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Publication Details

Bennett, W. W., Teasdale, P. R., Panther, J. G., Welsh, D. T. and Jolley, D. F. (2011). Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of AsIII by 3-mercaptopropyl-functionalized silica gel. Analytical Chemistry, 83 (21), 8293-8299.

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Keywords

Speciation, dissolved, inorganic, arsenic, diffusive, gradients, thin, films, selective, binding, AsIII, mercaptopropyl, functionalized, silica, gel, CMMB

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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This journal article is available at Research Online: http://ro.uow.edu.au/scipapers/3215

Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of As^{III} by 3-mercaptopropyl-functionalized silica gel

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Abstract

A diffusive gradients in thin films (DGT) technique for selectively measuring As^{III} utilizes commercially available 3-mercaptopropyl-functionalized silica gel. Deployment of the new technique alongside the Metsorb-DGT for total inorganic arsenic allows the calculation of As^{III} directly and As^{V} by difference. Uptake of As^{III} by mercapto-silica was quantitative and elution with a mixture of 1 mol L^{-1} HNO_3 and 0.01 mol L^{-1} KIO_3 gave a recovery of 85.6 ± 1.7%. DGT validation experiments showed linear accumulation of As^{III} over time (R^2 >0.998). Accumulation was unaffected by varying ionic strength (0.0001–0.75 mol L^{-1} $NaNO_3$) and pH (3.5–8.5). Deployment of mercapto-silica DGT and Metsorb DGT in seawater spiked with As^{III} and As^{V} demonstrated the ability of the combined approach to accurately quantify both species in the presence of potential competing ions. Ferrihydrite DGT, which has been previously reported for the measurement of total inorganic arsenic, was evaluated in seawater and shown to underestimate both As^{III} and As^{V} at longer deployment times (72 h). Reproducibility of the new mercapto-silica DGT technique was good (relative standard deviations <9%) and the average method detection limit was sufficiently low to allow quantification of ultra-trace concentrations of As^{III} (0.03 μg L^{-1}; 72 h deployment).

Introduction

The toxicity and bioavailability of environmental contaminants can be strongly influenced by their chemical speciation. In recent years, the importance of speciation analysis has been recognized by the environmental monitoring and assessment community, leading to the development of an increasing number of speciation techniques.[1] Unfortunately, speciation analysis is often complex and subject to problems related to species instability upon the removal of samples from the environment.[2] The problems associated with ex situ speciation measurements can be overcome by utilizing in situ measurement techniques. The in situ measurement of speciation enables accurate speciation analysis and can provide a time-integrated measurement of the contaminant concentration, which is more representative than traditional spot sampling measurements.[3]

Arsenic is an environmental contaminant whose toxicity and bioavailability are significantly influenced by speciation. The reduced inorganic arsenic species, arsenite (As^{III}), is more toxic than the oxidized inorganic species, arsenate (As^{V}), and the common organic forms, monomethyl arsenic (MMA) and dimethyl arsenic (DMA), are less toxic than the inorganic forms.[4] Arsenic is of particular concern in drinking waters, where it can significantly impact upon human health.[5] The monitoring of arsenic has traditionally involved the use of spot sampling followed by laboratory speciation analysis using HPLC-ICPMS, if required. This can provide an unrepresentative sample and there is the potential for changes in speciation to occur during transport and storage of the sample.[2] Some methods have attempted to reduce this problem by processing samples on-site through solid phase extraction cartridges to reduce the likelihood of changes in speciation.[6] This approach, however, does not address the unrepresentative nature of spot sampling and is problematic in high ionic strength waters such as seawater.

The diffusive gradients in thin films (DGT) technique has previously been used to measure total inorganic arsenic[7-9]. It has also been shown to provide highly representative information and, due to the in situ nature of the technique, avoid problems associated with changes in sample speciation.[10] This makes DGT an ideal candidate for modification to allow in situ speciation analysis of dissolved inorganic arsenic. This has been attempted by Panther and co-workers[11] by deploying two sets of DGT devices, one set with negatively charged perfluorosulfonated ionomer diffusive membranes (Nafion) and the other with the standard polyacrylamide hydrogel. As^{III} and As^{V} were speciated based on their charge with the uncharged As^{III} species (at neutral pH) passing through the Nafion membrane much faster than the charged As^{V}, allowing the concentrations of both oxidation states to be calculated. The use of this technique, however, is likely to be limited to low to moderate ionic strength waters, as at high ionic strengths the charged membrane could rapidly become saturated with major cations, rendering it ineffective. An alternative approach for in situ speciation of inorganic arsenic is to use selective adsorption of one or both species. This has been demonstrated previously by Ernstberger and co-workers[12] who used Chelex-100 to selectively measure Cr^{III} in the presence of Cr^{VI} and Bennett and co-workers[7] who used a titanium dioxide-based adsorbent (Metsorb) to selectively measure Se^{IV} in the presence of Se^{VI},.

In this research we take advantage of the selective adsorption of As^{III} by a mercaptopropyl-functionalized silica gel (mercapto-silica). Mercapto-silica has been previously used as a DGT binding agent for methylmercury,[13] but this is the first time it has been described for the selective measurement of As^{III} by DGT. Howard and co-workers[14] investigated mercapto-silica for batch preconcentration applications and confirmed that it selectively adsorbed As^{III} in the presence of As^{V}, monomethylarsonate (MMA) and dimethylarsinate (DMA). Additionally, they showed that adsorption was quantitative in seawater and over the pH range 1.5 – 8.5. In this study, mercapto-silica was evaluated as a selective As^{III} binding phase in the DGT technique and was deployed alongside the

Metsorb DGT method for total inorganic arsenic,[7] thus allowing the speciation of inorganic arsenic to be determined based on the differential measurement of As^{V}. This new approach for inorganic arsenic speciation was comprehensively evaluated over environmentally relevant pH and ionic strength ranges and tested in seawater.

