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Development and application of a HPIC-ICP-MS method for the redox arsenic speciation in river sediment pore waters

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A new sensitive chromatographic method has been developed for As speciation determination in anoxic pore waters. Starting from aliquots of 25 µL, the different As species As(III), As(V), $MMAA^V$ and $DMAA^V$ were separated in less than 4 min by HPIC-ICP-MS using the IonPac® AG7-AS7 anion-exchange column set and dilute HNO_3 as mobile phase. The detection limits were below or equal to 0.25 µg L^{-1} for each As species, which makes the method efficient to determine As speciation in poorly-contaminated sediments. In addition, no precipitation of iron and manganese (hydr)-oxides was observed since the anoxic samples were systematically carefully manipulated under nitrogen atmosphere. Chlorides were eliminated by the chromatographic separation, thus making possible speciation analysis in estuarine or seawater samples. The use of internal standard was not necessary due to good signal stability (<10%) at *m/z* 75 over 4 h of analysis. An environmental application has also been successfully performed in the Marque River (Northern France). Inorganic As species were detected in pore waters at low concentrations [below 1 and 10 µg L^{-1}, for As(V) and As(III) respectively]. Others As species, identified as thioarsenic species, were also detected.

1 Introduction

Understanding the behavior of arsenic species in surface sediment is still challenging.[1] Indeed, studies on arsenic speciation in pore waters remain scanty because the sedimentary matrix is both complex and anoxic. Sampling is a delicate process as sediments and pore waters must be kept out of oxygen until analysis to avoid any modifications of the redox speciation of elements such as Fe, Mn, S and As. In addition, the volume available for analysis is often very limited, and arsenic concentration can be very low (a few µg L^{-1}) in poorly-contaminated sites.

While a number of analytical techniques can be used to determine arsenic speciation, such as voltammetry,[2] hydride generation,[3] or even capillary electrophoresis,[4] the combination of chromatographic separation with element-specific spectrometric detection has proven to be the most useful strategy for analyzing the speciation of arsenic species at trace levels.[5,6] High-performance liquid chromatography (HPLC) is commonly used as a separation technique of arsenic species either in ion-pairing, ion-exchange, ion-exclusion or even size-exclusion modes.[7] Among these modes, anion exchange chromatography is the most frequently used technique due to the frequent anionic nature of arsenic species [mainly As(III), As(V), $MMAA^V$ (monomethyl arsenic acid) and $DMAA^V$ (dimethyl arsenic acid)] in natural waters. Anionic arsenic species are separated in the column by anion-exchange interactions and eluted by competitive anions (*e.g.* acetates, carbonates, nitrates, phosphates, sulfates) present in the mobile phase.[8,9] In terms of detection, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) has become one of the most popular techniques for arsenic measurement due to its versatility and its sensitivity.[10]

Several changes in As speciation have also been noticed using HPLC-ICP-MS. For example, Zheng *et al.*[11] observe an advanced reduction step of As(V) to As(III) in sediment pore waters that is marked by the high proportion of thioarsenical species. Xie *et al.*[12] could monitor changes in As speciation over time during toxicity testing experiments using *Chironomus tentans.* They suspect that a detoxification occurs due to the bacterial growth in solution *via* the oxidation of As(III) to As(V). Such examples demonstrate the power of HPLC-ICP-MS to characterize the redox fate of As in aquatic environments.

To better understand the fate of As in surface sediments with the above-mentioned constrains, a sensitive and reliable analytical method for determining the arsenic species in sediment pore water has been developed and optimized. Since only a small volume (a few mL) of pore waters can be commonly

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extracted from 1 cm slices of sediment cores, the development of a High Performance Ion Chromatography – Inductively Coupled Plasma – Mass Spectrometry (HPIC-ICP-MS) method has emerged. The three main objectives of the proposed method are: (i) removing efficiently isobaric and polyatomic interferences during the chromatographic and/or through the use of the collision/reaction cell; (ii) reaching an effective separation of As(III), As(V), $MMAA^V$ and $DMAA^V$ by HPIC-ICP-MS without any modifications of the original speciation, together with (iii) operational effectiveness of the method applied on pore waters extracted from non-contaminated river sediments by arsenic.

2 Experimental

2.1 Reagents, materials and solutions

All solutions are prepared using ultrapure water (Milli-Q gradient, Millipore, $\rho = 18.2$ MΩ cm) and named further in the text MQ water. As(V) standard solution (1 g L^{-1}) is obtained from Merck [CertiPur, (H_3AsO_4) in 4% (v/v) HNO_3]. Solutions of As(III), $DMAA^V$ and $MMAA^V$ (1 g L^{-1}) are prepared in 2% (v/v) HNO_3 (Fischer scientific, Optima grade) from As_2O_3 (Fluka, analytical grade), $(CH_3)_2AsO_2Na\cdot 3H_2O$ (Acros organic, pure) and $CH_3AsNa_2O_3\cdot 6H_2O$ (Supelco, Analytical) salts, respectively. Note that the dissolution of As_2O_3 is initially improved in a dilute NaOH solution as described by Panther *et al.*,[13] before adding HNO_3. Prior to use, speciation analyses are performed weekly to check the stability of As species in non-acidified standard solutions. Calcium and chlorides solutions (1 g L^{-1}) used in this study are purchased from Merck (Analytical grade), H_3BO_3 and $NaS_2\cdot 9H_2O$ salts from Sigma (Analytical grade), certified waters for As content (SLRS-4 and SLEW-3) from NRCC (National Research Council Canada).

