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Sampling of Dissolved Inorganic Sb^{III} by Mercapto-Functionalized Silica-based Diffusive Gradients in Thin-Films Technique

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Abstract

The mercapto-functionalized silica (MPS) diffusive gradients in thin-films (DGT) device, for the first time, was characterized by the determination of dissolved inorganic Sb^{III}. The performance of MPS–DGT was assessed by (1) determining the diffusion coefficient of Sb^{III} in polyethersulfone membrane, (2) assessing an uptake efficiency and digestion efficiency of MPS for Sb^{III}, (3) investigating the effect of pH, ionic strength (as $NaNO_3$) and foreign ions on performance of MPS–DGT for Sb^{III} species, and (4) assessing the validation of MPS–DGT for the measurement of dissolved inorganic Sb^{III} in spiked waters. The diffusion coefficient of Sb^{III} measured in PES membrane by a diffusion cell was $(3.05\pm0.09)\times10^{-6}$ cm^2 s^{-1}. There was a tendency toward higher adsorption affinity for Sb^{III} compared with the Sb^{V}. Mass *vs.* time deployments of MPS–DGT at pH 6 (0.01 mol L^{-1} $NaNO_3$) demonstrated linear uptake of Sb^{III} (R^2=0.9973). The MPS–DGT was independent of ionic strength (0.001–0.7 mol L^{-1} $NaNO_3$ at pH 5) and pH (3–8, 0.01 mol L^{-1} $NaNO_3$) for the measurement of Sb^{III}. The presence of foreign ions (such as Ca^{II}, Mg^{II}, Cd^{II}, Zn^{II}, Cu^{II}, As^{III} and Sb^{V}) has no significant influence on the uptake of Sb^{III} by MPS–DGT. MPS–DGT can quantitatively measure the concentration of dissolved inorganic Sb^{III} in spiked etching wastewater. In spiked natural freshwater, the concentration of dissolved inorganic Sb^{III} obtained by MPS–DGT is significant lower than the concentration of added Sb^{III} due to the presence of natural organic matter (8.7 mg C L^{-1}) which would have complexed a fraction of the added Sb^{III} and have changed the speciation of added Sb^{III}. The MPS–DGT device can potentially be used as a tool of speciation measurement for Sb^{III} in aqueous environments.

Keywords: Diffusive Gradients in Thin-Films, Speciation; Antimony

1. Introduction

Antimony (Sb) is listed as a priority pollutant by the U.S. Environmental Protection Agency due to its toxicity.[1] Different species of Sb in environment may show great differences in chemical behavior and is a critical factor influencing their toxicity.[2] Sb^{III} species are usually more toxic than Sb^{V}.[3] Determination of the chemical speciation of Sb in environment is important to get additional information about its chemical forms, mobility, availability, geochemical behavior and toxicity.[4] It is essential to develop the reliable methods for monitoring and sampling the different species of Sb in environmental samples.

The diffusive gradients in thin-films (DGT) technique has been developed by Davison and Zhang [5] and become one of the most promising in situ sampling and measurement techniques for trace metals in natural waters, soils and sediments.[6] The DGT device contains a diffusion layer (*e.g.* polyacrylamide hydrogel,[7] dialysis membrane,[8] nylon membrane [9] or chromatography paper [10]) which allows solute species below a size threshold to pass and a binding layer which is behind the diffusive layer.[5] The binding layer usually comprises a binding agent which can bind the metal species across a diffusion layer.[5] Garmo and co-workers investigate DGT device with a gel-layer incorporating chelex-100 resin as the binding agent and a hydrated polyacrylamide gel as the diffusion gel (Chelex–DGT) for the measurement of 55 elements, and find that Chelex-DGT is capable of measuring 24 elements accurately, whereas, for the element of Sb^{III}, linear uptake with time is not observed by Chelex–DGT indicating that this metal is not quantitatively collected by Chelex–100 resin and can not be measured by Chelex–DGT. [11] Recently, precipitated ferrihydrite has been used as a DGT binding agent for the measurement of Sb^{V}, As^{V}, V^{V} and Se^{VI}.[12] Panther and co-workers reported a new DGT device using a titanium dioxide-based adsorbent as the binding agent for the measurement of a variety of anionic species such as Sb^{V}, As^{V}, V^{V}, Mo^{VI} and W^{VI}.[13] However, the studies on the sampling and measuring of Sb^{III} by DGT technique in

water are still insufficient. Such constraint should be rectified by the incorporation of Sb alternative binding agents. Previous researches have reported that the compounds containing thiol groups have strong affinity for Sb^{III} [14] and can be used for the separation of Sb^{III} from the mixed solution of Sb^{III} and Sb^{V} [15] because the thiol groups as "soft acid" has a high affinity for "soft" Sb^{III} ions and a low affinity for "hard" Sb^{V} ions. The objective of this work is to take advantage of mercapto-functionalized silica (MPS) as the DGT binding agents for the selective measurement of Sb^{III} species. MPS has been previously used as a DGT binding agent for As^{III}, [16] methylmercury[17]. However, it has not been investigated for the selective measurement of Sb^{III} by DGT. In this work, the validation of MPS–based DGT device (MPS–DGT) for the measurement of Sb^{III} and the influence of a range of pH (3–8) and electrolyte concentrations (0.0001–0.7 mol L^{-1} as $NaNO_3$) on its performance were investigated. Finally, the application for the measurement of Sb^{III} in water was assessed.

