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Determination of total arsenic using a novel Zn-ferrite binding gel for DGT techniques: Application to the redox speciation of arsenic in river sediments

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ABSTRACT

A new laboratory-made Zn-ferrite ($ZnFe_2O_4$) binding gel is fully tested using Diffusive Gradient in Thin films (DGT) probes to measure total As [including inorganic As(III) and As(V), as well as MonoMethyl Arsenic Acid ($MMAA^V$) and DiMethyl Arsenic Acid ($DMAA^V$)] in river waters and sediment pore waters. The synthesis of the binding gel is easy, cheap and its insertion into the acrylamide gel is not problematic. An important series of triplicate tests have been carried out to validate the use of the Zn-ferrite binding gel in routine for several environmental matrixes studies, in order to test: (i) the effect of pH on the accumulation efficiency of inorganic As species; (ii) the reproducibility of the results; (iii) the accumulation efficiency of As species; (iv) the effects of the ionic strength and possible competitive anions; and (v) the uptake and the elution efficiency of As species after accumulation in the binding gel. All experimental conditions have been reproduced using two other existing binding gels for comparison: ferrihydrite and Metsorb® HMRP 50. We clearly demonstrate that the Zn-ferrite binding gel is at least as good as the two other binding gels, especially for pH values higher than 8. In addition, by taking into consideration the diffusion rates of As(III) and As(V) in the gel, combining the 3-mercaptopropyl [accumulating only As(III)] with the Zn-ferrite binding gels allows for performing speciation studies. An environmental study along the Marque River finally illustrates the ability of the new binding gel to be used for field studies.

1. Introduction

Both toxicity and bioavailability of arsenic are strongly dependent on its chemical speciation. While several possible oxidation states are listed in the literature, the two most common states of arsenic observed in sediments are +III and +V. Reduced inorganic species, *i.e.* arsenite [As(III)], are more toxic than the oxidized inorganic ones, *i.e.* arsenate [As(V)]. In addition, the common organic As(V) species, such as MonoMethyl Arsenic(V) Acid [$MMAA^V$] and DiMethyl Arsenic(V) Acid [$DMMA^V$], are generally known to be less toxic than inorganic As species [1]. All these species also have their own physical and chemical characteristics, resulting in various degrees of mobility according to the biogeochemical properties of the matrix [2,3]. More particularly, in sediments where strong redox gradients occur within the first cm below the water–sediment interface, the geochemical behavior of As is still not fully understood [1]. The study of the aqueous speciation of As in pore waters is still challenging since the sediment matrix is anoxic and complex, and the concentrations of As are low (a few $\mu g\,L^{-1}$ or less).

Classical *ex situ* approaches are used to determine the concentration profiles of As speciation. They are generally divided into several steps: (i) sediment core sampling; (ii) core cutting into slices under nitrogen atmosphere; (iii) centrifugation of slices under N_2; (iv) filtration of the supernatants under N_2; (v) possible addition of stabilizing agents; and finally (vi) analyses of pore waters with speciation tools, *e.g.* voltammetry [4], hydride generation [5], High Performance Ionic Chromatography–Inductively Coupled Plasma Mass Spectroscopy (HPIC-ICP–MS) [6–8], *etc.* Due to high number of steps required, these approaches may be a source of potential errors (*e.g.* filtration and/or addition of stabilizing agents [9–11]) modifying the original As speciation. Moreover the spatial resolution using these techniques is very low (in the range of 1–2 cm). Consequently, *in situ* measurement techniques (notably diffusive gel methods) seem to be an interesting alternative to replace at least partially traditional *ex situ*

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Table 1
Selected examples of DGT binding gels used for determining As speciation. The values highlighted in bold correspond to those used in this paper.

Binding agent	pH range of use	Eluent	Elution efficiency (%)				Diffusion coefficients ($\times 10^{-6}$ cm^2 s^{-1}), corrected to 25 °C				Experimental conditions		References
			As(III)	As(V)	$DMAA^V$	$MMAA^V$	As(III)	As(V)	$DMAA^V$	$MMAA^V$	[As] (µg L^{-1})	pH	
3-Mercaptopropyl functionalized silica gel	3.5–8.5	HNO_3 1 M KIO_3 10^{-2} M	85.6 ± 1.7				9.24 ± 0.24				20	8.2	[14]
Ferrihydrite	3–8	HNO_3 1 M	74.3 ± 0.1	78.5 ± 0.5									[41]
		NaOH 1 M	87.0 ± 16.4	100.7 ± 9.2	100.6 ± 15.0	108.2 ± 10.7							[16]
							10.1 ± 0.20	6.28 ± 0.32			250	5–6	[42]
							5.95 ± 0.30	4.90 ± 0.13			?	5	[15]
							7.45 ± 0.04	6.05 ± 0.05			?	8.1	[17]
Ferrihydrite/Nafion membrane	3–7	HClcc	100 ± 5	n.a.									[15]
Metsorb®	3.5–8.5	NaOH 1 M	**81.2 ± 1.1**	**75.2 ± 1.5**	71.2	79.2	10.5 ± 0.25	6.83 ± 0.13			20	7.0	[14,38]
	4–8.2	NaOH 1 M H_2O_2 1 M		92.1 ± 2.5									[43]
$ZnFe_2O_4$ (this study)	4.5–9	HNO_3 1 M	**100**	**100**	**100**	**100**	**7.2 ± 0.70**	**4.2 ± 0.60**	**0.58 ± 0.12**	**3.25 ± 0.70**			Present study
ZrO	2–9	NaOH 1 M H_2O_2 1 M	92.1 ± 4	91.2 ± 3.4			10.5 ± 0.38	7.02 ± 0.31					[18]

approaches with the aim to improve spatial resolution as well as to minimize artefacts in the determination of pore water composition.

The Diffusive Gradient in Thin film (DGT) technique, which associates the processes of mass transport through a diffusive gel with accumulation within a chelating binding gel [12,13], has been used to determine inorganic As speciation by using two DGT probes with different selectivities [14] (Table 1). In that case, one binding gel was strictly selective to As(III) and contained 3-mercaptopropyl functionalized silica (3MP) as a binding agent. However, the 3MP binding gel presents some disadvantages, such as brittleness and complex for synthesis. As(III) is also determined with binding gels sensitive to total As species but covered with an anionic membrane barrier (*e.g.* Nafion membrane) inhibiting the diffusion of anionic species in the range of pH 3–7 [15]. The determination of total As content is possible from several binding gels with a binding agent such as ferrihydrite [16], Metsorb® HMRP 50 [17], ZrO [18]. Note that, Metsorb® HMRP 50 and ZrO binding gels are not well adapted to arsenic determination at low concentration due to some inherent analytical problems induced by the elution step with NaOH eluent [19]. The ferrihydrite binding gel is more appropriate for determining the total As content, because HNO_3 eluent is more compatible for Inductively Coupled Plasma Mass Spectrometry (ICP–MS) measurements. However, the pH range of use is strongly limited to pH values below 8, a value that is frequently exceeded in surface sediment and overlying waters [1].

The aim of this study is to propose, validate and apply in field conditions a new binding gel (zinc ferrite, $ZnFe_2O_4$) for the determination of total inorganic As in the range of pH frequently encountered in aquatic systems (*i.e.*, ranging from 5 to 9) [1]. This binding gel is costless, easy and quick to manufacture, to handle manually and to dissolve during the elution step. In addition, zinc ferrite appears to be a good candidate as it is insoluble at environmental pH values and has a high point of zero charge favourable in the accumulation of anionic As species. After describing the manufacture and performance of the new binding gel compared with the other pre-existing ones (3MP, ferrihydrite and Metsorb®), a field application is proposed for speciation determination of As in surface sediments sampled in the Marque River (northern France).