Experimental

Reagents, materials and solutions. All experimental and reagent solutions were prepared using deionised water (Milli-Q Element, Millipore). As^{III} and As^{V} solutions were prepared from 1000 mg L^{-1} NIST-certified speciation standard solutions (High Purity Standards; Charleston, SC). Monomethylarsonate (MMA) and dimethylarsinate (DMA) solutions were prepared by dilution of 2000 mg L^{-1} stock solutions prepared by dissolving disodium methyl arsenate (Supelco) or sodium cacodylate hydrate (Fluka), respectively, in 0.001 % (v/v) HCl (Suprapur; Merck). 3-mercaptopropyl-functionalised silica gel (Sigma-Aldrich, St. Louis, MO), 200-400 mesh, was used as a selective DGT binding agent for reduced inorganic arsenic (As^{III}). Metsorb (Graver Technologies; Glasgow, DE) was used as a DGT binding agent for total inorganic arsenic, as reported previously.[7] The performance of Metsorb was also evaluated against ferrihydrite, another adsorbent used as a DGT binding agent for total inorganic arsenic, which was prepared as described by Panther and co-workers.[15]

Arsenic analysis. Dissolved metal concentrations were determined by inductively coupled plasma – mass spectrometry (ICPMS, Agilent 7500a). Yttrium (m/z 89) was used as an internal standard and quality control standards were analysed regularly throughout the analysis to ensure correction of instrument drift. The oxide ion ratio (CeO: Ce) was tuned prior to every analytical run, with typical values of 0.4 – 0.5 %. The oxide ion ratio is considered an indicator of plasma robustness; values of 0.5 % or less are indicative of a plasma capable of minimising ionization suppression and the polyatomic

ArCl (m/z 75) interference that can make analysis of trace concentrations of arsenic difficult.[16] Spiked seawater samples were diluted 50 fold and ICPMS analysis incorporated ArCl interference correction equations to minimise the effect of chloride. Speciation confirmation of most deployment solutions used strong anion exchange solid phase extraction (SAX-SPE) as described previously.[7] Briefly, 10 mL of sample was collected and immediately passed through a SAX-SPE cartridge (Supelco) at a flow rate of 2 mL per minute. This first fraction was retained for analysis of As^{III} - a neutral species not adsorbed on the cartridge. As^{V} in the sample was retained on the cartridge and eluted with 5 mL of 2 mol L^{-1} nitric acid (Baseline, Seastar). Both fractions were analysed for total arsenic by ICPMS. SAX-SPE samples were taken at the conclusion of an experiment to confirm that no speciation changes had occurred. SAX-SPE was not possible on very high ionic strength solutions such as seawater, but based on results from the other solutions it is unlikely that speciation shifts occurred over the relatively short deployment times.

Gel preparation. Agarose-crosslinked polyacrylamide diffusive (0.08 cm thickness) gels were prepared according to Zhang and Davison (1995)[17]. For the preparation of mercapto-silica binding gels, bisacrylamide-crosslinked polyacrylamide was used in place of the standard agarose-crosslinked polyacrylamide as it resulted in more homogeneous distribution of the mercapto-silica. 1 g dry mass of mercapto-silica was added per 10 mL of bisacrylamide-crosslinked polyacrylamide gel stock solution (see DeVries and Wang[18] for instructions on the preparation of gel solution). 200 μL of ammonium persulfate (Chem-Supply Pty. Ltd.) and 8 μL of N,N,N',N'-tetramethyl ethylenediamine (TEMED; Merck) were added and the mixture was stirred well before being cast. The gel mixture was cast between two Perspex plates, as the gels were more easily removed from Perspex rather than glass plates. The spacer used was 0.05 cm as the bisacrylamide gels shrunk slightly upon hydration, resulting in a binding gel with 0.04 cm thickness. The mercapto-silica binding agent settled on the lower side of

the gel during casting and this side was placed facing up when assembled in DGT devices. Gels were fragile and required careful handling to avoid breakage. Metsorb and ferrihydrite binding gels were prepared as described previously.[7, 15]

Assembly of DGT samplers. DGT sampler mouldings were obtained from DGT Research Limited (Lancaster, UK). Pistons and caps were washed in 10% (v/v) HNO_3 (AR Grade, Merck) and then three times in deionised water before use. Samplers were assembled and then stored at <4°C in double, plastic zip lock bags, with several millilitres of water in the outer bag to ensure a humid environment.

Analysis of DGT samplers. Following deployment of DGT samplers, the Metsorb binding gels were removed and eluted in 1 mL of 1 mol L^{-1} NaOH solution, as described previously,[7] giving an elution efficiency of 81.2% and 75.2% for As^{III} and As^{V}, respectively. Mercapto-silica binding gels were eluted in 1 mol L^{-1} HNO_3 with 0.01 mol L^{-1} KIO_3 as recommended previously.[14, 19] Ferrihydrite binding gels were eluted in 1 mol L^{-1} HNO_3. Following deployment in seawater, gels were rinsed by immersion in 5 mL of deionised water for 1 h to remove excess unbound salts, prior to elution. Eluent solutions were diluted at least ten-fold prior to analysis by ICPMS. Time averaged solution concentrations (C_{DGT}) were determined using the DGT equation (1):[17]

$$C = \frac{M\Delta g}{DtA} \tag{1}$$

The concentration (C, ng mL^{-1} = µg L^{-1}) is calculated based on the mass of analyte in the binding gel (M, ng), the thickness of the diffusive path length (Δg, cm), the diffusion coefficient of the analyte (D, cm^2 s^{-1}), the duration of the deployment (t, seconds) and the area of the sampler exposed to the solution (A, cm^2). Diffusion coefficients used for the calculation of As^{III} and As^{V} concentrations were 10.1×10^{-5} cm^2 s^{-1} and 7.09×10^{-6} cm^2 s^{-1}, respectively, recalculated from previous work[7] using updated elution efficiencies.