2. Experimental section

2.1 Reagents, materials, and solutions

All experimental and reagent solutions were prepared with deionized water. Sb^{III} standard was obtained as potassium antimonyl tartrate (Aldrich, 99.95% purity). The stock solutions of Sb^{III} (1000 mg L^{-1}) and Sb^{V} (1000 mg L^{-1}) were prepared by potassium antimonyl tartrate and potassium hexahydroxyantimonate (Sigma-Aldrich), respectively. The working solutions were prepared by series dilution of the stock solutions immediately prior to their use. Polyethersulfone membrane (PES, pore diameter 0.2 μm, Φ 25 mm, thickness 165±5 μm) was obtained from Kenker, USA. MPS (200–400 mesh), acrylamide, ammonium peroxydisulfate, bis-acrylamide, tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich. The patented agarose-derived cross-linker was purchased from DGT Research Ltd., UK. The other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All chemicals used in this work were of analytical grade and used without

further purification. Plastic containers and glassware were cleaned by soaking in diluted HNO_3 (10%) and were rinsed with deionized water prior to use. All the metal stock solutions (1000 mg L^{-1}) were obtained from the National Research Center for Standard Materials (NRCSM, Beijing, China).

2.2 Preparation of binding layer

MPS binding layer was prepared as described previously.[16,17a] 1 g of dry mass of MPS was added per 10 mL of pre-gel solution (15% acrylamide and 0.3% DGT cross-linker). 70 μL of 10% freshly prepared ammonium persulfate and 25 μL TEMED were added, and the mixture was stirred well before casting. The mixture solution of gel was cast between two glass plates and placed in an oven at 45 °C for 1 h, afterwards the binding gel was peeled off. It required careful handling to avoid breakage. The 2.5 cm diameter disks of binding gel was cut and stored in deionized water. The thickness of hydrated gels was 0.50±0.05 mm.

2.3 Uptake and digestion

Uptake of disks of MPS binding gel for Sb^{III} was investigated in batch experiments. 10 mL of aqueous solutions containing different initial concentrations of Sb^{III} (0.1, 0.5, and 1 mg L^{-1}) and 0.01 mol L^{-1} $NaNO_3$ at pH 5 were equilibrated with individually exposing the discs of binding gel (n=5) for at least 24 h, and then the disks were taken to determine the mass of Sb^{III} remaining in solution. The uptake efficiency of the disks of binding gel for Sb^{III} was calculated as the following equations:

$$E_{uptake}\ (\%) = 100C_i/C_f \qquad (1)$$

where E_{uptake} represents the uptake efficiency (%); C_i and C_f are the initial and final concentrations of Sb^{III} (mg L^{-1}) in solution, respectively. The Sb^{III} adsorbed onto the disks of MPS binding gel was carried out in a microwave acid digestion unit (Microwave Digestion System Start D, Milestone, Sorisole, Italy). A disk of MPS binding gel was put into PTFE vessels, and 3 mL of suprapure concentrated HNO_3, 2 mL of suprapure concentrated HCl, and

2 mL of HF were added. The digestion was allowed to 1200 W of potency and 140 °C over 30 min and then maintained at 140 °C for 45 min. After digestion, the digested solutions were filtered and transferred into a 25 mL volumetric flask, and the volume was completed with a 1% solution of HCl (v/v). The digestion efficiency of Sb^{III} from the disks of MPS binding gel was calculated by the following equations:

$$E_{digestion}(\%) = \frac{100 C_{digestion} V_{digested}}{(C_i - C_f) V_{initial}} \quad (2)$$

where $E_{digestion}$ represents the digestion efficiency (%); $V_{digested}$ and $V_{initial}$ are the volumes of digested solution of disk and initial solution of Sb^{III}, respectively. A similar procedure was followed for the uptake and digestion efficiencies of Sb^{V}.

2.4 Assembly of DGT samplers

Pistons and caps were washed in 10% (v/v) HNO_3 and then rinsed nine times with deionized water before use. MPS settled on one side of the gel in the forming process, and this side was placed facing up when assembled in DGT devices. The binding gel was covered by PES membranes. The front cap was pressed tightly. Samplers were sealed in plastic bags and stored at 4 °C.

2.5 Measurement of diffusion coefficients

PES membranes were immersed in 1 mol·L^{-1} HNO_3 for 24 h before being thoroughly rinsed with deionized water until the pH approached 7, then stored in 0.01mol·L^{-1} $NaNO_3$ until use. By storing PES membranes in $NaNO_3$ it served to pre-wet the membrane, which aided assembly and facilitated expansion of the membrane.[18] The diffusion coefficients of Sb^{III} ions through the PES membrane in 0.01 mol·L^{-1} $NaNO_3$ were determined using a specially designed diffusion cell as described by Zhang et al..[19] The diffusion cell comprised two 150 mL of compartments with an interconnecting 20 mm diameter opening. A 25 mm diameter of PES membrane known thickness was placed on the opening, provided the only connection for mass transport between two compartments and allowed the diffusion of Sb^{III} ions from a

source solution containing high concentration into a receiving solution which initially contains no Sb^{III} ions. 150 mL of 0.01 mol L^{-1} $NaNO_3$ containing 100.0 mg L^{-1} of Sb^{III} ions with pH at 5 as a source solution was put into compartment A, and 150 mL of 0.01 mol L^{-1} $NaNO_3$ with the same pH as receiving solution was put into compartment B. The high concentration (100.0 mg L^{-1}) of Sb^{III} ions in compartment A was used to ensure that the concentration depletion of metal ions during diffusion process was negligible. Both compartments were stirred continuously at 300 rpm using an overhead stirrer. Samples were taken from both compartments (50 μL for compartment A and 100 μL for compartment B with the same volume of the corresponding original solution replaced in each compartment) at 15 min intervals up to 90 min and measured by AFS. The measurements were repeated for five times. In order to test the influence of a diffusive boundary layer (DBL) on the diffusion coefficients of Sb^{III} through PES membrane, the different stirring rates from 50 to 500 rpm were performed in the source solution. Here, the experimentally determined values of diffusion coefficients, D, were calculated using Eq. (3):