2. Experimental

2.1. Reagents, materials and solutions

All solutions are prepared using ultrapure water (Milli-Q gradient, Millipore, called after in the text MQ). As(V) standard solution (1 g L^{-1}) is obtained from Merck (CertiPur). 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, puriss for analysis), $(CH_3)_2AsO_2Na \cdot 3H_2O$ (Acros organic, pure) and $CH_3AsNa_2O_3 \cdot 6H_2O$ (Supelco Analytical), respectively. Prior to use, speciation analyses are performed weekly to check the stability of As species in standard solutions.

Plastic containers and DGT components (DGT research Ltd.) are acid-cleaned in 10% (v/v) HNO_3 and rinsed thoroughly with ultrapure water prior to use. In order to check the stability of temperature and pH, the test solutions are regularly controlled throughout each experiment. The stability of the concentrations of As species is controlled as well, by sampling at the beginning and at the end of each experiment aliquots for ICP–MS determination.

Concentrations of dissolved elements are determined by using an ICP–MS (X series, Thermo Elemental). ICP–MS spectrometer is calibrated using standard solutions prepared in 2% (v/v) HNO_3. Ge

(Astasol, Czech Metrology institute) is used as internal standard to account for instrument drifts. It is added *on line* in all samples at around 15 μg L^{-1} using a trident kit (Glass expansion) that is connected next to the peristaltic pump.

Arsenic speciation in solution is determined by coupling ICP–MS to a High Performance Ion Chromatography (HPIC; Dionex ICS 5000+ TC and SP) following the procedure described by Gorny et al. [6].

2.1.1. Synthesis and characterization of $ZnFe_2O_4$ particles

The synthesis of zinc ferrite precipitate is performed in laboratory by precipitation at pH 11 following the procedure described by Hu et al. [20]. Precipitation occurs according to Eq. (1):

$$2Fe^{3+} + Zn^{2+} + 8OH^- \rightarrow ZnFe_2O_4\ (s) + 4H_2O \quad (1)$$

First, 20 mmol of $ZnCl_2$ (Acros Organics) and 40 mmol of Fe $(NO_3)_3 \cdot 6H_2O$ (Acros Organics) is dissolved in 200 mL of MQ water. The pH of the resulting mixture is then adjusted precisely to 11 using a 1 M NaOH solution (Backer analysis) while stirring vigorously. The mixture is heated at reflux (70 °C) for 2 h to obtain a characteristic orange-red $ZnFe_2O_4$ precipitate. After the formation of the precipitate, the supernatant solution is removed by centrifugation. $ZnFe_2O_4$ particles are washed 3 times with ultrapure water in order to remove the dissolved salts (*i.e.* Cl^-, NO_3^-, Na^+ and OH^-); the separation between the liquid and the solid phase is performed by centrifugation (2500 rpm during 20 min). Wet $ZnFe_2O_4$ particles are finally stored at 4 °C in the dark before incorporation in an agarose–polyacrylamide hydrogel.

Grain size distribution of wet $ZnFe_2O_4$ particles is determined by laser granulometry (Malvern Master-sizer 3000 hydro LV). The air-dried and calcinated $ZnFe_2O_4$ particles are analyzed by X-ray diffraction, using a D8 advance Bruker AXS diffractometer equipped with a Cu anode (CuK_{alpha}) and a 1D LynxEye PSD detector. The specific surface area of zinc ferrite particles is measured with a Brunaeur, Emmett and Teller (BET) surface area analyzer (Sorptomatic 1990 Carlo Erba) at −196 °C [21]. To characterize the point of zero charge of $ZnFe_2O_4$ particles, the zeta potential of $ZnFe_2O_4$ solution at 50 g L^{-1} is determined at 25 °C in a pH range comprised between 2.5 and 12 using a Zetasizer Nano ZS90 Zetameter (Malvern Instruments).

2.2. General DGT procedures

2.2.1. Gel and binding gel preparation

The preparation of DGT pistons and probes is carried out according to Zhang et al. [22] and Price et al. [17] procedures. The "DGT pistons" (DGT Research Ltd.) are 2.5 cm in diameter with a window of 2.0 cm in diameter and the DGT probes (DGT Research Ltd.) are 180 × 40 mm^2, with a window of 150 × 18 mm^2 in contact with the sediment. An agarose–polyacrylamide hydrogel consisting of 15% acrylamide (Merck) and 0.3% agarose derived cross linker (DGT Research Ltd.) is selected as a diffusive gel. Different binding agents are used to make the binding gels, *i.e.* 3-mercaptopropyl functionalized silica gel (Sigma-Aldrich, St. Louis, MO) for As(III), Metsorb® HMRP 50 (Graver technologies, Glasgow, DE, USA) and $ZnFe_2O_4$ for total As. 0.3–0.5 g equivalent dry of these binding agents are mixed with a 3.5 mL polyacrylamide gel solution [22]. Afterwards, 20 μL of freshly prepared ammonium persulphate initiator 10% (w/v) (Merck, electrophoresis) and 6 μL of *N*, *N*,*N*′,*N*′-tetramethylethylenediamine (99%, Merck, GR for analysis) are added and well mixed. These solutions are then cast between two acid-cleaned glass plates separated by a 0.5 mm plastic spacer and immediately placed into a 45 °C oven for 45 min. Once the binding gel is completely polymerized, it is removed from the glass plates, rinsed 3 times and placed into a MQ water bath until reaching complete hydration. To prepare the ferrihydrite binding gel, the diffusive gels made previously are placed into a 0.1 M Fe $(NO_3)_3$ bath for at least 2 h. Once the equilibrium is reached, the gels are rinsed briefly with MQ water in order to remove the excess of reagents and are then placed in a 2-(N-morpholino)ethanesulfonic acid (MES) buffer solution (0.05 M; Acros Organics) adjusted at pH 6.7 in order to precipitate ferrihydrite in the gels. The new ferrihydrite binding gels are finally removed from the buffer solution after 30 min of contact, rinsed, and stored in MQ water. Note that the thickness of all the prepared binding gels is 0.8 mm after total hydration. DGT probes are assembled as detailed in Zhang et al. [22] using a 0.45 μm cellulose nitrate membrane filter (Sartorius, Germany).

2.2.2. Elution time

After deployment, the DGT pistons or probes are recovered and rinsed with ultrapure water before the binding gels are put into pre-weighted clean plastic tubes. Each binding gel is weighed and then placed in 2 mL of eluent for 24 h before analysis. The eluent is composed, in this study, of ultrapure nitric acid (1 M) for 3MP, ferrihydrite and $ZnFe_2O_4$ binding gels, and, in addition contain KIO_3 at 0.01 mol L^{-1} for the treatment of the 3MP binding gel (Table 1). A sodium hydroxide eluent (1 M) is exclusively used for Metsorb® binding gel.

