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# Determination of Carbonyl Sulfide and Hydrogen Sulfide Species in Natural Waters Using Specialized Collection Procedures and Gas Chromatography with Flame Photometric Detection

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Hydrogen sulfide in natural waters can be found as dissolved uncomplexed species (i.e., "free sulfide",  $\text{H}_2\text{S}_{\text{aq}} + \text{HS}^- + \text{S}^{2-}$ ), as dissolved metal sulfide complexes ("complexed sulfide"), and as particulate metal sulfides. To examine the distribution of hydrogen sulfide species and carbonyl sulfide in natural waters, a technique for their sampling and simultaneous determination was developed. Contamination and loss are minimized by using trace metal-clean and hermetic sampling techniques and apparatus. The analytical method is based on stripping an acidified 1–300-mL sample with helium, liquid nitrogen-cooled trapping of the evolved gases, followed by gas chromatographic separation and flame photometric detection. To eliminate storage artifacts, determinations are made in the field immediately after sample collection. Detection limits are 0.2 pmol/L for total dissolved sulfide and 1.3 pmol/L for OCS. Precision is better than 5% (relative standard deviation) for both sulfur compounds at the 50 pmol/L level. The method can also determine hydrogen sulfide in the headspace of a sample ( $\text{H}_2\text{S}_\text{g}$ ); this concentration can in turn be used to calculate the concentration of free sulfide that is in equilibrium with  $\text{H}_2\text{S}_\text{g}$ . In combination with selective chemical treatments, the method can also be applied to the determination of acid-volatile sulfide and chromium-reducible sulfur in suspended particles. The procedures have been used to analyze a variety of natural water and sediment samples.

## INTRODUCTION

It has become increasingly important to distinguish between natural and anthropogenic sources of sulfur to the atmosphere because these sources are of equal magnitude<sup>1</sup> and because tropospheric sulfur has been proposed as a negative feedback to the global warming of Earth.<sup>2</sup> The natural flux of sulfur gases into the atmosphere is dominated by oceanic emissions. Dimethyl sulfide and carbonyl sulfide (OCS) represent over 95% and 1% of this flux, respectively, while the flux of hydrogen sulfide ( $\text{H}_2\text{S}$ ) is  $\leq 1\%$ .<sup>1,3</sup> A direct link between the biogeochemical cycles of the latter two gases has been proposed since the hydrolysis of dissolved OCS yields hydrogen sulfide.<sup>4</sup> Hydrogen sulfide is a weak diprotic acid that exists as  $\text{H}_2\text{S}_{\text{aq}}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$ ; collectively, these three dissolved, uncomplexed species can be termed "free sulfide". However, both  $\text{HS}^-$  and  $\text{S}^{2-}$  can react with metals to form dissolved metal sulfide

complexes and precipitates (e.g., refs 5 and 6), and thus may affect trace metal cycling. Therefore, hydrogen sulfide dissolved in natural waters can exist as "complexed sulfide" and free sulfide ( $\text{H}_2\text{S}_{\text{aq}} + \text{HS}^- + \text{S}^{2-}$ ); "total dissolved sulfide" is the sum of free sulfide and complexed sulfide that are dissolved in water. For these reasons, the simultaneous determination of OCS and total dissolved sulfide in the aquatic environment is useful to the study of these important sulfur gases, as well as to the study of trace metals.

Because total dissolved sulfide and OCS are highly reactive and are found at pico- to nanomolar concentrations in oxygenated natural waters,<sup>3,8,9,11</sup> determinations in the field are necessary. There are several methods for the shipboard determination of either total sulfide<sup>7,8</sup> or OCS<sup>9,10</sup> in oceanic waters. However, these methods do not afford the simultaneous determination of both compounds at the picomolar concentrations encountered in oligotrophic waters. In particular, the photoionization detector used by Cutter and Oatts<sup>7</sup> is not sensitive to OCS, while other procedures do not use sample acidification that enables the quantitative recovery of total sulfide as  $\text{H}_2\text{S}_\text{g}$ .

In this paper we describe sampling procedures and analytical techniques for the simultaneous determination of total dissolved sulfide (i.e., complexed sulfide plus free sulfide) and OCS in a variety of natural waters. Sampling procedures are specially designed to minimize contamination and loss; they are followed by the gas stripping of an acidified sample, cryogenic trapping, gas chromatography, and quantification of the evolved  $\text{H}_2\text{S}_\text{g}$  and  $\text{OCS}_\text{g}$  using a flame photometric detector (FPD). Low detection limits allow the use of small samples while maintaining good precision. In addition, these procedures have been applied to the determination of total inorganic sulfide in suspended particles and extended to the determination of headspace hydrogen sulfide ( $\text{H}_2\text{S}_\text{g}$ ). This determination allows the concentration of free sulfide that is in equilibrium with  $\text{H}_2\text{S}_\text{g}$  to be calculated. Complexed sulfide can then be estimated from the difference between total dissolved sulfide and free sulfide.

## EXPERIMENTAL SECTION

**Sampling Apparatus.** Water column samples are acquired using Teflon-coated Go-Flo sampling bottles (General Oceanics) modified to allow their pressurization by filtered (0.2  $\mu\text{m}$ ) nitrogen gas. The air bleed and sampling valves are replaced by a nylon

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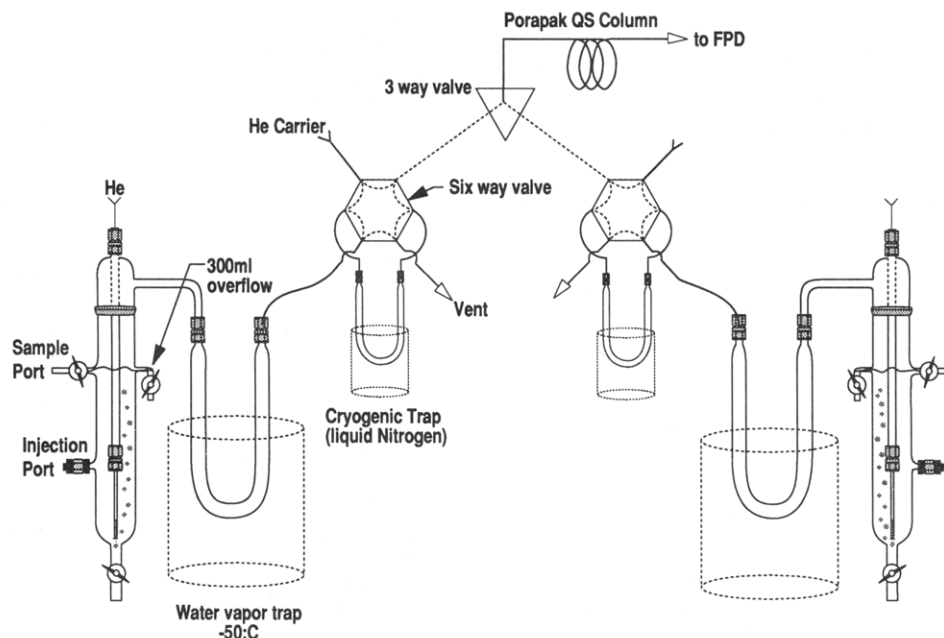