$$D = M \cdot \Delta g / A \cdot C \cdot t \quad (3)$$

M is the diffusion mass of Sb^{III} ions from a source solution with analyte concentration (C) into receiving solution, after passing through a diffusive layer of area (A) and thickness (Δg) over a deployment time (t). The diffusion coefficient of Sb^{III} ions at different temperatures can be corrected according to Stokes-Einstein equation.[20]

$$\frac{D_1\eta_1}{T_1} = \frac{D_2\eta_2}{T_2} \quad (4)$$

where D_1 and D_2 are diffusion coefficients at absolute temperature T_1 and T_2, respectively. η_1 and η_2 are viscosities of water at T_1 and T_2, respectively.

2.6 Accumulation over time

To estimate accumulation and measurement of Sb^{III} species over time by MPS–DGT, five sets

of triplicate DGT devices were deployed in 40 L of a well-stirred 0.01 mol L^{-1} of $NaNO_3$ solution spiked with 100 μg L^{-1} of Sb^{III} at 25 °C. The triplicate probes were removed at 24, 48, 72, 96 and 120 h, while grab samples of deployment the solution were taken at each time point and the concentration of Sb^{III} in the solution were measured by AFS as well as for changes in speciation. The MPS–DGT devices are validated by testing the relationship between the mass of analyte accumulated in the binding layer (M) and the deployment time (t) with a solution of known concentration. C_{DGT} is the concentration measured by the DGT technique in solution and can be predicted by the DGT equation:

$$M = D \cdot A \cdot C_{DGT} \cdot t / \Delta g \quad (5)$$

where, A is diffusive layer of area and Δg is diffusive layer of thickness. The experimental procedures were repeated with Sb^{V} to confirm that MPS binding agent would not accumulate Sb^{V} from solution.

2.7 Effects of pH, ionic strength and foreign ions

To test the effects of solution pH on the performance of MPS–DGT, fifteen replicates of DGT devices were deployed in 30 L of $NaNO_3$ solutions (0.01 mol L^{-1}) spiked with 100 μg L^{-1} of Sb^{III} in the pH range 3–8 at 25 °C over periods of time from 24 to 120 h with a 24–hour interval. The pH was adjusted as required using dilute HCl or KOH. The effect of ionic strength of solution on the performance of DGT was investigated by adjusting the ionic strength of a Sb^{III} solution (100 μg L^{-1}) via the addition of $NaNO_3$. The ionic strengths of the deployment solutions were range from 0.001 to 0.7 mol L^{-1} (0.001, 0.005, 0.01, 0.05, 0.1, 0.2 and 0.7 mol L^{-1}). Most natural waters fall into this range. [17a] DGT devices were deployed in 30 L of continuously stirred Sb^{III} solutions with different concentrations of $NaNO_3$ at pH 5 for 120 h with a 24–hour interval. To investigate the effect of the foreign ions on the uptake of Sb^{III}, MPS–DGT devices were deployed in 40 L of a well-stirred 100 μg L^{-1} Sb^{III} of solution containing different foreign ions at 25 °C for 120 h with a 24–hour interval. The foreign ions

and their concentrations in this study are listed in Table 1. The deployment solution was equilibrated overnight to obtain a stable pH or ionic strength.

2.8 Application to waters in the laboratory

The validation of the MPS–DGT were investigated by deploying DGT devices in 30 L of 0.45 μm-filtered natural waters or etching wastewater spiked with 100 μg L^{-1} Sb^{III} for 24, 48, 72, 96 and 120 h. Grab samples of bulk solution were taken at the beginning and in the end of each deployment. The concentrations of Sb^{III} and total Sb were measured. Prior to deployment of DGT devices, the colloidal material which had coagulated during sample storage was removed from solution by filtering. The natural waters and industrial wastewater were immediately pre-filtered under vacuum through qualitative filter papers before filtering through a 0.45 μm cellulose nitrate membrane in the laboratory. Major cation concentrations, dissolved organic carbon (DOC) and pH of mine wastewater were also shown in Table 2. The concentrations of DOC were measured using a Dohrmanne DC-190 TOC analyzer (USA).

2.9 Detection limit of DGT method

The detection limit of DGT method was determined by calculating 3 times the standard deviation (3σ) of three DGT binding gel blanks and applying Eq. 5 for specific time frames (1 day, 3 days, 5 days and 7 days).[21]

2.10 Antimony analysis

A commercial two channel hydride generation nondispersive atomic fluorescence spectrometer (AFS, Model AFS-2202E, Beijing Haiguang Instrument Co., Beijing, China) equipped with a quartz argon−hydrogen flame atomizer, a quartz gas−liquid separator, and coded high intensity hollow cathode lamps of Sb were used for the measurement of Sb^{III} and total Sb concentrations in solution according to the steps described by Deng et al..[22] The concentration of Sb^{III} in solution was determined directly by AFS. The total concentration of Sb^{III} and Sb^{V} in solution was measured as follow: In 10 mL aliquot of filtered sample, 2 mL

of KI stock solution, 2 mL of 8-hydroxyquinoline stock solutions and 11 mL of HCl (conc.) were added to obtained a 25 mL of final solution. [22] This solution was put aside for 20 min at room temperature, and then determined by AFS. The concentration of Sb^{V} was obtained by subtracting Sb^{III} from the total inorganic Sb of Sb^{III} and Sb^{V}.

