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Environmental Toxicology and Chemistry, Vol. 24, No. 12, pp. 3043–3047, 2005

Printed in the USA
0730-7268/05 $12.00 + .00

MEASURING SULFIDE ACCUMULATION IN DIFFUSIVE GRADIENTS IN THIN FILMS BY MEANS OF PURGE AND TRAP FOLLOWED BY ION-SELECTIVE ELECTRODE

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(*Received* 27 *January* 2005; *Accepted* 24 *June* 2005)

Abstract—A procedure for measuring in situ sulfide concentrations by coupling diffusive gradients in thin films (DGT) to solid-state ion-selective electrodes (ISE) is described and evaluated. Laboratory tests were performed to evaluate the coupling of these techniques, and these results were compared to the previously used methods of computer imaging densitometry (CID) and methylene blue. An average elution efficiency of 89%, as detected by ISE, was determined for a series of solutions containing amounts of sulfide ranging from 0.009 to 2.50 μmol. The validity of the standard mass-transfer equation for sulfide accumulation by DGT probes and subsequent detection by ISE was tested by measuring the mass of sulfide collected over time and with respect to varying diffusive gel thicknesses. Regressions of the sulfide mass accumulation versus the independent variables of time and inverse diffusive thickness proved to be linear. The use of DGT coupled to ISE provides a preconcentration method for sulfide that improves the detection limit (DL) over other techniques. This alternative method provides quantitative measurements of DGT-captured sulfide from solutions with a detection limit of at least 0.1 μmol/L for a 24-h deployment. The DGT technique also provides potential advantages in understanding sulfide speciation over existing methods.

Keywords—Sulfide In situ Diffusive gradients Thin films Ion-selective electrode

INTRODUCTION

Dissolved sulfide species are dominant ligands for many metals in anoxic natural waters [1–5] and also might be important metal ligands in the fully oxygenated environments [6–13]. Chemical equilibrium calculations suggest that sulfide controls the speciation of some metals at concentrations below the detection limit of routine analytical techniques, such as spectrophotometry or ion-selective electrodes (ISE) [12]. Routine methods for dissolved sulfide analysis at submicromolar concentrations, therefore, are needed in order to provide accurate assessments of metal speciation, bioavailability, and toxicity.

A variety of in situ and ex situ spectrophotometric, electrochemical, and chromatographic techniques for measuring dissolved sulfide exist in the chemical literature. Each method has its own set of advantages and disadvantages. Classic ex situ spectrophotometric methods (i.e., variations on methylene blue) are used most widely [12,14,15], but suffer from the need for specific reagent concentrations over different sulfide concentration ranges, departures from Beer's law at higher sulfide concentrations, and the potential for the strong acid used in the analysis to release methylene blue–reactive sulfides from loosely complexed or more labile metal sulfides, thus overestimating the true free-sulfide concentration [12]. Additionally, dissolved organic matter present in environmental samples may contribute to absorptive interferences [12,15]. The use of an ex situ sulfide solid-state ISE offers a very wide dynamic range, but requires the use of a strongly basic buffer, sulfide antioxidant buffer, for sample preservation. This buffer also includes a strong metal-complexing agent, ethylenediaminetetraacetic acid. Like methylene blue, this method could suffer from artifacts due to the potential release of sulfides from metal and other complexes. Other electrochemical techniques, such as voltammetry, are prone to electrode fouling, resulting in altered oxidation and reduction potentials on the surface of the electrode and ambiguous sulfide peaks [16]. Furthermore, and most importantly, the levels at which sulfide may control the complexation of metals in solution are at concentrations below the method detection limit of most classical methods.

Diffusive gradients in thin films are in situ analytical sensors used in speciation and preconcentration studies of labile ions, often metals [17–19]. The probes perform an in situ fractionation of chemical species by means of a semipermeable membrane, and this separation of chemical species is a kinetically based process rather than an equilibrium process [19]. During their deployment in solutions or natural waters, DGT probes continually accumulate ions. The mass of ions collected is proportional to the concentration of the ions in the bulk solution and can be quantified by means of a mass-transport equation [18,19]. Analysis of the fractionated sample is completed in the laboratory by an appropriate analytical method.