Figure 1. Schematic of the analytical system for the simultaneous determination of total dissolved sulfide and OCS.

connector (No. NY-600-1-OR; Swagelok) and by a  $3/8$ -in. Teflon plug valve (Berghoff America), respectively. Samples are transferred from the Go-Flo's into 4-L polyethylene Cubitainers (Cole-Parmer) whose caps are modified to accommodate two ports. One port is fitted with  $3/8$ -in.-i.d. Tygon tubing that can be closed by a Mohr clamp. The second port has  $1/8$ -in.-o.d. Teflon tubing extending 25 cm into the Cubitainer, while the other end of the tubing is fitted with a two-way polycarbonate stopcock (Cole-Parmer). The first port is used for sample transfer, and the second one permits the complete expulsion of air bubbles.

Porewater samples are obtained using a pressurized core barrel assembly described by Jahnke.<sup>12</sup> For each sampling port on the core barrel, a porous polyethylene rod (40 × 2 mm, 120 mesh; Porex) is used to prefilter the sample into a gas-tight syringe (10 mL; Hamilton). These syringes are fitted with a three-way stopcock to allow rinsing and removal of air from the syringe barrel while isolating the sample from the atmosphere.

The sampling gear is cleaned using detergent wash (Micro), distilled, deionized water rinsing, acetone rinsing (for Cubitainers and syringes only), a 1-day soak in 0.5 M HCl, and three deionized water rinses.

**Analytical Apparatus.** The analytical system consists of two main components that are represented in Figure 1. The stripping/trapping component is largely from the apparatus used for total dissolved sulfide<sup>7</sup> and metalloid determinations.<sup>13</sup> The internal volume (300 mL) of the stripping vessel is gravimetrically calibrated by filling with deionized water until overflow (Figure 1). The gas dispersion tube is made of Goretex microporous tubing.<sup>7</sup> The sample and drain ports have Teflon stopcocks, while the reagent injection port is a Teflon fitting (Swagelok) housing a Teflon-backed, silicone rubber septum. For samples where OCS and total dissolved sulfide concentrations exceed 100 pmol/L, a 50-mL stripper can be used. A chemical scrubber that retains  $H_2S_2$  is used for the determination of OCS concentrations in samples with  $\geq 2 \mu\text{mol/L}$  total dissolved sulfide (e.g., sediment porewaters). The scrubber is placed between the stripper and water trap and consists of a 5-cm length of  $1/4$ -in.-o.d. Teflon tubing housing a strip of Whatman AF/41 filter paper (10 × 2.5 cm) tightly wound in a roll. The filter paper is impregnated with a 2% (w/v) solution of silver nitrate. The water vapor trap is a borosilicate glass U-tube (36 cm long, 14-mm i.d.<sup>13</sup>) immersed in 2-propanol held at  $-50^\circ\text{C}$  by a cryogenic probe (Neslab).  $H_2S_2$  and  $OCS_2$  stripped from the sample are collected in a cryogenic trap made of U-shaped borosilicate glass tubing ( $1/4$ -in. o.d.) loosely packed with silanized glass wool

(Supelco<sup>13</sup>). A simpler trap consisting of 40 cm of  $1/8$ -in. Teflon tubing that is loosely packed with silanized glass wool may be used with 50-mL stripping vessels. The cryogenic trap is connected to a six-way stainless steel valve (Teflon-filled rotor; Valco). With the valve in the *strip/trap* position, helium stripping gas passes through the cryogenic trap before being vented to the atmosphere, and the carrier gas flows directly to the chromatographic column. In the *inject* position, the carrier gas passes through the cryogenic trap while the stripping gas is directly vented to the atmosphere. All connections are made with Teflon Swagelok fittings and Teflon tubing. To minimize adsorption, all internal glass surfaces are treated with dimethyldichlorosilane. To process two samples simultaneously, two identical stripping and trapping apparatuses are interfaced to a single gas chromatograph by a three-way stainless steel valve (Teflon-filled rotor; Valco).

The quantification component of the apparatus includes a chromatographic column held at  $40^\circ\text{C}$  in a gas chromatograph (Hewlett-Packard Model 5890 II) that is equipped with a FPD maintained at  $170^\circ\text{C}$  (HP Model 19258A). The column is Teflon tubing (0.16 mm i.d. × 180 cm) packed with acetone-washed, 50/80 mesh Porapak QS.<sup>14</sup> The analog output signal from the detector is processed using a Hewlett-Packard 3396A plotter/integrator. Hydrogen (75 mL/min) and air (100 mL/min) are used for the FPD flame, while helium (zero grade) is used as the stripping gas (120 mL/min) and the carrier gas (30 mL/min). To purify the stripping gas, a 1-m coil of copper tubing ( $1/4$ -in. o.d.) is packed with Carbosieve SIII (60/80 mesh; Supelco) and held in liquid nitrogen. The response of the FPD is optimized by doping the hydrogen gas with carbonyl sulfide from a permeation device (62 ng of OCS/min.; Metronics) held at  $40^\circ\text{C}$  in a thermostated water bath.

**Reagents and Standards.** Two certified  $H_2S$  and OCS permeation devices (Metronics) are maintained at  $40^\circ\text{C}$  in a thermostated water bath. These devices are used to calibrate the instrument for  $H_2S$  and OCS and are weighed at 3-month intervals to monitor their permeation rates (7.02 pmol of  $H_2S/s$  and 4.05 pmol of OCS/s). Pure, compressed  $H_2S$  and OCS are obtained from Matheson, and anhydrous sodium sulfide is obtained from Alfa. Metal solutions are atomic absorption spectroscopy standards (Baker).