Dissolved Fe and Mn concentrations are determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; Varian Vista Pro, axial view). Chlorides and phosphates determination are performed with a Dionex™ ion chromatography [equipped with a separation column (IonPac AG18, 4 mm internal diameter (i.d.) × 50 mm coupled with IonPac AS18, 4 mm i.d., × 250 mm), an eluent generator (EG50) and an electrochemical detector (ED40)]. Arsenic measurements are carried out using Inductively Coupled Plasma Mass spectrometry (ICP-MS; X series, Thermo Elemental).

2.2 Instrumentation

Chromatographic separation. A Thermo Scientific™ Dionex™ ICS-5000+ High-Performance Ion Chromatography (HPIC), consisting of an injector (25 μL PEEK injection loop), a simple gradient pump, a thermal compartment module and an eluent degasser, is used as a separating system. Separation of arsenic species is performed using a Thermo Scientific™ Dionex™ IonPac AG7 guard column (10 μm particle diameter, 2 mm i.d. × 50 mm) coupled with a Thermo Scientific™ Dionex™ IonPac AS7 analytical column (10 μm particle diameter, 2 mm i.d. × 250 mm). The flow rate of the mobile phase is fixed at 400 μL min^{-1}. The outlet of the HPIC column is directly connected to the nebulizer of the ICP-MS using a 25 cm PEEK capillary tubing (125 μm i.d.). Note that in addition to the vacuum degasser, the mobile phases stock solutions are purged continuously with helium to eliminate the presence of dissolved oxygen.

ICP-MS. A single quadrupole ICP-MS instrument, Thermo Elemental™ X-series is used as a detector. It is equipped with a Micromist™ concentric nebulizer (Glass expansion), an impact bead spray chamber (SCP Sciences) cooled at 3 °C, a quartz torch (SCP Sciences, 1.5 mm injector) and with platinum sampler and skimmer cones (SCP Sciences). Analyses are performed either in the normal mode or in the CCT mode (Collision Cell Technology™) using helium and hydrogen as additional gases with the aim to reduce the presence of polyatomic interfering ions. Operating conditions and data acquisition parameters are listed in Table 1. Plasma parameters are tuned daily to get optimal signals using a mixture of PlasmaCal and AccuTrace (SCP Sciences) solutions at 10 μg L^{-1}. Treatment of chromatograms is carried out by integrating the peak area with the Thermo Elemental PlasmaLab 2.5 software.

2.3 Application of the speciation method to anoxic sediment of Marque River

The optimized method is applied to analyze As speciation in pore waters from a riverine site (Marque River, North of France). Arsenic content in the surface sediments (0–20 cm) (data not shown) is presently close to the regional background concentrations {$[As]_{background} \sim 8$ mg kg^{-1} in sedimentary parent materials for $[Al]_{background} \sim 36$ g kg^{-1} (ref. 14)}. The enrichment factor in the sampling site normalized to Al is always lower than 1.1 [for more details concerning enrichment factor calculations, see for instance[15]].

Three sediment cores have been collected in the Marque River on February 2014 using a manual corer with a 35 cm perspex tube (7.5 cm i.d.). E_h and pH measurements are carried out by potentiometry in the first core. Electrodes are inserted in holes situated every cm all along the tube and previously covered with tape. For that purpose, a platinum electrode (Mettler Toledo; 0.5 cm external diameter) and a glass electrode (Mettler Toledo, 1 cm external diameter) are used as working electrodes to measure E_h and pH, respectively. Both electrodes are combined with an Ag/AgCl ([KCl] = 3 M) reference electrode, with a potential equal to 0.22 V *versus* the Hydrogen Normal Electrode (HNE). All potential values reported here are expressed *versus* the HNE electrode. The second core is introduced in a glove box previously flushed with nitrogen, and sliced every 1–2 cm after removing the overlying water. Back to the laboratory, each sediment slice is introduced in a centrifugation tube in order to extract interstitial water using a X 340 Prolabo centrifuge (rotation radius: 20 cm) for 20 min at a rotation speed of 2500 rpm. Pore waters are then filtered under nitrogen, on a 0.45 μm membrane (Sartorius filters, cellulose acetate membrane). An aliquot of the liquid is immediately acidified at 2% (v/v) with HNO_3 (Merck, suprapur) for the analysis of total As, Fe and Mn concentrations using spectrometric methods, whereas the remaining volume is used for analysis of As speciation using HPIC-ICP-MS within the same day. Finally, an AgI-DGT probe is inserted in the third core for a 24 h exposition

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Table 1 Optimized ICP-MS and HPIC settings

	Parameters	Normal mode	CCT mode
ICP-MS	R.f. power (W)	1400	
	Nebulizer	Micromist® concentric nebulizer	
	Spray chamber	Impact bead spray chamber, cooled at 3 °C	
	Ion sampling		
	Sampler cone	Platinum	
	Skimmer cone	Platinum, xs	
	Extraction (V)	−550 to −500	
	Hexapole[b] (V)	3[a]	-6[a]
	Pole bias[b] (V)	5[a]	-8[a]
	Argon flow rates		
	Outer (mL min^{-1})	16.0[a]	
	Intermediate (mL min^{-1})	1.10[a]	
	Aerosol carrier (mL min^{-1})	0.80[a]	
	Gas flow rates		
	H_2 (mL min^{-1})	n.a.	0.5
	He (mL min^{-1})	n.a.	3.5
	Data acquisition parameters		
	Monitoring mass	*m/z* 51 (chlorides interferences) and 75	
	Scanning mode	Transient	
	Dwell time (ms)	250–400	
HPIC	Anion-exchange columns	IonPac™ AG7 (2 mm i.d. × 50 mm) and AS7 (2 mm i.d. × 150 mm)	
	Mobile phase A	1 mM HNO_3	
	Mobile phase B	50 mM HNO_3	
	Gradient program	0–1 min 100% A 2–3 min 100% B 4–8 min 100% A	
	Flow rate (μL min^{-1})	400	
	Temperature (°C)	30	
	Injected volume (μL)	25	

[a] Variable as a function of daily signal optimization. [b] A Kinetic Energy Discrimination (KED) is applied by 2 V of potential difference between the hexapole and pole bias to attenuate polyatomic interference.

in a thermostatic chamber fixed to the field temperature, with the aim to measure sulfide concentrations as a function of depth.[16] Note that prior to deployment, the DGT probe is de-oxygenated with a flux of N_2 for 24 h in a 0.01 M $NaNO_3$ solution. After deployment, the probe is rinsed quickly with MQ water and put in a well humidified plastic box before treatment. The sulfide concentrations are determined as a function of the gray scale density related to each standard with a flatbed scanner (300 dpi). Overlying water is also sampled and treated like pore waters (but under oxic conditions in this case).

