

1-1-2011

Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of AsIII by 3-mercaptopropyl-functionalized silica gel

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Recommended Citation

Bennett, William W.; Teasdale, Peter R.; Panther, Jarad G.; Welsh, David T.; and Jolley, Dianne F.: Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of AsIII by 3-mercaptopropyl-functionalized silica gel 2011, 8293-8299.
<https://ro.uow.edu.au/scipapers/3215>

Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of AsIII by 3-mercaptopropyl-functionalized silica gel

Abstract

A diffusive gradients in thin films (DGT) technique for selectively measuring AsIII 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 AsV by difference. Uptake of As III by mercapto-silica was quantitative and elution with a mixture of 1 mol L⁻¹ HNO₃ and 0.01 mol L⁻¹ KIO₃ gave a recovery of 85.6 ± 1.7%. DGT validation experiments showed linear accumulation of AsIII over time (R² > 0.998). Accumulation was unaffected by varying ionic strength (0.0001-0.75 mol L⁻¹ NaNO₃) and pH (3.5-8.5). Deployment of mercapto-silica DGT and Metsorb DGT in seawater spiked with AsIII and AsV 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 AsIII and AsV 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 ultratrace concentrations of AsIII (0.03 µg L⁻¹; 72 h deployment). 2011 American Chemical Society.

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

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.

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

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21 **Abstract**

22 A diffusive gradients in thin films (DGT) technique for selectively measuring As^{III} utilizes
23 commercially available 3-mercaptopropyl-functionalized silica gel. Deployment of the new technique
24 alongside the Metsorb-DGT for total inorganic arsenic allows the calculation of As^{III} directly and As^{V}
25 by difference. Uptake of As^{III} by mercapto-silica was quantitative and elution with a mixture of 1 mol
26 L^{-1} HNO_3 and 0.01 mol L^{-1} KIO_3 gave a recovery of $85.6 \pm 1.7\%$. DGT validation experiments showed
27 linear accumulation of As^{III} over time ($R^2 > 0.998$). Accumulation was unaffected by varying ionic
28 strength (0.0001–0.75 mol L^{-1} NaNO_3) and pH (3.5–8.5). Deployment of mercapto-silica DGT and
29 Metsorb DGT in seawater spiked with As^{III} and As^{V} demonstrated the ability of the combined approach
30 to accurately quantify both species in the presence of potential competing ions. Ferrihydrite DGT,
31 which has been previously reported for the measurement of total inorganic arsenic, was evaluated in
32 seawater and shown to underestimate both As^{III} and As^{V} at longer deployment times (72 h).
33 Reproducibility of the new mercapto-silica DGT technique was good (relative standard deviations
34 $< 9\%$) and the average method detection limit was sufficiently low to allow quantification of ultra-trace
35 concentrations of As^{III} (0.03 $\mu\text{g L}^{-1}$; 72 h deployment).

36

37 **Introduction**

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

47
48 Arsenic is an environmental contaminant whose toxicity and bioavailability are significantly influenced
49 by speciation. The reduced inorganic arsenic species, arsenite (As^{III}), is more toxic than the oxidized
50 inorganic species, arsenate (As^{V}), and the common organic forms, monomethyl arsenic (MMA) and
51 dimethyl arsenic (DMA), are less toxic than the inorganic forms.⁴ Arsenic is of particular concern in
52 drinking waters, where it can significantly impact upon human health.⁵ The monitoring of arsenic has
53 traditionally involved the use of spot sampling followed by laboratory speciation analysis using HPLC-
54 ICPMS, if required. This can provide an unrepresentative sample and there is the potential for changes
55 in speciation to occur during transport and storage of the sample.² Some methods have attempted to
56 reduce this problem by processing samples on-site through solid phase extraction cartridges to reduce
57 the likelihood of changes in speciation.⁶ This approach, however, does not address the unrepresentative
58 nature of spot sampling and is problematic in high ionic strength waters such as seawater.