Distilled, deionized (DDI) water with a specific resistance of  $18 \text{ M}\Omega\text{-cm}$  is used in all experiments. All acids are reagent grade (Baker); phosphoric acid is diluted with DDI water to a concentration of 1.5 mol/L, and HCl is diluted to 4.0 mol/L. A

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chromium(II) solution is prepared by passing 1 mol/L chromium chloride (dissolved in 1 mol/L HCl) through a Jones reductor column.<sup>15</sup> Immediately after preparation, this reagent is sealed under nitrogen atmosphere to prevent its oxidation.

**Procedures. (a) Determination of Total Dissolved Sulfide and OCS in Water.** Immediately after the sample is acquired using a Go-Flo sampling bottle, the bottle is pressurized (7 kPa) with filtered nitrogen, and the sample is passed through a polycarbonate filter (0.4- $\mu$ m pore size, 142-mm diameter; Nuclepore) held in a Teflon filter holder and hermetically transferred into a Cubitainer. The Cubitainer should be rinsed with the sample three times, and while being filled, air bubbles are rapidly and completely expelled through the Teflon tubing and two-way valve. In addition, exposure to light should be minimized by covering the Cubitainer while it is being filled. The filtered sample is analyzed immediately for total dissolved sulfide and OCS, or it can be refrigerated (4 °C) in the dark until analysis ( $\leq 2$  h).

For analysis, a 300-mL sample is hermetically transferred from a Cubitainer into the stripper with rinsing, while the stripping gas flow is stopped and the six-way valve is set on *strip/trap*. The cryogenic trap is then immersed in liquid nitrogen and stripping gas flow started. Twelve milliliters of 1.5 mol/L phosphoric acid is immediately injected into the stripper and the timing of stripping/trapping begun. After 20 min of stripping, the six-way valve is set on *inject* (ensure that the three-way valve is set to interface the proper strip/trap apparatus) and the trap removed from the liquid nitrogen; the integrator is started at this time. After 60 s, the six-way valve is returned to the strip/trap position. The stripper is drained and is ready for the next analysis. Using conditions given above, retention times are approximately 4.3 min for  $\text{H}_2\text{S}$  and 6.8 min for OCS. Elevated total dissolved sulfide and OCS concentrations in coastal and estuarine waters allow a 50-mL stripper and an all-Teflon cryogenic trap to be used. The amount of acid injected is reduced to 2 mL and the stripping/trapping time decreased to 15 min.

**(b) Determination of Total Dissolved Sulfide and OCS in Porewaters.** Sediment cores in the special core barrel are pressurized with nitrogen to 250 kPa, and sediment porewater samples are hermetically extracted from the sediments into 10-mL gas-tight syringes fitted with three-way stopcocks. With the stopcocks closed to isolate the samples from the atmosphere, the syringes can be refrigerated (4 °C) in the dark until analysis ( $\leq 2$  h), although immediate analysis is preferred.

A 50-mL stripper is filled with 25 mL of deionized water and 2 mL of 1.5 mol/L phosphoric acid. With the trap in liquid nitrogen and using a gas-tight syringe, a sample aliquot (0.1–5 mL) is filtered (0.4- $\mu$ m pore size, polycarbonate membrane; Nuclepore) and injected through the reagent port of the stripper using a platinum needle. The sample is analyzed for total dissolved sulfide and OCS as described above. Multiple determinations can be performed without draining the stripper until 25 mL of porewaters has been analyzed.  $\text{H}_2\text{S}_g$  can interfere with the quantification of OCS for porewaters with total dissolved sulfide concentrations of  $\geq 2 \mu\text{mol/L}$ . In this case, a sulfide scrubber is inserted in the gas stream between the stripper and the water trap, and no acid is added to the sample.

**(c) Determination of Acid-Volatile and Chromium-Reducible Sulfur in Suspended Particulate Matter.** Using nitrogen overpressure (7 kPa), a known volume of water (5–30 L) from a Go-Flo sampling bottle is passed directly through a polycarbonate filter (0.4- $\mu$ m pore size, 142-mm diameter; Nuclepore) placed in an all-Teflon filter holder. The filter is folded, placed in a polyethylene vial, and immediately frozen until analysis. The analytical procedure of Cutter and Oatts<sup>7</sup> is modified for the sequential analyses of acid-volatile and chromium-reducible sulfide. A filter is placed in a 50-mL stripper with 10 mL of deionized water. After a 2-min purge with helium stripping gas, the cryogenic trap is immersed in liquid nitrogen and 10 mL of 1 mol/L HCl is added. After 15 min of stripping and trapping, the six-way valve is set to *inject*, and the procedure for total dissolved sulfide described above is followed; this yields the concentration of particulate acid volatile sulfide (pAVS).

After 2 min, the cryogenic trap is immersed in liquid nitrogen, and 4 mL of concentrated HCl and 10 mL of Cr(II) solution are introduced in the stripper. After 20 min of stripping/trapping,  $\text{H}_2\text{S}_g$  retained on the cryogenic trap is determined as above, yielding the concentration of particulate chromium-reducible sulfur (pCRS).

**(d) Determination of  $\text{H}_2\text{S}_g$  in the Headspace of a Sample.** In a Cubitainer containing 3 L of sample is introduced 400 mL of high-purity helium gas through one of the ports on the cap. The Cubitainer is shaken for 30 s to equilibrate gas and liquid phases. The stripping gas tubing and the tubing leading to the cryogenic trap are connected by a Teflon tee, thus bypassing the stripper/U-tube assembly. The third arm of the tee is connected to an all-Teflon injection port similar to that on the stripping vessel. The gas flow rate through the tee (i.e., stripping gas) is reduced to 30 mL/min. The trap is immersed in liquid nitrogen, and 10–100 mL of headspace is then injected into the tee at a rate of 90 mL/min using a gas-tight syringe fitted with a platinum needle. Two minutes after the injection is completed, the determination of  $\text{H}_2\text{S}_g$  follows the procedure given above for total dissolved sulfide. Along with the measurement of sample pH, temperature, and salinity, this procedure is used to determine the concentration of free sulfide in equilibrium with the concentration of  $\text{H}_2\text{S}_g$  (i.e.,  $\text{H}_2\text{S}_{aq} + \text{HS}^- + \text{S}^{2-}$ ).