Uptake and elution. Uptake efficiency of As^{III} by mercapto-silica was tested by individually exposing gel discs (n=9) to 5 mL of solution containing 500 ng of As^{III} in 0.01 mol L^{-1} $NaNO_3$. A similar procedure was followed for ferrihydrite, but gel discs were exposed to 1000 ng of either As^{III} (n=3) or As^{V} (n=3). Although the elution efficiency of ferrihydrite has been previously determined for concentrated HCl,[8] it was not possible to use this procedure due to interference of chloride with the ICP-MS analysis of arsenic. Therefore, the elution efficiency was determined in 1 mol L^{-1} HNO_3. The solutions containing the gels were left for at least 24 h and then samples were taken to determine the mass of analyte remaining in solution. Gels were then eluted and analysed as described in the previous section. Samples of the uptake solutions were also analyzed (after acidification) to determine the mass of arsenic remaining in solution. The mass of adsorbed arsenic, and thereby the uptake and elution efficiencies, were calculated by difference.

Uptake of organic arsenic species. The uptake of MMA and DMA by Metsorb was evaluated by exposing gel discs to 5 mL of 100 ng mL^{-1} MMA (n=3) or DMA (n=3). The concentration remaining in solution was measured by ICPMS. Gel discs were eluted with 1 mol L^{-1} NaOH, as described for inorganic arsenic species, diluted and analysed by ICPMS. Mercapto-silica has been previously demonstrated to be selective for As^{III} only,[14] even in the presence of MMA and DMA.

Accumulation over time. The initial evaluation of the mercapto-silica technique followed closely the procedures reported by Bennett and co-workers for Metsorb.[7] Briefly, the evaluation of the accumulation of As^{III} over time was done in 7 L of 0.01 mol L^{-1} $NaNO_3$ spiked with 20 μg L^{-1} As^{III} at 24.7 ± 0.5°C; triplicate probes were removed at 8, 12, 16, and 24 h. Grab samples of the deployment solution were taken at each time point and analysed by ICPMS as well as for changes in speciation by SAX-SPE. The experiment was repeated with As^{V} to confirm that the mercapto-silica binding phase

would not accumulate As^V from solution. Both Metsorb[7] and ferrihydrite[8] have been tested previously for the linear accumulation of As^{III} and As^V over time.

Effect of pH and ionic strength. The effect of pH was evaluated by deploying triplicate mercapto-silica DGT probes for ~6 h in 3 L of 50 μg L^{-1} of both As^{III} and As^V in 0.01 mol L^{-1} $NaNO_3$ prepared at pH 3.5, 5, 7 and 8.2. The pH was adjusted as required using dilute HNO_3 or NaOH and the temperature of each deployment solution was measured during the experiment. The pH 8.2 solution was buffered with 0.001 mol L^{-1} $NaHCO_3$ to ensure a stable pH for the duration of the experiment. Metsorb DGT probes were also deployed in the same solutions to simulate field deployment of both types of DGT probe in order to measure As^{III} and total inorganic arsenic (As^{III} + As^V).

Similarly, the effect of ionic strength was evaluated by deploying triplicate mercapto-silica DGT probes for 5.5 h in separate 3 L solutions of 100 μg L^{-1} As^{III} or As^V prepared at ionic strengths of 0.0001, 0.001, 0.1 and 0.75 mol L^{-1} $NaNO_3$. The temperature of each deployment solution was measured during the experiment and dilute HNO_3 or NaOH was used to adjust the solutions to pH 6.7 ± 0.5. In both pH and ionic strength experiments, grab samples were analysed for As^{III}, As^V and total arsenic (see 'Arsenic analysis' section).

Capacity of Metsorb, mercapto-silica and ferrihydrite. The As^{III} and As^V capacities of Metsorb, mercapto-silica and the previously reported ferrihydrite adsorbent, were determined following the procedure outlined by Panther and co-workers.[20] DGT probes containing each adsorbent were deployed in solutions of either 0.01 mol L^{-1} $NaNO_3$ or 0.2 μm–filtered (Isopore GTBP; Millipore) natural seawater, spiked with 15 mg L^{-1} of either As^{III} or As^V. Deployment times varied from 20 min to 9 h, with one DGT probe for each of the 8 – 10 time points per adsorbent, in order to capture the linear

accumulation of arsenic and the plateau once the capacity of the adsorbent was reached. Preliminary results for the As^{III} capacities of Metsorb and ferrihydrite indicated that they were lower than estimated, and experiments were repeated at 5 mg L^{-1} As^{III} to allow more accurate determinations.