59

60 The diffusive gradients in thin films (DGT) technique has previously been used to measure total
61 inorganic arsenic⁷⁻⁹. It has also been shown to provide highly representative information and, due to the
62 in situ nature of the technique, avoid problems associated with changes in sample speciation.¹⁰ This
63 makes DGT an ideal candidate for modification to allow in situ speciation analysis of dissolved
64 inorganic arsenic. This has been attempted by Panther and co-workers¹¹ by deploying two sets of DGT
65 devices, one set with negatively charged perfluorosulfonated ionomer diffusive membranes (Nafion)
66 and the other with the standard polyacrylamide hydrogel. As^{III} and As^V were speciated based on their
67 charge with the uncharged As^{III} species (at neutral pH) passing through the Nafion membrane much
68 faster than the charged As^V, allowing the concentrations of both oxidation states to be calculated. The
69 use of this technique, however, is likely to be limited to low to moderate ionic strength waters, as at
70 high ionic strengths the charged membrane could rapidly become saturated with major cations,
71 rendering it ineffective. An alternative approach for in situ speciation of inorganic arsenic is to use
72 selective adsorption of one or both species. This has been demonstrated previously by Ernstberger and
73 co-workers¹² who used Chelex-100 to selectively measure Cr^{III} in the presence of Cr^{VI} and Bennett and
74 co-workers⁷ who used a titanium dioxide-based adsorbent (Metsorb) to selectively measure Se^{IV} in the
75 presence of Se^{VI},

76

77 In this research we take advantage of the selective adsorption of As^{III} by a mercaptopropyl-
78 functionalized silica gel (mercapto-silica). Mercapto-silica has been previously used as a DGT binding
79 agent for methylmercury,¹³ but this is the first time it has been described for the selective measurement
80 of As^{III} by DGT. Howard and co-workers¹⁴ investigated mercapto-silica for batch preconcentration
81 applications and confirmed that it selectively adsorbed As^{III} in the presence of As^V,
82 monomethylarsonate (MMA) and dimethylarsinate (DMA). Additionally, they showed that adsorption
83 was quantitative in seawater and over the pH range 1.5 – 8.5. In this study, mercapto-silica was
84 evaluated as a selective As^{III} binding phase in the DGT technique and was deployed alongside the

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

89

90 **Experimental**

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

102

103 **Arsenic analysis.** Dissolved metal concentrations were determined by inductively coupled plasma –
104 mass spectrometry (ICPMS, Agilent 7500a). Yttrium (m/z 89) was used as an internal standard and
105 quality control standards were analysed regularly throughout the analysis to ensure correction of
106 instrument drift. The oxide ion ratio (CeO: Ce) was tuned prior to every analytical run, with typical
107 values of 0.4 – 0.5 %. The oxide ion ratio is considered an indicator of plasma robustness; values of 0.5
108 % or less are indicative of a plasma capable of minimising ionization suppression and the polyatomic

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

121

122 **Gel preparation.** Agarose-crosslinked polyacrylamide diffusive (0.08 cm thickness) gels were
123 prepared according to Zhang and Davison (1995)¹⁷. For the preparation of mercapto-silica binding gels,
124 bisacrylamide-crosslinked polyacrylamide was used in place of the standard agarose-crosslinked
125 polyacrylamide as it resulted in more homogeneous distribution of the mercapto-silica. 1 g dry mass of
126 mercapto-silica was added per 10 mL of bisacrylamide-crosslinked polyacrylamide gel stock solution
127 (see DeVries and Wang¹⁸ for instructions on the preparation of gel solution). 200 µL of ammonium
128 persulfate (Chem-Supply Pty. Ltd.) and 8 µL of N,N,N',N'-tetramethyl ethylenediamine (TEMED;
129 Merck) were added and the mixture was stirred well before being cast. The gel mixture was cast
130 between two Perspex plates, as the gels were more easily removed from Perspex rather than glass
131 plates. The spacer used was 0.05 cm as the bisacrylamide gels shrunk slightly upon hydration, resulting
132 in a binding gel with 0.04 cm thickness. The mercapto-silica binding agent settled on the lower side of