3 Results and discussion

3.1 Optimization of the chromatographic separation

Separation of As species [As(III), As(V), $DMAA^V$ and $MMAA^V$] is performed using AG7-AS7 anion-exchange columns that allow separation of the anionic As species. Nitric acid is chosen as a mobile phase with the aim to determine the As speciation in anoxic and filtered pore waters while limiting the precipitation of iron and manganese (hydr)-oxides.

Optimisation of the chromatographic conditions is carried out using solutions containing As(III), As(V), $DMAA^V$ or $MMAA^V$ at 10 μg L^{-1}. The eluent composition is firstly studied by varying the concentration of HNO_3 from 0.1 to 50 mmol L^{-1} in order to reach a good compromise between sensitivity of the method, separation of As species and duration of the chromatographic analysis. The evolution of the retention times and peak heights as a function of the eluent concentration and pH is presented in Fig. 1(A) and (B).

As shown in Fig. 1(A), the retention time of As(III) does not change ($t_r = 1$ min) whatever the pH of the mobile phase. This can be explained by the fact that As(III) exists as a neutral species in acid solutions (H_3AsO_3; $pK_{a_1} = 9.22$). As a result, there is no interaction between As(III) and the anion exchange groups of the columns. The observations are similar for $DMMA^V$ ($pK_a = 6.2$), and only minor changes in the retention times ($t_r \sim 3.15$ min) and peak heights (~11 000 cps) are noticed in the working pH range. In contrast, the retention of both As(V) ($pK_{a_1} = 2.3$) and $MMAA^V$ ($pK_{a_1} = 3.4$) is strongly dependent on the pH of the mobile phase. Indeed, retention times are found to increase when the pH of the mobile phase steps up, and are accompanied by a significant reduction of the peak heights. This is explained by a higher affinity of the deprotonated As(V) and $MMAA^V$ forms [*i.e.* $H_2AsO_4^-$ and $CH_3As(O)_2(OH)^-$] for the stationary phase. Conversely, at the lower pH values, both As(V) and $MMAA^V$ are protonated, thus decreasing their affinity for the stationary phase.

The separation of As(III), As(V), $DMAA^V$ and $MMAA^V$ can be carried out in the isocratic mode with a concentration of HNO_3 in the mobile phase ranging from 1 to 10 mmol L^{-1}; above 10 mmol L^{-1} HNO_3 solution, the co-elution of organic As(V) species has been evidenced. However, the implementation of a pH gradient has shown to improve the separation. Results of the optimised method are presented in Fig. 2. The validation of the method is performed by injecting a mixture of the different As species at 10 μg L^{-1}. Triggering of the pH gradient (*i.e.* by increasing the HNO_3 concentration from 1 mM to 50 mM) is performed just after the elution of As(III) in order to avoid the co-elution of As(III) and $MMAA^V$, and to decrease the elution time of both $DMMA^V$ and As(V). The optimal retention times of As(III), $MMAA^V$, $DMMA^V$ and As(V) are 1.0, 1.7, 3.3 and 3.9 min, respectively. The chromatographic resolution (R_s) between each As species is determined using the following equation (eqn (1))[17]

$$R_s = \frac{1.176 \times (t_{r2} - t_{r1})}{W_{h1} + W_{h2}} \quad (1)$$

with t_r the retention time (min) and W_h the width measured at half peak height (cps).

For the operating conditions presented in Fig. 2, the achieved resolutions are satisfactory with the following values: $R_{s\ As(III)/MMAA^V} = 6.0$; $R_{s\ MMAA^V/DMAA^V} = 9.1$; $R_{s\ DMAA^V/As(V)} = 3.9$.

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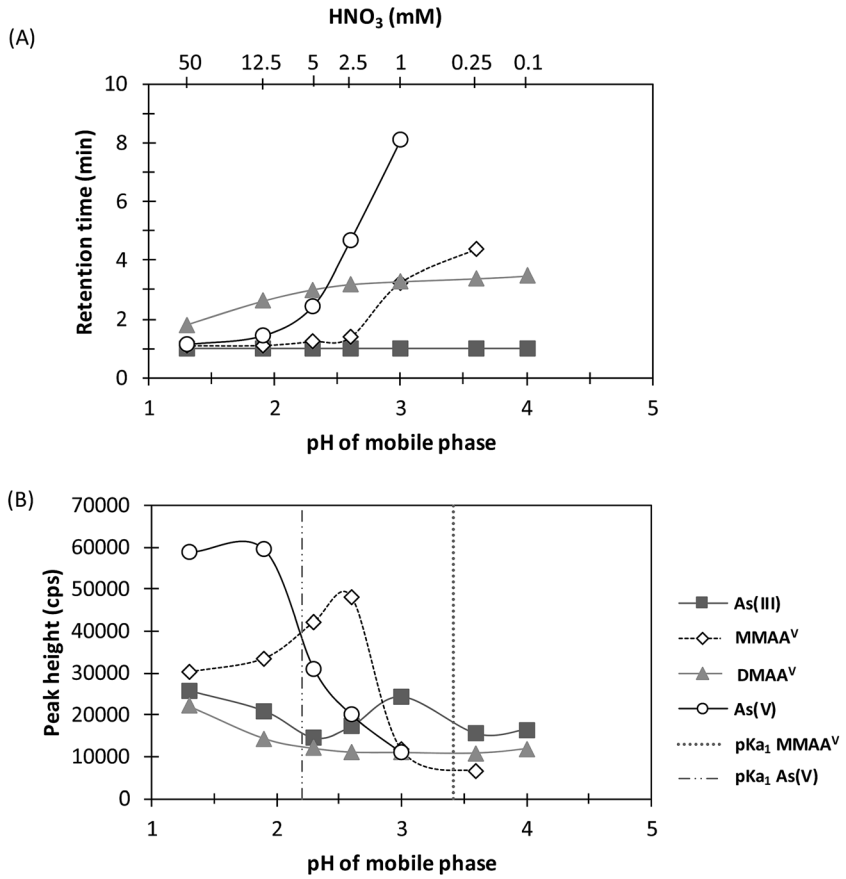