The DGT technique has been applied to dissolved sulfide analysis [20]. This technique differs from most other in situ sulfide measurements in that it records only the dissolved sulfide species that pass through the polyacrylamide gel and it integrates sulfide concentration through time. Diffusive gradients in thin films specific for sulfide have been analyzed by computer-imaging densitometry (CID) and methylene blue methods [20–23]. Both methods have drawbacks. For DGT probes quantified by CID, the image intensity for field samples can exceed the upper limits of the calibration curve [20,21] due to black saturation of the gray scale. The usage of the methylene blue technique can be rather time consuming due

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to the required reagent ranges necessary for various sulfide concentrations. In addition, both methods do not have a sufficiently low detection limit (DL) (~0.3 μmol/L) [20,24]. By coupling DGT and an ISE, one can take advantage of the unvarying reagent concentrations used in preparing sulfide antioxidant buffer [25], the dynamic linear range of the ISE, and the ability of a DGT probe to specifically preconcentrate dissolved sulfide to achieve a lower DL and more consistent results. This laboratory study was undertaken to address the feasibility of using the diffusive gradients in thin films–ion selective electrode (DGT-ISE) approach to measure the sulfide in solution and of potentially lowering the DL as compared to those of the classical and DGT-CID methods.

MATERIALS AND METHODS

Probe assembly

Silver iodide (AgI) binding and diffusive gels were prepared with minor changes to methods described previously [18,20]. The AgI binding gels were prepared from a stock solution of polyacrylamide that was composed of 15% (by volume) acrylamide (Roche Diagnostics, Indianapolis, IN, USA) and 0.3% (by volume) agarose-based cross linker (DGT Research, Lancaster, UK). The stock solution then was placed on ice. Approximately 0.6 g of finely ground AgI (Alfa Aesar, Ward Hill, MA, USA) was added to 6 ml of the polyacrylamide stock solution in a clean 50-ml centrifuge tube. Silver iodide ($K_{sp} = 8.51 \times 10^{-17}$) is insoluble in the binding gel. This solution was mixed vigorously using a Mini Vortexer (VWR International, Buffalo Grove, IL, USA) until a dispersed suspension was achieved. An aliquot of 42 μl of freshly prepared 10% (by weight) ammonium persulfate (Fisher Scientific, Pittsburgh, PA, USA) and 15 μl of 99% *N,N,N′,N′*,-tetramethylethylenediame (Sigma, St. Louis, MO, USA) were added to the suspension. Ammonium persulfate is the initiator and *N,N,N′,N′*,-tetramethylethylenediame is the catalyst for polymerization. This mixture was inverted once and pipetted carefully into a mold. If the formation of air bubbles was noticed during transfer, the mold was tilted carefully to allow for their release. Polymerization of the solution occurs in less than 2 min. Chilling the stock solution was found to slow the polymerization process and allow for complete filling of the mold. The mold consisted of two offset sheets of glass (15 × 7.5 cm) with a 0.37-mm thick plastic spacer inserted between them, held together using binder clips. The two glass sheets typically were offset by a few millimeters. The filled mold was wrapped completely with aluminum foil in order to exclude light and then held at 45°C for 60 min to cure the polymer. After curing, the AgI binding gel was placed into Milli-Q® 18-MΩ water (Millipore, Bedford, MA, USA) for 24 h in order to hydrate and rinse the gel. The binding gels then were transferred to a freshly prepared 0.01-mol/L $NaNO_3$ (Fisher Scientific) solution for storage before probe assembly. All hydrated binding gels were between 0.37 and 0.40 mm thick. Binding gel thickness was measured under a microscope.

Diffusive gels of various thicknesses were produced using 10 ml of the stock solution, 70 μl of 10% (by weight) ammonium persulfate, and 25 μl of 99% *N,N,N′,N′*,-tetramethylethylenediame. The gels were cast, set, hydrated, and stored in the same manner as described above. Diffusive gels of 0.4 and 0.8 mm thickness also were obtained commercially (DGT Research).