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

136

137 **Assembly of DGT samplers.** DGT sampler mouldings were obtained from DGT Research Limited
138 (Lancaster, UK). Pistons and caps were washed in 10% (v/v) HNO₃ (AR Grade, Merck) and then three
139 times in deionised water before use. Samplers were assembled and then stored at <4°C in double,
140 plastic zip lock bags, with several millilitres of water in the outer bag to ensure a humid environment.

141

142 **Analysis of DGT samplers.** Following deployment of DGT samplers, the Metsorb binding gels were
143 removed and eluted in 1 mL of 1 mol L⁻¹ NaOH solution, as described previously,⁷ giving an elution
144 efficiency of 81.2% and 75.2% for As^{III} and As^V, respectively. Mercapto-silica binding gels were
145 eluted in 1 mol L⁻¹ HNO₃ with 0.01 mol L⁻¹ KIO₃ as recommended previously.^{14, 19} Ferrihydrite binding
146 gels were eluted in 1 mol L⁻¹ HNO₃. Following deployment in seawater, gels were rinsed by immersion
147 in 5 mL of deionised water for 1 h to remove excess unbound salts, prior to elution. Eluent solutions
148 were diluted at least ten-fold prior to analysis by ICPMS. Time averaged solution concentrations (C
149 DGT) were determined using the DGT equation (1):¹⁷

$$C = \frac{M\Delta g}{DtA} \quad (1)$$

150 The concentration (C , ng mL⁻¹ = μg L⁻¹) is calculated based on the mass of analyte in the binding gel
151 (M , ng), the thickness of the diffusive path length (Δg , cm), the diffusion coefficient of the analyte (D ,
152 cm² s⁻¹), the duration of the deployment (t , seconds) and the area of the sampler exposed to the solution
153 (A , cm²). Diffusion coefficients used for the calculation of As^{III} and As^V concentrations were 10.1×10^{-5}
154 cm² s⁻¹ and 7.09×10^{-6} cm² s⁻¹, respectively, recalculated from previous work⁷ using updated elution
155 efficiencies.

156

157 **Uptake and elution.** Uptake efficiency of As^{III} by mercapto-silica was tested by individually exposing
158 gel discs (n=9) to 5 mL of solution containing 500 ng of As^{III} in 0.01 mol L⁻¹ NaNO₃. A similar
159 procedure was followed for ferrihydrite, but gel discs were exposed to 1000 ng of either As^{III} (n=3) or
160 As^V (n=3). Although the elution efficiency of ferrihydrite has been previously determined for
161 concentrated HCl,⁸ it was not possible to use this procedure due to interference of chloride with the
162 ICP-MS analysis of arsenic. Therefore, the elution efficiency was determined in 1 mol L⁻¹ HNO₃. The
163 solutions containing the gels were left for at least 24 h and then samples were taken to determine the
164 mass of analyte remaining in solution. Gels were then eluted and analysed as described in the previous
165 section. Samples of the uptake solutions were also analyzed (after acidification) to determine the mass
166 of arsenic remaining in solution. The mass of adsorbed arsenic, and thereby the uptake and elution
167 efficiencies, were calculated by difference.

168

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

174

175 **Accumulation over time.** The initial evaluation of the mercapto-silica technique followed closely the
176 procedures reported by Bennett and co-workers for Metsorb.⁷ Briefly, the evaluation of the
177 accumulation of As^{III} over time was done in 7 L of 0.01 mol L⁻¹ NaNO₃ spiked with 20 µg L⁻¹ As^{III} at
178 24.7 ± 0.5°C; triplicate probes were removed at 8, 12, 16, and 24 h. Grab samples of the deployment
179 solution were taken at each time point and analysed by ICPMS as well as for changes in speciation by
180 SAX-SPE. The experiment was repeated with As^V to confirm that the mercapto-silica binding phase

181 would not accumulate As^{V} from solution. Both Metsorb⁷ and ferrihydrite⁸ have been tested previously
182 for the linear accumulation of As^{III} and As^{V} over time.