Fig. 1 Influence of the mobile phase concentration and pH on the retention time (A) and peak height (B) using the IonPac® AG7-AS7 columns ([As(III)] = [As(V)] = [DMAA^V] = [MMAA^V] = 10 μg L^{-1}).

3.2 Analytical performance of the HPIC-ICP-MS method

Calibration range. The calibration is performed with standard solutions up to 20 μg L^{-1} (*i.e.*, 0, 0.5, 1, 2, 5, 10 and 20 μg L^{-1}) to cover the range of concentrations commonly encountered in pore waters. Analytical performances are summarized in Table 2. Supposing a linear response within the concentrations range chosen, an acceptable coefficient of determination is attained ($R^2 > 0.995$).

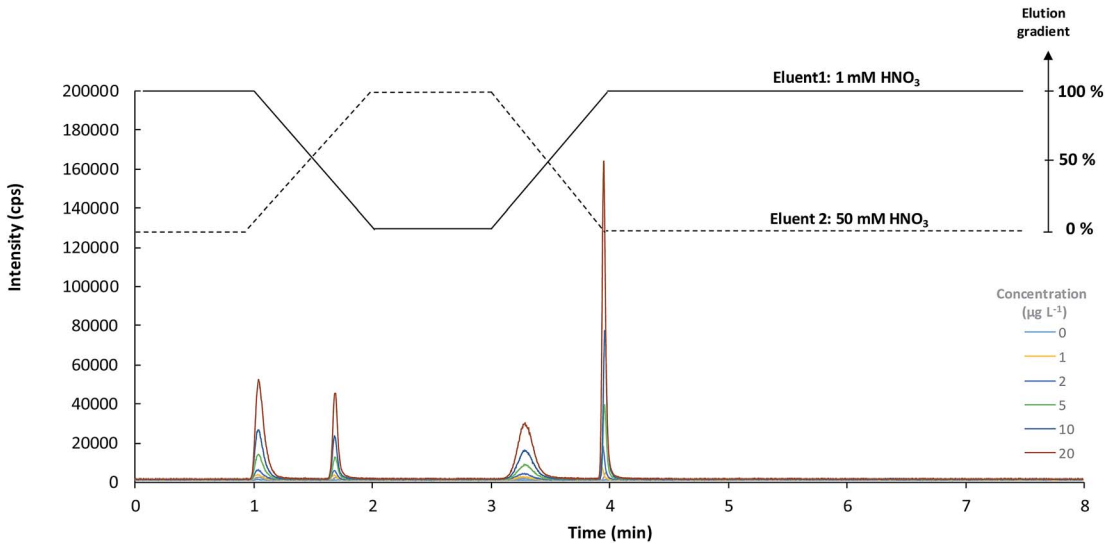

Fig. 2 HPIC-ICP-MS chromatograms at *m*/*z* 75 obtained for a solution containing 20 μg L^{-1} of As(III), As(V), DMMA^V and MMAA^V after optimization of separation onto the AG7-AS7 columns. The optimized gradient of HNO_3 concentration is also presented as a function of time.

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Table 2 Figures of merit for the separation and the detection by ICP-MS [in normal mode and with the Collision Cell Technology (CCT)] of As(III), As(V), $MMAA^V$ and $DMAA^V$ using IonPac® AG7–AS7 columns. Note that the detection limit values are expressed as As species concentrations

	Retention time (min)	Slope (kcps L ms^{-1} μg^{-1})		Blank (cps)		Coefficient of determination		Detection limit ($\mu g\ L^{-1}$)	
		Normal	CCT	Normal	CCT	Normal	CCT	Normal	CCT
As(III)	1	12.6	2.4	238	83	0.999	0.999	0.20	0.25
$DMAA^V$	1.7	8.0	1.6	19	16	0.999	0.999	0.15	0.25
$MMAA^V$	3.3	8.5	1.6	269	311	0.999	0.999	0.25	0.50
As(V)	3.9	15.4	3.1	72	24	0.999	0.999	0.05	0.10

Detection limits. The detection limits (DL) (expressed as As species concentrations) are estimated for each species based on the noise intensity of the baseline (I_0) (with DL = $3I_0$), and are experimentally checked with standard solutions close to the calculated DL. Results are presented in Table 2 for each As species. DL are below or equal to 0.5 $\mu g\ L^{-1}$ for each As species whatever the analytical mode used. The results are in the same order of magnitude or slightly higher compared to those gathered by Komorowicz and Barałkiewicz[5] (LD of As species >0.25 $\mu g\ L^{-1}$).

