* 1977; 24:63–65. [PubMed: 18962027]
- Kim MJ, Nriagu J, Haack S. Carbonate ions and arsenic dissolution by groundwater. *Environ. Sci. Techno.* 2000; 34:3094–3100.
- Kim M. Separation of inorganic arsenic species in groundwater using ion exchange method. *Bull. Environ. Contam. Toxicol.* 2001; 67:46–51. [PubMed: 11381311]
- Korte N, Fernando Q. A review of arsenic (III) in groundwater. *Critical Reviews in Environmental Control.* 1991; 21:1–39.
- Larsen E. Method optimization and quality assurance in speciation analysis using high performance liquid chromatography with detection by inductively coupled plasma mass spectrometry. *Spect. Acta Part B.* 1998; 53:253–265.
- Le X, Yalcin S, Ma M. Speciation of submicrogram per liter levels of arsenic in water: On-site species separation integrated with sample collection. *Environ. Sci. Technol.* 2000; 34:2342–2347.
- Le X, Ma M. Short-column liquid chromatography with hydride generation atomic fluorescence detection for the speciation of arsenic. *Anal. Chem.* 1998; 70:1926–1933. [PubMed: 9599587]
- Le X, Ma M, Wong N. Speciation of arsenic compounds using high-performance liquid chromatography at elevated temperature and selective hydride generation atomic fluorescence detection. *Anal. Chem.* 1996; 68:4501–4506.

- Londesborough S, Mattusch J, Wennrich R, Fres J. Separation of organic and inorganic arsenic species by HPLC-ICP-MS. *Anal. Chem.* 1999; 363:577–581.
- Lopez-Molinero A, Villareal A, Aznar Y, Benito M, Castillo J. Chemical vaporization of arsenic (III) chloride for arsenic determination by inductively coupled plasma atomic emission spectroscopy. *App. Spectr.* 2001; 55:1277–1282.
- Lopez-Molinero A, Castillo J, Chamorro P, Callizo A. Flame atomic absorption spectrometric determination of arsenic after volatilization of As (III) with chloride ions. *Mikrochimica Acta.* 1999; 131:225–230.
- Malik AH, Khan ZM, Mahmood Q, Nasreen S, Z.A. Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries. *J. Hazardous Materials.* 2009; 168(1):1–12.
- Martin I, Lopez-Gonzalves M, Gomez M, Camara C, Palacios M. Evaluation of high-performance liquid-chromatography for the separation and determination of arsenic species by online high-performance liquid-chromatographic hydride generation atomic-absorption spectrometry. *J. Chrom.B: Biom. Appl.* 1995; 66:101–109.
- Masscheleyn P, Delaune R, Patrick W. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* 25:1414–1419. 1991.
- Masscheleyn P, Delaune R, Patrick W. A hydride generation atomic-absorption technique for arsenic speciation. *J. Env. Q.* 1991; 20:96–100.
- Michel P, Averty B, Colandini V. Improvement in arsenic speciation, using hydride generation and atomic-absorption spectrophotometry. *Mikrochimica Acta.* 1992; 109:35–38.
- Mattusch J, Wennrich R. Determination of anionic, neutral, and cationic species of arsenic by ion chromatography with ICPMS detection in environmental samples. *Anal. Chem.* 1998; 70:3649–3655. [PubMed: 21644711]
- Miller G, Norman D, Frisch P. A comment on arenic species separation using ion exchange. *Water Research.* 2000; 34:1397–1400.
- Moller A, Scholz F. Differential-pulse voltammetric determination of total arsenic following its volatilization as AsH₃ and absorption in silver nitrate solution. *Anal. Proceedings.* 1995; 32:495–497.
- Narsito H, Agterdenbos J. Study of arsenic (III) and arsenic (V) reduction and of arsine decomposition in hydride-generation atomic-absorption spectrometry. *Anal. Chim. Acta.* 1987; 197:315–321.
- National Research Council (NRC). Arsenic in drinking water. Washington: National Academy Press; 2001.
- Ochsenkuhn-Petropolu M, Ochsenkuhn K, Milonas I, Parassakis G. Separation and speciation of inorganic and methylarsenic compounds in marine samples *Can. J. of App. Spec.* 1995; 40:61–65.
- Pacey G, Ford J. Arsenic speciation by ion-exchange separation and graphite-furnace atomic-absorption spectrophotometry. *Talanta.* 1981; 28:935–938. [PubMed: 18963033]
- Phillips DJ. Arsenic in aquatic organisms: a review, emphasizing chemical speciation. *Aquat. Toxicol.* 1990; 16:151–186.
- Puttemans F, Vandenwinkel P, Massart D. The determination of arsenic by electrothermal atomic-absorption spectrometry after liquid liquid extraction. *Anal. Chim. Acta.* 1983; 149:123–128.
- Rohr U, Meckel L. Determination of arsenic in glass and raw materials for glass via quartz-tube hydride generation AAS after separation by solvent extraction. *Fres. J. Anal. Chem.* 1992; 342:370–375.
- Russeva E, Havezov I, Detcheva A. Arsenic speciation in waste-waters by extraction chromatography followed by atomic-absorption spectrometry. *Fres. J. Anal. Chem.* 1993; 347:320–323.
- Shiomi, K. Arsenic in the Environment Part I. Nriagu, J., editor. New York: John Wiley & Sons; 1994. p. 261-293.
- Shkinev V, Spivakov S, Shkinev V, Vorob'eva G, Zolotov Y. Dialkyltin salts as extractants in methods for the determination of arsenic and phosphorus. *Anal. Chim. Acta.* 1985; 167:145–160.
- Simon G, Huang H, Penner-Hann JE, Kesler SE, Kao LS. Oxidation state of gold and arsenic in gold-bearing arsenian pyrite. *Am. Mineral.* 1999; 84:1071–1079.
- Spivakov S, Shkinev V, Vorob'eva G, Zolotov Y. Extraction of arsenic (V) and phosphorus (V) by dioctyltin dichloride from metal-salt solutions. *J. Appl. Chem. USSR.* 1983; 56:716–720.