183

184 **Effect of pH and ionic strength.** The effect of pH was evaluated by deploying triplicate mercapto-
185 silica DGT probes for ~6 h in 3 L of $50 \mu\text{g L}^{-1}$ of both As^{III} and As^{V} in $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ prepared at
186 pH 3.5, 5, 7 and 8.2. The pH was adjusted as required using dilute HNO_3 or NaOH and the temperature
187 of each deployment solution was measured during the experiment. The pH 8.2 solution was buffered
188 with $0.001 \text{ mol L}^{-1} \text{ NaHCO}_3$ to ensure a stable pH for the duration of the experiment. Metsorb DGT
189 probes were also deployed in the same solutions to simulate field deployment of both types of DGT
190 probe in order to measure As^{III} and total inorganic arsenic ($\text{As}^{\text{III}} + \text{As}^{\text{V}}$).

191

192 Similarly, the effect of ionic strength was evaluated by deploying triplicate mercapto-silica DGT
193 probes for 5.5 h in separate 3 L solutions of $100 \mu\text{g L}^{-1} \text{ As}^{\text{III}}$ or As^{V} prepared at ionic strengths of
194 0.0001, 0.001, 0.1 and $0.75 \text{ mol L}^{-1} \text{ NaNO}_3$. The temperature of each deployment solution was
195 measured during the experiment and dilute HNO_3 or NaOH was used to adjust the solutions to $\text{pH } 6.7 \pm$
196 0.5 . In both pH and ionic strength experiments, grab samples were analysed for As^{III} , As^{V} and total
197 arsenic (see 'Arsenic analysis' section).

198

199 **Capacity of Metsorb, mercapto-silica and ferrihydrite.** The As^{III} and As^{V} capacities of Metsorb,
200 mercapto-silica and the previously reported ferrihydrite adsorbent, were determined following the
201 procedure outlined by Panther and co-workers.²⁰ DGT probes containing each adsorbent were deployed
202 in solutions of either $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ or $0.2 \mu\text{m}$ -filtered (Isopore GTBP; Millipore) natural
203 seawater, spiked with 15 mg L^{-1} of either As^{III} or As^{V} . Deployment times varied from 20 min to 9 h,
204 with one DGT probe for each of the 8 – 10 time points per adsorbent, in order to capture the linear

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

208

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

220

221 **Results and Discussion**

222 **Uptake and elution.** The uptake efficiency of As^{III} by mercapto-silica binding gels was >99%. This
223 indicates quantitative adsorption of As^{III} by mercapto-silica. The average elution efficiency was
224 determined to be 85.6 ± 1.7% (n=9) following elution for at least 24 h in 1 mol L⁻¹ HNO₃ with 0.01 mol
225 L⁻¹ KIO₃. This value is consistent with previously reported elution efficiencies for DGT techniques.¹⁷
226 The elution efficiencies of As^{III} and As^V from ferrihydrite using 1 mol L⁻¹ HNO₃ were 74.3 ± 0.1% and
227 78.5 ± 0.5%, respectively. This compares well with the elution efficiencies reported by Luo and co-

228 workers⁹ for precipitated ferrihydrite gels and those previously reported for As^{III} and As^V from Metsorb
229 using 1 mol L⁻¹ NaOH.⁷