2.2.3. Calculation of DGT concentration

The As(III) concentration ($C_{As(III)}$ in μg L^{-1}) in the solution measured by the use of the 3MP DGT is estimated using Eq. (2) [22].

$$C_{As(III)} = M_{As(III)}\Delta g/(D_{As(III)}tA) \quad (2)$$

where $M_{As(III)}$ is the accumulated mass of As(III) (μg), Δg the thickness of both the diffusive gel and the filter membrane (dm), $D_{As(III)}$ is the diffusion coefficient of As(III) in the gel ($dm^2\ s^{-1}$), t is the deployment time (s) and A is the exposure area (dm^2). The As (V) concentration ($C_{As(V)}$ in μg L^{-1}) is achieved indirectly (Eq. (3)–(5)) by subtracting the fraction of As(III) from the total amount of As accumulated onto the ferrihydrite, Metsorb® or ferrite binding gels.

$$M_{total} = M_{As(III)} + M_{As(V)} \quad (3)$$

$$M_{total} = tA/\Delta g_*(C_{As(III)}D_{As(III)} + C_{As(V)}D_{As(V)}) \quad (4)$$

$$C_{As(V)} = (M_{total}\Delta g/tA - C_{As(III)}D_{As(III)})/D_{As(V)} \quad (5)$$

where M_{total} and $M_{As(V)}$ are the mass accumulated of total As and As(V) respectively (μg), $D_{As(V)}$ is the diffusion coefficient of As(V) in the diffusive gel ($dm^2\ s^{-1}$). Since organic As(V) species concentration is very low in sediment pore waters [1], it is assumed that they will not contribute significantly to overestimating the As (V) fraction measured by DGT. The diffusion coefficients, as determined in the present study, and elution factors (3MP and Metsorb® binding gels) are used for calculating the DGT-measured concentrations (Table 1). Since ferrihydrite and $ZnFe_2O_4$ particles are totally dissolved in 1 M HNO_3 after 24 h, the elution factor for ferrihydrite and $ZnFe_2O_4$ binding gel is 100% for total As.

2.3. Laboratory evaluation of the $ZnFe_2O_4$-DGT performances

For performance evaluation of the new $ZnFe_2O_4$ binding gel in DGT pistons, all the experiments are carried out in triplicate. Standard deviations are displayed graphically. In total, over 300 DGT pistons have been used for this study.

2.3.1. Evaluation of diffusion coefficients

The accumulation of As species over time is determined by deploying seven sets of triplicate DGT pistons using $ZnFe_2O_4$ binding gel in 6 L polypropylene (PP) containers of either As(III), As(V), $DMAA^V$ or $MMAA^V$ at 25 μg L^{-1} in a buffered solution [0.1 M H_3BO_3 (Acros organics)] adjusted to pH 7.5 with a 1 M NaOH solution. Accumulation tests of organic As(V) species (although generally negligible in sediment pore waters [1]) are also performed in order to evaluate the selectivity of $ZnFe_2O_4$ binding gels. All of these experiments are carried out in a thermostatic room (20 °C) to maintain steady state conditions in solution during DGT pistons exposition. Pistons are removed after deployment times of 0, 0.25, 0.5, 1, 2, 3, 6, 9 and 24 h, washed with ultrapure water and stored at 4 °C in a sealed plastic bag until elution.

Diffusion coefficients, D_i (dm^2 s^{-1}), are calculated using Eq. (6):

$$D_i = (\text{slope}_* \Delta g)/C_i A \quad (6)$$

where A (dm^2) is the exposed area, Δg (dm) is the thickness of diffusive gel and membrane filter, and C_i (μg dm^{-3}) is the concentration of As species in the buffer solution [22]. The slope (μg^{-1} s^{-1}) was calculated from linear interpolation of the mass of As species as a function of the deployment time.

2.3.2. Effective elution time

A set of DGT pistons using ferrite binding gels are placed into 6 L plastic containers (PP) with ultrapure water and a spiking solution of As(III) or As(V) at 1 g L^{-1} to adjust As concentration at 25 μg L^{-1}. After a 24 h deployment, the $ZnFe_2O_4$ binding gels are eluted using 2 mL of 1 M HNO_3. To optimize the elution time for the complete arsenic elution, several elution times are tested in triplicate: 0, 1, 3, 6, 9 and 24 h. Note that neither different concentrations of HNO_3 nor the use of other eluents (*e.g.* HCl, H_2SO_4, H_3PO_4 or NaOH) have been tested here. Indeed, spectral interferences are commonly encountered in ICP–MS analysis when using HCl eluent [23] especially for arsenic, and non-spectral interferences (signal suppression, plasma instability and/or deposition on ICP–MS cones) can be produced when using H_2SO_4, H_3PO_4 or NaOH eluents [19,24,25].

2.3.3. Selectivity and complexing capacity as a function of pH

To evaluate the pH range of performance of the $ZnFe_2O_4$ binding gel, $ZnFe_2O_4$-DGT probes are deployed in 6 L plastic containers (PP) with either inorganic As(III) or As(V) (10 and 25 μg L^{-1} tested) and pH ranging from 5 to 9 by addition of a buffer. Buffer solutions at 0.1 M are prepared from CH_3CO_2H solution [96%, Merck] ($pH_{buffer}=5$), sodium 2-(N-morpholino)ethanesulfonate [Acros Organics] ($pH_{buffer}=6$), sodium 4-(2-hydroxyethyl)-1-piperazineethanesulfonate [Acros Organics] ($pH_{buffer}=7$) and H_3BO_4 salts [Merck, pro analysis] ($pH_{buffer}=8$ and 9). pH values of these five solutions were adjusted using HNO_3 (1 M) or NaOH (1 M) solutions. The last experiments are performed in the same conditions using different sets of DGT probes coupled with the other binding gels (*i.e.*, 3MP, ferrihydrite and Metsorb®) for comparison. Note that in this study, organic As(V) species ($MMAA^V$ and $DMAA^V$) are not taken into account since they are not detected during the field study.

2.3.4. Sorption capacity

The sorption capacity of $ZnFe_2O_4$ binding gel (*i.e.*, the maximum amount of analyte linearly accumulated according to DGT theory [26]) are determined by deploying DGT probes in borate buffer solution adjusted at pH 7.5 spiked at 10 mg L^{-1} of each inorganic As components separately. Several deployment times are tested in triplicate: 0, 1, 2, 3, 4, 7, 13 and 15 h.

2.3.5. Effect of Ionic strength on DGT performance

To examine the efficiency of the $ZnFe_2O_4$ binding gel inside a wide ionic strength range at $pH=5\pm0.2$, DGT probes are placed into plastic containers spiked at 10 μg L^{-1} of each inorganic As compound separately with the following concentrations of $NaNO_3$: 0, 0.01, 0.1 and 1 mol L^{-1}.

2.3.6. Effect of natural competing anions on binding gel performances

To compare the accumulation efficiency of the binding gels (ferrihydrite, Metsorb® or $ZnFe_2O_4$) for measuring total As in the presence of potential anionic species found in natural waters, DGT probes are deployed in 2 L plastic containers (PP) with either inorganic As(III) or As(V) (25 μg L^{-1} tested) in the presence of phosphates (10 mg L^{-1} prepared from an Astasol standard solution at 1 g L^{-1}), sulfates [2 g L^{-1} prepared from Na_2SO_4 (Prolabo, RP normapur)] or chlorides [20 g L^{-1} prepared from NaCl (Prolabo, RP normapur)], at pH 8.5 [prepared with a mixture of boric acid (0.1 mol L^{-1}) and sodium hydroxide for adjusting the pH value (Merck, proanalysis)]. These values correspond to concentrations commonly found in river sediment pore waters for phosphates [27], and in seawaters for chlorides and sulfates [28].

