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Application of microwave digestion to the preparation of sediment samples for arsenic speciation

Abstract Several extraction procedures are described allowing arsenic speciation in sediments. The extraction of organometallic compounds such as dimethylarsinic acid or monomethylarsonic acid is quite simple since these compounds are stable in the different extraction media (HCl/HNO_3, H_3PO_4, ammonium oxalate) and are easily released independent of the extraction mode (magnetic stirring or microwave solubilization). Extraction yields are higher than 96% for these two arsenic forms. An HCl/HNO_3 microwave solubilization procedure allows the quantitative solubilization of mineral arsenic, but the differentiation between the two oxidation states is not possible owing to the oxidation of As(III) to As(V). Extractions with orthophosphoric acid or ammonium oxalate allow the solubilization of mineral arsenic with extraction yields ranging from 90 to 95% and the differentiation between As(III) and As(V). Nevertheless, the amount of As(III) is underestimated owing to its partial oxidation. The usefulness and advantages of microwave solubilization compared with conventional extraction procedures are discussed.

Introduction

Arsenic may accumulate in soils and sediments due to the use of arsenical pesticides, application of fertilizers, irrigation, oxidation of volatile arsines in air, dust from the burning of fossil fuels and disposal of industrial, municipal and animal wastes [1].

In soils and sediments arsenic may exist in different chemical forms such as mineral arsenic (arsenite and arsenate) of two oxidation states (As(III) and As((V)) or organometallic compounds such as dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA). Since the toxicological and biological importance of arsenic greatly depends on its chemical form [2], it is necessary to speciate it, i.e. to quantify the amounts of the individual species involved.

In recent years, several analytical techniques allowing the differentiation of the chemical forms of an element have been developed (mainly techniques involving gas or liquid chromatography coupled with elemental specific detectors), but the development of extraction procedures allowing the solubilization of the different chemical forms of arsenic without any changes of their partition was neglected. The development of such extraction methods is complicated because the different species show a different behaviour.

The knowledge of the kind of adherence of arsenic in soils (adsorption, precipitation etc.) may be very useful to select extraction media. A few authors studied these retention mechanisms [3–9]. Livesey and Huang [3], who examined precipitation or adsorption as possible mechanisms of the arsenate retention by soils, showed that the retention does not occur by precipitation reactions but by adsorption reactions. Arsenate adsorption maxima were found to be linearly related to the amounts of aluminium and iron extractable by ammonium oxalate. Whereas chloride, nitrate and sulfate have no significant effect on the arsenate adsorption, phosphate substantially suppresses the adsorption of arsenic, the extent of suppression varying significantly from one soil to another. Wauchope [8] and Holm [9], who studied the adsorption behaviour of the four principal arsenic compounds (As(III), DMA, MMA and As(V)) in soil, found that the retention occurs by the adsorption on amorphous hydroxides and that the adsorption decreases from arsenate to MMA, As(III) and DMA, phosphate ions being more strongly retained than arsenic forms.

In this work, several extraction procedures were tested with a sediment spiked with the four arsenic compounds. The extracts were analyzed by HPLC-ICP-MS [10].

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Experimental

Spiking of the sediment

10 kg of a lake sediment were ground, homogenized and, after sieving, the fraction below 90 μm was kept for spiking. One part of this sediment (3 kg) was bottled and kept in the dark as blank without any further treatment (sediment S11A). The second part (3 kg) was suspended in approximately 30 L of water for a week. Then, concentrated solutions of the appropriate arsenic salts were added (As(III) as As_2O_3 in 1 mol/L NaOH, As(V) as sodium arsenate, MMA and DMA as monomethylarsonic and dimethylarsinic sodium salts in methanol solution). After a three-day contact period, the spiked sediment was filtered from the solution. The residue was firstly dried in darkness to prevent a photo-oxidation of As(III) to As(V) and finally drying was accomplished at room temperature. Then, the sediment was ground and homogenized (sediment S11B). Due to possible interconversions amongst arsenic species and/or adsorption processes on the walls of the containers used, this technique of spiking does not allow the estimation of the actual quantity of each species adsorbed.