230

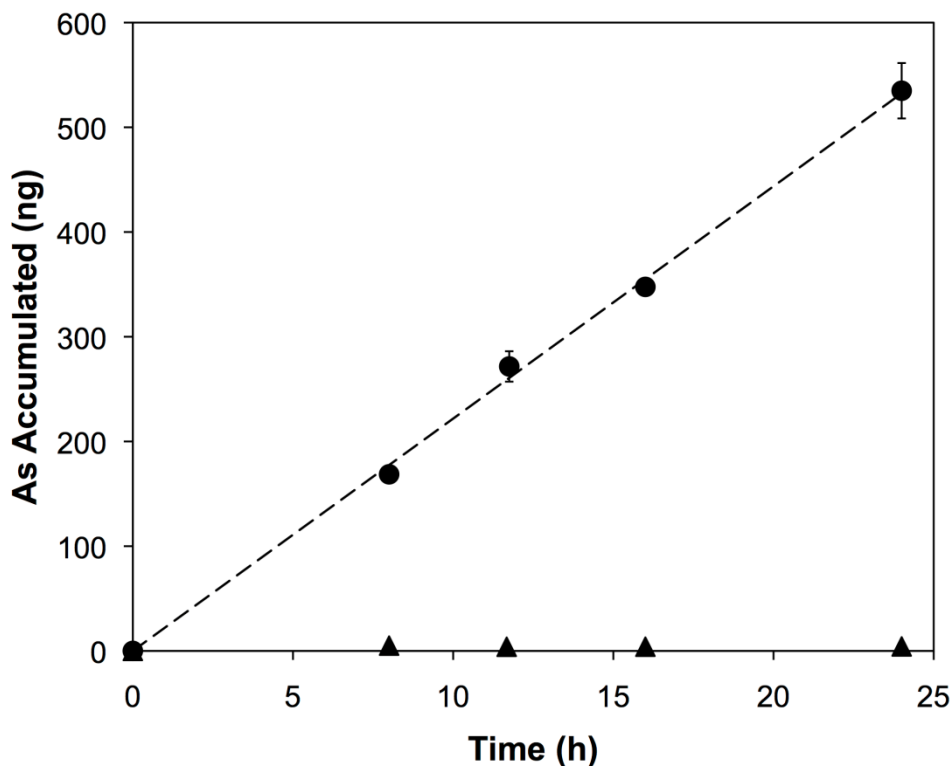
231 **Uptake of organic arsenic species.** Mercapto-silica has been shown to be selective for As^{III} in the
232 presence of monomethylarsonate (MMA) and dimethylarsinate (DMA),¹⁴ so the DGT As^{III}
233 measurement will represent the true As^{III} concentration. Conversely, titanium dioxide, the compound
234 Metsorb is based on, has been shown to adsorb MMA and DMA.²² To determine if Metsorb also
235 adsorbs these species, binding gel discs were exposed to MMA and DMA solutions. Accumulation of
236 MMA and DMA was 98.8% and 37.0%, respectively, and both species were eluted at 71.2% and
237 79.2% efficiency in 1 mol L⁻¹ NaOH. Therefore, it is possible that organic arsenic species, if present,
238 may contribute to the total “inorganic arsenic” measurement by Metsorb DGT. Previous studies have
239 shown that organic forms of arsenic typically account for less than 10-20% of total dissolved arsenic.^{23,}
240 ²⁴ Therefore, the potential degree of overestimation of total inorganic arsenic concentrations by
241 Metsorb DGT is within acceptable limits, although the possible contribution of organic arsenic species
242 should be seriously considered when deploying in highly productive areas that may have higher
243 proportions of organic species.²³

244

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

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

256



257

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

262

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

266 (h), the thickness of the diffusive layer (Δg , cm), the area of the diffusive layer available for diffusion
267 (A , cm²) and the concentration of the solution (C , ng mL⁻¹) (Eq. (2)).