Performance in seawater. The efficacy of the mercapto-silica, Metsorb and ferrihydrite DGT techniques, were investigated by deploying DGT probes in 3 L of 0.2 μm-filtered natural seawater (35 ppk salinity). In this study ferrihydrite and Metsorb were evaluated in seawater as they are both DGT techniques that have been reported for the measurement of total inorganic arsenic,[7, 8] but neither technique has been evaluated in seawater. Seawater was selected for the evaluation of these techniques, as it is one of the most challenging environmental matrices in terms of competing ions and potential interferences. Mercapto-silica, Metsorb and ferrihydrite DGT probes were deployed in triplicate in separate solutions containing As^{III} or As^{V} at 100 μg L^{-1} or 50 μg L^{-1}. Deployments were for 7, 15, 24 and 72 h. Grab samples were taken at the beginning and end of each deployment to determine arsenic concentrations. A DGT-measured concentration to bulk solution concentration ratio (C_{DGT}: C_{SOLN}) between 0.85 and 1.15 is considered to be indicative of adequate analyte recovery.[21]

Results and Discussion

Uptake and elution. The uptake efficiency of As^{III} by mercapto-silica binding gels was >99%. This indicates quantitative adsorption of As^{III} by mercapto-silica. The average elution efficiency was determined to be 85.6 ± 1.7% (n=9) following elution for at least 24 h in 1 mol L^{-1} HNO_3 with 0.01 mol L^{-1} KIO_3. This value is consistent with previously reported elution efficiencies for DGT techniques.[17] The elution efficiencies of As^{III} and As^{V} from ferrihydrite using 1 mol L^{-1} HNO_3 were 74.3 ± 0.1% and 78.5 ± 0.5%, respectively. This compares well with the elution efficiencies reported by Luo and co-

workers[9] for precipitated ferrihydrite gels and those previously reported for As^{III} and As^{V} from Metsorb using 1 mol L^{-1} NaOH.[7]

Uptake of organic arsenic species. Mercapto-silica has been shown to be selective for As^{III} in the presence of monomethylarsonate (MMA) and dimethylarsinate (DMA),[14] so the DGT As^{III} measurement will represent the true As^{III} concentration. Conversely, titanium dioxide, the compound Metsorb is based on, has been shown to adsorb MMA and DMA.[22] To determine if Metsorb also adsorbs these species, binding gel discs were exposed to MMA and DMA solutions. Accumulation of MMA and DMA was 98.8% and 37.0%, respectively, and both species were eluted at 71.2% and 79.2% efficiency in 1 mol L^{-1} NaOH. Therefore, it is possible that organic arsenic species, if present, may contribute to the total "inorganic arsenic" measurement by Metsorb DGT. Previous studies have shown that organic forms of arsenic typically account for less than 10-20% of total dissolved arsenic.[23, 24] Therefore, the potential degree of overestimation of total inorganic arsenic concentrations by Metsorb DGT is within acceptable limits, although the possible contribution of organic arsenic species should be seriously considered when deploying in highly productive areas that may have higher proportions of organic species.[23]

Accumulation over time. The linear accumulation of As^{III} by mercapto-silica DGT, as shown in Figure 1, demonstrates that the DGT equation can be used to predict time-averaged solution concentrations based on the measured mass of arsenic accumulated in the binding gel. The selectivity of mercapto-silica DGT for As^{III} is demonstrated by the negligible accumulation of As^{V}, relative to As^{III}. The mass of As^{V} accumulated by the binding phase, once corrected for the mass of dissolved As^{V} that would simply equilibrate within the gel, is less than 1 ng for all time points with no increase observed over time. This indicates that no As^{V} is binding over time to the mercapto-silica, and thus that this technique should not suffer any interference from As^{V} even when the ratio of As^{V} to As^{III} is large.

To eliminate any chance of a positive interference from As^V, it is recommended that the mercapto-silica binding gel be washed in 5 mL of distilled water prior to elution, to allow any As^V present in the porewater of the gel to diffuse out.