3. Results and discussion

3.1. Surface characterization of zinc ferrite particles

The freshly prepared $ZnFe_2O_4$ particles have a size ranging from 0.5 to 50 μm. More precisely, the volume diameter of particles defining the 10%, 50% and 90% of the cumulative volume undersize is 4.58, 13.2 and 29.4 μm, respectively. The XRD diffraction analysis of the air-dried powder shows no peaks indicating that amorphous material is formed during the synthesis of the $ZnFe_2O_4$ particles. Once the powder has been calcined at 450 °C (48 h), only the characteristic peaks of $ZnFe_2O_4$ (Franklinite) have been identified using the JCPDS-International Center for Diffraction Data (ICDD) (JCPDS-ICDD file 22-1012). The specific surface area of the air-dried $ZnFe_2O_4$ particles is 152 m^2 g^{-1}. This value is relatively close to those of the ferrihydrite (180 m^2 g^{-1}) [29] and Metsorb® particles (196 m^2 g^{-1}) [22], suggesting similar sorption capacities. The point of zero charge of $ZnFe_2O_4$ particles is around 8.1 (Fig. 1), which is higher than the one reported for ferrihydrite (7.5) [29] and Metsorb® particles (5.8) [22]. As a result, the number of cationic exchange sites should be more important for $ZnFe_2O_4$ particles than ferrihydrite and Metsorb® particles when pH is basic which is the case in most of sea or riverine water bodies. Consequently, stronger electrostatic interactions should be observed

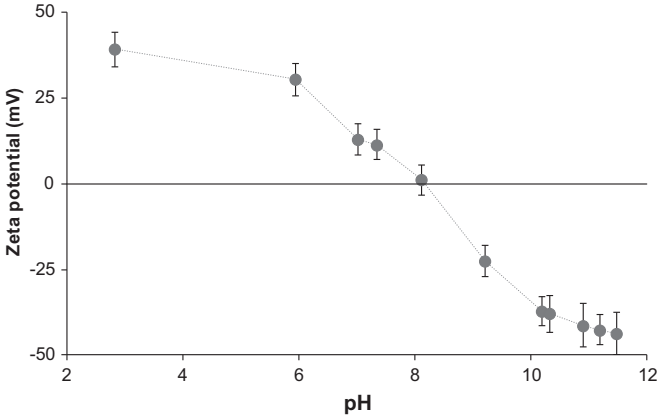

Fig. 1. Zeta potential of $ZnFe_2O_4$*vs* pH.

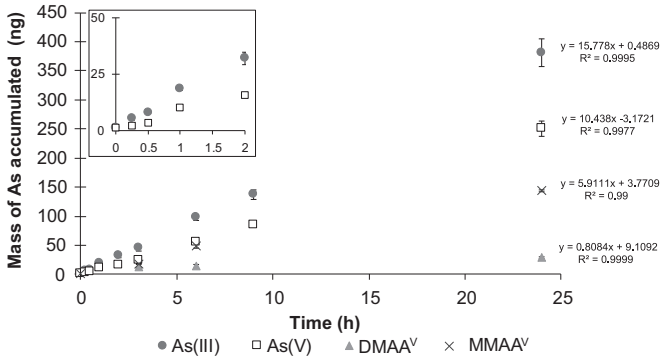

Fig. 2. Mass of As accumulated on $ZnFe_2O_4$ binding gel *vs* time. The linear regression coefficients and equation are plotted for the set of points. Experimental conditions: [As]=20 μg L^{-1}; pH 7.50 ± 0.2.

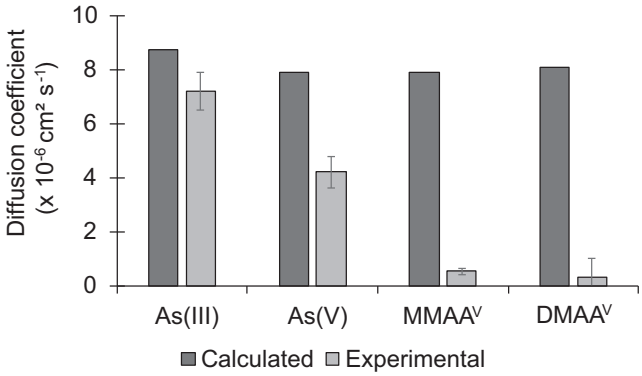

Fig. 3. Comparison of the diffusion coefficient values obtained by calculation (Eq. (8)) and experimentally.

between $ZnFe_2O_4$ surface sites and anionic arsenic species at high environmental pH values, leading to a better As accumulation on the Zn-ferrite binding gel.

3.2. Mass accumulation over time

To validate the performances of the new Zn-ferrite binding gel as a DGT binding agent, its capacity to accumulate target species through time must be evaluated. For that purpose, the accumulation kinetic of arsenic species [As(III), As(V), $DMAA^V$ and $MMAA^V$] onto the Zn-ferrite binding gel is studied separately up to 24 h of DGT deployments in solutions. As shown in Fig. 2, a lower accumulation rate is observed for inorganic As(III) and As (V) species over the first 30 min of deployment, corresponding to the diffusion time of analytes through the membrane filter and diffusive gel before the establishment of a steady-state concentration-gradient. The residence time t_r (min) of dissolved As species in the membrane filter and the diffusive gel can be estimated using Eq. (7) [30]:

$$t_r = (\Delta g')^2/2D \quad (7)$$

where $\Delta g'$ is the thickness of the membrane filter and diffusive gel (dm), and D the diffusion coefficient of species ($dm^2\ s^{-1}$). The residence times estimated using Eq. (7) are 11 and 18 min for As (III) and As(V), respectively. These results are consistent with the delay before a linear regime can be observed. After the transient period [15 and 30 min for As(III) and As(V), respectively], a linear regime is observed for each analyte with a strong linearity ($R^2 \geq 0.99$). These results confirm that the $ZnFe_2O_4$ binding gel is an appropriate sorbent to be used in DGT probes to sample total As species (including methylated species) in aquatic systems.

3.3. Diffusion coefficient

The diffusion experiments described above also allow the evaluation of the diffusion coefficients (D_i) for each arsenic species at fixed temperature using Eq. (6). The calculated D_i values are given in Table 1, and are of the same order of magnitude than values found in the literature (Table 1). The relatively scattered values can be explained by both different experimental conditions (*e.g.* ionic strength, pH, As concentration tested and counter ions) and the manufacturing processes of DGT (*e.g.* chemical composition or porosity changes of the diffusive gel, [30]). In this study, the mobility of As through the diffusive gel is classified in the following order: As(III) > As(V) > $MMAA^V$ > $DMAA^V$. This result is in accordance with Eq. (8) [31], where the diffusive coefficient of an arsenic compound in water is found to be inversely proportional to the cubic root of its molar mass although other parameters such as hydration level of the gel, pH and ionic strength of solution are also important [32,33].

$$D_i = 3.3 \times 10^{-5}/Mw^{1/3} \quad (8)$$

In Eq. (8), D_i is the diffusion coefficient ($cm^2\ s^{-1}$) and Mw is the molar mass of the fully protonated species ($g\ mol^{-1}$). Calculated diffusion coefficients of the fully protonated As species are displayed in Fig. 3. Important differences are observed for $DMMA^V$ and $MMAA^V$ between the experimental and the calculation determinations. Underestimation of the diffusion coefficients (determined experimentally) may result in a low accumulation on $ZnFe_2O_4$ binding gel at pH 7.5. Indeed, several studies have already established that increasing substitution of methyl to hydroxyl groups of As(V) decreases As sorption on aluminum and iron oxide surfaces [34–36].

3.4. Elution efficiency

Several elution times of $ZnFe_2O_4$ binding gel are tested after As exposition to evaluate the optimal recovery rate of each inorganic As species. The recovery rate of arsenic increases through the progressive dissolution of $ZnFe_2O_4$ particles dispersed in the polyacrylamide gel during elution. The release of As(III) occurs faster than As(V), suggesting different chemical bondings between inorganic As species and the surface sites of $ZnFe_2O_4$. Indeed, it is usually recognised that As(III) is more labile than As(V) [37]. The highest recovery rates are obtained after 24 h of elution where a complete dissolution of $ZnFe_2O_4$ particles has occurred, allowing for the total release of As(III) and As(V). Methylated As(V) species are also totally eluted after 24 h.

Consequently, $ZnFe_2O_4$ binding gels are eluted in 2 mL of 1 M HNO_3 for 24 h, and an elution factor of 1 is applied in the C_{DGT} calculations for all the experiments. Furthermore, As species can also be eluted using diluted NaOH (Table 1), but the quantification of As concentration in the NaOH matrix is challenging due to a strong attenuation of signal [decrease of As ionization efficiency due to high sodium content] in ICP–MS measurements [17].