- Szpunar J, McSheehy S, Polee K, Vacchina V, Mounicou S, Rodriguez I, Lobinski R. Gas and liquid chromatography with inductively coupled plasma mass spectrometry detection for environmental speciation analysis - advances and limitations. *Spectrochim. Acta B*. 2000; 55:779–793.
- Tesfalidet S, Agrium K. Volatilization of arsenic as the trichloride for sample introduction in atomic spectroscopy. *Anal. Chem*. 1988; 60:2031–2035.
- Tseng WP, Chu HM, How SW, Fong JM, Lin CS, Yeh S. Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. *J. Nat. Cancer Inst*. 1968; 40:453–463. [PubMed: 5644201]
- Tye C, Haswell S, O'Neill P, Bancroft K. High-performance liquid-chromatography with hydride generation atomic-absorption spectrometry for the determination of arsenic species with application to some water samples. *Anal. Chim. Acta*. 1985; 169:195–200.
- Volke P, Merkel B. Using of a new field analysis method to investigate the stability of arsenic and its inorganic species in aquatic systems. *Acta Hydrochim. Et Hydro*. 1999; 27:230–238.
- World Health Organization (WHO). *Drinking Water Guidelines and Standard*. 1996.
- Wu M, Kuo TL, Hwang YH, Chen CJ. Dose-response relation between arsenic concentration in well water and mortality from cancers and vascular diseases. *Am. J. Epidemiol*. 1989; 130:1123–1113.
- Yalcin S, Le X. Low pressure chromatographic separation of inorganic arsenic species using solid phase extraction cartridges. *Talanta*. 1998; 47:787–796. [PubMed: 18967383]

Figure 1.
Arsenic speciation scheme

Figure 2.
Elution curves for As (V)-MMA separation

Table 1

Furnace temperature program for As analysis.