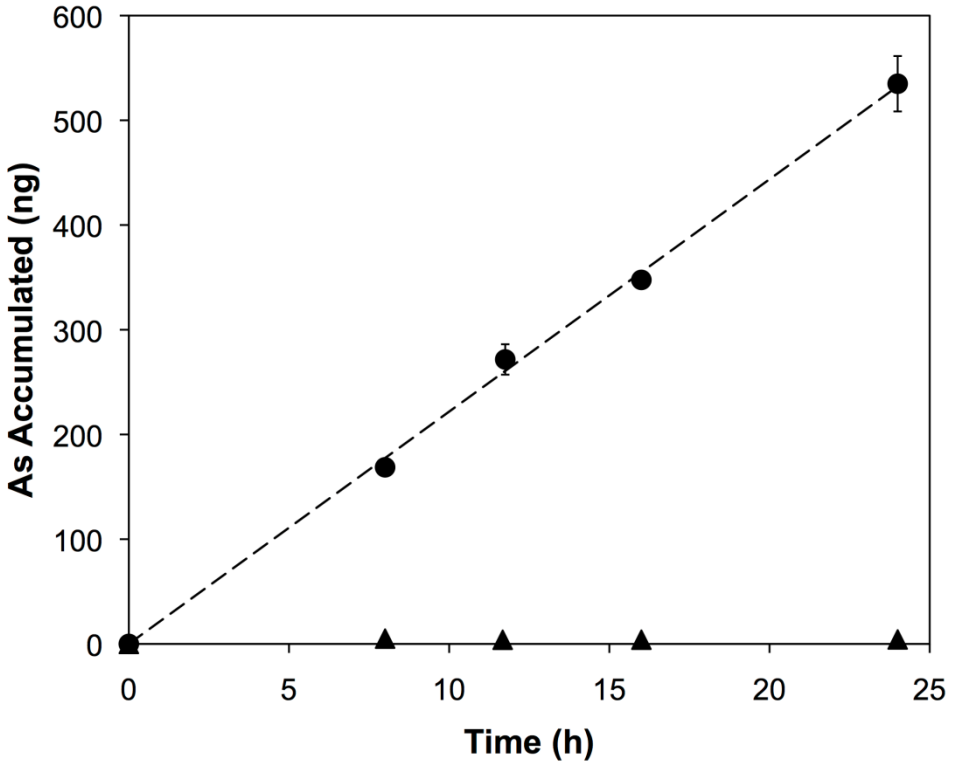

Figure 1. Mass of As^{III} and As^V accumulated over time by mercapto-silica DGT in separate solutions of either 20 μg L^{-1} As^{III} (●) or 20 μg L^{-1} As^V (▲). Data points are means (n=3) ± 1 standard deviation. Speciation was confirmed by SAX-SPE. Dashed line is the linear regression (R^2 = 0.998) used to calculate the diffusion coefficient of As^{III} (9.04×10^{-6} cm^2 s^{-1}).

The linear relationship between deployment time and the mass of As^{III} accumulated allows the estimation of a diffusion coefficient. The effective diffusion coefficient (D, cm^2 s^{-1}) was calculated using the slope (α) of the linear regression of the mass of analyte (ng) accumulated in the gel over time

(h), the thickness of the diffusive layer (Δg, cm), the area of the diffusive layer available for diffusion (A, cm^2) and the concentration of the solution (C, ng mL^{-1}) (Eq. (2)).

$$D = \frac{\alpha \Delta g}{AC} \tag{2}$$

The effective As^{III} diffusion coefficient estimated from mercapto-silica DGT deployments of (9.04 ± 0.24) × 10^{-6} cm^2 s^{-1} agrees well with the value previously estimated using Metsorb DGT deployments[7] (D_{MSIL}: $D_{METSORB}$ = 0.9). Additionally, a recent study reported a diffusion coefficient in water for As^{III} of 11.1 × 10^{-6} cm^2 s^{-1}, measured using modified Taylor dispersion procedures.[25] This value is within 10% of the value measured by Metsorb DGT and within 20% of the value measured by mercapto-silica DGT.[7] This consistency of diffusion coefficients measured in polyacrylamide hydrogel and in water indicates that the diffusion of As^{III} is only slightly restricted by the polyacrylamide gel, contrary to results reported for other anions such as As^{V} and PO_4^{3-}.[7, 26] This is most likely because As^{III}, unlike As^{V} and PO_4^{3-}, is uncharged at neutral pH and thus not affected by any charge present within the hydrogel or filter membrane; this electrostatic interaction has been suggested as the reason for the slower diffusion of some anions in DGT samplers.[7, 26] However, recent research by Garmo and co-workers has shown that the agarose-crosslinked polyacrylamide gels typically used for DGT do not have charged surfaces capable of interacting with diffusing species, but rather interact with cations by adsorption.[27, 28] Nitrocellulose filter membranes, however, have been found to possess a negative charge[27] that could interact with diffusing anions such as As^{V} and PO_3^{3-} and reduce the effective diffusion coefficient, while having little effect on the diffusion of uncharged As^{III}. This electrostatic effect should be negligible at higher ionic strengths such as that of seawater where the charges on the filter membrane will be screened by the high concentration of ions in solution.[28]

Effect of pH and ionic strength. The effect of pH and ionic strength on the accumulation of As^{III} by mercapto-silica DGT was tested to ensure that the technique would perform as expected under conditions typical of natural waters. The accumulation of As^{V} was also investigated to ensure that mercapto-silica would selectively accumulate As^{III} across the pH and ionic strength ranges tested. Table 1 shows the measurement of As^{III} by mercapto-silica DGT in the presence of As^{V}. Metsorb DGT was deployed alongside the mercapto-silica DGT to validate the concept of deploying both types of DGT in the determination of inorganic arsenic speciation. The measurement of arsenic speciation in the deployment solution by SAX-SPE allowed direct comparison of the DGT-measured speciation estimates to the actual speciation. The total arsenic concentration calculated by the addition of SAX-SPE-measured As^{III} and As^{V} concentrations showed good agreement with the total arsenic concentration measured in grab samples by ICP-MS (recoveries of 100-107%).

Table 1. Effect of pH on the selective measurement of As^{III} by mercapto-silica (C_{MSIL}) DGT in a solution containing both 50 μg L^{-1} As^{III} and 50 μg L^{-1} As^{V}. Total arsenic was measured by Metsorb DGT. C_{SOLN} was measured by SAX-SPE.

pH	As^{III}			Total Arsenic (As^{III} + As^{V})		
	C_{MSIL} μg L^{-1}	C_{SOLN} μg L^{-1}	C_{MSIL}/C_{SOLN}	$C_{METSORB}$ μg L^{-1}	C_{SOLN} μg L^{-1}	$C_{METSORB}/C_{SOLN}$
3.5	44.3 ± 2.0	44.5	1.00 ± 0.05	116 ± 2.9	97.9	1.18 ± 0.03
5.0	36.0 ± 3.0	44.5	0.81 ± 0.07	108 ± 3.5	99.1	1.09 ± 0.04
7.0	43.7 ± 1.2	49.3	0.89 ± 0.02	107 ± 5.8	104.2	1.03 ± 0.06
8.2	49.8 ± 1.2	45.9	1.09 ± 0.03	101 ± 5.7	101.5	1.00 ± 0.06