3.5. Sorption capacity

To ensure accurate calculation of As concentration through Eqs. (2) and (5), it is necessary to estimate the maximal sorption capacity of $ZnFe_2O_4$ binding gel. Consequently, accumulation kinetic experiments with high As concentration (10 mg L^{-1}) have been performed to determine this capacity for each inorganic As species. As presented Fig. 4, the mass of inorganic As species accumulated by $ZnFe_2O_4$ binding gel agrees well with calculated DGT

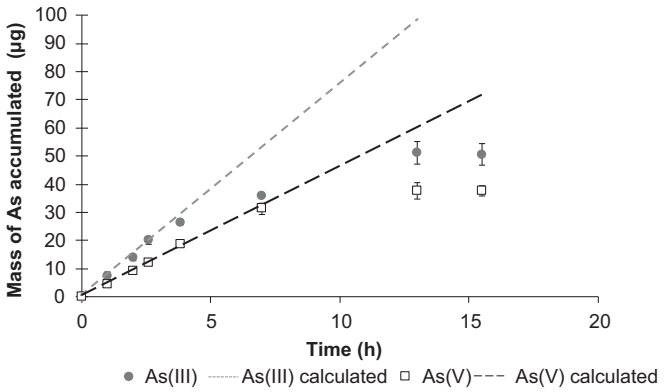

Fig. 4. Results of capacity experiment showing mass of inorganic As species accumulated by $ZnFe_2O_4$ binding gel as a function of time. The dotted line represents the predicted accumulated mass of inorganic As species calculated using the DGT equation. Experimental conditions: [As] = 10 mg L^{-1}; pH 7.50 ± 0.2.

response (dotted line) up to 3.5 and 7 h for As(III) and As(V), respectively. These results show also once again the better As(III) mobility into the diffusive gel than that of As(V).

The sorption capacities of $ZnFe_2O_4$ binding gel reach up to 54 000 and 37 000 ng for As(III) and As(V), respectively. For approximately the same amount of sorbent in binding gel (0.3–0.4 g), ferrihydrite and Metsorb® binding gels have lower capacity for As (III), their sorption capacity being respectively 22 500 and 8500 ng [38]. As for As(V), the sorption capacity decreases as follows: Metsorb® (82 000 ng) > $ZnFe_2O_4$ (37 000 ng) > ferrihydrite (31 500 ng) [38]. Finally, these results suggest that $ZnFe_2O_4$ binding gel is far from the saturation when the deployments of the DGT are performed for several days in aquatic systems with As concentrations at µg L^{-1} levels.

3.6. Effect of pH and Ionic strength

Several pH and ionic strengths are tested to assess the validity

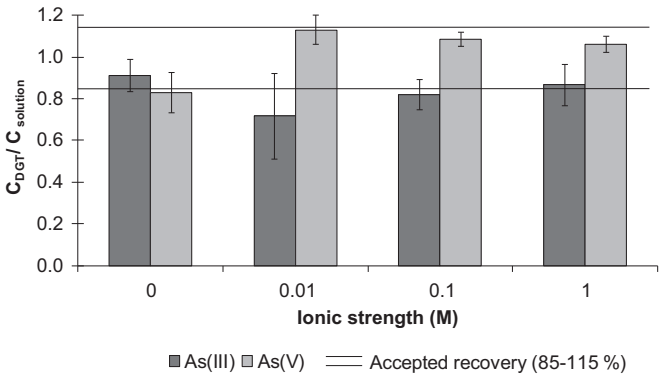

Fig. 6. Influence of ionic strength on the performance of $ZnFe_2O_4$-binding gel. Experimental conditions: [As] = 20 µg L^{-1}; pH 5 ± 0.2.

range of the $ZnFe_2O_4$ binding gel. These performances are also compared with the other binding gels (3MP, ferrihydrite and Metsorb®) from triplicate experiments performed simultaneously.

The influence of pH on the accumulation efficiency of As(III) and As(V) is presented in Fig. 5. Two limits are added to the graph to underline acceptable DGT performances assuming a 15% error for $C_{DGT}/C_{solution}$ [14]. DGT measurements using $ZnFe_2O_4$ binding gel are quantitative for a pH ranging from 5 to 9 and regardless the ionic strength (Fig. 6). These results highlight that this binding gel is a fully operational passive sampler for the determination of total dissolved As concentration in the pH range of natural waters (both freshwaters and seawaters).

Acceptable results for As(III) and As(V) are also obtained using ferrihydrite and Metsorb® binding gels in pH ranging from 5 to 8 (Fig. 5B and C). However, the As(III) concentration (C_{DGT}) is underestimated by 20–30% using the ferrihydrite binding gel between approximately pH 5 and 7, and an overestimation is observed for As(V) using the Metsorb® binding gel for pH > 8, contrary to the $ZnFe_2O_4$ binding gel. Note that the lack of reproducibility encountered with the Metsorb® binding gel can be related to

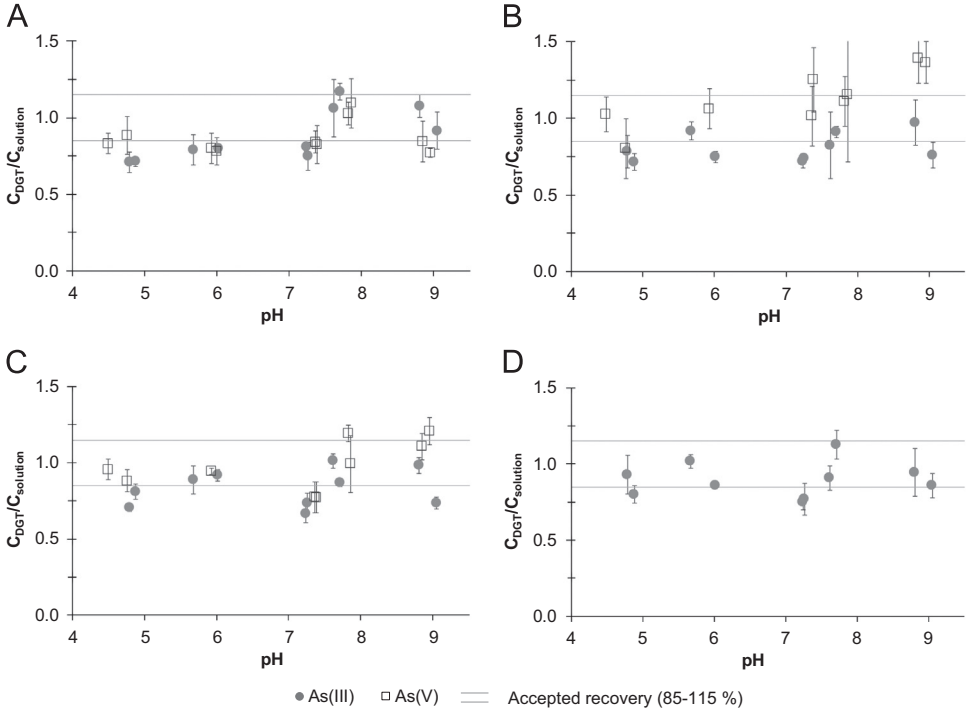

Fig. 5. Influence of pH (4–9) on the performance of (A) ferrihydrite, (B) Metsorb®, (C) $ZnFe_2O_4$ and (D) 3MP binding gels in standard solutions. Experimental conditions: [As] = 10–20 µg L^{-1}.