Extraction and digestion procedures

Apparatus. Two microwave ovens were used: a closed system (CEM, India Trail, NC), model MDS-81D developed from the in-house system and the Prolabo A300 automated microwave digestion system (max. energy 200W).

Microwave dissolution in the presence of HCl-HNO_3-H_2O_2 (determination of the total arsenic concentration). A multistage heating program was developed. 7 mL HCl and 3 mL HNO_3 were added to 0.5–1 g of sediment. The solution was treated at 40 W for 5 min, then at 50 W for 10 min and after adding 7 mL HCl and 3 mL HNO_3 at 60 W for 10 min. After cooling and addition of 1 mL H_2O_2, the microwave dissolution was continued at 40 W for 5 min and finally, after addition of 5 mL of water, at 50 W for 5 min.

Microwave digestion in the presence of HCl-HNO_3 (arsenic speciation). 5 mL HNO_3 and 10 mL HCl were added to 200 mg of sediment and the microwave power was set at 20 W for 12 min.

Digestion in PTFE bombs (CEM oven). The determination of total arsenic was performed by a three-step digestion. Typically, a 500 mg sample weight was taken.

First step: addition of 5 mL HNO_3 and 3 mL $HClO_4$, power set at 120 W for 15 min and at 150 W for 15 min.

Second step: after cooling, addition of 2 mL of conc. HF, power set at 150 W for 15 min.

Third step: after cooling, additional 5 mL HCl were added, power set at 180 W for 15 min.

Analysis procedure

For arsenic speciation the samples were analyzed by coupling high-performance liquid chromatography (HPLC) with inductively coupled plasma mass spectrometry (ICP-MS).

HPLC. The HPLC apparatus included a binary gradient system (Model 302, Gilson), a syringe-loading injector (Model 7125, Rheodyne) with a 20 μL injection loop and an anion-exchange column Hamilton PRP X 100 (Hamilton Company), 250 mm × 4.1 mm i.d., (10 μm).

Mobile phases. Mobile phase A was prepared by mixing a 0.01 mol L^{-1} $(NH_4)H_2PO_4$ (Sigma) solution with 0.01 mol L^{-1} $(NH_4)_2HPO_4$ (Sigma) solution to reach pH 6.5. Mobile phase B is a 0.1 mol L^{-1} $(NH_4)_2HPO_4$ (pH 7.95) solution. The mobile phases were filtered through a 0.45 μm filter under vacuum. 2% (v/v) acetonitrile (HPLC grade, Prolabo) were added to each mobile phase after filtration. The arsenic compounds were separated with an ionic strength gradient:

$$\underset{0\%\,B}{} \xrightarrow{3.4\ min} \underset{0\%\,B}{} \xrightarrow{0.1\ min} \underset{50\%\,B}{} \xrightarrow{3\ min} \underset{50\%\,B}{} \xrightarrow{0.1\ min} \underset{0\%\,B}{}$$

ICP-MS. The ICP-MS spectrometer was a VG Plasma Quad (2 + EDR) (vacuum generator,) operated with an Henry Radio generator. The general operating conditions used are summarized in Table 1.

To couple the HPLC system to the ICP-MS, a PTFE capillary (10 cm × 0.25 mm i.d.) was connected from the exit of the column to the entrance of the nebulizer. The mass spectrometer was operated in SIM mode at m/z = 75. An integrator (Shimadzu CR3A) was connected to the ICP-MS to monitor the chromatograms.

To optimize the mass spectrometer for the arsenic signal, the PTFE capillary from the column was disconnected and an arsenic

Table 1 Operating conditions for ICP-MS and ICP ARL 3580

	ICP ARL 3580	ICP-MS (VG Plasmaquad)
Torch	Type Fassel, monobloc	Type Fassel, monobloc
Nebulizer	Type Meinhardt	Type Meinhardt
Spray chamber	Type ARL	Type Scott, cooled at 0°C
Incident power	1200 W	1400 W
Gas flow rates		
Auxiliary gas	1 L min^{-1}	1 L min^{-1}
Coolant gas	12 L min$^{-1\,a}$	14 L min$^{-1\,a}$
Injector gas	0.8 L min$^{-1\,a}$	0.8 L min$^{-1\,a}$
Sample introduction flow rate	1 mL min^{-1}	1 mL min^{-1}
"Sampler" cone	–	Ni or Pt (orifice diameter 1mm)
"Skimmer" cone	–	Ni (orifice diameter 0.75 mm)
Pressures		
Interface	–	1 mbar
Quadrupole	–	$2 \cdot 10^{-6}$ bar
Wavelengths	λ (As) = 193.760 nm	–
	λ (Fe) = 259.940 nm	
	λ (Al) = 308.220 nm	