3. Results and discussion

3.1 Uptake and digestion

The uptake efficiencies of MPS binding gel disks for Sb^{III} from 0.1, 0.5, and 1 mg L^{-1} Sb^{III} solution were >99%, while the uptake efficiencies of Sb^{V} from 0.1, 0.5, and 1 mg L^{-1} Sb^{V} solution were 8.4±4.6, 9.3±3.8 and 10.5±3.2 %. These results indicate that MPS binding gel disks can selectively quantitative accumulate Sb^{III} from aqueous solution. Previous studies have observed the selective adsorption of Sb^{III} by thiol-functionalized sorbents due to the strong interactions of Sb^{III} with the thiolate sulfur.[14a,23] Accurate calculation of Sb^{III} by MPS–DGT requires the quantitative and reproducible recovery of metal ions captured in MPS binding gels. Concentrated acids digest and destroy the structure of the gels, with complete release of Sb^{III} from the binding gels disks. Prior to analysis of Sb by AFS, parts of the polyacrylamide re-precipitated, making a filtration or centrifugation step necessary.[13] The high acid matrix does not affect the measurement of AFS for Sb^{III} or Sb^{V}. The values of $E_{digestion}$ for Sb^{III} or Sb^{V} by MPS binding gels disks were 97.7±2.6 and 98.1±3.3 % (mean value ± standard deviation), respectively, which was very close to the digestion efficiency of the precipitated ferrihydrite containing gel described by Luo and co-workers.[12] The low standard deviations indicated that the digestion procedure was reproducible.

3.2 Diffusion coefficient in the PES membrane

The DGT-labile concentration is accurately determined relying on the use of diffusion coefficient. For Sb^{III}, applying the Stokes−Einstein equation for temperature correction (Eq. 4), the diffusion coefficient obtained from Eq 3 in PES membrane was $(3.05\pm0.09)\times10^{-6}$ cm^2

s^{-1} at pH 5 and temperature 25 °C. There are no published diffusion coefficient data for Sb^{III} measured using a diffusion cell. For Sb^{V}, the diffusion coefficient measured using a diffusion cell ($(1.71\pm0.15)\times10^{-6}$ cm^2 s^{-1}) is ~19 % of the diffusion coefficients in water (9.05×10^{-6} cm^2 s^{-1}) [24] at 25 °C and lower than the value reported by Panther et al. $(6.04\pm0.12)\times10^{-6}$ cm^2 s^{-1}) [12] and published by Öterlund et al. $(5.55\pm0.20)\times10^{-6}$ cm^2 s^{-1}) [25]. The differences might arise from the composition variations of diffusion layers.

The diffusion coefficient of Sb^{III} is independent on pH in a 0.01 mol L^{-1} of $NaNO_3$ matrix (as shown in Figure 1a). There are only small discrepancies of diffusion coefficient at the different pH values. For a constant pH 5, the diffusion coefficient of Sb^{III} in PES membrane was independent of ionic strength in the range of 1–200 mmol L^{-1} and decreased at the ionic strength of 700 mmol L^{-1} (as shown in Figure 1b), indicating that the high ionic strengths had effects on the diffusion of Sb^{III} through PES membrane as a result of the change of solution viscosity and/or the competition diffusion between Sb^{III} and nitrate.

In poorly moving waters, the DBL thickness becomes significant compared with the diffusive layer thickness. This need arises as a result of the diffusion coefficient of metal ions in bulk solution being similar to the diffusion coefficients in the polyacrylamide gels.[8] The diffusive gradient within the DBL can also limit the overall mass transport. With the PES membrane diffusive layer described here, changing rates of stirring from 50 to 500 rpm had virtually no influence on the diffusion coefficients of Sb^{III} through PES membrane in the diffusion experiments (Figure1c). These experimental results indicate that a DBL does not become significant, even in slower moving waters and the transport across the membrane is the rate-limiting step even under the most critical conditions because the diffusion coefficient in the membrane is lower than the diffusion coefficient in the bulk solution. Although the diffusion coefficient of Sb^{III} in aqueous solution has not been reported in the literature, diffusion coefficient of 7.0×10^{-6} cm^2 s^{-1} for Sb^{III} in 1 mol L^{-1} of HNO_3 solution has been

previously reported.[26] The diffusion coefficients of metals have been significantly affected by ionic strengths of solution and decrease with the increase of ionic strengths.[8,27] In this work, the same trend has been obtained. We may speculate that the diffusion coefficients of Sb^{III} in natural freshwater may be greater than the diffusion coefficients in 1 mol L^{-1} of HNO_3 solution. Diffusion coefficient of Sb^{III} in PES membrane will always be lower than the diffusion coefficient of the metal ions in solution, the formation of a DBL layer at the membrane interface will usually have a very minor contribution to the overall mass transport. This means the thickness of the membrane can be used as Δg in the DGT equation under most deployment conditions without needing to correct for the DBL thickness.

