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The abilities of various extractants to recover four arsenic species [As(III), As(V), dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA)] from soils spiked with 20 μg $g^{-1}$ As were investigated. The extractants were water, buffer solutions (citrate and ammonium dihydrogen phosphate), acidic solutions (phosphoric acid and acetic acid), a basic solution (sodium hydroxide) and household chemicals (vinegar and Coca Cola). Gentle shaking at room temperature with each extractant for 24 h gave different recoveries for the different arsenic species. With 0.1 M NaOH solution 46% As(III), 53% DMA, 100% MMA and 84% As(V) were recovered. A rapid extraction procedure using a sonicator probe has been developed to obtain higher extraction efficiencies. Extracts of arsenic-spiked soil, SRM 2711 Montana soil and SRM 2709 San Joaquin soil were analyzed by HPLC-ICP-MS. In the SRM water extracts, DMA and MMA were identified in addition to inorganic arsenic. The solution detection limits (3*s*) were 0.1, 0.12, 0.13 and 0.15 ng $mL^{-1}$ for As(III), DMA, MMA and As(V), respectively for HPLC-ICP-MS.

## Introduction

Arsenic is widely distributed in nature and is commonly associated with the ores of metals like copper, lead and gold. Arsenic can exist in four oxidation states: As(-III), As(0), As(III) and As(V). Elemental arsenic occurs rarely, whereas traces of toxic arsines can be detected in gases emanating from anoxic environments.[1] The predominant form of inorganic arsenic in aqueous, aerobic environments is arsenate [As(V) as $H_2AsO_4^-$ and $HAsO_4^{2-}$], whereas arsenite [As(III) as $H_3AsO_3$ and $H_2AsO_3^-$] is more prevalent in anoxic environments. Humans are primarily exposed to arsenic through drinking water and foods. Inorganic arsenic is more toxic than organic forms, and is classified as a carcinogen. Arsenic can occur in agricultural soils in some regions, as a consequence of the use of arsenic containing pesticides and herbicides.[1–3] Other contributing sources for arsenic in the soils are industrial and mine wastes.[4] Contamination of soils due to irrigation with groundwater with high arsenic content from natural origin is widely reported since it affects large areas in the world. Arsenic in soils and sediments is mainly present as the inorganic forms (arsenate and arsenite), the organic compounds MMA and DMA may also be present in lower amounts.[5] These methylated species can originate from microorganism mediated oxidation–reduction reactions.[6] Arsenic extraction and speciation in contaminated soils is a topic of current interest.[7–9] One major difficulty is the extraction of arsenic from soils. Since arsenic compounds can be associated with the soil matrix to different degrees depending on a number of factors, any given solvent may not provide a sufficient extraction. In assessing the toxicity of contaminated soil, what is of concern is bioavailable arsenic. For this reason, less aggressive solvents are studied in extracting arsenic from soils.

Another consideration is that more aggressive solvents are capable of chemically altering arsenic species, making subsequent speciation difficult. It is therefore important that methods of extraction be developed that are capable of extracting a sufficient quantity of the available arsenic, while maintaining the chemical integrity of the original species. There are many extraction procedures to evaluate metal availability in soils,[10–14] which can be divided into two groups: sequential extraction and simple extraction. Both procedures are time-consuming because they need long mechanical shaking times.

The concentration of arsenic in the soils of various countries range from 0.1 to 40 μg $g^{-1}$ but the values vary considerably among geographic regions.[15] Most states and municipalities in the USA consider soil to be in need of clean-up if the concentration of arsenic is above 20 μg $g^{-1}$. The principal factors influencing the concentration of arsenic in soils are nature of the parent rock and human activities. Factors such as climate, the organic and inorganic components of the soils and redox potential status also will affect the concentration of the various arsenic compounds in the soils. There are a few reports of arsenic-speciated reference materials for soils and sediments.[5,7,9,16–18]

The aim of this research work was to examine a wide range of extraction procedures for the four common arsenic species in soils. Various extractants with both a gentle shaker and as an alternative rapid extraction procedure the use of a sonicator probe were investigated. Total arsenic was determined by ET-AAS. To obtain chemical speciation information soil extracts were analyzed by HPLC-ICP-MS. Another objective of the study was to evaluate simple extractions with household chemicals such as Coca Cola and vinegar. This work is in support of on-going collaborative studies with middle school students and teachers.