The concentration of As^{III} in the combined solution of As^{III} and As^{V} was accurately determined by the mercapto-silica DGT technique, with most C_{MSIL}/C_{SOLN} values between 0.89 and 1.09. This confirms that mercapto-silica DGT is selectively measuring As^{III} in the presence of As^{V}. The recovery for pH 5

(C_{MSIL}: C_{SOLN} = 0.81) is slightly less than expected, although still within acceptable limits for a field speciation method. The Metsorb DGT, which was simultaneously deployed in the same experimental solution, measured total arsenic accurately, although there was slight overestimation of total arsenic at pH 3.5. This overestimation could be due to an increase in the ratio of $H_2AsO_4^-$ to $HAsO_4^{2-}$ with decreasing pH, as it is likely that the diffusion coefficient of $H_2AsO_4^-$ is larger than $HAsO_4^{2-}$ due to the higher degree of protonation. This increase in diffusion coefficient with degree of protonation is observed for the diffusion coefficients of $H_2PO_4^-$ and HPO_4^{2-}, which are analogues of the As^V oxyanions.[29]

The effect of ionic strength on the accumulation of As^{III} by mercapto-silica DGT is shown as Figure 2. Accumulation was quantitative and consistent across the ionic strength range 0.0001 mol L^{-1} to 0.75 mol L^{-1}, with all average C_{DGT}: C_{SOLN} values between 0.90 and 0.98. These results suggest that this technique can be accurately used in the majority of natural fresh and marine waters, although further testing in seawater is necessary to ensure that competing anions other than nitrate do not interfere with the measurement of As^{III} by mercapto-silica (see section "Performance in seawater"). Accumulation of As^V by the mercapto-silica DGT was negligible for all tested ionic strengths, confirming the selectivity of mercapto-silica DGT for As^{III} at various ionic strengths.

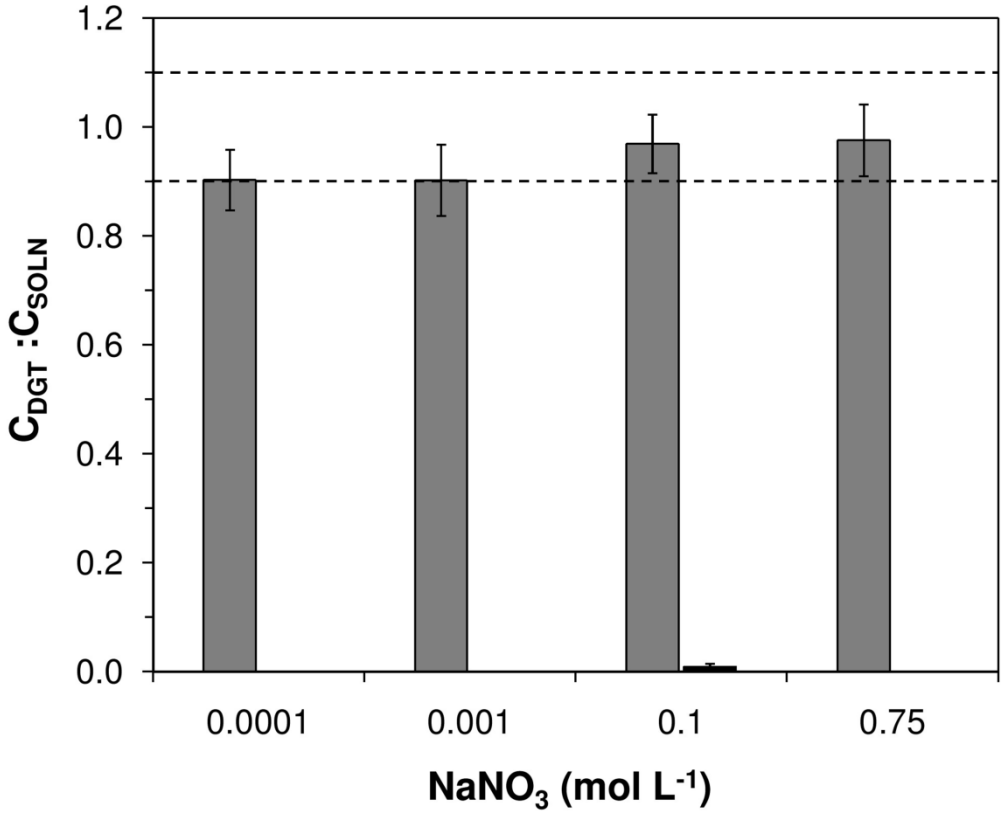

Figure 2. The effect of ionic strength (mol L^{-1} $NaNO_3$) on the accumulation of As^{III} (gray) by mercapto-silica DGT. Dotted lines indicate a C_{DGT}: C_{SOLN} ratio of 0.9 – 1.1. The accumulation of As^{V} (black) by the mercapto-silica was negligible (C_{DGT}: C_{SOLN} < 0.01).

Capacity of Metsorb, mercapto-silica and ferrihydrite. Recent results from Panther and co-workers[20] have shown an effect of adsorbent capacity on the measurement of phosphate by Metsorb and ferrihydrite DGT samplers. Ferrihydrite, with a measured phosphate capacity of <50% the capacity of Metsorb, was shown to underestimate dissolved phosphorus by 45% compared to Metsorb DGT when deployed in seawater for 96 h.[20] Therefore, it is important to determine the capacity of new adsorbents to enable estimation of potential field deployment times.