**(e) Calibration.** Calibration is carried out using  $\text{H}_2\text{S}_g$  and  $\text{OCS}_g$  from two permeation devices diluted in a stream of helium (120 mL/min). To calibrate the system, the six-way valve is set on *inject* and the effluent from the permeation devices passes through the cryogenic trap via the six-way valve. While the cryogenic trap is immersed in liquid nitrogen, the valve is switched to the *trap* position for known periods of time (typically 5, 10, 15, 20, and 25 s) and then back to *inject*. When the trap is removed from liquid nitrogen,  $\text{H}_2\text{S}$  and OCS are swept into the chromatographic column. A linear, least-squares fit of peak areas vs amount of  $\text{H}_2\text{S}_g$  and  $\text{OCS}_g$  retained on the trap is used as a calibration curve.

## RESULTS AND DISCUSSION

**Sample Acquisition.** The elimination of sampling artifacts is essential for the accurate determination of dissolved sulfur gases at picomolar concentrations. As an example, dissolved sulfide species readily form insoluble compounds with transition and "B"-type metals<sup>16</sup> that may affect the recovery of total dissolved sulfide. In addition, contamination from the atmosphere or emissions from fossil fuel combustion must be avoided. Several procedures are used to overcome these potential problems, including the use of Go-Flo bottles that are cleaned following trace metal-clean procedures.<sup>17</sup> For identical reasons, the filters for particulate sulfide speciation are also collected using trace metal-clean procedures and apparatus.

Previous work has shown that Go-Flo bottles can contaminate water samples for OCS.<sup>9</sup> Therefore, cleaned sampling bottles are checked for contamination by the following procedure. Aliquots of deionized water with a known OCS concentration are analyzed as described above after 2, 4, 6, and 24 h of being placed in the Go-Flo. An increase in OCS concentration with time warrants another cleaning and testing. A similar check is performed at the first sampling station by comparing the concentrations of OCS in water samples taken from the same depth using different Go-Flo's. Only bottles that show no contamination with these two procedures are used. It has been our experience that new Go-Flo's and Go-Flo's which have been repaired with PVC cement are severely contaminating.

To overcome the problem of atmospheric contamination, the Go-Flo's are pressurized with filtered nitrogen, ensuring

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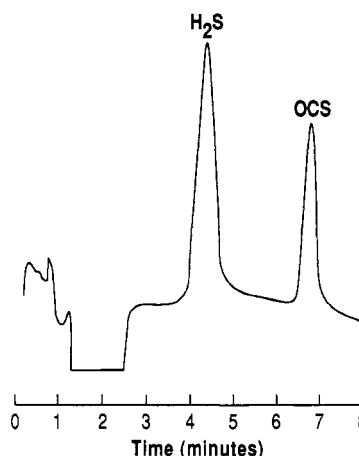
that air does not enter the bottle and contaminate the sample while it is being withdrawn. Potential contamination by the pressurizing gas is assessed in the blanking procedure described above. To eliminate gas exchange between the sample and the atmosphere, hermetic transfer steps are used throughout the procedure. For manipulating large samples, Cubitainers can expand or collapse without air bubbles being introduced. Gas-tight syringes function similarly for smaller samples (i.e.,  $\leq 50$  mL). When samples cannot be analyzed immediately, they are refrigerated in the dark to prevent the production of carbonyl sulfide via photolysis<sup>18</sup> and to slow the oxidation of total dissolved sulfide.<sup>19</sup>

Due to  $10^2$ – $10^4$ -fold supersaturation of OCS in sediment porewaters, loss of OCS from discrete core sections can be significant. Therefore, a hermetically sealed, pressurized core barrel<sup>12</sup> is used; additional advantages include ease of operation and rapidity of porewater sampling. This apparatus was checked for contamination by filling the core barrel with deionized water having a known OCS concentration and treating it as a sample; no contamination was apparent.

**Apparatus for the Determination of Total Dissolved Sulfide and OCS.** Gas stripping and cryogenic trapping is commonly used for the determination of volatile sulfur compounds.<sup>7,9,20</sup> A drawback of this general method is that the stream of stripping gas becomes laden with water vapor which can clog the cryogenic trap. This problem has been circumvented using different approaches, including chemical water traps,<sup>20</sup> Nafion dryers,<sup>9</sup> and progressive immersion of the cryogenic trap in liquid nitrogen using a motorized laboratory jack.<sup>10</sup> Cooled U-tubes have also been used to remove water vapor.<sup>7,20</sup> A silanized glass U-tube was chosen for this work because the reactivity of  $\text{H}_2\text{S}_g$  precludes the use of chemical scrubbers with oxidative or acid/base properties such as magnesium perchlorate or potassium carbonate.

Different trapping schemes have been used for the gas chromatographic determination of gaseous sulfur compounds, including preconcentration onto solid adsorbents<sup>20–22</sup> and cryogenic trapping.<sup>10,20</sup> For optimum recovery and simplicity, liquid nitrogen-cooled trapping was chosen. The construction of cryogenic traps varies, but usually comprises silanized glass beads or silanized glass wool packed in U-shaped glass tubing that can be heated to quickly volatilize the sulfur compounds.<sup>20</sup> The low boiling points of hydrogen sulfide and carbonyl sulfide do not require heating of the cryogenic trap to quantitatively desorb them, and thus  $1/8$ -in.-o.d. Teflon tubing (loosely packed with silanized glass wool) can also be used. This all-Teflon cryogenic trap is simpler to prepare than glass traps because it does not require silanization or glass/Teflon connectors. However, for the determination of total dissolved sulfide and OCS in a large seawater sample (i.e., 300 mL), glass U-tube traps are used because the amount of  $\text{CO}_2$  stripped from an acidified 300-mL sample can clog the smaller bore, all-Teflon cryogenic trap. Carryover of  $\text{H}_2\text{S}_g$  or  $\text{OCS}_g$  from one sample to the next was not observed using either type of cryogenic trap.