3.3 Accumulation over time

The MPS–DGT was validated by examining the relationship between the mass of Sb^{III} accumulated in MPS and the deployment time with a Sb^{III} or Sb^{V} solution with fixed concentration. The measured mass of Sb^{III} accumulated by MPS–DGT increased linearly with deployment time over 120 h (R^2=0.9973) and fitted the theoretical line which calculated from the known solution concentrations (Figure 2). Based on these data, the concentrations of Sb^{III} were calculated using Eq. (5). The fraction of labile Sb^{III} in synthetic solution was 94.5± 3.2% of the soluble Sb^{III} concentration, where free species dominated, however, the linear uptake of Sb^{V} with time is not observed by MPS–DGT (Figure 2). This result is consistent with the low uptake efficiency of MPS for Sb^{V}, suggesting that accumulation of Sb^{V} is limited by thermodynamic factors.[28] Previous studies have observed the weak coordination interactions of Sb^{V} by thiol groups.[29] These results partially confirm that the new MPS–DGT devices meets the assumptions of the DGT equation, ensuring that the concentration of analyte at the interface between the binding gel and diffusive layer was effectively zero. These results confirm that MPS can be used as an appropriate DGT binding agent for the selective accumulation of Sb^{III}.

3.4 Effect of pH

In order to test the effect of the solution pH on the uptake of Sb^{III} by MPS binding gel, MPS–DGT devices were deployed in synthetic solution at different pH from 3 to 8. Figure 3a shows the ratio of DGT-measured concentrations (C_{DGT}) to the independently measured concentrations of the bulk solutions (C_{SOLN}) over a range of pH values. The results showed that the uptake of Sb^{III} by MPS-DGT devices was satisfactory in pH range of 3–8, indicating that the charge of bulk solution pH did not significantly affect the uptake performance of Sb^{III} by MPS-DGT. The pH of natural fresh waters normally falls into this range.

3.5 Effect of Ionic Strength

To visualize the effect of the ionic strength on uptake of Sb^{III} by MPS–DGT, the ratios of C_{DGT}/C_{SOLN} is plotted versus the log value of the ionic strength. At ionic strengths range from 0.001 to 0.7 mol L^{-1}, the values of C_{DGT} for Sb^{III} were close to C_{SOLN} (Figure 3b). This suggests that varying the ionic strength of the solution over 3 orders of magnitude did not have a substantial effect on the uptake of Sb^{III} by the MPS–DGT.

3.6 Interference Test

MPS gel probably also retain other elements besides Sb^{III} in water samples, such as Zn^{II}, Cu^{II}, Pb^{II}, Cd^{II} and As^{III}.[30] The results illustrated in Table 1 show that with one exception, the ratios of C_{DGT}/C_{SOLN} were in the range of 0.9–1.1. The presence of Ca^{II}, Mg^{II}, Cd^{II}, Zn^{II}, Pb^{II}, Cu^{II}, As^{III} and Sb^{V} ions in the sample solution had no obvious influence on the uptake of MPS–DGT for Sb^{III} under the selected conditions due to the thermodynamically strong interactions between Sb^{III} ions and thiol groups.[14a] Thus, MPS-DGT device clearly offers a high selectivity for Sb^{III} ions.

3.7 Detection limit

The standard deviation of Sb^{III} blank values for 3 DGT binding gels was 0.05 μg. The detection limit for each DGT mass is, therefore, 0.15 μg (3 ×0.05 μg). Using Eq 5 with a

standard DGT configuration (3.14 cm^2 exposure window area, 110 μm diffusive gel), and assuming a pH of 5 and temperature of 25 °C, the method detection limits (MDL) for DGT over time frames of 1 day, 3 days, 5 days and 7 days are 1.99, 0.664, 0.498, and 0.285 ng L^{-1}, respectively. As the environmental concentration of Sb^{III} is likely to be in the ng/L range, the data show that low ng L^{-1} detection limits can be achieved for the deployment time at least 3 days.

3.8 Performance in spiked waters

To evaluate the performance of the DGT method for the uptake of dissolved inorganic Sb^{III} in waters, DGT devices were deployed in natural freshwater and an etching wastewater spiked with Sb^{III}. No Sb^{III} could be detected in the river water and etching wastewater by direct measurement of AFS, and hence samples were spiked with aliquots of Sb^{III} to give a Sb^{III} concentration of ~100 μg L^{-1}. Reproducibility of MPS–DGT in the spiked waters was very good, with relative standard deviations of less than 6%. For etching wastewater, the value of C_{DGT}/C_{SOLN} (0.95±0.05) between 0.9 and 1.1 is obtained, indicating that the fraction of dissolved inorganic Sb^{III} measured by MPS–DGT is in good agreement with the added Sb^{III} concentration, and MPS–DGT can quantitatively measure the concentration of dissolved inorganic Sb^{III} in etching wastewater over the 5 day deployment. Such good agreement indicates that the coexisting ions in etching wastewater have no influence on the uptake of dissolved inorganic Sb^{III} by MPS–DGT. For natural freshwater, C_{DGT} (58.1±3.4 μg L^{-1}) is significantly lower than C_{SOLN} (90.2±4.2 μg L^{-1}). It is possible that the speciation of added Sb^{III} have be changed by the presence of natural organic matter (such as humic acid) in the natural freshwater, which may be affecting the uptake of MPS–DGT for dissolved inorganic Sb^{III} due to the interactions between Sb^{III} ions and natural organic matter.[31] Buschmann et al. [32] report that over 30 % of total Sb^{III} may be bound to natural organic matter under environmentally relevant conditions. Tella and Pokrovski found that Sb^{III} can form complexes

with the natural organic matter having O- and N-functional groups and 35% of total dissolved Sb^{III} binds to aqueous natural organic matter via carboxylic and hydroxy-carboxylic groups.[33] The MPS–DGT estimates are in a good agreement with the literature values On the other hand, prior to direct AFS measurements, samples were filtered through a 0.22 μm pore-size membrane and acidified. Acidification may release Sb^{III} binding with natural organic matter which remain in the sample, and contributing to the higher value of C_{SOLN} than C_{DGT}. Thus, these results obtained in spiked waters demonstrate the potential and robustness of MPS–DGT to assess Sb^{III} in common water.