[a] These values are optimized each day

solution (20 µg L^{-1}) containing 2% acetonitrile was continuously delivered at 1 mL min^{-1} into the ICP-MS system by a peristaltic pump. Both the ion lens voltages of the instrument and the plasma operating conditions were optimized for maximum arsenic sensitivity.

ICP. An ARL 3580 instrument operating under the conditions described in Table 1, was used for the determination of Fe, Al and total arsenic.

Arsenic standard solutions. Stock solutions of arsenic compounds (1 g L^{-1}) were prepared, respectively, from As$_2$O$_3$ (Merck) in NaOH (Prolabo), Na$_2$HAsO$_4 \cdot$ 7H$_2$O (Aldrich) and AsCH$_3$O$_3$Na$_2 \cdot$ 6H$_2$O (Carlo Erba), all dissolved in water. These stock solutions were stored at room temperature (20° C) in darkness. Dilute solutions for analysis were prepared daily.

Results and discussion

Determination of the total As content of the sediments S11A and S11B

The total arsenic content of the sediments S11A and S11B was determined by ICP or ICP-MS after digestion in PTFE bombs or HCl/HNO$_3$/H$_2$O$_2$ microwave digestion. The sediments S11A and S11B contained 32 ± 1 mg (As) kg^{-1} and 250 ± 5 mg (As) kg^{-1} as As, respectively. These concentration values were used to calculate the global extraction yields of arsenic in later stages of the project.

Arsenic speciation after HCl/HNO$_3$ microwave digestion

Stability of the arsenic compounds during the digestion

The stability of arsenic single species solutions (As(III), DMA, MMA, As(V) each at 5 mg As L^{-1}) during a microwave HCl/HNO$_3$ digestion was evaluated (conditions see Experimental). Except for As(III), which is quantitatively oxidized to As(V), all the other compounds are stable during such a digestion: DMA and MMA recoveries were (99 ± 3)% and (102 ± 2)%, respectively.

Arsenic speciation after the digestion

Since the arsenic compounds with the exception of As (III) are stable during microwave HCl/HNO$_3$ digestion, this procedure was applied to arsenic speciation in the sediments S11A and S11B. The results indicated that such a digestion procedure allows the dissolution of the whole arsenic content of sediments S11A and S11B (extraction yield: ≈100%). The non-spiked sediment S11A only contains mineral arsenic (32.2 ± 0.9 mg As kg^{-1}), whereas the sediment S11B contains both mineral and organometallic arsenic compounds in the following proportions: 186.1 ± 5.1 mg As kg^{-1} (74.7%), 21.6 ± 1.1 mg As kg^{-1} (8.7%) and 41.2 ± 1.2 mg As kg^{-1} (16.6%) for mineral arsenic, DMA and MMA, respectively. These concentrations of the arsenic species in the sediment were used to calculate the

extraction yields of mineral arsenic, DMA and MMA in later stages of the project.

Extraction of sediment S11B with phosphate solutions

In order to preserve the integrity of the As(III)/As(V) speciation, a much milder solubilization technique had to be adopted. Extractions with phosphate solutions were realized. First of all, the stability of the different arsenic compounds was studied under various conditions.

Stability of arsenic compounds in orthophosphoric acid with magnetic stirring or microwave digestion

Stability of standard solutions prepared in H$_3$PO$_4$. The stability of arsenic compounds in orthophosphoric acid solutions (0.3 mol L^{-1} or 0.9 mol L^{-1}) was evaluated. Single species solutions containing 190, 177, 300 and 480 µg L^{-1} of As(III), DMA, MMA and As(V) (as As) were prepared and a 15 mL aliquot was subjected to either magnetic stirring for 10 min or microwave energy (20 W) for 10 min. For each compound the recoveries, ranging from 98% to 102%, indicated that arsenic compounds are stable in 0.3 or 0.9 mol L^{-1} orthophosphoric acid, independent of the solubilization mode.