Packings used for the chromatographic separation of gaseous sulfur compounds include Chromosil 310 and 330 and Porapak QS. The latter is a silanized Porapak Q and can resolve the large  $\text{CO}_2$  peak (evolved from acidified seawater) from the much smaller and neighboring  $\text{H}_2\text{S}$  and OCS peaks. In addition, Porapak QS held at 40 °C retains nonpolar compounds such as dimethyl sulfide. This is useful when



**Figure 2.** Chromatogram showing the separation of  $\text{CO}_2$  (0.1 mmol/L, negative peak) from  $\text{H}_2\text{S}$  (48.5 pmol/L) and OCS (79.2 pmol/L) in a 300-mL seawater sample.

samples are analyzed over long periods of time because there is no need for more than a daily 30-min column bake-out at 110 °C to elute high-boiling compounds. An example chromatogram of a 300-mL seawater sample shows that OCS and  $\text{H}_2\text{S}$  are well separated from each other and the negative  $\text{CO}_2$  peak (Figure 2).

In sediment porewaters where total dissolved sulfide concentrations reach millimolar levels, nanomolar concentrations of OCS cannot be accurately quantified due to chromatographic interference. However, OCS can be determined by removing  $\text{H}_2\text{S}_g$  from the stripping gas using a silver nitrate scrubber. Filter paper moistened with silver nitrate has been shown to quantitatively retain  $\text{H}_2\text{S}_g$  while retaining less than 1% of the OCS.<sup>23,24</sup> For the apparatus used here, repeated injections of 424 pmol of OCS into the strip/trap apparatus show that  $97.8 \pm 2.2\%$  ( $n = 8$ ) of the OCS passes through the  $\text{H}_2\text{S}_g$  scrubber. With a single scrubber, over 100 mL of porewater samples can be analyzed without  $\text{H}_2\text{S}_g$  interference.

The use of flame photometric detectors for the quantification of sulfur compounds has been the choice of many investigators because of their selectivity and sensitivity. In the reducing flame of the detector, the dissociation of S–S dimers formed during combustion of sulfur compounds radiates at 393 nm. The nonlinear response of the detector's photomultiplier tube to the concentration of sulfur in the flame has been described by d'Ottavio et al.,<sup>25</sup> who showed that doping the flame with a background sulfur concentration linearizes and increases the sensitivity of the detector. The detector used here is doped with 62 ng of OCS/min, increasing the sensitivity of the FPD by a factor of 20 (at the 20 pmol of S level) while maintaining a wide working range (0–140 pmol of S).

In their method for the determination of nanomolar levels of total dissolved sulfide, Cutter and Oatts<sup>7</sup> used a standard solution of  $\text{Na}_2\text{S}$  for calibration that was prepared daily. However, such solutions cannot be accurately prepared in the field. Moreover, the calibration for OCS requires a gas standard. The calibration of the FPD for hydrogen sulfide was examined in the laboratory using a liquid standard (i.e.,  $\text{Na}_2\text{S}$  dissolved in water) added to the stripper and treated as a sample and a gas standard from a permeation device that was trapped directly. A comparison between the calibrations

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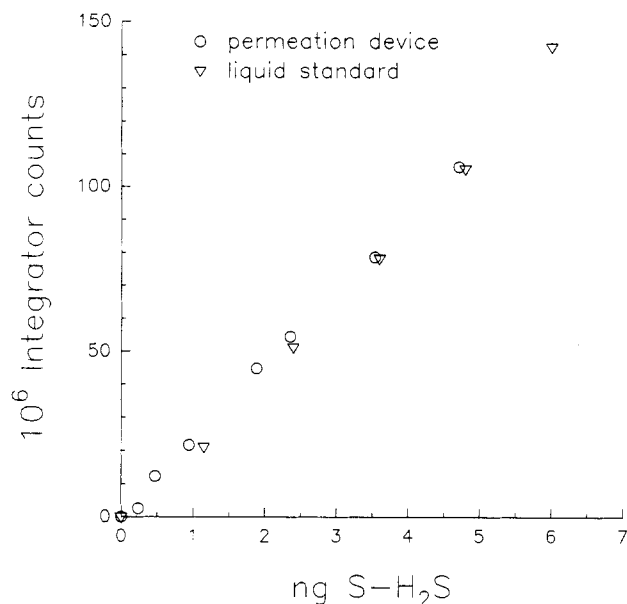
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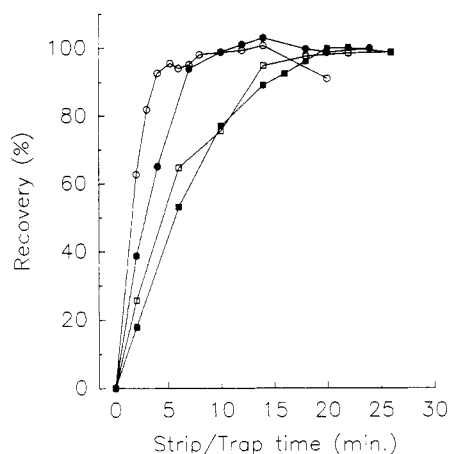
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**Figure 3.** Comparison of FPD calibrations for  $\text{H}_2\text{S}$  using a liquid standard run through the entire analytical procedure (triangles) and by direct trapping of  $\text{H}_2\text{S}$  from a permeation device (circles).

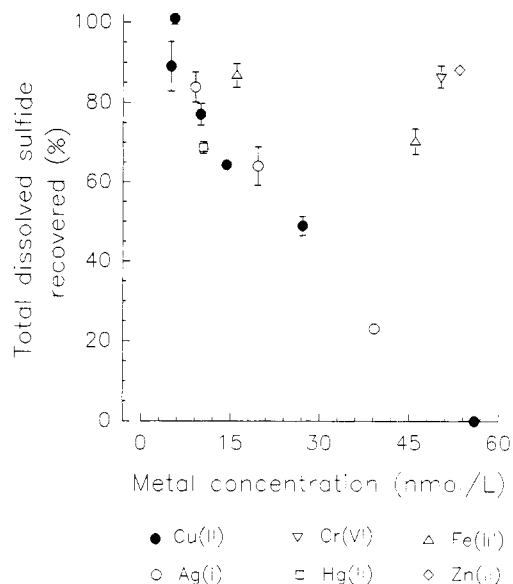


**Figure 4.** Recoveries of total dissolved sulfide and OCS as a function of stripping and trapping time. For the 300-mL stripper, hollow squares represent total dissolved sulfide, while filled squares are OCS. For the 50-mL stripper, hollow circles are total dissolved sulfide and filled circles are OCS. Recoveries are calculated from the concentrations determined using gas calibrations.

obtained using the  $\text{H}_2\text{S}$  permeation device and the liquid standard is shown in Figure 3. This comparison demonstrates that the two calibration methods are equivalent. Furthermore, the calibration using permeation devices is linear from 0 to 140 pmol of S, with correlation coefficients being  $>0.998$ .