4. Conclusions

In this study, a reliable DGT device with MPS as the binding agents and PES membranes as the diffusion layer was developed for the selective measurement of Sb^{III} in aquatic system. This paper presents the first published measurements of the diffusion coefficient of Sb^{III} in PES membranes. The change in diffusion coefficient at high ionic strength of 0.7 mol L^{-1} $NaNO_3$ is possibly due to the change of solution viscosity or the competition diffusion. Over the pH range of 3–8 and ionic strengths from 0.001 to 0.7 mol L^{-1}, the mass of Sb^{III} accumulated by MPS–DGT agreed well with the mass of Sb^{III} which predicted from the known solution composition. Furthermore, the presence of cations at concentrations up to 1–3 fold higher than those in synthetic solution, has no significant influence on the uptake of Sb^{III} by MPS-DGT. The precision of the results from replicate DGT devices were generally higher than 90%. The competition adsorption between Sb^{III} and Hg^{II} onto MPS affects the accumulation of Sb^{III} by MPS–DGT. When MPS-DGT was applied to spiked etching wastewater in the laboratory, a good agreement was obtained between the C_{DGT} and C_{SOLN}. In spiked natural freshwaters, C_{DGT} is significant lower than C_{SOLN} due to interactions between Sb^{III} ions and natural organic matter. This work has demonstrated that the suitability of MPS–DGT for the measurement of inorganic Sb^{III} species in natural waters is likely to be

useful for the assessment of Sb^{III} availability in natural waters. Future research may involve testing the suitability of MPS–DGT to assess Sb^{III} in water under field conditions and determine whether DGT assessment of Sb^{III} matches with availability in waters.

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424 **Figure captions**

425 Figure 1. Diffusion coefficient as a function of pH (a) and ionic strength (b). Data has been
426 adjusted using eq 4 for temperature of 25 °C. Error bars represent the standard deviation of
427 repeated experiments.

428 Figure 2. Dependence of mass of Sb^{III} and Sb^{V} accumulated by MPS–DGT on deployment
429 time. The dashed line is the theoretical slopes calculated from known concentrations of Sb^{III}
430 in solution.

431 Figure 3. (a) Effect of pH on the performance of MPS–DGT, assessed by the ratio of C_{DGT} to
432 C_{SOLN}, accounting for the change with pH at 25 °C. Ionic strength was kept at 0.01 mol L^{-1} for
433 all experiments. (b) Effect of ionic strengths on the performance of MPS–DGT at pH 5 at 25
434 °C. Mean values and error bars of triplicate measurements are given. The solid lines indicate
435 ±10% of the C_{DGT}/C_{SOLN} ratio.

436 **Table 1** Effects of the foreign ions on the uptake of Sb^{III} by MPS–DGT

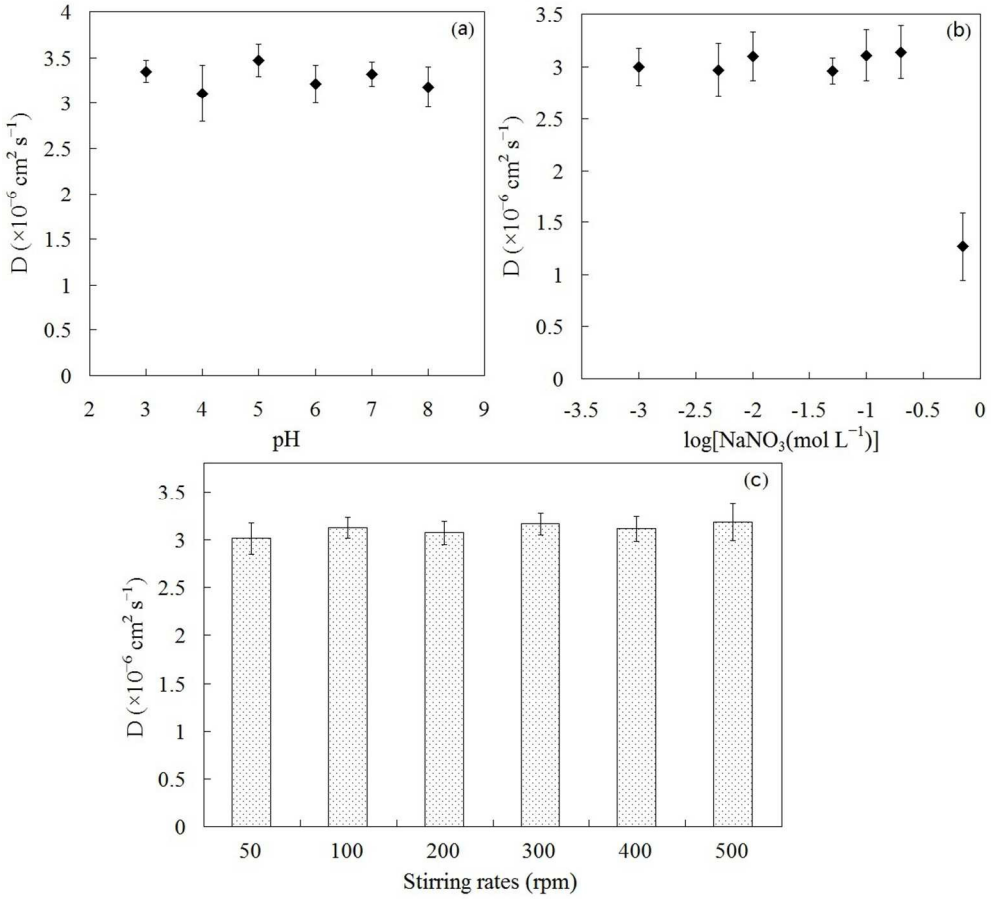
Foreign Ions	Concentrations of foreign ions (mg L^{-1})	Tolerance ratios ($C_{foreign\ ions}/C_{SbIII}$)	C_{DGT} (μg L^{-1})	C_{SOLN} (μg L^{-1})	Ratios of C_{DGT}/C_{SOLN}
Ca^{II}	100	1000	98.7±2.4	100.8±1.1	0.98±0.03
Mg^{II}	100	1000	99.8±2.3	100.5±1.2	0.99±0.03
Cd^{II}	1	10	96.9±2.4	100.1±1.1	0.97±0.03
Zn^{II}	1	10	96.4±2.0	99.8±0.8	0.97±0.02
Cu^{II}	1	10	93.5±3.1	100.5±1.0	0.93±0.04
Pb^{II}	1	10	95.1±2.9	100.8±0.8	0.94±0.03
Ni^{II}	1	10	99.8±2.5	98.8±0.8	1.01±0.03
As^{III}	0.1	1	94.7±2.2	99.8±1.8	0.95±0.03
As^{III}	1	10	92.1±3.2	100.1±1.8	0.92±0.04
Sb^{V}	0.1	1	98.2±2.3	103.4±3.1	0.95±0.03
Sb^{V}	1	10	96.8±2.8	105.4±3.4	0.92±0.03