Study of polyatomic interferences. A major limitation of ICP-MS is the spectral interferences arising from the formation of both polyatomic and isobaric ions in the plasma. The major potential mass spectral interferences for As (m/z = 75; only 1 single stable isotope) are polyatomic ions $^{40}Ar^{35}Cl^+$ and $^{38}Ar^{37}Cl^+$.[8] A study of these interferences is carried out by increasing the concentration of chlorides (up to 1000 mg L^{-1}) to a solution containing 10 $\mu g\ L^{-1}$ of each inorganic As species. Chromatograms are recorded in the normal measurement mode to better visualize the formation of interference peaks. In parallel, the m/z = 51 is monitored to detect the potential interfering peak of chloride through the formation of the ions $^{35}Cl^{16}O^+$.[18] The interfering peak linked to the presence of chlorides is observed after about 5.7 min for chloride concentrations higher than 20 mg L^{-1} (Fig. 3). However, using the optimized eluting conditions presented Table 1, the chloride signal does not interfere with the peak of As(V) ($R_{s\ As(V)/Cl}$ = 5.8). Analysis of filtered seawater is also carried out to test the impact of a higher chloride concentration (Fig. 4). As expected, chlorides are eluted after inorganic As(V) with a sufficient resolution ($R_{s\ As(V)/Cl}$ = 1.36) to envisage analysis of arsenic speciation in estuarine and marine waters.

Possible $^{36}Ar^{39}K^+$ and $^{42}Ca^{16}O_2{}^+$ polyatomic interferences are also studied, but no peaks are detected at m/z 75 for concentrations of calcium and potassium up to 1000 mg L^{-1}. Finally, the present HPIC-ICP-MS procedure appears to be robust enough to determine arsenic in pore waters without necessarily requiring the use of the CCT measurement mode, and thus allowing better detection limits of As species.

Signal stability over time. Standard solutions containing all the As species studied (10 $\mu g\ L^{-1}$) are analysed during 4 hours in order to ensure the stability of HPIC-ICP-MS method over time.

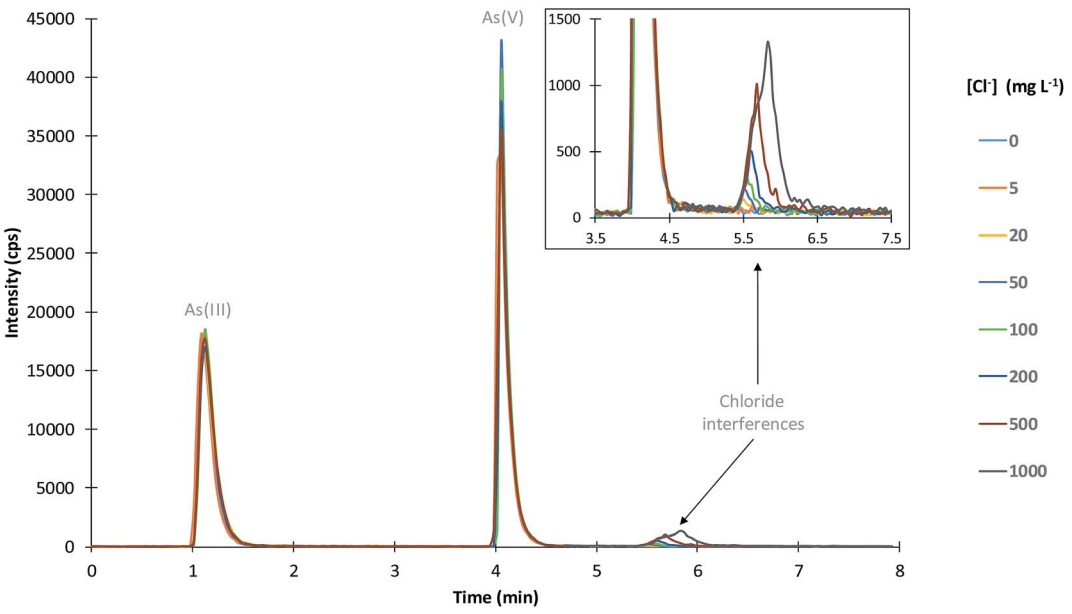

Fig. 3 HPIC-ICP-MS chromatograms at m/z 75 obtained for a solution containing 10 $\mu g\ L^{-1}$ of each inorganic As species and in presence of chlorides at different concentrations.

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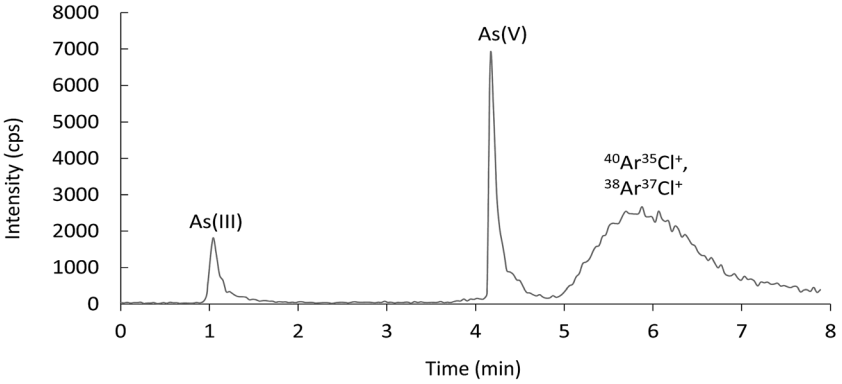

Fig. 4 HPIC-ICP-MS chromatograms at *m*/*z* 75 obtained for a filtered (at 0.45 μm) sample of seawater from North Sea (France).

This duration also corresponds to the time expected for analysing all the samples of pore waters after a typical field campaign. The measurements show an excellent reproducibility with less than 10% uncertainty (Fig. 5), suggesting that an internal standard is not necessary to correct a signal drift at *m*/*z* 75. Nevertheless, quality controls are necessary every 5–10 samples to ensure the proper functioning of the speciation method.