## Experimental

### Instrumentation

An ELAN 5000 or ELAN 6000 inductively coupled plasma mass spectrometer (PerkinElmer Sciex, Norwalk, CT, USA) was used as an HPLC detector. Samples were introduced into the ICP-MS with a cross flow nebulizer, and a Scott type double pass spray chamber. The ICP-MS conditions are listed in Table 1. The chromatographic system consisted of a liquid chromatograph model (Applied Bio Systems/ 400 solvent delivery system, San Jose, CA, USA). Injections were made with a model 7725 injection valve (Rheodyne, Cotati, CA, USA). Table 1 describes the chromatographic conditions for the HPLC-ICP-MS experiments. The outlet of the HPLC anion-exchange column was connected to the nebulizer of the ICP-MS instrument by a 20 cm × 0.25 mm polyether ether ketone (PEEK) tube.

Data were collected using PerkinElmer ELAN software in the graphics mode, processed with PeakFit™ (version 4) software and plotted with Microsoft Excel software.

A PerkinElmer 4100ZL atomic absorption spectrometer equipped with longitudinal Zeeman–background correction and a transversely heated graphite atomizer (THGA) tube, fitted with an integral L'vov platform (PerkinElmer part number BO504053) was used. The arsenic electrodeless discharge lamp (EDL) from PerkinElmer was powered by a PerkinElmer system 2 EDL and operated at 350 mA. A slit width of 0.7 nm and a wavelength of 193.7 nm were selected for the experiments. A PerkinElmer AS–70 autosampler was used. The optimized instrumental conditions are listed in Table 2.

An ultrasonic probe (Sonics and Materials Inc. Danbury, CT, USA) and a MDS 2100 microwave oven (CEM corporation) with PTFE vessels were used during sample preparation. The microwave digestion program is given in Table 3.

## Reagents and samples

All solutions were prepared in 18 MΩ deionized water from a Barnstead E-pure system (Barnstead, USA). Phosphoric acid (EM Science, Germany), acetic acid (Aldrich Chemicals, USA), ammonium dihydrogen phosphate (AnalaR, BDH Chemicals, UK), citric acid anhydrous powder (JT Baker), hydrochloric acid and sodium hydroxide pellets (Mallinckrodt, USA), were used. The daily working standards for arsenic species were prepared from stock solutions (1000 mg $L^{-1}$) prepared from $NaAsO_2$ (Aldrich, USA), $Na_3AsO_4.7H_2O$ (Fisher Scientific, USA), $(CH_3)AsO_3Na_2.6H_2O$ (ChemService, USA) and $(CH_3)_2AsO(OH)$ (Pfaltz & Bauer, USA) by dissolving accurately weighed solid material in deionized water. These stock solutions were kept at 4 °C in darkness. Stock solutions were diluted daily to prepare calibration standards in deionized water. Palladium nitrate (10000 mg $L^{-1}$) and magnesium nitrate (10000 mg $L^{-1}$) solutions for ET-AAS analysis were obtained from PerkinElmer. For the microwave digestions nitric acid, hydrofluoric acid and 30% (v/v) hydrogen peroxide (Fisher Scientific, NJ, USA) were obtained.

The soil samples used in this study were collected from Western Massachusetts and had an average pH of 6.2 and medium clay content. Standard reference materials investigated were NIST SRM 2711 (Montana soil, moderately elevated trace elements) and NIST SRM 2709 (San Joaquin soil) with certified arsenic concentrations of 105 ± 8 μg $g^{-1}$ and 17.7 ± 0.8 μg $g^{-1}$ respectively.