$$D = \frac{\alpha \Delta g}{AC} \quad (2)$$

268

269 The effective As^{III} diffusion coefficient estimated from mercapto-silica DGT deployments of $(9.04 \pm$
270 $0.24) \times 10^{-6}$ cm² s⁻¹ agrees well with the value previously estimated using Metsorb DGT deployments⁷
271 ($D_{\text{MSIL}}: D_{\text{METSORB}} = 0.9$). Additionally, a recent study reported a diffusion coefficient in water for As^{III}
272 of 11.1×10^{-6} cm² s⁻¹, measured using modified Taylor dispersion procedures.²⁵ This value is within
273 10% of the value measured by Metsorb DGT and within 20% of the value measured by mercapto-silica
274 DGT.⁷ This consistency of diffusion coefficients measured in polyacrylamide hydrogel and in water
275 indicates that the diffusion of As^{III} is only slightly restricted by the polyacrylamide gel, contrary to
276 results reported for other anions such as As^V and PO₄³⁻.^{7, 26} This is most likely because As^{III}, unlike As^V
277 and PO₄³⁻, is uncharged at neutral pH and thus not affected by any charge present within the hydrogel
278 or filter membrane; this electrostatic interaction has been suggested as the reason for the slower
279 diffusion of some anions in DGT samplers.^{7, 26} However, recent research by Garmo and co-workers has
280 shown that the agarose-crosslinked polyacrylamide gels typically used for DGT do not have charged
281 surfaces capable of interacting with diffusing species, but rather interact with cations by adsorption.^{27,}
282 ²⁸ Nitrocellulose filter membranes, however, have been found to possess a negative charge²⁷ that could
283 interact with diffusing anions such as As^V and PO₃³⁻ and reduce the effective diffusion coefficient,
284 while having little effect on the diffusion of uncharged As^{III}. This electrostatic effect should be
285 negligible at higher ionic strengths such as that of seawater where the charges on the filter membrane
286 will be screened by the high concentration of ions in solution.²⁸

287

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

299

300 **Table 1. Effect of pH on the selective measurement of As^{III} by mercapto-silica (C_{MSIL}) DGT in a**
 301 **solution containing both 50 µg L⁻¹ As^{III} and 50 µg L⁻¹ As^V. Total arsenic was measured by**
 302 **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

303

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

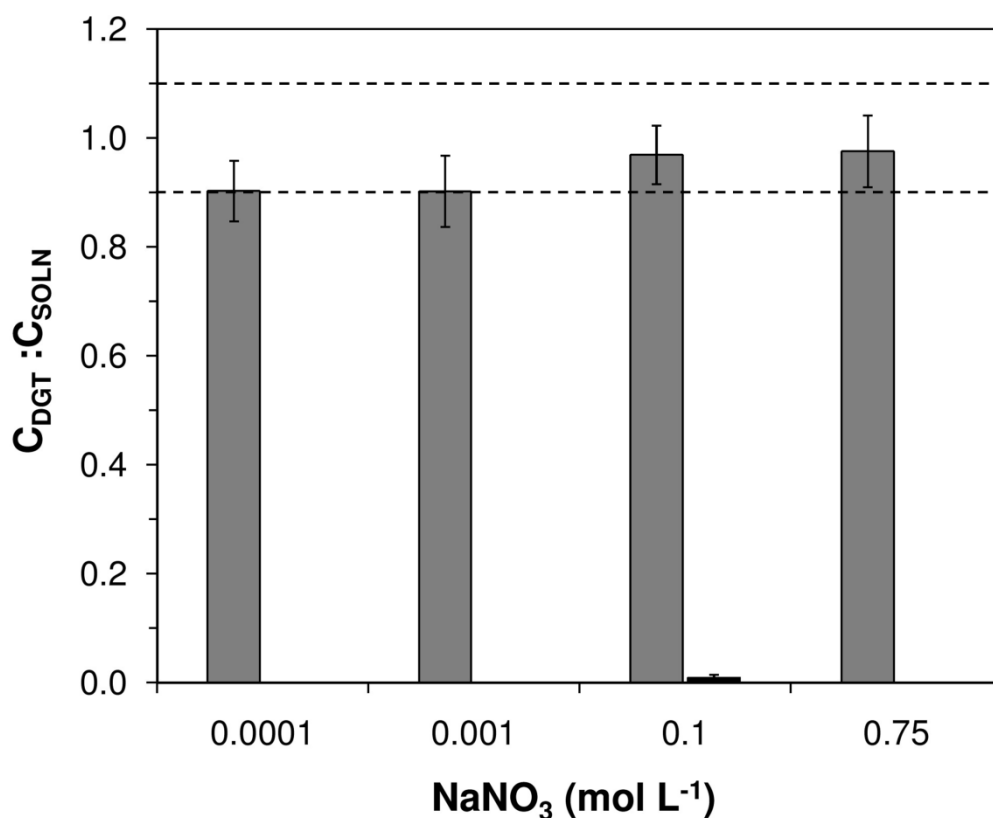
307 ($C_{MSIL}: C_{SOLN} = 0.81$) is slightly less than expected, although still within acceptable limits for a field
308 speciation method. The Metsorb DGT, which was simultaneously deployed in the same experimental
309 solution, measured total arsenic accurately, although there was slight overestimation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