Addition of an internal standard (such as antimony, germanium, indium, iridium or rhodium) to samples and standard solutions is generally achieved during HPLC-ICP-MS measurements of As speciation in complicated matrixes that are more impacted by drift signals (*e.g.*, enzymatic extract of marine organisms, sediment or soil extracts and human urine).[18–22] However, in the present case, this approach is not used for several reasons: (i) to prevent a possible modification of the initial As speciation since the internal standard is usually acidified, thus leading to possible redox reactions [like photo-oxidation of As(III) in the presence of dissolved Fe(III)], decomposition of methylated species…;[23–26] (ii) due to the difficulty to add the internal standard in a glove bag; and/or (iii) due to the possible presence of these elements in pore waters. In this study, preliminary tests using germanium as internal standard have been performed using a trident kit, allowing addition of the internal standard at the column outlet without any modifications of the original sample. However, these tests systematically lead to an intense peak deformation (essentially tailing) due to a perturbation of the chromatographic path.

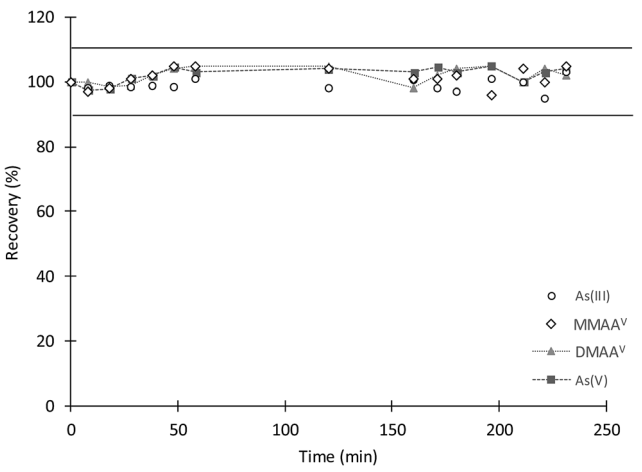

Fig. 5 Stability test of the optimized HPIC-ICP-MS procedure over the time for the studied As species.

Besides, no salt deposit on the Pt cones of ICP-MS is observed using dilute HNO_3 as a mobile phase after 4 h of analyses. The present operating conditions are therefore more adapted to ICP-MS measurements than those using phosphate mobile phases, which are known to obstruct and/or damage cones presumably through the deposition of P_4O_{10}.[27] Additionally, for pH > 5,[9,28] phosphate mobile phases are not compatible with As speciation measurement in pore waters. Indeed, Fe(II) present at potential high concentrations (commonly >1 mg L^{-1}) in the samples can precipitate as (hydr)-oxides after a rapid re-oxidation and/or form various Fe–P compounds of low solubility [*e.g.* vivianite[29]].

Accuracy. Accuracy of the HPIC-ICP-MS method is checked using certified waters (SLRS-4 and SLEW-3) towards total As contents. Since there is no commercially available reference material specifically relative to As speciation, the analytical accuracy is evaluated only in terms of total concentration [*i.e.*, the sum of As(III) and As(V) concentrations]. Besides, accuracy of the sample preparation step cannot be taken into account since no certified raw sediments are available. Once the reference water sample analyzed, a standard deviation E_n is calculated with the following equation (eqn (2), ISO 3534 (ref. 30)), with a confidence level of 95%, the difference is statically considered as insignificant if $E_n < 2$:

$$E_n = \left| (x_i - x_{cert}) \Big/ \sqrt{\left(u_i^2 + u_{cert}^2\right)} \right| \quad (2)$$

with x_i the concentration measured, x_{cert} the certified reference concentration, u_i the standard deviation of the measurements, and u_f the standard deviation associated to the certified reference value.

As presented in Table 3, the differences between the measured and the certified reference values are not significant ($E_n < 2$), meaning that the accuracy of the IC-ICP-MS for total As determination is acceptable.

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Table 3 Accuracy assessment of the HPIC-ICP-MS procedure (normal mode) by using water reference materials. E_n is related to a standard deviation (see eqn (2) in the text for more details)

	As(III) (μg L^{-1})	As(V) (μg L^{-1})	Total As (μg L^{-1})	As_{ref} (μg L^{-1})	E_n
SLRS-4 river water	0.48 ± 0.5	0.13 ± 0.1	0.61 ± 0.06	0.68 ± 0.06	0.82
SLEW-3 estuarine water	1.08 ± 0.11	0.11 ± 0.01	1.19 ± 0.19	1.34 ± 0.09	0.69