**Table 1** Instrumental operating conditions

| | |
|---|---|
| ICP-MS Parameters | |
| Forward power | 1000 W |
| Plasma flow | 15 L $min^{-1}$ |
| Auxiliary flow | 0.8 L $min^{-1}$ |
| Nebulizer flow | 0.8 L $min^{-1}$ |
| Isotopes monitored | $^{75}As$ and $^{77}Se$ |
| Resolution | Normal |
| Scanning mode | Peak hop |
| Dwell time | 1000 ms |
| HPLC Parameters | |
| Column | Hamilton PRP X-100, 10 μm anion exchange column (150 mm × 4.1 mm) |
| Mobile phase | 10 mM ammonium dihydrogen phosphate (pH 5.8) |
| Flow rate | 1 mL $min^{-1}$ |
| Injection volume | 100 μL |

**Table 2** Furnace heating program for arsenic determination

| Step | Temperature/°C | Ramp time/s | Hold time/s | Argon flow rate/ mL $min^{-1}$ |
|---|---|---|---|---|
| Drying 1 | 110 | 1 | 20 | 250 |
| Drying 2 | 130 | 20 | 30 | 250 |
| Pyrolysis | 1200 | 30 | 20 | 250 |
| Atomization | 2200 | 0 | 5 | 0 |
| Clean out | 2400 | 1 | 2 | 250 |

**Table 3** Microwave digestion program

| Step | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Power[a] (%) | 10 | 45 | 66 | 66 |
| Pressure/PSI | 20 | 40 | 85 | 100 |
| Time/min | 2:00 | 5:00 | 10:00 | 30:00 |
| Temp/°C | 120 | 140 | 160 | 180 |

[a] 1000 W full power

### Extractants for arsenic in soils

The range of extractants tested were deionized water; 5.0% (v/v) glacial acetic acid (5 mL glacial acetic acid in 100 mL of deionized water); 1 M phosphoric acid (6.2 mL of concentrated acid in 100 mL of deionized water); 10 mM citrate buffer (0.1938 g of citric acid powder in 100 mL deionized water with a few mL of 0.1 M sodium hydroxide solution to obtain a pH of 3); 0.1 M sodium hydroxide solution (pH ~12); 10 mM ammonium dihydrogen phosphate (0.5862 g of solid material in 500 mL deionized water and 50 μL of ammonium hydroxide to obtain a pH of 5.8); degassed Coca Cola® (pH ~ 3) and household vinegar (Heinz distilled white vinegar).

## Soil preparation

A sterile soil donated from the University of Massachusetts Plant and Soil Science department was passed through a 250 μm sieve. From this sieved soil, 20 g portions were placed in each of six 400 mL beakers to which was added 150 mL of deionized water. To one of the beakers 0.400 mL 1000 ppm As(III) was added drop wise with continuous constant stirring. The remaining beakers received the other arsenic species [DMA, MMA, and As(V)] and a soil with a mixture of the four arsenic species was prepared. Another beaker contained "reagent" blank soil.

## Soil sample pretreatment

These six beakers containing the soils were dried in an oven at 70 °C for one week. A glass rod was used to break up the dry soil. A previous study by other research workers indicated that soils treated at 20 °C, 40 °C and 100 °C did not lose arsenic.[7] For the present study arsenic-spiked soils were pretreated at 70 °C, and the total arsenic was measured.

## Analytical procedure

### Extraction efficiency

The soil samples (0.2 g) were accurately weighed into a 15 mL centrifuge tube. To each centrifuge tube 5 mL of a given extractant was added accurately. A sonication probe was placed in the sample for 20 min for the sample to become fully homogenized by ultrasonic agitation at a 50% power output setting. The resulting solutions were centrifuged for 15 min and the supernatant was used for arsenic determination. An aliquot of the clear supernatant was then directly transferred into a sample cup placed on the autosampler tray by means of a Pasteur pipette. A portion (10 μL) of the soil extract was then taken by the autosampler along with 10 μL of modifier, containing 5 μg $Pd(NO_3)_2$ and 3 μg of $Mg(NO_3)_2$, and injected into the graphite furnace. To estimate recoveries for the milder extraction methods, 0.2–0.3 g of the soil samples were digested with 9 mL of $HNO_3$ and 3 mL of HF (USEPA method 3502). The microwave conditions described in Table 3 were used to digest the samples. During preliminary experiments 0.2 g of the soil samples were digested (using microwave program in Table 3) with 2 mL of $HNO_3$ and 1 mL of $H_2O_2$ to determine acid leachable arsenic content in the soils. After this treatment, the soil digests were filtered (Whatman filter paper no. 42), transferred and made up to volume with de-ionized water in 10 mL calibrated flasks. The