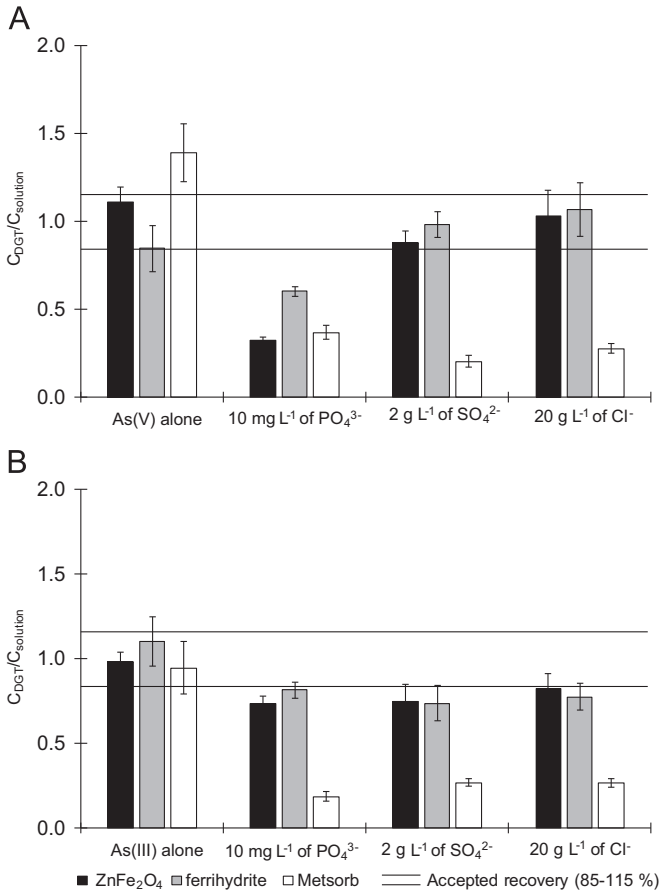

Fig. 7. Effects of competing anions for the determination of (A) As(V) and (B) As(III) using ferrihydrite, Metsorb® and $ZnFe_2O_4$. Experimental conditions: [As]= 20 μg L^{-1}; pH=8.5.

the NaOH eluent, which is necessary for the elution of As species. Besides, the quantification limit, as determined with 10 DGT-blanks, is very high for the Metsorb® binding gel (~50 ng) compared with the 3MP, ferrihydrite and $ZnFe_2O_4$ binding gels (~5 ng). Consequently, the Metsorb® binding gel is less useful for the determination of total As at ultra-trace levels. 3MP binding gel accumulates selectively As(III) (Fig. 5D) with an acceptable sorption capacity whatever the pH values.

Finally, these tests reveal that the determination of As redox speciation in the aquatic systems is reliable through the deployment of two different DGT probes, *i.e.* the $ZnFe_2O_4$ binding gel for total As determination and the 3MP binding gel for As(III). The ferrihydrite binding gel also produces good results for pH > 7, whereas Metsorb® binding gel shows more scattered results whatever the pH.

3.7. Effect of competing anions

Additional experiments were performed at pH 8.5 to clarify the effects of competing anions (chlorides, phosphates and sulphates) on the accumulation efficiency of inorganic As species onto ferrihydrite, Metsorb® and $ZnFe_2O_4$ binding gels.

Results are displayed in Fig. 7. Accumulation of inorganic As species on the Metsorb® binding gel always displays interferences (recovery < 40%) whatever the competing anions. Due to a relatively low pH_{PZC} (5.8), the amount of positive surface sites of the Metsorb® binding gel may limit the accumulation of As species in presence of other anions like chlorides and sulfates. These results are inconsistent with those obtained by Bennett et al. [14], but the pH value is not mentioned in their study, limiting the present discussion. Regarding our results, it appears that the Metsorb® binding gel is not appropriate for determining As speciation in seawater and/or in phosphates-rich matrix.

Conversely, acceptable results are obtained in the presence of chlorides and sulfates using ferrihydrite and $ZnFe_2O_4$ binding gels. However, the presence of phosphates mainly affected the quantification of As(V) concentration at 40% and 60% of recovery respectively for the $ZnFe_2O_4$ and ferrihydrite binding gels. In both cases, phosphates appear to be the main competing ion due to their chemical similarity with As(V) [1]. Finally, the most adapted binding gels for measuring total As in marine and riverine sediment pore waters are the ferrihydrite and $ZnFe_2O_4$, although phosphates at high concentrations partly hinder the response of inorganic As(V) species. Note further that chlorides which are sampled by the binding agents used (ferrihydrite, Metsorb® and $ZnFe_2O_4$), can also impact ICP–MS measurements by generating spectral interferences. Complementary studies dedicated on the selectivity of these binding gels for chlorides should be carried out, thus permitting to select the binding gel accumulating the lower content of chlorides.

3.8. Validation of As speciation

Prior to field deployment, we ensured that the determination of As redox speciation using the combination of Zn-ferrite and 3MP binding gels was valid by comparing the results with HPIC-ICP–MS measurements. For that purpose, the two different DGT were mounted in triplicate back-to-back on vertical plastic holders and were deployed in a borate buffer solution adjusted to pH 8 with As(III)/As(V) weight ratio of 1/0, 3/1, 1/1 and 0/1 (the total concentrations of arsenic never exceeded 50 μg L^{-1}). After 24 h of exposition, binding gels were eluted (following the optimized procedure described in Section 3) and the concentrations of As in the eluates measured by ICP–MS. Initial As(III) concentrations were directly calculated from Eq. (2), and As(V) concentrations obtained indirectly from Eq. (5). In parallel, the As redox speciation in the deployment solution were monitored with ICP–MS and HPIC-ICP–MS.

Correct recoveries between the sum of inorganic As and total As species were obtained between ICP–MS and DGT techniques (> 85%). In addition, the arsenic redox signature is similar whatever the speciation tool used (either the DGT probes or the HPIC-ICP–MS), as shown in Table 2. These preliminary results clearly confirm that the DGT techniques using a combination of binding gels disposed back to back can be a powerful speciation tool for the study of arsenic in aquatic environments.

Table 2
Comparison for the measurement of As speciation [considering inorganic As(III) and As(V) species] between DGT technique and HPIC-ICP–MS.

Theoretical speciation		Speciation obtained by HPIC-ICP–MS method	Speciation obtained by HPIC-ICP–MS method	Speciation obtained by DGT technique	
As(III) (%)	As(V) (%)	As(III)(%)	As(V)(%)	As(III)(%)	As(V)(%)
0	100	100.0 ± 10.0	< LD	100 ± 5.1	< LD
70	30	69.6 ± 8.7	30.4 ± 3.8	69.3 ± 6.1	30.7 ± 7.6
50	50	48.8 ± 6.0	51.2 ± 6.3	44.2 ± 6.2	55.8 ± 10
100	0	3.4 ± 0.9	96.64 ± 4.3	< LD	100 ± 14

Table 3
Values of Eh (*vs* SHE), pH, and concentrations of As(III) and As(V) determined by the combination of 3MP with either zinc ferrite, ferrihydrite or Metsorb® in overlying water and pore waters of the Marque River. Abbreviation: n.d.: the difference of As accumulation in the 3MP and the other binding gel is less than 20% and does not permit to quantify precisely As(V) concentration; SHE: Standard Hydrogen Electrode.