3.3 Application of the speciation method to anoxic pore waters in the Marque River

The optimized method is applied to assess the As speciation in pore waters of the Marque River. Results are displayed in Fig. 6. In the water column, both inorganic As(III) and As(V) species have similar concentrations (~0.5 μg L^{-1}). No trace of methylated species is detected. At the water–sediment interface, a strong redox gradient occurs due to early diagenetic processes. E_h values are found to drop from approximately 415 to −10 mV within the 3 first cm and remain quite constant below 3 cm depth. The reduction of Mn and Fe (hydr)-oxides is also clearly underlined with maximal values of dissolved Mn^{2+} and Fe^{2+} at −2 cm (~1.7 mg L^{-1}) and −3 cm (~20 mg L^{-1}), respectively, indicating that Mn oxides are reduced slightly before Fe ones. Conversely to Chaillou *et al.*,[31] who estimated the As(V) content as the difference between total As and As(III) concentrations, our protocol allows to estimate directly each As species in the samples without calculation. Inorganic As(III) is the dominant specie all over the profile with a maximal value (weight ratio of As(III)/As(V) ~ 37) just below the water–sediment interface, suggesting that As(V) may be reduced slightly before Fe and Mn oxides and/or with the most reducible ones. This result also suggests that a fraction of As(V) should be rather adsorbed onto oxides surface than scavenged in the mineral structure. Inorganic As(V) species are detected in the 8 first cm depth of the core with concentrations closed to the detection limit. The proportion of As(V) accounted for less than 10% of total As. The second reduction/dissolution zone of Fe in the sediments (6–14 cm) does not promote a release of As(V) and/or As(III) in the pore water, confirming the quantitative reduction of As within the water–sediment interface. In addition, similarly to the overlying water, no methylated As species are detected in the pore waters. By comparing the total concentrations of As measured by ICP-MS with the sum of As species measured by HPIC-ICP-MS, the recovery is fairly good for the 6 first cm ($R^2 = 0.995$), suggesting that the analytical procedure is fully optimized and is not subject to matrix effects [35–55 mg L^{-1} of chlorides in pore waters (Fig. 6)] and/or artifacts associated to sample handling (*e.g.* sorption of As species on filter and/or precipitation with (hydr)-oxides due to the presence of oxygen).

Below 6 cm, a significant difference in the arsenic recovery is noticed (Fig. 6) and is accompanied by several chromatographic peaks not clearly identified, one being generally still more intense at 4.2 min (Fig. 7). In anoxic environments where the

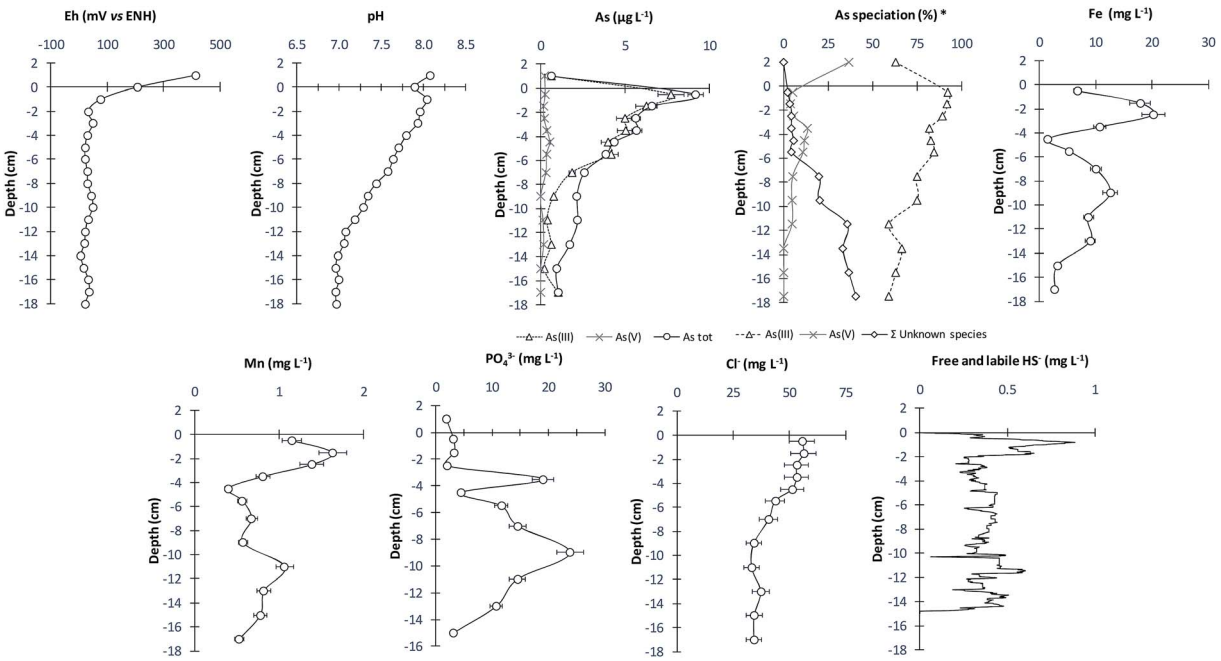

Fig. 6 Concentration profiles of As speciation, pH, potential redox (E_h), total element contents (As, Fe and Mn), chlorides, phosphates and sulfides (only free and/or labile fraction) in pore waters from a sediment core sampled in the Marque River in February 2014. *: Calibration of the peak area of thio-arsenical species is done using the calibration slope of As inorganic species, since no standards of As–S species are commercially available.