ET-AAS injection temperature was 20 °C and the furnace heating program was run under the optimized conditions shown in Table 2. Calibration standards of As(III), DMA, MMA and As(V) were used to determine the arsenic in the different spike soil extracts, and As(V) standards were used for the total arsenic determination in microwave acid digests.

### Method development

The coupling of HPLC with ICP-MS offers several advantages because of the high sensitivity, multi-element capability, large dynamic range and isotope ratio measurement capabilities. There are many applications where investigators used a strong quaternary amine anion-exchanger (Hamilton PRP X-100 column) for the separation of arsenic compounds using HPLC-ICP-MS.[19–22] The method developed by Yehl *et al.*[16] was slightly modified for the present arsenic speciation work. After investigating different mobile phase solutions and pH conditions with the anion exchange column (Hamilton PRP X-100) ammonium dihydrogen phosphate (10 mM at pH 5.8) was selected to give the optimum separation for the four arsenic species in less than 10 min. By monitoring both $^{40}Ar^{35}Cl$ and $^{40}Ar^{37}Cl$ (*m*/*z* 75 and 77) the interference of chloride on arsenic measurement was investigated. The low chloride concentrations in all the extracts did not interfere with the arsenic separation and detection.

For total arsenic determination in microwave digested soil samples and soil extracts, ET-AAS was used. The atomization and pyrolysis temperatures were optimized for As(III), DMA, MMA and As(V). Calibration data were obtained for aqueous arsenic(III), arsenic(V), monomethylarsonate (MMA) and dimethylarsinate (DMA) using Pd and $Mg(NO_3)_2$ as the modifier. The blank soil matrix was also used to prepare calibration standards to investigate any soil matrix effects. The blank soil was sonicated with 200 mL deionized water and centrifuged. The supernatant solution was used to make arsenic(III) calibration standards to examine soil matrix effects when determined by ET-AAS. It was found that the soil matrix does not interfere with arsenic determination by comparing the slopes of the calibration graphs, which were not statistically different (*t*-test, 95% confidence level).

For extraction of arsenic species, preliminary experiments were performed by shaking on a wrist-action shaker; but, subsequently all extractions, including those of the SRM, were performed with the help of the ultrasonic probe.

## Results and discussion

### Determination of total arsenic content

Total arsenic concentrations in the soil microwave digests were measured by ET-AAS. The results for the spiked soils and standard reference material (SRM) are presented in Table 4. Using $HNO_3$ and HF for the microwave acid digestion released the total arsenic content from the soils, where as the $HNO_3/H_2O_2$ did not release the total arsenic from the spiked soils and SRM 2711. Results obtained by this procedure (without HF) were used to calculate leach recoveries. A leach recovery value of 89.1% was obtained for the