Depth (cm)	Eh (mV *vs* SHE)	pH	total As (μg L^{-1})	[As(III)] by 3MP (μg L^{-1})	[As(V)] by Zn-ferrite (μg L^{-1})	[As(V)] by ferrihydrite (μg L^{-1})	Bias *vs* Zn-ferrite (%)	[As(V)] by Metsorb® (μg L^{-1})	Bias *vs* Zn-ferrite (%)
2.2	154	7.89	0.71	0.29	n.d.	n.d.		n.d.	
1.2	154	7.89	0.71	0.29	n.d.	n.d.		n.d.	
-0.80	116	7.53	6.00	0.36	0.41	0.44	6	n.d.	
-1.80	111	7.44	5.71	0.51	2.00	2.15	7	n.d.	
-2.80	101	7.46	5.65	0.65	3.29	3.54	7	1.53	53
-3.80	106	7.22	6.26	1.30	2.34	2.50	6	n.d.	
-4.80	72	7.19	7.32	2.21	1.19	1.24	4	1.71	43
-5.80	64	7.07	8.67	1.66	3.29	3.52	7	7.93	140
-6.80	64	7.02	9.32	1.14	4.72	5.07	7	7.57	60
-7.80	74	6.96	9.76	1.43	3.69	3.95	7	6.27	70
-8.80	65	6.93	9.95	1.27	2.38	2.54	7	4.02	69

4. Application of the speciation method to anoxic sediment of marque river

Several sediment cores were collected in the Marque River (50°40′53.2″N 3°06′45.7″E) in March 2014 using a manual corer with a 35 cm perspex tube (7.5 cm diameter). This non-contaminated sampling site towards As was chosen to evaluate DGT technique performance regarding As redox speciation. The site is characterized by a high fine fraction (~90% of sediment particles < 63 μm), by about 5% of organic carbon content and by 1% of particulate inorganic carbon (unpublished work). Since the river flow is relatively low and fluvial traffic has stopped for years, the sediment column is not disturbed by massive re-suspension events allowing the observation of a clear redox gradient at the water–sediment interface. Note that prior to deployment, the DGT probes are de-oxygenated by immersing them for 24 h in a container with $NaNO_3$ (0.01 M) solution. After deployment, the probes are rinsed quickly with MQ water and placed in a well humidified plastic box before laboratory treatment. Each binding gel is then cut into 10-mm intervals using a Plexiglas gel cutter, weighed in tubes and then eluted in a 2 mL eluent for 24 h prior to ICP–MS analysis.

The results are displayed in Table 3. The overlying waters are poorly oxygenated and sediments are anoxic with Eh values down to 68 mV [*vs* Standard Hydrogen Electrode (SHE)]. A gradual decline in pH values, from 7.9 to 6.8, is observed with depth in the sediment, a result of active mineralization of the labile organic matter [39].

As the sediment is anoxic and the water poorly oxygenated, As (III) concentrations in overlying and pore waters are easily measured using the 3MP binding gel, with a global increase of As(III) concentration when redox potential values are decreasing. The calculations of As(V) concentrations from the deployment of the ferrihydrite and $ZnFe_2O_4$ binding gels provide similar results, with a bias below 10% all along the sediment core. Conversely, the results obtained by using the Metsorb® binding gel show significant differences with a bias generally exceeding 50%. Neither is the use of the Metsorb® binding gel appropriate for the measurement of As(V) in the pore waters of these sediments, nor least because the detection limit of our protocol for this binding gel was too high. Also, an unexpected detection of As(V) was observed in these sediments suggesting that some ligands, *e.g.* sulfides, may stabilize dissolved As(V) in anoxic pore waters [1]. This hypothesis is going to be studied further by using of HPIC-ICP–MS in pore waters and standard solutions of thioarsenic species.

In addition, significant differences between total As concentrations (measured by ICP–MS after pore water centrifugation under nitrogen and filtration of the supernatant) and the sum of inorganic As species estimated by the DGT technique (from values obtained with the 3MP and $ZnFe_2O_4$ binding gels) are observed. This can be attributed to two several possible phenomena: (i) the selective accumulation of only-free and kinetically labile species by DGT probes that does not include all the As species; and/or (ii) a rapid depletion of As species in the pore waters due to their accumulations in the DGT binding gel, resulting in a lower estimation of the calculated concentrations [40]. Further studies are underway to clarify these differences.

5. Conclusion

A new laboratory-made Zn-ferrite doped binding gel, has been fully tested in DGT probes for the measurement of total As [including inorganic As(III) and As(V), as well as $MMAA^V$ and $DMAA^V$] in sediment pore waters. The performance of the $ZnFe_2O_4$ binding gel has been established through accumulation tests as a function of pH, ionic strength and competing anions, and then compared with commonly-used binding gels (ferrihydrite and Metsorb®) for the determination of total arsenic. Several key points have emerged:

- The Zn-ferrite binding gel is at least as efficient as the two other binding gels, especially for pH values higher than 8 due to its high point of zero charge.
- The quantification limit is higher for the Metsorb® binding gel (−50 ng) than for the 3MP, ferrihydrite and $ZnFe_2O_4$ binding gels (−5 ng). In addition, the reproducibility of the results obtained with the Metsorb® binding gel is weaker than those obtained with the other binding gels.
- A better sorption capacity for As(III) is obtained with $ZnFe_2O_4$ compared to ferrihydrite and Metsorb binding gels.
- The Zn-ferrite and ferrihydrite binding gels are well adapted to total As measurement at low concentration (< 20 μg L^{-1}) due to the compatibility of HNO_3 eluent with ICP–MS measurements, as opposed to the Metsorb® binding gel that needs a basic eluent like NaOH.
- The most common binding gels for measuring total As in marine and riverine sediment pore waters are the ferrihydrite and $ZnFe_2O_4$ binding gels, although phosphates at high concentrations hinder the response of inorganic As(V) species. These results demonstrate that mathematical treatments of the results obtained by DGT should be considered in the future to account for interferences of competing ions.
- The methodology for determining As speciation by the DGT techniques (combination of two DGT probes with different selectivities) has been fully validated by HPIC-ICP–MS in synthetic solutions.

In addition, an environmental application has been successfully performed in the sediments of the Marque River demonstrating that the DGT technique can be used as a tool for speciation studies. However, no information is currently available on the possible accumulation of thio-arsenical species (which are commonly found in anoxic pore waters) on the four binding gels tested (3MP, ferrihydrite, Metsorb® and $ZnFe_2O_4$). Future research is therefore required on this specific point. Complementary studies should also be carried out to ensure no changes in the chemical properties and sorption capacity of $ZnFe_2O_4$ over time. This is an important point to get reproducible results, especially for routine applications when important series of binding gels are produced and stored several weeks before use.