The capacities of Metsorb, mercapto-silica and ferrihydrite for As^{III} and As^{V} in both 0.01 mol L^{-1} $NaNO_3$ and 0.2 μm-filtered natural seawater were measured using short-term deployments over time at high concentrations of As^{III} or As^{V} (Table 2). The capacities were determined by identifying the highest mass accumulated by DGT that still agreed (C_{DGT}: $C_{PREDICTED}$ >0.85) with the predicted linear uptake. The capacities reported should therefore be referred to as DGT capacities, which is the maximum mass bound by the binding phase during the linear accumulation phase, as the total capacities may be higher but are not relevant due to the non-linear uptake. The capacity of the adsorbents was tested in seawater, as it has been shown that competing ions in seawater may lower the effective capacity of a DGT adsorbent.[20]

Table 2. Measured DGT capacities (ng) for As^{III} and As^{V} of Metsorb, mercapto-silica and ferrihydrite DGT samplers in 0.01 mol L^{-1} $NaNO_3$ and 0.2 μm-filtered natural seawater.

Matrix	As^{III} Capacity (ng)			As^{V} Capacity (ng)	
	Metsorb	Mercapto-silica	Ferrihydrite	Metsorb	Ferrihydrite
0.01 mol L^{-1} $NaNO_3$	8500	77500	22500	82000	31500
0.2 μm-filtered natural seawater	7500	>129000	20000	52000	11500

Metsorb and ferrihydrite exhibited a lower capacity for arsenic in seawater compared to 0.01 mol L^{-1} $NaNO_3$. This is expected based on the higher concentration and range of potentially competing ions present in seawater, which presumably bind to the adsorbent and reduce the available binding sites for arsenic. Conversely, mercapto-silica had a higher capacity for As^{III} in seawater compared to 0.01 mol L^{-1} $NaNO_3$, for reasons unknown. Mercapto-silica is a highly selective binding agent for As^{III} due to the strong complexation of H_3AsO_3 by thiol (S-H) groups.[30] The strength of this interaction is confirmed by the fact that seawater has no negative effect on the adsorption of As^{III} by mercapto-silica.

Metsorb has a lower capacity for As^{III} but a higher capacity for As^{V} compared to ferrihydrite. It may appear, therefore, that Metsorb could be more susceptible to interference when measuring As^{III} due to competing ions reducing the effective capacity of the adsorbent, as described for PO_4^{3-} by ferrihydrite DGT by Panther and co-workers.[20] However, the selectivity of an adsorbent for the target analyte is critical to the overall performance of that technique for exposure times typical of field deployments (3 – 4 days). Capacity experiments were only performed over <12 h, which does not allow competing ions in solution to diffuse through the diffusive gel and bind to the adsorbent in the same quantity that a longer deployment time would. This means that the effect of competing ions on the effective capacity of the adsorbent is underestimated by the short-term experiments typically used for adsorbent capacity estimation. In order to evaluate the performance of different adsorbents, longer deployments must be made at lower analyte concentrations.

Performance in seawater. Mercapto-silica DGT was evaluated in 0.2 μm-filtered natural seawater to demonstrate the robustness of the technique (Table 3). Metsorb and ferrihydrite, the two adsorbents previously reported[7, 8] for the measurement of total inorganic arsenic by DGT, were also included for evaluation. This is the first time either of these adsorbents has been evaluated for the measurement of arsenic in seawater. Seawater was chosen for the evaluation of these techniques due to the high concentrations of potential competing ions present, which should aid in identifying DGT techniques that lack sufficient selectivity and/or capacity for the desired analyte.

Table 3. Ratios of DGT-measured solution concentrations (C_{DGT}) to ICP-MS-measured solution concentrations (C_{SOLN}) for Metsorb, mercapto-silica and ferrihydrite DGT deployed over time in 0.2 μm-filtered natural seawater spiked with As^{III} or As^{V} at 100 μg L^{-1} or 50 μg L^{-1}. Ratios that indicate non-quantitative accumulation (C_{DGT}: C_{SOLN} <0.85) are highlighted in bold. Uncertainties were calculated based on the standard deviations of both the DGT-measured concentrations and the measured grab samples.

Deployment Time (h)	As^{III} C_{DGT}: C_{SOLN}			As^{V} C_{DGT}: C_{SOLN}	
	Metsorb	**Mercapto-silica**	**Ferrihydrite**	**Metsorb**	**Ferrihydrite**
7	1.09 ± 0.12	1.16 ± 0.08	1.04 ± 0.07	1.15 ± 0.24	1.03 ± 0.12
15	0.99 ± 0.07	1.08 ± 0.08	0.89 ± 0.06	0.95 ± 0.06	1.08 ± 0.24
24	1.04 ± 0.07	1.10 ± 0.07	0.90 ± 0.08	0.99 ± 0.08	0.86 ± 0.07
72	0.85 ± 0.02[a]	1.04 ± 0.07	**0.80 ± 0.04**[a]	1.07 ± 0.14	**0.78 ± 0.08**

[a] Experiments performed in 50 μg L^{-1} As^{III}

Mercapto-silica DGT accurately measured As^{III} in seawater, including for deployment times of 72 h, indicating that the new mercapto-silica DGT technique is suitable for the in situ measurement of As^{III} for deployment times typically used in the field. Panther and co-workers recently determined that evaluation of DGT techniques over typical in situ deployment times was important when evaluating a new technique, as evaluation over shorter deployment times (<24 h) could mask poorly performing adsorbents.[20]

As^{III} accumulation for 72 h was initially tested at 100 μg L^{-1} for both Metsorb and ferrihydrite, but only measured 78% and 57%, respectively, of the ICPMS-measured solution concentration. The accumulated mass theoretically predicted at this deployment time is the same as the measured DGT capacity of Metsorb for As^{III} (7500 ng), which explains the somewhat lower uptake in this case. To