The diffusive and binding gels were assembled into a piston-design DGT sampling probe that was used for all solution laboratory and field studies. A piston assembly with a 2-cm diameter sample window and an appropriate 2.5-cm diameter gel cutter were obtained commercially (DGT Research) [18]. Gels were handled and cut on a clean electrophoresis gel-handling sheet (Diversified Biotech, Boston, MA, USA). The DGT sampling probes were assembled carefully to prevent air bubbles from becoming trapped between the layers of polyacrylamide gel. It is important that the resin or ligand imbedded within the binding gel be facing upward. Care was taken to ensure that the full depth of the piston assembly was filled by polyacrylamide gel, in order to prevent leakage of sample fluid around the diffusive layer. The total depth of the piston assembly was approximately 1.34 mm. Polyacrylamide gel spacers were used when needed to allow for a secure fit. No filter membranes were used in this laboratory study. All fully assembled probes were stored in a 0.01-mol/L deoxygenated $NaNO_3$ solution inside an anaerobic (nitrogen-filled) vinyl chamber glove box (Coy Laboratory, Grass Lake, MI, USA). Probes remained within the glove box at least one week before use because it was observed that the plastic pistons slowly bleed oxygen. Fresh, 0.01-mol/L deoxygenated $NaNO_3$ was added daily.

Elution of sulfide from binding gel

Sulfide accumulated by the AgI binding gel was liberated by a modified version of the acid-volatile sulfide (AVS) purge and trap extraction method [26,27]. The AVS apparatus consisted of a sealed round-bottom flask and water-cooled condenser system, purged with nitrogen. The AgI sample gel was rinsed with Milli-Q water, patted dry with a clean tissue, and placed into a 100-ml three-neck round-bottom Pyrex® flask (Corning, Acton, MA, USA). The two side necks were fitted with silicone stoppers (Cole Parmer, Vernon Hills, IL, USA) with Teflon® tubing ports. One port delivered a continual flow (~100 ml/min) of high-purity oxygen-free nitrogen gas. The other port was fitted with a female Luer lock to two-way valve (Cole Parmer) through which 10 ml of 12-mol/L deoxygenated HCl (J.T. Baker, Phillipsburg, NJ, USA) was delivered by a plastic syringe (Henke-Sass Wolf, Tuttlingen, Germany). Prior to the addition of acid, nitrogen was allowed to flow over the gel sample for 5 min to ensure that oxygen had been purged from the reaction vessel. The round-bottom flasks were heated at 65°C for 2 h. The nitrogen and evolved hydrogen-sulfide gas (H_2S) departed the distillation apparatus through the top of the condenser by way of a Teflon line and was trapped in 25 ml of sulfide antioxidant buffer [25]. The condensers atop each round-bottom flask prevented HCl vapor from entering into the traps.

Analysis of sulfide in traps following elution

Analyses of sulfide traps were performed using a silver and sulfide solid-state ISE and a reference electrode (Thermo Electron, Beverly, MA, USA). A six-point calibration curve was made daily from a stock solution. The saturated sulfide stock solution was prepared by washing a crystal of $Na_2S{\cdot}9H_2O$ (Sigma) with deionized water, drying it with a tissue, and dissolving it in a few milliliters of deoxygenated, deionized water. This stock solution was stored under nitrogen in a glove box. Production of secondary standards and the standardization of stock solution by means of lead titration were performed daily. A 0.1-mol/L $Pb(ClO_4)_2$ standard was used as the titrant (Thermo Electron).

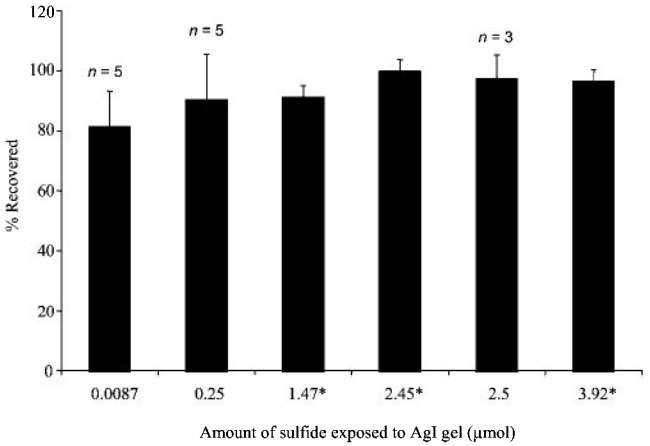

Fig. 1. Elution efficiency of sulfide from AgI binding gel. Sulfide mass determined by ion selective electrode are represented by columns with no symbols; sulfide mass determined by methylene blue [20] are represented by columns with an asterisk (*).