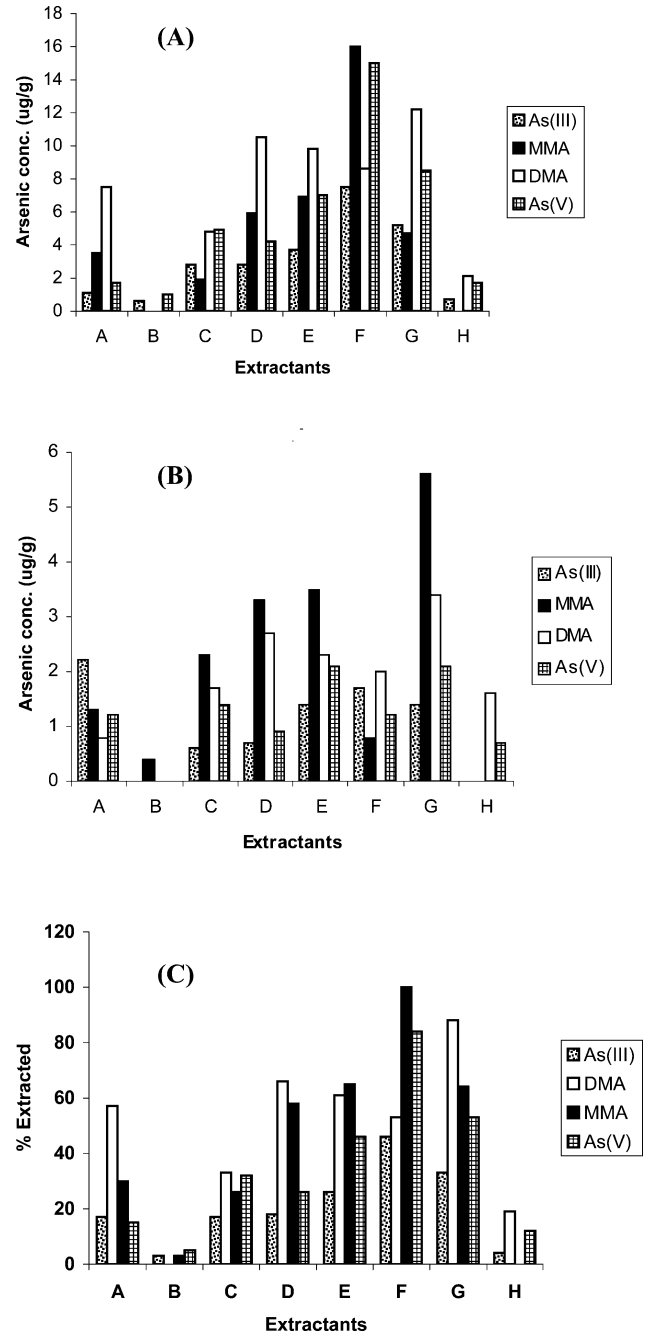


**Fig. 1** (A) Arsenic extraction from spiked soils after 24 h, (B) further arsenic extracted after 1 week, (C) % of arsenic extracted (after 24 h value + 1 week value) based on total arsenic content after microwave digestion ($HNO_3$ + HF digestion). The extractants used were A—deionized water; B—1 M phosphoric acid; C—Coca Cola; D—5% acetic acid; E—Heinz vinegar; F—0.1 M NaOH; G—10 mM citrate buffer; H—10 mM ammonium dihydrogen phosphate.

**Table 4** Total arsenic in spiked soils and standard reference material

| | Spiked soils/μg g$^{-1}$[ab] | | | | | | SRM 2711/ μg g$^{-1}$[c] |
|---|---|---|---|---|---|---|---|
| Microwave digestion method | Blank[d] | As(III) | DMA | MMA | As(V) | Mix | Measured value |
| 9 mL $HNO_3$ + 3 mL HF | N.D. | 20.4 ± 3.9 | 19.8 ± 1.1 | 15.3 ± 1 | 20.1 ± 1.7 | 18.8 ± 2.4 | 98.5 ± 5 |
| 2 mL $HNO_3$ + 1 mL $H_2O_2$ | N.D. | 16.1 ± 0.8 | 16.9 ± 1.1 | 13.9 ± 0.6 | 16.7 ± 0.7 | 15.9 ± 0.3 | 80.2 ± 4.1 |

[a] Mean ± 95% C.L. ($n$ = 3) for microwave digestion ($HNO_3$ + HF). [b] Mean ± S.D. ($n$ = 2) for microwave digestion ($HNO_3$ + $H_2O_2$). [c] NIST SRM 2711 certified value 105 ± 8 μg g$^{-1}$; leach recovery value 86%. [d] N.D. below the detection limit (3*s*) 80 ng g$^{-1}$.