Stability of arsenic compounds in H$_3$PO$_4$ and in the presence of the control sediment S11A. The influence of concomitant elements in the matrix was studied: elements such as Fe or Al (co-extracted with arsenic species) may affect the stability of the arsenic compounds. In order to investigate this possibility, 100 mg of the non-spiked sediment S11A were suspended in 15 mL of H$_3$PO$_4$ solutions (0.3 or 0.9 mol L^{-1}) containing known arsenic concentrations. "Pseudo-extractions" were realized during 10 min (microwave solubilization or magnetic stirring). Recoveries for each compound were calculated by comparing the peak areas with those obtained from standard solutions (the quantity of arsenic released by the control sediment S11A under these solubilization conditions was subtracted).

For DMA and MMA recoveries ranged from 98% to 102%, independent of the arsenic concentration of the initial solution (ranging from 80 to 320 µg L^{-1} as As). The results indicate that the speciation of these two compounds is not affected by the presence of concomitant elements.

After a "pseudo extraction" with 0.3 mol L^{-1} orthophosphoric acid and with magnetic stirring, As(III) recovery was found to be 95% and no significant variation of the As(V) peak area was observed. In 0.3 mol L^{-1} orthophosphoric acid with microwave solubilization and in 0.9 mol L^{-1} orthophosphoric acid with microwave energy or magnetic stirring, As(III) recoveries were lower (between 94 and 70%); concurrently, an increase of As(V) peak area was observed, implying that As(III) was partially oxidized to As(V). In general, the fraction of As(III)
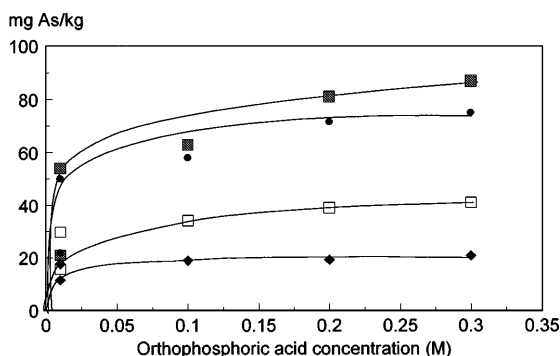
oxidized increased with the orthophosphoric acid concentration (perhaps because more elements are coextracted) and was greater in the case of a microwave solubilization (heating of the solution might have increased the oxidation rate). It must be kept in mind that As(III) concentrations are susceptible to underestimation during extractions with orthophosphoric acid.

Stability of arsenic compounds in a basic medium. A systematic study of the stability of arsenic compounds under basic conditions was not carried out. A few preliminary experiments were conducted: "pseudo-extractions" in the presence of the non-spiked sediment S11A, at pH 12 (Na₃PO₄). The results indicated that all compounds are stable except for As(III) wich is rapidly oxidized to As(V) (approximately 90% of As(III) is oxidized to As(V) within 10 min of magnetic stirring).

The aim of this stability study was to evaluate parameters that may influence the speciation of arsenic compounds during the extractions. However, it is not possible to exactly simulate the different processes occurring during an extraction since the real situation is far more complex.

Extraction of sediment S11B

Influence of orthophosphoric acid concentration. The influence of orthophosphoric acid concentration on the extractability of arsenic compounds was studied for acid concentrations ranging from 0.01 to 0.3 mol L^{-1}. 100 mg of sediment were extracted with 15 mL of solution with magnetic stirring during 10 min in darkness. The results are summarized in Fig. 1. The extractability of all the arsenic compounds increases with increasing phosphate concentration. There is a competition between phosphate and arsenic species for the adsorption sites on the sediment. In the presence of 0.3 mol L^{-1} phosphoric acid, DMA and MMA are quantitatively extracted (96% and 99.5% recoveries for DMA and MMA), whereas the recovery of mineral arsenic is only 87% under the same conditions. These results show that organometallic compounds are more easily desorbed than mineral ones, which can be related to their greater size compared to the phosphate ions [11]. These results are in agreement with the relative adsorption strengths given by Wauchope [8] and Holm [9]. Moreover, this extraction procedure allows the presence of As(III) in the sediment S11B to be detected at a concentration at or above 87 mg (As) kg^{-1}, which represents 47% of mineral arsenic. This concentration is probably underestimated since a fraction of As(III) can be oxidized to As(V) during the extraction process.