315

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

324

325



326

327 **Figure 2. The effect of ionic strength (mol L⁻¹ NaNO₃) on the accumulation of As^{III} (gray) by**
 328 **mercapto-silica DGT. Dotted lines indicate a C_{DGT} : C_{SOLN} ratio of 0.9 – 1.1. The accumulation of**
 329 **As^V (black) by the mercapto-silica was negligible (C_{DGT} : C_{SOLN} < 0.01).**

330

331

332 **Capacity of Metsorb, mercapto-silica and ferrihydrite.** Recent results from Panther and co-
 333 workers²⁰ have shown an effect of adsorbent capacity on the measurement of phosphate by Metsorb
 334 and ferrihydrite DGT samplers. Ferrihydrite, with a measured phosphate capacity of <50% the capacity
 335 of Metsorb, was shown to underestimate dissolved phosphorus by 45% compared to Metsorb DGT
 336 when deployed in seawater for 96 h.²⁰ Therefore, it is important to determine the capacity of new
 337 adsorbents to enable estimation of potential field deployment times.

338

339 The capacities of Metsorb, mercapto-silica and ferrihydrite for As^{III} and As^V in both 0.01 mol L⁻¹
 340 NaNO₃ and 0.2 μm-filtered natural seawater were measured using short-term deployments over time at
 341 high concentrations of As^{III} or As^V (Table 2). The capacities were determined by identifying the highest
 342 mass accumulated by DGT that still agreed (C_{DGT}: C_{PREDICTED} >0.85) with the predicted linear uptake.
 343 The capacities reported should therefore be referred to as DGT capacities, which is the maximum mass
 344 bound by the binding phase during the linear accumulation phase, as the total capacities may be higher
 345 but are not relevant due to the non-linear uptake. The capacity of the adsorbents was tested in seawater,
 346 as it has been shown that competing ions in seawater may lower the effective capacity of a DGT
 347 adsorbent.²⁰

348

349 **Table 2. Measured DGT capacities (ng) for As^{III} and As^V of Metsorb, mercapto-silica and**
 350 **ferrihydrite DGT samplers in 0.01 mol L⁻¹ NaNO₃ 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

351

352 Metsorb and ferrihydrite exhibited a lower capacity for arsenic in seawater compared to 0.01 mol L⁻¹
 353 NaNO₃. This is expected based on the higher concentration and range of potentially competing ions
 354 present in seawater, which presumably bind to the adsorbent and reduce the available binding sites for
 355 arsenic. Conversely, mercapto-silica had a higher capacity for As^{III} in seawater compared to 0.01 mol
 356 L⁻¹ NaNO₃, for reasons unknown. Mercapto-silica is a highly selective binding agent for As^{III} due to the
 357 strong complexation of H₃AsO₃ by thiol (S-H) groups.³⁰ The strength of this interaction is confirmed
 358 by the fact that seawater has no negative effect on the adsorption of As^{III} by mercapto-silica.