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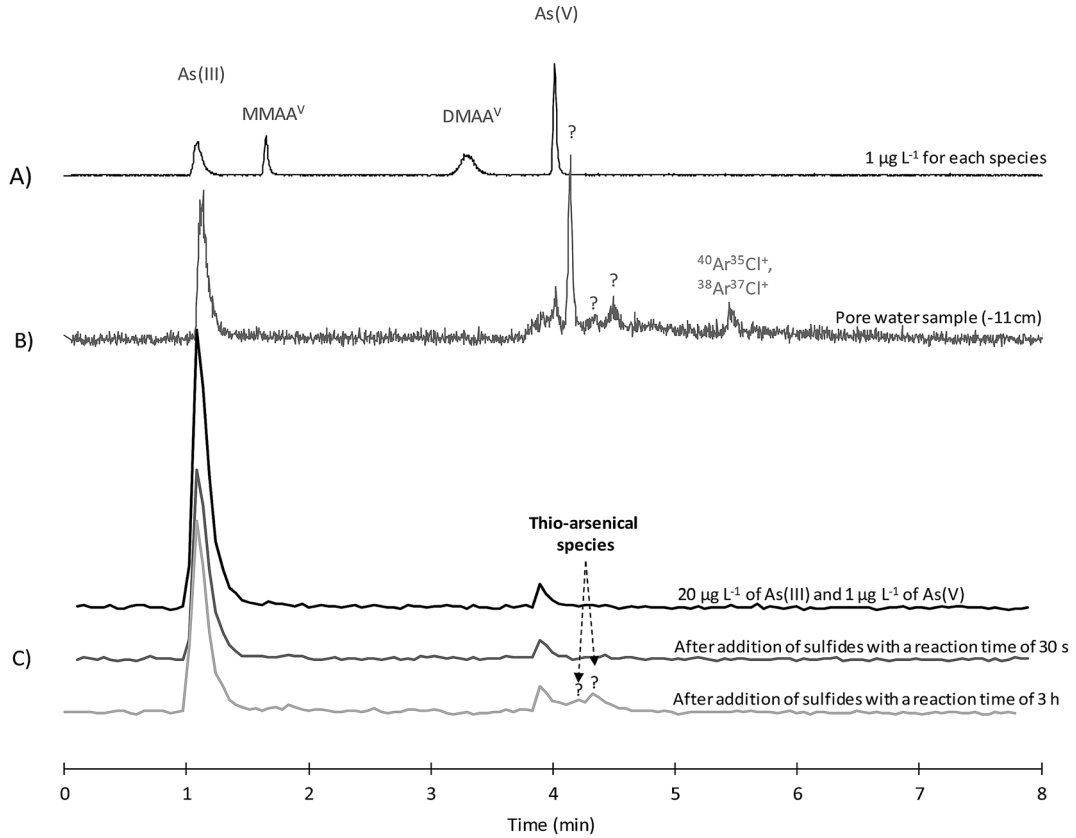

Fig. 7 HPIC-ICP-MS chromatograms: (A) in a standard solution containing 1 µg L^{-1} of each As species; (B) in a pore water sample from the Marque river sediment at 11 cm depth (ICP-MS signal × 5); and (C) in a model solution containing a mixture of inorganic As(III), inorganic As(V) and HS^-, showing the generation of thio-arsenical species as a function of the time.

presence of sulfides is evidenced, the formation of thioarsenic species such as thioarsenites ($AsO_{3-x}S_x^{3-}$ with $x = 1$ to 3) and thioarsenates ($AsO_{4-x}S_x^{3-}$with $x = 1$ to 4) may occur.[32,33] However, dedicated studies to these species in anoxic sediments remain scanty. The existence of such species cannot be ruled out in our case, not only because the consumption of sulfates occurs in sediments (and probably close to the water interface) but also because sulfides species are clearly evidenced by AgI-DGT probes (Fig. 6). In order to go further on the possible As–S associations, new investigations have been carried out in a de-oxygenated 0.1 M H_3BO_3 solution adjusted to pH 8 by addition of 1 M NaOH and containing As(III) (20 µg L^{-1}), As(V) (1 µg L^{-1}) and sulfides (2 mg L^{-1}). As(V) is deliberately added at a low concentration for a better discrimination against the thioarsenic species. Evolution of As speciation in that solution is monitored as a function of the time by HPIC-ICP-MS with the aim to detect the potential formation of thioarsenic species. All the operations are performed in a glove bag under nitrogen atmosphere, and each aliquot is filtered (0.45 µm) before analysis. Results are shown in Fig. 7. The As(III) concentration is found to decrease down to 15 µg L^{-1} just after the addition of sulfides, and remained then stable for the rest of the experiment. The emergence of new peaks attributed to As–S species could be noticed after 1 h of reaction time confirming the low kinetic formation of thioarsenic species observed by Rochette *et al.*[34] and Zhang *et al.*[35] Since the formation of thioarsenic species is controlled by low kinetic processes, it would be therefore not surprising to generate such species in buried sediments where the re-oxidation processes (due to bioturbation and/or sediment resuspension) is rather limited. Indeed, it is observed in the pore waters of the Marque River that the proportion of thioarsenic species increases below 6 cm of depth accounting for almost 40% of the total arsenic content (based on chromatographic peaks area) (Fig. 6).

4 Conclusion

A HPIC-ICP-MS method has been successfully developed in this paper to determine the speciation of arsenic at trace level (up to 20 µg L^{-1}) and without stabilizing agents in sediment pore waters. The present method takes also into account of all problems relative to the oxidative precipitation of Fe(II) and Mn(II). Overall, the As species As(III), As(V), MMAA^V and DMAA^V are separated in less than 4 min using a set of IonPac® AG7-AS7 anion-exchange columns and a gradient of HNO_3 (1–50 mM). The detection limits are equal to or below 0.5 µg L^{-1} for each As species, which is of paramount importance for determining As speciation in poorly-contaminated sediments. Only small volumes of sample are required (25 µL) for analysis, which is really suitable for analyzing pore waters since the volume

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available for all the analyses (*e.g.*, alkalinity, anions, dissolved organic carbon, and elemental composition) is often limited to a few mL. In addition, the presence of chlorides in the sample which are known to produce strong interferences in arsenic analyses with low resolution ICP-MS ($^{40}Ar^{35}Cl^{+}$ and $^{38}Ar^{37}Cl^{+}$), do not interfere using our HPIC-ICP-MS method. In the present case, chlorides are efficiently removed during chromatographic separation, allowing for As speciation analyses in estuarine or seawater samples without employing the collision/reaction mode.

The optimized method has been further applied to the determination of As species in pore waters of the Marque River. Inorganic As species have been detected at low concentrations [<1 and <10 μg L^{-1} for As(v) and As(iii), respectively], while the presence of $DMAA^{V}$ and $MMAA^{V}$ has not been evidenced. Other As species have been identified as thioarsenic species, but their chemical characterization still requires further investigations. Finally, this method can be used in routine for environmental studies to better understand the fate of As under redox changes due for instance, to early diagenetic processes.

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