SRM 2711, which is in good agreement with the NIST leach recovery value (86%) for SRM 2711. This kind of leaching procedure is a good approach for the evaluation of the "pseudo-total" arsenic content in soils and sediments by means of an acidic-oxidative attack that avoids the use of hydrofluoric acid.

### Extraction of the arsenic species from spiked soils

During preliminary studies gentle wrist action shaking was used with the different extractants to determine the easily extractable arsenic content in spiked soils. The centrifuge tubes containing the spiked soils (0.2 g) and extractants (5 mL) were capped and placed on the wrist-action shaker for 24 h. The resulting solutions were centrifuged for 15 min and the supernatant was separated from the soil and used for arsenic determination. To the remaining soil, a further 5 mL of the extractant was added and left on the gentle shaker for 1 week, centrifuged for 15 min and the arsenic content in the supernatant was determined by ET-AAS. The effect of various extractants on recovering As(III), DMA, MMA and As(V) from soils, and the influence of extraction time is shown in Fig. 1. The highest extraction efficiency was obtained when NaOH or the citrate buffer was used as extractants. The extractants studied in the extraction procedure were capable of extracting differing amounts of arsenic from the soils (Fig. 1). With a high pH extractant such as, 0.1 M NaOH, 46% As(III), 53% DMA, 100% MMA and 84% As(V) were extracted. Whereas in acidic conditions, with a citrate buffer at pH 3, 33% As(III), 88% DMA, 64% MMA and 53% As(V) were extracted from the spiked soils. In a similar study where extractions were performed at different pH values, the highest amount of arsenic [As(III) and As(V)] extracted was for high pH extractants.[13,23] No organically bound arsenic was present in the soil samples examined.[23] Household chemicals were able to extract significant amounts of arsenic species from soils. In a previous study the main ingredients of Coca Cola®, phosphoric acid (*ca*. 6 mM), reducing sugars and carbon dioxide was found to extract micronutrients (Fe, Cu, Zn and Mn) from soils.[24] In the present study 17% As(III), 33% DMA, 26% MMA and 32% As(V) were extracted from soils using degassed Coca Cola®.

### Optimization of extraction using an ultrasonic probe

The arsenic-spiked soils were used to evaluate the extraction efficiency when a powerful sonicator probe was used with the different extractants. The sonication time to extract the arsenic from the soil was optimized with different extractants (water, citrate buffer and sodium hydroxide). The soil extracts were injected into the graphite furnace after spending varying amounts of sonication time, ranging from 0 to 45 min. Three replicates were run of each sample. The peak area increased steadily, reaching a maximum after 20–25 min for the sonicator probe. No further increase in peak area was observed after these times. It was therefore decided to sonicate the soil samples for 20–25 min using the sonicator probe. The effect on the sonication time with the sonicator probe is illustrated in Fig. 2. After 20 min of sonication 4 μg $g^{-1}$ As for the water extraction, 12 μg $g^{-1}$ As for the citrate extraction and 15 μg $g^{-1}$ As for the NaOH extraction were obtained, corresponding to *ca*. 23%, 71% and 88% extraction efficiencies for the arsenic(V) spiked soil. The extraction efficiencies for DMA and MMA spiked soils were *ca*. 85% and 98%, respectively for the NaOH extractant and *ca.* 68% and 58%, respectively for the water extractants. This ultrasonic extraction procedure was applied to SRM 2711 and SRM 2709 to detect any methylated arsenic species.