437

438 **Table 2** Major cation concentrations, dissolved organic carbon and pH value of the Hun river
439 water and etching wastewater [a]

Measured parameters	Water samples	
	Hun river water	Etching wastewater
$[K^{I}]$ /mg L^{-1}	7.8±1.1	2.1±0.6
$[Na^{I}]$ /mg L^{-1}	38.4±8.2	20.9±7.3
$[Ca^{II}]$ /mg L^{-1}	62.5±2.5	25.5±2.1
$[Mg^{II}]$/mg L^{-1}	19.7±1.1	8.8±1.0
$[Cd^{II}]$ /mgL^{-1}	N.D.	2.1±0.2
$[Cu^{II}]$ /mgL^{-1}	N.D.	58.8±0.2
$[Pb^{II}]$ /mgL^{-1}	N.D.	32.7±0.3
$[Sb^{III}]$ /mgL^{-1}	N.D.	N.D.
[DOC]/ mg C L^{-1}	8.7±0.8	0.7±0.3
pH	7.3±0.1	4.6±0.1

440 [a] Major cation concentrations were measured by FAAS after appropriate dilution except Sb.
441 [b] N.D. means not detected.



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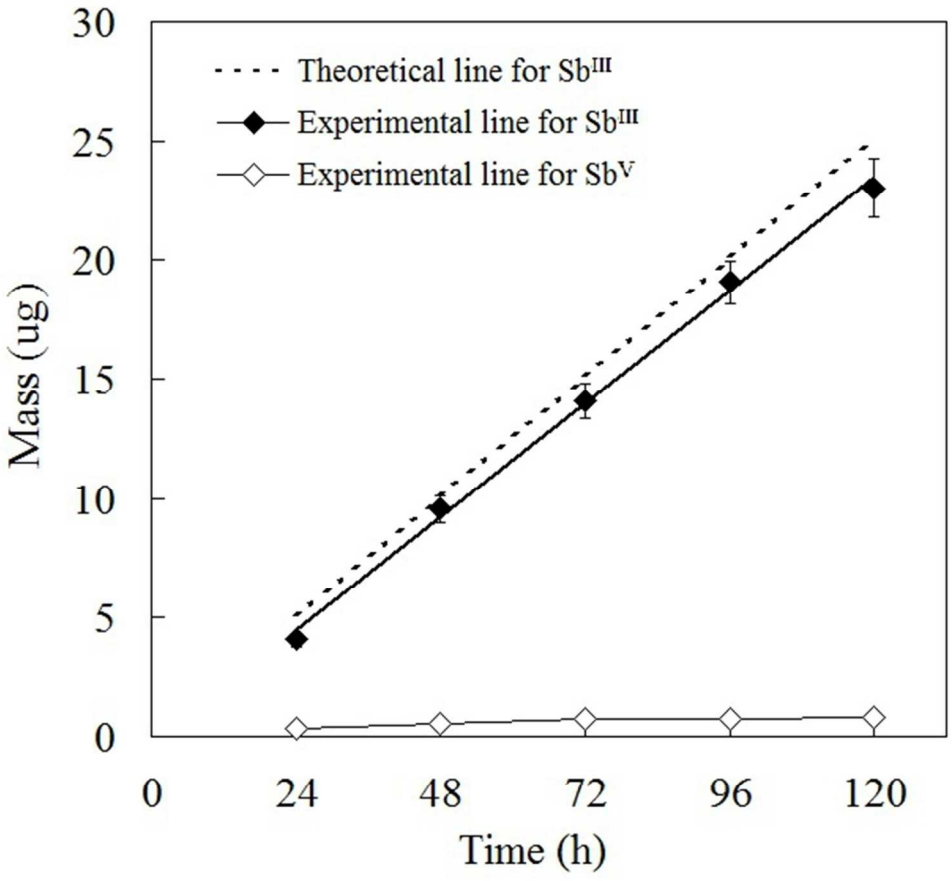