**Conditions for the Determination of Total Dissolved Sulfide and OCS.** With the chromatographic parameters established, the recoveries of total dissolved sulfide and OCS were examined as a function of the stripping/trapping time. Additionally, the effects of two different acids and various trace metals on the recovery of total dissolved sulfide were investigated. With respect to the latter, dissolved metals readily form insoluble compounds and soluble complexes with free sulfide<sup>5,6,16</sup> that may not be determined using the experimental conditions given here.

The effect of stripping and trapping time was investigated in two experiments. Dissolved sulfide (added as  $\text{Na}_2\text{S}$ ) or OCS (added as gaseous OCS; both at 160–200 pmol/L) in deionized water was stripped at 120 mL/min for different lengths of time. The results presented in Figure 4 show that quantitative recovery for both gases is achieved in less than



**Figure 5.** Recovery of 50 nmol/L total dissolved sulfide as a function of the concentration of six individual trace metals. Error bars are  $\pm$  one standard deviation ( $n = 3$ ).

15 min for 50-mL samples and in less than 20 min for 300-mL samples. However, 15- and 20-min stripping times are used so that the determination is relatively time independent.

In a second series of experiments, the effect of acid concentration and type on the recovery of total dissolved sulfide and OCS was investigated. Aliquots of DDI water or Sargasso Sea water containing total dissolved sulfide and OCS (at the 0.2 nmol/L level) were analyzed using varying acid concentrations. Total dissolved sulfide was quantitatively recovered using 2 mL of 1.5 mol/L phosphoric acid in a 50-mL sample (final pH 1.7); the recovery of OCS was unaffected by this acid concentration. Hydrochloric acid (4 mol/L) was also tested in stripping/trapping experiments. Quantitative recovery of total sulfide was achieved in deionized water and Sargasso Sea water with 0.4 mL of 4 mol/L HCl. For Sargasso Sea water, the recovery of total dissolved sulfide decreased rapidly with increasing amounts of HCl added; this effect was not observed with DDI water. The reasons for the loss of total sulfide in Sargasso Sea water are unclear, but similar to the observation of Cutter et al.,<sup>13</sup> we speculate that free chlorine present in the HCl reacts with hydrogen sulfide when HCl is introduced to seawater. Because of this problem, acidification with phosphoric acid is used for all samples.

A third series of experiments were designed to examine the effects of trace metals on the recovery of total dissolved sulfide. Distilled, deionized water was placed into a Cubitainer, purged with nitrogen for 1 h at 300 mL/min to remove dissolved oxygen; the solution was then amended with a trace metal. Added trace metals were copper [5–56 nmol of  $\text{Cu(II)/L}$ ], zinc (53 nmol/L), mercury (10.4 nmol/L), iron [16–46 nmol of  $\text{Fe(III)/L}$ ], silver (9–39 nmol/L), and chromium [50 nmol  $\text{Cr(VI)/L}$ ]. To minimize contamination, trace metal additions to the Cubitainers were performed in a class 100 clean room using trace metal-clean plasticware. In every case,  $\text{H}_2\text{S}_g$  was then introduced in the Cubitainer to achieve a final dissolved concentration of 50 nmol/L. Total dissolved sulfide was then determined in triplicate using the method described above. From these experiments, it appears that copper, mercury, and silver sulfide complexes are not completely acid labile at high concentrations (Figure 5), while zinc, iron, and chromium sulfide complexes are acid labile and total dissolved sulfide can be quantitatively recovered. The slight decrease in recovery with  $\text{Fe(III)}$  is likely due to oxidation since the same



behavior was not observed with Fe(II). The recovery of total dissolved sulfide in the presence of copper did not improve by increasing the final acid concentration to 12 mol of  $\text{H}_3\text{PO}_4/\text{L}$  or to 10 mol of  $\text{HCl}/\text{L}$ . Total dissolved sulfide in copper sulfide complexes can be recovered using an acidic chromium-(II) solution (refer to next section); however, this procedure is rather cumbersome for large water samples. However, the concentrations of metals and total dissolved sulfide examined in this experiment are much greater than those found in seawater, and thus the results may not be directly applicable.

The degree of metal interference on the determination of total dissolved sulfide in seawater (i.e., the formation of non-acid-labile metal sulfide complexes) was evaluated using typical concentrations found in natural waters. Trace metals were added individually to Cubitainers containing deoxygenated Sargasso Sea water that had been amended immediately beforehand with  $\text{H}_2\text{S}_g$  to give a total dissolved sulfide concentration of 1 nmol/L. Trace metals were added so that their concentrations matched the maximum of these ions found in seawater [Cu(II), 6 nmol/L; Cd(II), 1.1 nmol/L; Ni(II), 12 nmol/L; Pb(II), 0.15 nmol/L; Zn(II), 9 nmol/L<sup>26</sup>]. These metals were chosen because they form strong metal sulfide complexes<sup>5,6</sup> and because their concentrations are sufficiently high enough in the upper ocean to warrant their consideration. The results in Figure 5 indicate that silver and mercury sulfides may not be recoverable. However, with maximum seawater concentrations of 15 pmol/L for Ag and 10 pmol/L for Hg,<sup>26</sup> these metals should not cause significant interference. Analysis of the resulting solutions for total dissolved sulfide showed full recovery within experimental error for all cases except Cu(II). At a Cu(II) concentration of 6 nmol/L, none of the 1 nmol/L total dissolved sulfide was recovered. Thus, total dissolved sulfide is operationally defined since it does not include sulfide in dissolved copper sulfide complexes. However, the procedure for total dissolved sulfide includes all the other significant metal sulfide complexes likely to be encountered in most natural waters.