359

360 Metsorb has a lower capacity for As^{III} but a higher capacity for As^{V} compared to ferrihydrite. It may
361 appear, therefore, that Metsorb could be more susceptible to interference when measuring As^{III} due to
362 competing ions reducing the effective capacity of the adsorbent, as described for PO_4^{3-} by ferrihydrite
363 DGT by Panther and co-workers.²⁰ However, the selectivity of an adsorbent for the target analyte is
364 critical to the overall performance of that technique for exposure times typical of field deployments (3
365 – 4 days). Capacity experiments were only performed over <12 h, which does not allow competing ions
366 in solution to diffuse through the diffusive gel and bind to the adsorbent in the same quantity that a
367 longer deployment time would. This means that the effect of competing ions on the effective capacity
368 of the adsorbent is underestimated by the short-term experiments typically used for adsorbent capacity
369 estimation. In order to evaluate the performance of different adsorbents, longer deployments must be
370 made at lower analyte concentrations.

371

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

379

380

381

382

383 **Table 3. Ratios of DGT-measured solution concentrations (C_{DGT}) to ICP-MS-measured solution**
 384 **concentrations (C_{SOLN}) for Metsorb, mercapto-silica and ferrihydrite DGT deployed over time in**
 385 **0.2 μm -filtered natural seawater spiked with As^{III} or As^{V} at $100 \mu\text{g L}^{-1}$ or $50 \mu\text{g L}^{-1}$. Ratios that**
 386 **indicate non-quantitative accumulation ($C_{DGT} : C_{SOLN} < 0.85$) are highlighted in bold.**
 387 **Uncertainties were calculated based on the standard deviations of both the DGT-measured**
 388 **concentrations and the measured grab samples.**

Deployment Time (h)	$\text{As}^{\text{III}} C_{DGT} : C_{SOLN}$			$\text{As}^{\text{V}} C_{DGT} : C_{SOLN}$	
	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	$0.85 \pm 0.02^{\text{a}}$	1.04 ± 0.07	$0.80 \pm 0.04^{\text{a}}$	1.07 ± 0.14	0.78 ± 0.08

389 ^a Experiments performed in $50 \mu\text{g L}^{-1} \text{As}^{\text{III}}$

390

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

397

398 As^{III} accumulation for 72 h was initially tested at $100 \mu\text{g L}^{-1}$ for both Metsorb and ferrihydrite, but only
 399 measured 78% and 57%, respectively, of the ICPMS-measured solution concentration. The
 400 accumulated mass theoretically predicted at this deployment time is the same as the measured DGT
 401 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 $50 \mu\text{g L}^{-1} \text{As}^{\text{III}}$ so
403 that the adsorbent capacity would not be reached. This resulted in a $C_{\text{DGT}}: C_{\text{SOLN}}$ 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 ($< 1.5 \mu\text{g L}^{-1}$)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 workers²⁰ 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 workers³¹ 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-workers²⁰ and Degryse and co-workers³¹ 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 ($0.03 \mu\text{g L}^{-1}$; 72 h deployment) and total inorganic
446 arsenic by Metsorb DGT ($0.03 \mu\text{g L}^{-1}$; 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

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

454

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

460

461 **Acknowledgements**

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

466

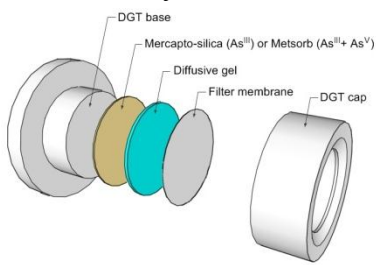
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