Figure 2. Dependence of mass of SbIII and SbV accumulated by MPS–DGT on deployment time. The dashed line is the theoretical slopes calculated from known concentrations of SbIII in solution.
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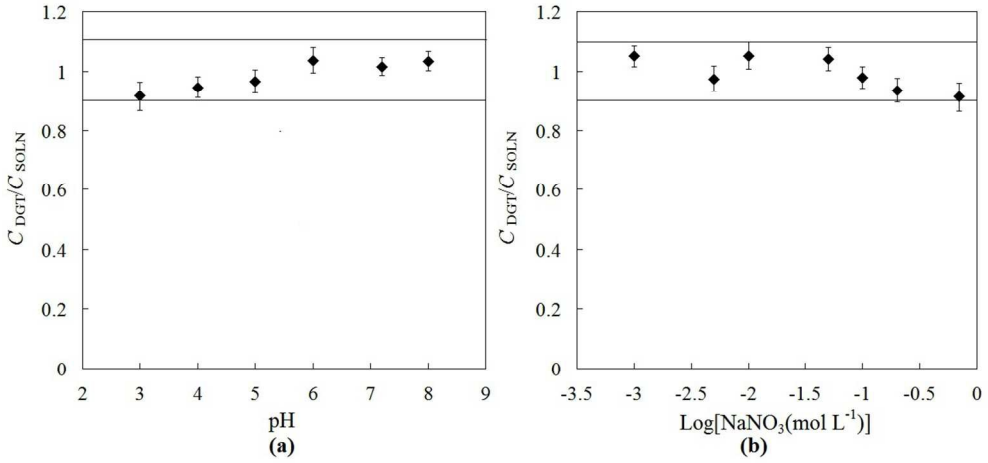

Figure 3. (a) Effect of pH on the performance of MPS–DGT, assessed by the ratio of CDGT to CSOLN, accounting for the change with pH at 25 ◦C. Ionic strength was kept at 0.01 mol L−1 for all experiments. (b) Effect of ionic strengths on the performance of MPS–DGT at pH 5 at 25 ◦C. Mean values and error bars of triplicate measurements are given. The solid lines indicate ±10% of the CDGT/CSOLN ratio.
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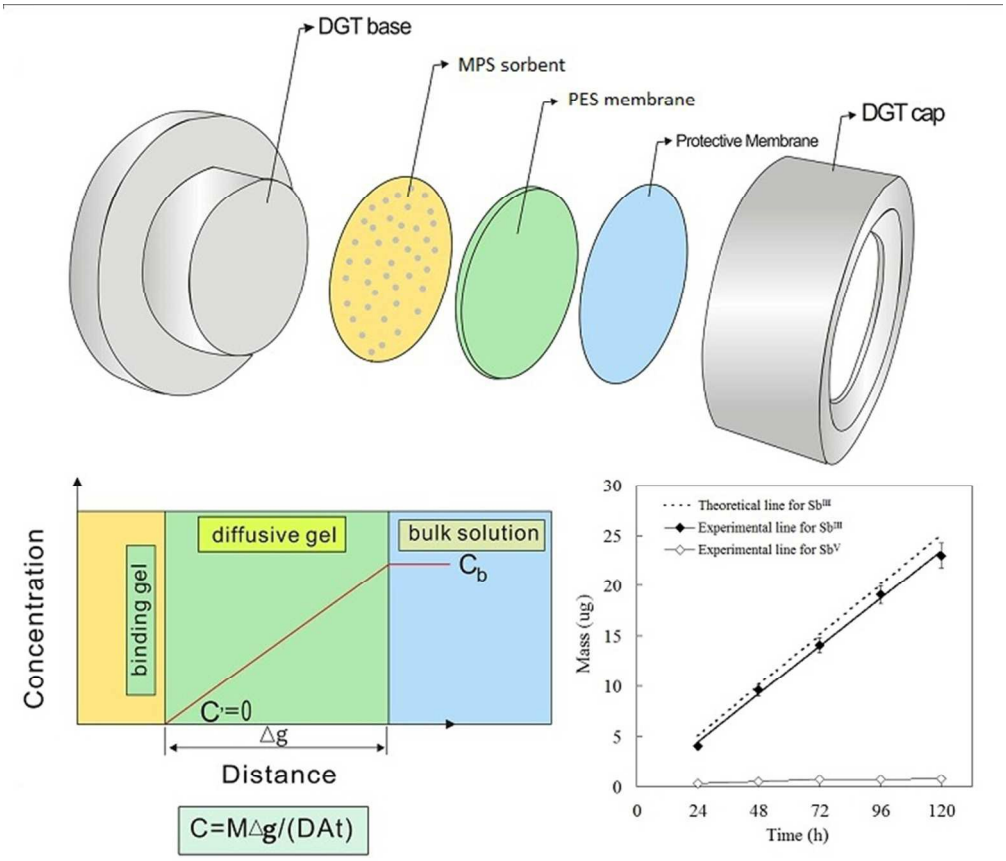

Graphical Abstract
67x58mm (285 x 285 DPI)