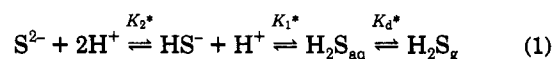
**Determination of Particulate Acid-Volatile Sulfide and Chromium-Reducible Sulfur.** Free sulfide can react with trace metals to form insoluble metal sulfides in the water column. The method to determine the concentration of these inorganic compounds on suspended particles was adapted from Cutter and Oatts.<sup>7</sup> In their sediment work, they showed that sulfide bound in iron monosulfide is quantitatively released as  $\text{H}_2\text{S}$  using 0.4 mol/L HCl, while Cr(II)/HCl reagent must be used to release  $\text{H}_2\text{S}_g$  from pyrite ( $\text{FeS}_2$ ). It should be noted that while the Cr(II)/HCl reagent reduces elemental sulfur to  $\text{H}_2\text{S}$ , it does not cleave C-S bonds in organic sulfur compounds,<sup>7</sup> and thus the chromium-reducible fraction only includes inorganic sulfur compounds.

To evaluate the applicability of these methods to the determination of other metal sulfide compounds, known (0.5 mg, ground to a fine powder) amounts of a metal sulfide compound ( $\text{Cu}_2\text{S}$ ,  $\text{CuS}$ ,  $\text{ZnS}$ ) were subjected to the 0.5 mol/L HCl and Cr(II)/HCl treatments. The  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  were obtained from Alfa, and  $\text{ZnS}$  was filtered from a solution of zinc acetate and sodium sulfide, then dried, and ground to a fine powder. Consistent with Cutter and Oatts,<sup>7</sup> the 0.5 mol/L HCl treatment quantitatively released  $\text{H}_2\text{S}_g$  from zinc sulfide ( $98.4 \pm 2.6\%$ ,  $n = 4$ ). However, the more rigorous Cr(II)/HCl treatment was necessary to recover  $\text{H}_2\text{S}_g$  from copper sulfide compounds ( $\text{H}_2\text{S}$  recovery  $101.4 \pm 3.8\%$ ,  $n = 6$ ). Considering the dissolved metal experiments discussed previously, particulate acid-volatile sulfide includes compounds such as  $\text{ZnS}$  and  $\text{FeS}$ . After these compounds are removed, particulate chromium-reducible sulfur includes

copper sulfide compounds, as well as pyrite.

**Determination of  $\text{H}_2\text{S}_g$ .** For the determination of  $\text{H}_2\text{S}_g$  in the headspace of a sample, conditions for cryogenic trapping are similar to those for total dissolved sulfide and OCS. The injection tee is made of Teflon to minimize loss of  $\text{H}_2\text{S}_g$ , and the cumulative gas flow rate (headspace + stripping) through the cryogenic trap is maintained at 120 mL/min to prevent sample breakthrough. To collect all  $\text{H}_2\text{S}_g$ , the trap is kept in liquid nitrogen for 2 min after the injection is completed. The determination of  $\text{H}_2\text{S}_g$  can be used to calculate the concentration of free sulfide (i.e.,  $\text{H}_2\text{S}_{aq} + \text{HS}^- + \text{S}^{2-}$ ) in a sample at in situ conditions of temperature, salinity, and pH. Along with the determination of total dissolved sulfide (as described above), the concentration of dissolved sulfide species complexed with metals in acid-labile complexes can then be estimated by difference between free and total dissolved sulfide concentrations.

The method used to calculate the concentration of free sulfide is based on the coupled equilibria shown in the following equation:



where  $K_1^*$  and  $K_2^*$  are the conditional dissociation constants (i.e., corrected for temperature and salinity using the equations in ref 27) and  $K_d^*$  is the conditional distribution coefficient (i.e., corrected for temperature and salinity using the solubility table in ref 28). The fraction of free sulfide with concentration  $C$  that exists as  $\text{H}_2\text{S}_{aq}$  is<sup>16</sup>

$$\alpha = \left( 1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^*K_2^*}{[\text{H}^+]^2} \right)^{-1} \quad (2)$$

and thus

$$[\text{H}_2\text{S}_{aq}] = \alpha C \quad (3)$$

If a pure helium headspace of volume  $V_g$  is introduced over a sample of volume  $V_l$  and allowed to equilibrate, then

$$\alpha C_0 V_l = [\text{H}_2\text{S}_{aq}] V_l + [\text{H}_2\text{S}_g] V_g \quad (4)$$

where  $C_0$  is the original concentration of uncomplexed, dissolved hydrogen sulfide. Since  $[\text{H}_2\text{S}_{aq}] = K_d^*[\text{H}_2\text{S}_g]$ , eq 4 can be rewritten as

$$C_0 = \frac{[\text{H}_2\text{S}_g]}{\alpha} \left( K_d^* + \frac{V_g}{V_l} \right) \quad (5)$$

Thus, the determination of  $\text{H}_2\text{S}_g$ , pH, temperature, and salinity of a sample (the latter two are necessary to adjust the conditional dissociation and distribution constants) allows the calculation of the concentration of free sulfide. At a given concentration of  $\text{H}_2\text{S}_{aq} + \text{HS}^- + \text{S}^{2-}$ , the quotient  $[\text{H}_2\text{S}_g]/\alpha$  presents the largest uncertainty for  $C_0$ . In particular, when the pH is greater than  $\text{p}K_1^*$ ,  $\alpha$  changes by a factor of 10 for each variation of 1 pH unit. Thus, an accurate determination of pH using a pH scale appropriate for the ionic strength of the water considered (e.g., ref 29) is necessary to reduce systematic error.

To evaluate this headspace method in DDI water, a Cubitainer containing 3.00 L of trace metal-clean water at 24 °C with a pH of 8.52 (adjusted with NaOH) and deoxygenated using a stream of helium (1 h at 300 mL/min) was amended with  $\text{H}_2\text{S}_g$  to give a concentration of 6.6 nmol/L. Using the procedure described above, the headspace concentration of  $\text{H}_2\text{S}_g$  was determined to be  $85.1 \pm 19.6$  pmol/L ( $n = 6$ ).

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Applying eq 5, the concentration of free sulfide was  $7.3 \pm 1.7$  nmol/L, in good agreement with the actual concentration of 6.6 nmol/L. To evaluate this method in seawater, a Cubitainer containing 3.00 L of Sargasso Sea water at 23 °C, with a pH of 8.29 and deoxygenated as above, was amended with  $\text{H}_2\text{S}_g$  to a final concentration of total dissolved sulfide of 51 nmol/L. This elevated concentration was chosen to minimize the impact of sulfide complexation by dissolved metals in the sample on the inventory of free sulfide. The concentration of  $\text{H}_2\text{S}_g$  determined in the headspace after equilibration was  $311 \pm 15$  pmol/L ( $n = 5$ ), which yields a concentration of free sulfide of  $47.0 \pm 2.3$  nmol/L ( $92 \pm 5\%$  recovery). Thus, the headspace method also appears to be reliable in a more complex matrix.