Influence of the pH. Considering the dissociation constants (K_a) of orthophosphoric acid and arsenic compounds, it may be possible to adjust the respective affinities of phosphate and arsenic ions for the adsorption sites by varying the pH of the solution. The influence of the pH on the extractability of the different arsenic compounds was evaluated for pH values ranging from 1.3 to 12.4, with magnetic stirring for 10 min and with a 0.3 mol L^{-1} phosphate solution. Results are summarized in Fig. 2. All the arsenic compounds exhibit the same behaviour and are preferentially extracted in an acidic medium. The extraction yields decrease rapidly to reach a minimum between pH 5 and 9. Above pH 9, the extractabilities increase, it is however no longer possible to distinguish between As(III) and As(V) due to the oxidation of As(III). These results show that arsenic species are preferentially released from their non-ionic forms at pH 1.3.

Influence of the extraction period. In order to improve the extraction yields of the compounds of interest, the extraction period was increased up to 2 h. These experiments were conducted at pH 1.3 (0.3 mol L^{-1} H₃PO₄). An increased contact time does not significantly influence the extraction yields of the arsenic compounds. Moreover, for extraction periods > 1 h a decrease of the As(III) concentration was observed, concurrently with an increase of the As(V) concentration, indicating that As(III) was progressively oxidized.
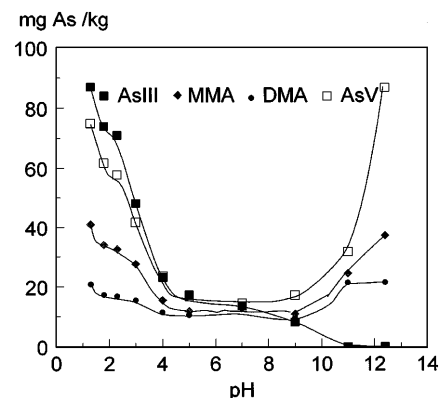

Fig. 1 Influence of orthophosphoric acid concentration on the extractability of arsenic compounds in sediment S11B. 200 mg of sediment S11B, suspended in 15 mL of H₃PO₄ solution, 10 min magnetic stirring, room temperature (22°C)

Fig. 2 Influence of the pH of the extractant solution on the extractability of arsenic compounds in sediment S11B. 200 mg of sediment S11B, suspended in 15 mL of a phosphate solution (0.3 mol L^{-1}), 10 min magnetic stirring, room temperature (22°C)

Influence of the solubilization mode (microwave solubilization or magnetic stirring). The influence of the solubilization mode was studied under the following conditions: 10 min contact time, same V/m ratio (200 mg of sediment extracted with 15 mL of solution), orthophosphoric acid concentration ranging from 0 to 0.3 mol L^{-1}. In general, for the same acidity, extraction yields are higher with microwave stirring; the weaker the acidity the more important the difference. The improvement of the extraction yield can be related to the heating of the solution. The influence of conventional heating, e.g. with a hot plate, was not studied since reproducible conditions are hard to achieve in case of such rapid extraction processes and the exact temperature reached in the open microwave digestion is hard to ascertain.

Relation between the quantities of Fe/Al and As extracted. According to literature [3–9] arsenic is preferentially attached to the sediment by specific adsorption at Fe and Al amorphous oxide sites. For each extract, the quantities of Fe and Al released in solution were determined by ICP. The results indicated that there is a linear relationship between the Fe/Al and As quantities. Fe or Al compounds present as amorphous oxides should not be labile; therefore, the exchange between As and phosphate ions should not govern the Fe or Al release. Arsenic is displaced by phosphate by a simple ion-exchange mechanism. The Fe/Al – phosphate complexes so formed are soluble and therefore result in an irreversible destruction of sites for As adsorption on the sediment.