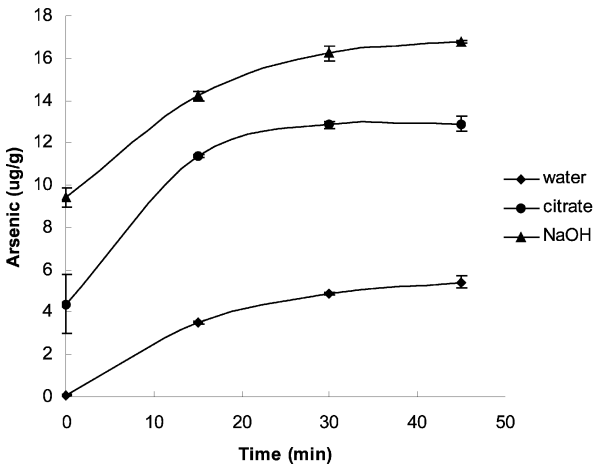


**Fig. 2** Effect on sonication time with the sonicator probe for extraction of arsenic from As(V) spiked soils. Error bars are ± 1 standard deviation ($n$ = 3).

### Arsenic speciation by HPLC-ICP-MS

The arsenic-specific chromatograms for soil extracts are shown in Fig. 3 with peaks identified based on retention time matching with

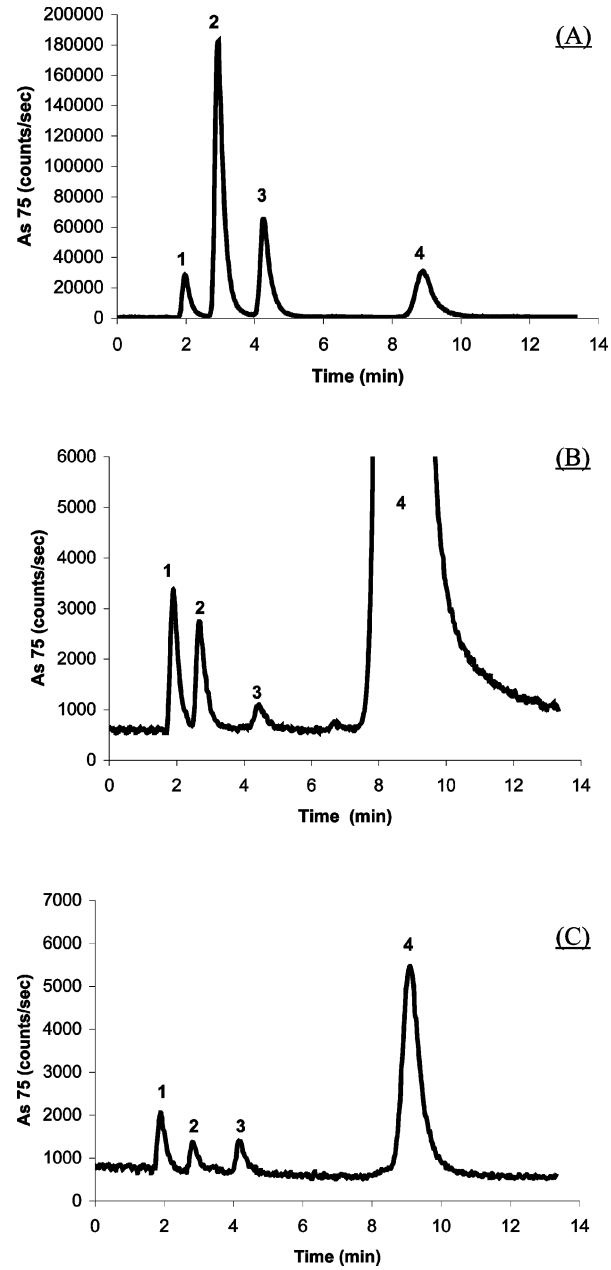


**Fig. 3** HPLC-ICP-MS arsenic speciation profiles of soil water extracts (A) Arsenic spiked soil mixture, (B) SRM 2711 moderate levels Montana soil, (C) SRM 2709 San Joaquin soil. **1**. Arsenite (As(III)); **2**. DMA; **3**. MMA; **4**. Arsenate (As(V)). Column: PRP X-100 anion-exchange column (10 μm particle size, 150 mm × 4.1 mm). Mobile phase: 10 mM ammonium dihydrogen phosphate (pH 5.8). Flow rate 1.0 mL $min^{-1}$. Injection volume 100 μL.