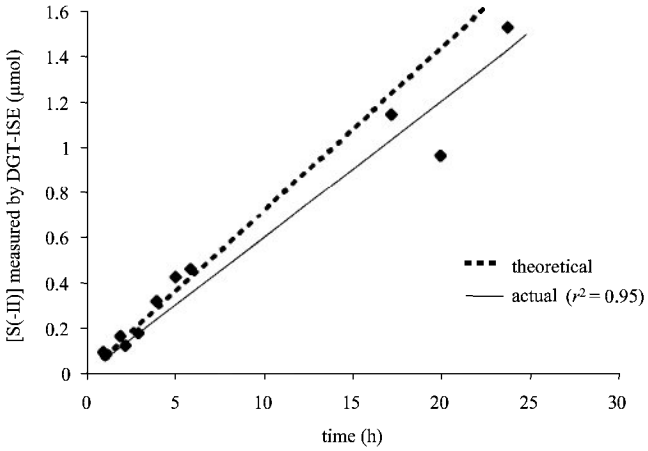

Fig. 2. Measured sulfide accumulation on diffusive gradients in thin films (DGT) probes with diffusive thickness of 0.42 mm as determined by diffusive gradients in thin films–ion selective electrode (DGT-ISE). The DGT probes deployed in 18 ± 1 μmol/L sulfide solutions for 24 h. The solid line generated by the least-squares method represents a regression of the actual sulfide accumulation.

Laboratory testing conditions

Unless otherwise stated, testing of dissolved sulfide uptake onto the AgI DGT probes was performed under an oxygen-free nitrogen environment at 25°C. Gel assemblies were exposed to standardized sulfide solutions (pH = 7) in 500-ml amber volatile organic compound (VOC) sampling containers (VWR International). Minimal headspace and the use of tightly sealing VOC containers helped to minimize the loss of sulfide through volatilization. The bottles were shaken on an orbital shaker table (Cole Parmer) at 85 rpm to prevent the formation of a diffusive boundary layer that can affect the mass transport of the ion of interest through the unstirred layer at the gel surface [28].

RESULTS AND DISCUSSION

Sulfide elution efficiency

Elution tests were performed to ensure that the recovery of sulfide from the binding gels was quantitative. Bare AgI binding gels, without a diffusive layer or piston assembly, were placed into VOC sampling containers with known quantities of dissolved sulfide for 12 h. Analysis of the remaining bulk solution within the VOC sampling containers demonstrated that no detectable sulfide remained. This suggests that the dissolved sulfide was transferred quantitatively to the binding gels. The percent recovery of sulfide from the gels as detected by ISE averaged 89 ± 8% (Fig. 1). This percent compared favorably to recoveries measured by an AVS extraction of sulfide from the binding gels followed by methylene blue detection (for samples containing over 1 μmol of sulfide). Even at nanomole levels of dissolved sulfide, an 81 ± 12% recovery was obtainable by the modified AVS extraction and subsequent ISE detection approach.

Validity of DGT equations

The validity of the standard mass-transfer equations for analyte accumulation by DGT probes can be tested by measuring the mass or amount of analyte collected over time and with respect to varying diffusive gel thicknesses. Both should be linear. The underlying principles and standard mass-transfer equation for DGT have been described in detail elsewhere [17–19]. The first validity test was conducted using fully loaded (0.42-mm thick diffusive layers and AgI binding gels) DGT probes deployed in an 18 ± 1 μmol/L solution of dissolved sulfide under the previously mentioned laboratory conditions. Over a 24-h time period, sulfide accumulation was linear with an r^2- value of 0.95 (Fig. 2).