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References

[1] J. Gorny, G. Billon, L. Lesven, D. Dumoulin, B. Madé, C. Noiriel, Arsenic behavior in river sediments under redox gradient: a review, Sci. Total Environ. 505 (2015) 423–434.
[2] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.
[3] T. Prohaska, G. Stingeder, Speciation of Arsenic, Handbook of Elemental Speciation II – Species in the Environment, Food, Medicine and Occupational Health, John Wiley & Sons, Ltd. (2005), p. 69–85.
[4] Y. He, Y. Zheng, D.C. Locke, Cathodic stripping voltammetric analysis of arsenic species in environmental water samples, Microchem. J. 85 (2007) 265–269.
[5] H.M. Anawar, Arsenic speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry, Talanta 88 (2012) 30–42.
[6] J. Gorny, D. Dumoulin, L. Lesven, C. Noiriel, B. Madé, G. Billon, Development and application of a HPIC-ICP–MS method for the redox arsenic speciation in river sediment pore waters, J. Anal. At. Spectrom. 30 (2015) 1562–1570.
[7] E. Terlecka, Arsenic speciation analysis in water samples: a review of the hyphenated techniques, Environ. Monit. Assess. 107 (2005) 259–284.
[8] R. Michalski, M. Jabłonska, S. Szopa, A. Łyko, Application of ion chromatography with ICP–MS or MS detection to the determination of selected halides and metal/metalloids species, Crit. Rev. Anal. Chem. 41 (2011) 133–150.
[9] P.M. Chapman, F. Wang, J.D. Germano, G. Batley, Pore water testing and analysis: the good, the bad, and the ugly, Mar. Pollut. Bull. 44 (2002) 359–366.
[10] B. Daus, J. Mattusch, R. Wennrich, H. Weiss, Investigation on stability and preservation of arsenic species in iron rich water samples, Talanta 58 (2002) 57–65.
[11] J.L. Gomez Ariza, E. Morales, D. Sanchez-Rodas, I. Giraldez, Stability of chemical species in environmental matrices, Trends Anal. Chem. 19 (2000) 200–209.
[12] M.-H. Tusseau-Vuillemin, R. Gilbin, M. Taillefert, A dynamic numerical model to characterize labile metal complexes collected with diffusion gradient in thin films devices, Environ. Sci. Technol. 37 (2003) 1645–1652.
[13] H. Zhang, W. Davison, Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution, Anal. Chem. 67 (1995) 3391–3400.
[14] W.W. Bennett, P.R. Teasdale, J.G. Panther, D.T. Welsh, D.F. Jolley, Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of AsIII by 3-mercaptopropyl-functionalized silica gel, Anal. Chem. 83 (2011) 8293–8299.
[15] J.G. Panther, K.P. Stillwell, K.J. Powell, A.J. Downard, Perfluorosulfonated ionomer-modified diffusive gradients in thin films: tool for inorganic arsenic speciation analysis, Anal. Chem. 80 (2008) 9806–9811.
[16] H. Österlund, M. Faarinen, J. Ingri, D.C. Baxter, Contribution of organic arsenic species to total arsenic measurements using ferrihydrite-backed diffusive gradients in thin films (DGT), Environ. Chem. 9 (2012) 55–62.
[17] H.L. Price, P.R. Teasdale, D.F. Jolley, An evaluation of ferrihydrite- and Metsorb™-DGT techniques for measuring oxyanion species (As, Se, V, P): effective capacity, competition and diffusion coefficients, Anal. Chim. Acta 803 (2013) 56–65.
[18] Q. Sun, J. Chen, H. Zhang, S. Ding, Z. Li, P.N. Williams, H. Cheng, C. Han, L. Wu, C. Zhang, Improved diffusive gradients in thin films (DGT) measurement of total dissolved inorganic arsenic in waters and soils using a hydrous zirconium oxide binding layer, Anal. Chem. 86 (2014) 3060–3067.
[19] B.P. Jackson, P.M. Bertsch, Determination of arsenic speciation in poultry wastes by IC-ICP–MS, Environ. Sci. Technol. 35 (2001) 4868–4873.
[20] J. Hu, I.M.C. Lo, G. Chen, Comparative study of various magnetic nanoparticles for Cr(VI) removal, Sep. Purif. Technol. 56 (2007) 249–256.
[21] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319.
[22] H. Zhang, W. Davison, R. Gadi, T. Kobayashi, In situ measurement of dissolved phosphorus in natural waters using DGT, Anal. Chim. Acta 370 (1998) 29–38.
[23] T.W. May, R.H. Wiedmeyer, A table of polyatomic interferences in ICP–MS, At. Spectrosc.—Norwalk Conn. 19 (1998) 150–155.
[24] A.A. Ammann, Arsenic speciation by gradient anion exchange narrow bore ion chromatography and high resolution inductively coupled plasma mass spectrometry detection, J. Chromatogr. A 1217 (2010) 2111–2116.
[25] E. Björn, W. Frech, Non-spectral interference effects in inductively coupled plasma mass spectrometry using direct injection high efficiency and microconcentric nebulisation, J. Anal. At. Spectrom. 16 (2001) 4–11.
[26] J.G. Panther, P.R. Teasdale, W.W. Bennett, D.T. Welsh, H. Zhao, Comparing dissolved reactive phosphorus measured by DGT with ferrihydrite and titanium dioxide adsorbents: anionic interferences, adsorbent capacity and deployment time, Anal. Chim. Acta 698 (2011) 20–26.
[27] L. Lesven, B. Lourino-Cabana, G. Billon, P. Recourt, B. Ouddane, O. Mikkelsen, A. Boughriet, On metal diagenesis in contaminated sediments of the Deûle river (northern France), Appl. Geochem. 25 (2010) 1361–1373.
[28] N. Gros, M.F. Camões, C. Oliveira, M.C.R. Silva, Ionic composition of seawaters and derived saline solutions determined by ion chromatography and its relation to other water quality parameters, J. Chromatogr. A 1210 (2008) 92–98.
[29] J. Zhu, M. Pigna, V. Cozzolino, A.G. Caporale, A. Violante, Sorption of arsenite and arsenate on ferrihydrite: Effect of organic and inorganic ligands, J. Hazard. Mater. 189 (2011) 564–571.
[30] H. Zhang, W. Davison, Direct in situ measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films, Anal. Chem. 72 (2000) 4447–4457.
[31] J. Buffle, Complexation Reactions in Aquatic Systems. An Analytical Approach, John Wiley & Sons Ltd., Chichester, 1988.
[32] W. Li, H. Zhao, P.R. Teasdale, F. Wang, Trace metal speciation measurements in waters by the liquid binding phase DGT device, Talanta 67 (2005) 571–578.
[33] M. Tanaka, Y. Takahashi, N. Yamaguchi, K.-W. Kim, G. Zheng, M. Sakamitsu, The difference of diffusion coefficients in water for arsenic compounds at various pH and its dominant factors implied by molecular simulations, Geochim. Cosmochim. Acta 105 (2013) 360–371.
[34] J. Zhang, R. Stanforth, S. Pehkonen, Effect of replacing a hydroxyl group with a methyl group on arsenic (V) species adsorption on goethite (α-FeOOH), J. Colloid Interface Sci. 306 (2007) 16–21.
[35] J. Zhang, R. Stanforth, Slow adsorption reaction between arsenic species and goethite (α-FeOOH): diffusion or heterogeneous surface reaction control, Langmuir 21 (2005) 2895–2901.
[36] H. Xu, B. Allard, A. Grimvall, Effects of acidification and natural organic materials on the mobility of arsenic in the environment, Water Air Soil Pollut. 57–58 (1991) 269–278.
[37] S. Fendorf, P.S. Nico, B.D. Kocar, Y. Masue, K.J. Tufano, Chapter 12—arsenic chemistry in soils and sediments, in: S. Balwant, G. Markus (Eds.), Developments in Soil Science, Elsevier, 2010, pp. 357–378.
[38] W.W. Bennett, P.R. Teasdale, J.G. Panther, D.T. Welsh, D.F. Jolley, New diffusive gradients in a thin film technique for measuring inorganic arsenic and selenium(IV) using a titanium dioxide based adsorbent, Anal. Chem. 82 (2010) 7401–7407.
[39] P.N. Froelich, G.P. Klinkhammer, M.L. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman, V. Maynard, Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis, Geochim. Cosmochim. Acta 43 (1979) 1075–1090.
[40] M.P. Harper, W. Davison, H. Zhang, W. Tych, Kinetics of metal exchange between solids and solutions in sediments and soils interpreted from DGT measured fluxes, Geochim. Cosmochim. Acta 62 (1998) 2757–2770.
[41] J. Luo, H. Zhang, J. Santner, W. Davison, Performance characteristics of diffusive gradients in thin films equipped with a binding gel layer containing precipitated ferrihydrite for measuring arsenic(V), selenium(VI), vanadium(V), and antimony(V), Anal. Chem. 82 (2010) 8903–8909.
[42] E. Moreno-Jiménez, L. Six, P.N. Williams, E. Smolders, Inorganic species of arsenic in soil solution determined by microcartridges and ferrihydrite-based diffusive gradient in thin films (DGT), Talanta 104 (2013) 83–89.
[43] J.G. Panther, R.R. Stewart, P.R. Teasdale, W.W. Bennett, D.T. Welsh, H. Zhao, Titanium dioxide-based DGT for measuring dissolved As(V), V(V), Sb(V), Mo (VI) and W(VI) in water, Talanta 105 (2013) 80–86.