Extraction of sediment S11B
with ammonium oxalate solutions

The specific technique devised in sequential extraction schemes to study various soil/sediment fractions was directly applied to examine the hydroxide fraction : ammonium oxalate acidified to pH 3 with oxalic acid [12]. The extraction of sediment S11B was carried out under the conditions described above (oxalate 0.3 mol L^{-1}, pH 3, V/m (mL/g) = 200). The results are summarized in Table 2. During oxalate extraction 91% of the total arsenic was released into the solution. DMA and MMA were quantitatively extracted, whereas only 90% of mineral arsenic was released. As(III) represents 50% of mineral arsenic, which is in good agreement with the value obtained during orthophosphoric acid dissolution.

Conclusion

Table 2 summarizes the results obtained for the different extraction procedures used throughout this study, and a few chromatograms are presented in Fig. 3. The extraction of organometallic compounds (DMA and MMA) is quite simple since these compounds are stable in the different extraction media and are easily released. HNO_3/HCl microwave digestion or extractions with orthophosphoric acid (0.3 mol L^{-1}, pH 1.3) or ammonium oxalate (0.3 mol L^{-1}, pH 3) give extraction yields superior or equal to 96%.

Mineral arsenic is quantitatively extracted during an HNO_3/HCl microwave digestion, but this procedure does not allow the differentiation between the two oxidation
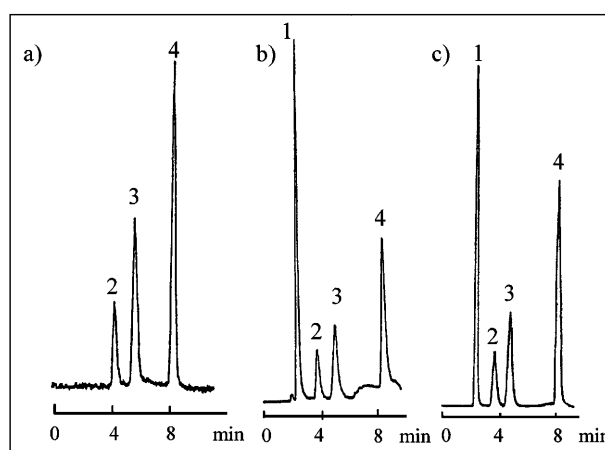
Fig. 3 Chromatograms of different extracts **a**: HNO_3/HCl extract; **b**: orthophosphoric acid extract; **c**: ammonium oxalate extract. *(1)* As(III); *(2)* DMA; *(3)* MMA; *(4)* As(V)

Table 2 Comparative study of the efficiency of the different solubilization procedures for arsenic speciation

Arsenic compound mg (As) kg^{-1}	HCl/HNO$_3$ microwave digestion	H$_3$PO$_4$ 0.3 mol L^{-1} pH 1.3[a]	H$_3$PO$_4$ 0.3 mol L^{-1} pH 1.3[b]	Ammonium oxalate 0.3 mol L^{-1} pH 3[a]
As (III)	–	87.0 ± 0.9	78.1 ± 2.0	84.0 ± 0.8
DMA	21.6 ± 1.1 (100%)	20.8 ± 0.5 (96%)	21.1 ± 1.1 (98%)	21.4 ± 0.9 (99%)
MMA	41.2 ± 1.2 (100%)	41.0 ± 0.3 (100%)	40.6 ± 0.5 (99%)	40.5 ± 1.4 (98%)
As(V)	–	75.1 ± 6.1	98.2 ± 4.0	82.9 ± 3.5
As mineral	186.1 ± 5.1 (100%)	165.0 ± 7.0 (89%)	176.3 ± 6.00 (95%)	166.9 ± 4.3 (90%)
As total	248.9 ± 7.4 (100%)	223.8 ± 7.8 (90%)	237.7 ± 7.6 (95%)	228.8 ± 6.6 (92%)

[a] 10 min magnetic "stirring"
[b] 10 min microwave solubilization

states (As(III), As(V)). Extractions with orthophosphoric acid or ammonium oxalate allow to detect the presence of As(III) in the spiked sediment at a concentration superior or equal to 87 mg (As) kg^{-1} and to extract 90 to 95% of mineral arsenic.

The usefulness of microwave dissolution for arsenic speciation has been shown in this study. Moreover, the results prove that there is a linear relationship between the quantities of Fe/Al and As desorbed.

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