A second validity test was performed by varying the diffusive gel thickness. Duplicate DGT probes with 0.52-, 0.67-, and 0.83-mm thick diffusive layers were deployed in a 17 ± 1 μmol/L solution of dissolved sulfide for 6 h (Fig. 3). The actual mass accumulated was in good agreement with the theoretical mass, estimated from the dissolved concentration and the mass-transfer equation. The mass, as a function of the reciprocal of diffusive gel thickness, had an r^2 value of 0.88 (Fig. 3). These results concur with those of a previous study of sulfide accumulation by DGT that used the densitometric analysis of dissolved sulfide over varying diffusive gel thickness [20].

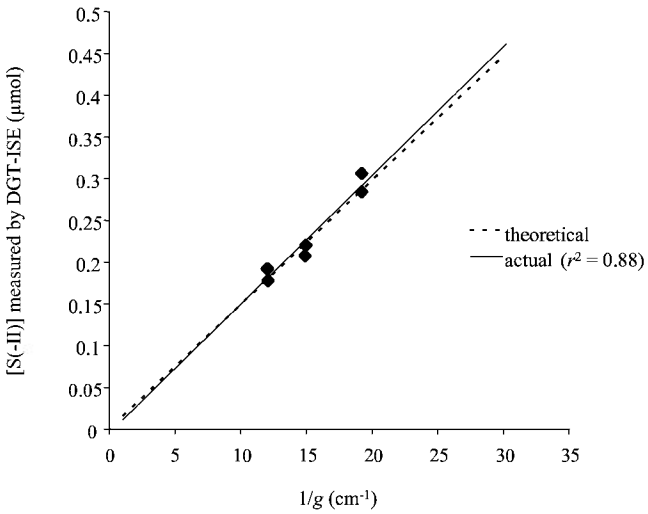

Fig. 3. Total sulfide accumulation over varying diffusive gel thickness (g) as determined by diffusive gradients in thin films–ion selective electrode (DGT-ISE). Diffusive gradients in thin films (DGT) probes deployed in 17 ± 1 μmol/L sulfide solutions for 6 h. The solid line generated by the least-squares method represents the regression of the actual sulfide accumulation. The dashed line calculated from the mass-transfer equation represents the theoretical sulfide accumulation.

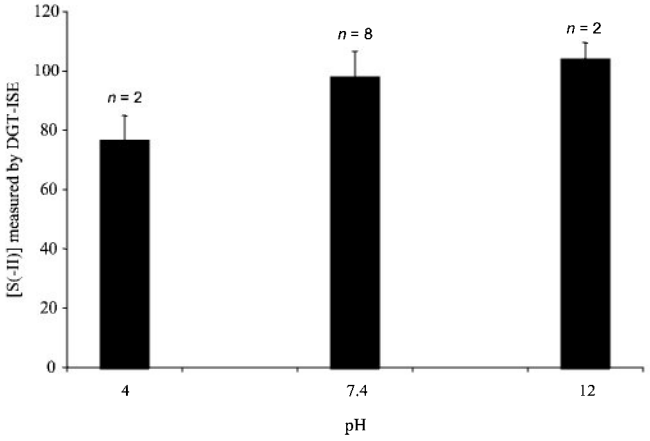

Fig. 4. Percent of total sulfide measured by diffusive gradients in thin films–ion selective electrode (DGT-ISE) at various pH values. Diffusive gradients in thin films (DGT) probes with diffusive thickness of 0.83 mm deployed in 25 ± 1 μmol/L sulfide solutions for 5 h.

Testing over pH gradient

The effect of pH on dissolved sulfide accumulation by the DGT probes was conducted by adjusting the pH of three solutions containing initial concentrations of 25 ± 1 μmol/L dissolved sulfide. These solutions were prepared in VOC containers under a nitrogen environment to minimize volatilization and oxidative loses. The pH = 4 and pH = 12 solutions were adjusted by the drop-wise addition of concentrated HCl and NaOH solutions, respectively. The pH = 7.4 solution was made with a phosphate buffer (Sigma). Complexation of dissolved sulfide to any anion within these solutions should not occur appreciably. Duplicate DGT probes with diffusive thickness of 0.83 mm were deployed in the three solutions for 5 h (Fig. 4). The lowest percent of total sulfide detected by a DGT device was for the pH = 4 solution (76 ± 8%).