Step	Temp, °C	Ramp, s	Hold, s	Read	Flow, mL/min
1	110	1	30		250
2	130	15	30		250
3	1200	10	20		250
4	2000	0	5	x	0
5	2400	1	3		250

Table 2

Interference among four arsenic species and capacity experiments (concentration in µg/L)

	As (III)	As (V)	MMA	DMA
Spiked	10	-	-	-
% recovery	99.5			
% S.D.	6.4			
Spiked	50		-	-
% recovery	98.6			
% S.D.	1.4			
Spiked	80			
% recovery	100.9			
% S.D.	1.8			
Spiked	100			
% recovery	101.9			
% S.D.	2.5			
Spiked	-	10	-	
% recovery		102.5		
% S.D.		6.1		
Spiked	-	50	-	
% recovery	1.8	98.2		
S.D.	5.4	2.4		
Spiked	-	80		
% recovery	15.8	81.7		
% S.D.	4.8	2.6		
Spiked	-	100		
% recovery	39.5	67.0		
% S.D.	2.7	1.8		
Spiked	-	-	10	-
% recovery	1.9		98.0	
% S.D.	3.4		6.0	
Spiked			50	
% recovery			100.1	
% S.D.			3.4	
Spiked		-	80	
% recovery	1.8		98.7	
% S.D.	2.4		2.2	

	As (III)	As (V)	MMA	DMA
Spiked	-		100	
% recovery	0.8		100.4	
% S.D.	6.8		1.5	
Spiked				10
% recovery	1.7			98.5
% S.D.	5.6			4.9
Spiked				50
% recovery				103.3
% S.D.				1.1
Spiked				80
% recovery	0.9			98.9
% S.D.	5.6			2.4
Spiked				100
% recovery	2.4			97.9
% S.D.	4.5			1.9

Table 3

Arsenic speciation in spiked samples

	As(III)	As(V)	MMA	DMA
Spiked ($\mu\text{g/L}$)	0	40	10	0
% recovery		86.5	92.3	
% RSD*		1.2	2.1	
Spiked	0	40	10	10
% recovery		89.5	94.3	105.5
% RSD		1.8	4.9	6.4
Spiked	40	40	10	10
% recovery	98.6	84.9	93.6	101.5
% RSD	2.0	1.4	3.8	5.2
Spiked	40	0	10	10
% recovery	112.3		98.9	99.8
% RSD	2.1		3.8	2.9
Spiked	40	40	10	0
% recovery	108.3	90.5	110.2	
% RSD	2.1	1.9	4.6	
Spiked	40	20	0	0
% recovery	97.3	83.6		
% RSD	3.9	2.6		
Spiked	40	40	0	10
% recovery	106.3	82.5		95.6
% RSD	3.0	2.1		5.3
Spiked	5	5	1	1
% recovery	87.5	78.7	100.9	108.3
% RSD	9.1	9.4	11.3	10.6
Spiked	20	10	5	5
% recovery	91.3	77.5	92.6	96.7
% RSD	3.7	6.7	6.9	6.6
Spiked	60	30	5	5
% recovery	93.8	84.4	93.4	97.5
% RSD	1.3	4.4	5.4	5.1
Spiked	30	60	5	5
% recovery	91.5	84.4	89.9	102.4
% RSD	3.5	6.4	7.4	5.6

	As(III)	As(V)	MMA	DMA
Spiked	60	40	0	0
% recovery	90.3	88.5		
% RSD	3.6	4.5		

Table 4

Results of the Arsenic speciation in groundwater samples

Sample	Total Hardness as CaCO ₃ , mg/L	As (III)	As (V)	MMA	DMA
Well	250	0.22	0.67		
Spiked		50	30	10	10
% recovery		98.5	86.9	97.4	105.2
% RSD		1.3	2.4	5.1	6.4
MSU tapwater	450	0.3	1.9		
Spiked		50	30	10	10
% recovery		95.5	84.4	98.9	101.5
% RSD		1.6	2.2	7.2	8.2