**Analytical Figures of Merit.** The detection limit for total dissolved sulfide and OCS in water samples was evaluated using five determinations of a blank consisting of deionized water (300 mL) degassed in the stripper with helium. The absolute detection limits ( $3\sigma$  of a blank) are 0.06 pmol of  $\text{H}_2\text{S}$  and 0.4 pmol of OCS. For a 300-mL sample, the relative detection limits are then 0.2 pmol/L for total dissolved sulfide and 1.3 pmol/L for OCS. Similarly, for a 1-mL sediment porewater aliquot, the relative detection limits are 60 pmol/L  $\text{H}_2\text{S}$  and 400 pmol/L OCS. The absolute detection limits for particulate acid-volatile sulfide and chromium-reducible sulfur were evaluated using five determinations of blank (unused) filters. The detection limits are 0.2 pmol of S as acid-volatile sulfide and 2 pmol of S as chromium-reducible sulfur. For a 30-L sample, this corresponds to relative detection limits of 0.007 pmol/L for particulate acid-volatile sulfide and 0.07 pmol/L for particulate chromium-reducible sulfur.

Using 0.06 pmol of  $\text{H}_2\text{S}$  as the absolute detection limit and a 100-mL headspace sample, the relative detection limit for  $\text{H}_2\text{S}_g$  is 0.6 pmol/L. At pH 8, a salinity of 35 practical salinity units (psu), and 25 °C, this corresponds to a relative detection limit of 52 pmol/L for free sulfide. In freshwater at pH 7 and at 25 °C, the relative detection limit for free sulfide is 3.5 pmol/L. It should be noted that the detection limit for free sulfide can be improved by a factor of 10 for each pH unit decrease until  $\text{p}K_1^*$  is reached. At concentrations of 20 pmol/L total dissolved sulfide or OCS, precision is 5% relative standard deviation for both sulfur compounds ( $n = 5$ ) and 4% relative standard deviation ( $n = 5$ ) at concentrations of  $\geq 5$  nmol/L. By varying the volume analyzed (1–300 mL), samples with total dissolved sulfide and OCS concentrations ranging from 0.2 pmol/L to 100 nmol/L can be analyzed.

**Application to Field Samples.** Using the methods described above, samples from a variety of environments have been analyzed for total dissolved sulfide and carbonyl sulfide; some of the resulting data are presented in Table I. For total dissolved sulfide and OCS in the water column, concentrations generally increase with proximity to land masses. Elevated OCS concentration in marine sediments is evidence for OCS production by diagenetic processes. Detectable concentrations of particulate acid-volatile sulfide and particulate chromium-reducible sulfur in the remote Pacific Ocean suggests that these compounds may be formed in the oxic water column. To illustrate how the methods presented above can be used to examine the interactions between metals and sulfide, an experiment was performed using 3.00 L of seawater (pH 8.27, 24 °C, 34.1 psu, collected at 8°59' N, 147°24' W). The water was amended with  $\text{H}_2\text{S}_g$  to a final concentration of 2.12 nmol/L. After a 10-min equilibration period and using the method described above, the concentration of  $\text{H}_2\text{S}_g$  in the headspace was  $7.37 \pm 1.0$  pmol/L ( $n = 3$ ), which corresponds to  $1.0 \pm 0.13$  nmol/L free sulfide using eq 5; total dissolved

**Table I. Total Dissolved Sulfide and OCS in Natural Waters<sup>a</sup>**

sample type and location	depth (m)	concn (pmol/L)	
		total diss sulfide	OCS
water column			
Pacific Ocean, 08/1991, 8°59' N, 147°24' W	5	46.0 ± 2.7	10.0 ± 0.4
	150	39.1 ± 1.5	22.3 ± 1.1
Pettaquamscutt River, RI, 08/1990	0.25	615 ± 27	636 ± 14
	3.85	1220 ± 40	415 ± 13
sample type and location	depth interval (cm)	concn (nmol/L)	
		total diss sulfide	OCS
sediment porewaters			
North Atlantic Ocean, 06/1990, 38°20' N, 73°31' W	0–2.5	34.9	37.4
Chesapeake Bay, 10/1991, 38°57' N, 76°45' W	interface	NA <sup>b</sup>	14.0 ± 0.9
	1–2	NA	24.7 ± 2.0
	4–6	NA	36.2 ± 2.1
lake 5.0, FL, 06/1990	5	69.2 ± 3.5	53.2 ± 5.7
sample type and location	depth (m)	concn (pmol/L)	
		pAVS	pCRS
suspended particulate matter			
Pacific Ocean, 08/1991, 8°59' N, 147°24' W	65	3.38	18.3
	150	4.43	67.3

<sup>a</sup> Triplicate determinations were performed on water column samples. Duplicate determinations were performed on sediment porewaters. Particulate sample concentrations were determined by single analysis. <sup>b</sup> NA, not analyzed.

<sup>a</sup> Triplicate determinations were performed on water column samples. Duplicate determinations were performed on sediment porewaters. Particulate sample concentrations were determined by single analysis. <sup>b</sup> NA, not analyzed.

sulfide was  $1.23 \pm 0.01$  nmol/L ( $n = 3$ ). With these concentrations, the fraction of the amended  $\text{H}_2\text{S}_g$  which remained free is 47% ( $1.0/2.12$ ), and the fraction of the added  $\text{H}_2\text{S}_g$  which reacted with metals such as copper is 42% [ $(2.12 - 1.23)/2.12$ ]. The remainder of the  $\text{H}_2\text{S}_g$  amendment (11%) is complexed with metals such as zinc, cadmium, and nickel. Thus, the headspace method allows an unobtrusive examination of the interactions between dissolved sulfide species and these metals at near in situ conditions. Moreover, in natural waters where total dissolved sulfide concentrations are  $>300$  pmol/L, determinations of dissolved sulfide and free sulfide can be used to directly evaluate sulfide-metal complexation. Overall, the results in Table I confirm that the methods described above are applicable to a variety of environments, while good precision is maintained for a wide range of concentrations. Furthermore, picomolar concentrations of total dissolved sulfide and OCS found in the open ocean demonstrate the need for contamination-free sampling and analytical methods.

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