At low pH, most of the sulfide is present in solution as H_2S and, thus, the low percentage of total sulfide detected by the method most likely is due to losses associated with the volatilization of dissolved H_2S from solution into the container headspace. Given the relative volume of air and water and the K_H for H_2S [29], the loss due to volatilization was estimated to be approximately 39%. This value is consistent with the lower recovery value, suggesting that sulfide loss to the headspace likely accounts for the low recovery at pH = 4. At pH = 7.4, the [H_2S] concentration is only about 30% of the total sulfide and, thus, potential losses due to volatilization are small (around 10%). At pH = 12, there should be no volatilization losses. Overall, these results demonstrate that sulfide diffusion and accumulation in the DGT probes are independent of pH, and that all sulfide species partition through the gel membrane.

Performance characteristics

Typical precision of DGT-ISE measurements for sulfide concentrations ranging between 25 and 250 μmol/L was approximately 5 to 15%, based on 15 replicates. The accuracy of the DGT-ISE measurement was within 10% for a series of 25-μmol/L solutions. The stock solution used to generate these working solutions was calibrated by a $Pb(Cl0_4)_2$ titration. Measurements were less accurate at pH values of 4 or below, probably due to the formation of volatile H_2S.

Detection limit estimates must consider both the variability of the blank measurement and the time of DGT deployment. For an 0.08-cm diffusive gel, the average mass of sulfide in the blank was 0.002 ± 0.002 μmol (n = 18), yielding an estimated DL of 0.006 μmol based on three times the standard deviation of the blank. Applying the mass-transfer equation to a 24-h deployment with a 0.08-cm diffusive thickness yields an estimated DL of 0.1 μmol/L. Just doubling the deployment time to 48 h would result in an estimated DL of 0.05 μmol/L. Blank gels also were extracted using the above-mentioned elution procedure.

CONCLUSION

The present study demonstrates that in situ sulfide concentrations in solution at the submicromolar level can be measured quantitatively by coupling DGT probes with an AVS extraction and subsequent ISE measurement of the trapped sulfide. Furthermore, all performance tests of the DGT-ISE compare favorably with previous results that were generated by DGT probes coupled to methylene blue and densitometric measurements. The dynamic linear range of the ISE (10^{-7} to 1 mol/L) enables sample analysis over extreme concentration ranges [25], which is an advantage over the other methods (CID or methylene blue). The DL determined in this study is 0.1 μmol/L (n = 18) for a 24-h deployment period using a 0.08-cm diffusive thickness and could be lowered significantly by extending the deployment time and using a thinner diffusive layer. This study's detection limit is slightly lower than the reported value of 0.26 μmol/L using DGT-CID over a 24-h deployment with a 0.08-cm diffusive thickness [20] and the reported value of 0.3 μmol/L using ex situ methylene blue [24]. Overall, the results in this study demonstrate that DGT-ISE is a suitable alternative to existing methods and that it provides a somewhat lower detection limit.

Finally, the DGT-ISE method was field tested and compared with parallel ex situ sulfide measurements using the Cline method and potentiometry. These findings will be discussed in detail in a future publication because we found differences between the various methods, as was found also by others [12]. We have investigated these differences in detail and can demonstrate that the DGT-ISE method, which produced lower concentrations, is less susceptible to artifacts than the other approaches. These findings support the idea that standard analytical techniques for sulfide measure different dissolved sulfide pools [9,12,15,30] and that DGT-ISE may provide a more robust and accurate measurement of the uncomplexed, dissolved sulfide in natural waters.

Acknowledgement—We thank C. Miller for advice and technical assistance. This work was supported in part by the U.S. Environmental Protection Agency (U.S. EPA) Science to Achieve Results grant (R827653–01–0) and National Science Foundation (NSF) grant (0451345), although the content may not necessarily reflect neither U.S. EPA's nor NSF's official agency positions. The work formed part of the Master of Science thesis of M.S. Rearick through the Marine Estuarine Environmental Science Program at the University of Maryland. Contribution 3897, University of Maryland Center for Environmental Science.

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