402 confirm this, probes were deployed for 72 h in filtered natural seawater spiked with 50 μg L^{-1} As^{III} so
403 that the adsorbent capacity would not be reached. This resulted in a C_{DGT}: C_{SOLN} ratio of 0.85 for
404 Metsorb, which shows that Metsorb functions accurately in seawater over longer deployment times. In
405 natural seawater, arsenic is typically present at much lower concentrations (< 1.5 μg L^{-1})[24] so adsorbent
406 capacity would not be approached in field deployments of Metsorb DGT. However, the measured
407 capacity of ferrihydrite in seawater (20000 ng) is far higher than the mass theoretically adsorbed after
408 72 h (7500 ng), but the technique only accumulated 57% of the predicted mass, indicating that the
409 capacity of the adsorbent may not accurately indicate the actual performance for realistic deployment
410 times. Rather, the selectivity of the binding agent for the target analyte appears to be more important to
411 the performance of DGT in challenging conditions such as seawater. Recent data from Panther and co-
412 workers[20] supports this finding, as it showed that ferrihydrite DGT did not accurately measure
413 dissolved reactive phosphorus (DRP) concentrations in seawater, even though the measured DRP
414 capacity of ferrihydrite had not been reached. They suggest that deployment in conditions where
415 competing ions such as bicarbonate are present leads to a decrease in the effective capacity of
416 ferrihydrite DGT, due to binding of bicarbonate to the adsorbent, effectively lowering the number of
417 available binding sites for DRP.[20] In their study, Metsorb accurately measured DRP under all tested
418 conditions, indicating that either the higher capacity of the Metsorb adsorbent resulted in sufficient
419 binding sites for DRP in the presence of bicarbonate, or that Metsorb is more selective for DRP
420 compared to ferrihydrite so that bound bicarbonate is easily replaced by DRP.[20] Degryse and co-
421 workers[31] also investigated the effect of competition by calcium on the accumulation of zinc by
422 Chelex-100 DGT in soil porewaters. They found that an increase in calcium concentration resulted in a
423 decrease in the distribution coefficient of zinc, indicating that competition from calcium caused a
424 decrease in the effective zinc capacity of the Chelex-100 binding phase. The findings of Panther and
425 co-workers[20] and Degryse and co-workers[31] are supported by our results from 72 h deployments of

426 ferrihydrite DGT samplers in seawater spiked with As^{V}, where they measured only 78% of the actual
427 solution concentration even though the bound mass of As^{V} was less than 25% of the measured capacity.
428 Metsorb DGT samplers measured 107% of the actual As^{V} concentration when deployed in the same
429 solution, indicating quantitative accumulation. These findings, and those of Panther and co-workers,[20]
430 indicate that Metsorb is more selective towards these oxyanionic species compared to ferrihydrite and
431 thus more suitable for the measurement of these species in situ over typical deployment times of
432 several days.
433

434 **Conclusion**

435 This work has evaluated a new approach for the in situ measurement of inorganic arsenic speciation.
436 By utilising mercapto-silica as an As^{III}-selective DGT adsorbent, in combination with Metsorb DGT for
437 measuring total inorganic arsenic, the speciation of both inorganic arsenic species can be determined.
438 This method represents a significant advance in speciation analysis of arsenic by allowing both
439 inorganic arsenic species to be measured in situ, thus avoiding changes in speciation typically
440 associated with traditional, ex situ analytical techniques. Furthermore, this technique has been
441 demonstrated to perform effectively in seawater, an area where speciation analysis of inorganic arsenic
442 is very difficult due to the high concentrations of chloride that interfere with ICPMS analysis. Method
443 detection limits, calculated by converting the standard deviation of multiple blank measurements into a
444 concentration by applying the DGT equation, were sufficiently low to allow quantification of ultra
445 trace concentrations of As^{III} by mercapto-silica DGT (0.03 $\mu g\ L^{-1}$; 72 h deployment) and total inorganic
446 arsenic by Metsorb DGT (0.03 $\mu g\ L^{-1}$; 72 h deployment).
447

448 Our results also support recent work that proposes adsorbent capacity as a key factor that should be
449 evaluated for new DGT techniques, especially when deployment in seawater is intended. The adsorbent

capacity of the mercapto-silica DGT technique is very high compared to all existing arsenic DGT techniques and it performed well over environmentally relevant pH and ionic strength ranges and in the complex matrix of seawater. The robustness of this technique, coupled with its high selectivity and capacity for As^{III}, make it an ideal adsorbent for the speciation of inorganic arsenic by DGT.

Future research should focus on the application of this new approach for the investigation of arsenic speciation in naturally and anthropogenically-contaminated waters, soils and sediments. Particular focus should be placed on the evaluation of this technique as a method for investigating the biogeochemistry of arsenic and assessing the status of groundwater sediments in areas where groundwater is used as a source of drinking water.

Acknowledgements

The authors thank the School of Environment, Griffith University, for the provision of a Ph.D scholarship for WWB. We also acknowledge the financial support of the NSW Environmental Trust (research project APP2006-RD-0059). The authors also thank Graver Technologies (www.gravertech.com) for the provision of the Metsorb product used in this study.

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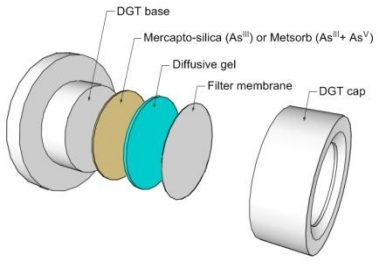
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