**Table 5** Arsenic concentrations (μg $g^{-1}$) in standard reference material water extracts

| Standard reference material | Certified total As/μg $g^{-1}$ | As(III) | DMA | MMA | As(V) | Sum in water extracts |
|---|---|---|---|---|---|---|
| SRM 2711 (Montana soil, moderate levels) | 105 ± 8 | 0.05 ± 0.01 | 0.04 ± 0.01 | 0.02 ± 0.01 | 7.3 ± 0.8 | 7.4 ± 0.8 |
| SRM 2709 (San Joaquin soil) | 17.7 ± 0.8 | 0.03 ± 0.01 | 0.02 ± 0.01 | 0.02 ± 0.01 | 0.11 ± 0.01 | 0.18 ± 0.04 |

Mean ± 95% C.L. ($n$ = 3).

standard chromatograms and spike experiments. The separation of the arsenic species can be explained by their p$K_a$ values. Arsenite [As(III)] elutes first ($t_R$ = 1.9 min) in the column void volume as it is fully protonated at pH 5.8 (p$K_a$ 9.2), and then DMA ($t_R$ = 2.8 min), MMA ($t_R$ = 4.1 min) and As(V) ($t_R$ = 8.5 min) eluted from the column. The peak area data were obtained using PeakFit™ (version 4) software and detection limits were calculated based on peak height. The resolution between As(III)–DMA was 1.5 and DMA–MMA was 1.6 indicating good chromatographic separation of the arsenic species. The HPLC-ICP-MS chromatograms of water extractable arsenic species in Montana soil (moderate levels) NIST SRM 2711 and San Joaquin soil NIST SRM 2709 are shown in Fig. 3. The presence of methylated arsenic species in the standard reference material is noteworthy. In the spiked soil mixture DMA and MMA is detected more than the inorganic arsenic species—arsenic(III) and arsenic(V). In Fig. 3a the presence of larger peak area for DMA and the higher extraction efficiency (Fig. 1) obtained for the water extraction from the DMA spiked soils suggests DMA is more water-soluble. Such water extractable arsenic species in soils can be washed away by rain water and enter the aquatic environment. Attempts were also made to analyze arsenic in the NaOH soil extracts, since this extractant gave the highest extraction efficiency. To obtain speciation profiles of the hydroxide extracts, pH adjustments were made by acidifying the extracts; however, a dark brown precipitate (probably humic material) that removed some of the arsenic. For further HPLC-ICP-MS experiments, only the water extracts were considered.

### Calibration and quantification

Quantification of arsenic species were based on peak heights, where the peak height response was linear up to 500 ng $mL^{-1}$ for all four arsenic species. The HPLC-ICP-MS detection limits were calculated using peak height response, which was 0.1 ng $mL^{-1}$ for As(III), 0.12 ng $mL^{-1}$ for DMA, 0.13 ng $mL^{-1}$ for MMA and 0.15 ng $mL^{-1}$ for As(V). Quantification of water extractable MMA and DMA in the standard reference material was calculated by external calibration (Table 5). As can be observed from the data, the highest concentration of arsenic extracted in the SRM was in the form of As(V). The arsenic species in the soil extracts were identified based on standard retention times. Table 5 shows quantification of arsenic species in soil water extracts for replicate analyses. Although the sum only represents about 10% of the total arsenic, the leach solution of spiked soil indicates that As(V) and As(III) are extracted to a similar extent, and thus it may be deduced that the SRM do not contain significant amounts of As(III).

## Conclusions

Ultrasonic probe extraction is a rapid procedure for extracting arsenic from arsenic-spiked soils and soil standard reference materials. The major water extractable most stable form of arsenic species in the SRM soils is arsenate (As(V)). Relatively small amounts of methylated arsenic species (MMA and DMA) were also identified in water extracts of NIST SRM 2711 and NIST SRM 2709. Generalization of arsenic species in soil standard reference material cannot be made without more extensive experiments on a wide range of soil samples.

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