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Determination of Dissolved Sulfide and Sedimentary Sulfur Speciation Using Gas Chromatography–Photoionization Detection

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The determination of dissolved sulfide and sedimentary sulfur is important to studies of trace element cycling in the aquatic environment. A method employing selective generation of hydrogen sulfide, liquid-nitrogen-cooled trapping, and subsequent gas chromatographic separation/photoionization detection has been developed for such studies. Dissolved sulfide is determined via acidification and gas stripping of a water sample, with a detection limit of 12.7 nM and a precision of 0.5% (relative standard deviation). With preconcentration steps, the detection limit is 0.13 nM. Hydrogen sulfide is generated from sedimentary acid volatile sulfides (AVS) via acidification, from greigite using sodium borohydride and potassium iodide, and from pyrite using acidic chromium(II). The detection limit for these sulfur species is 6.1 μg of S/g, with the precision not exceeding 7% (relative standard deviation). This method is rapid and free of chemical interference, and field determinations are possible. Numerous natural water and sediment samples have been analyzed by using the described procedures.

Sulfur enters into numerous biogeochemical reactions in the aquatic environment. In anoxic waters, the sulfate/sulfide redox couple is thought to control the free electron activity, particularly in the marine environment (*1*). Dissolved sulfide produced from microbial sulfate reduction in anoxic waters affects the solubility of trace elements such as iron (*2*). In anoxic sediments these insoluble metal sulfides can accumulate, or be remobilized through sedimentary diagenetic reactions (*3*). Iron sulfide minerals including pyrite (FeS_2) and mackinawite (FeS) are the most common metal sulfides in sediments and represent the major form of sedimentary sulfur (*4*). Berner et al. (*5*) have suggested that variations in the pyrite to mackinawite ratio may be used as a paleosalinity indicator, while Howarth (*6*) postulates that pyrite formation is an important part of microbial metabolism in salt marshes. Thus, determinations of dissolved sulfide and sedimentary sulfur speciation are important not only to investigations of sulfur itself but also to studies of trace elements in the aquatic environment.

Dissolved sulfide is typically determined by spectrophotometric procedures (*7*, *8*) which utilize multiple reagents and sample manipulations. The lowest detection limit reported for a spectrophotometric sulfide method is approximately 0.1 μmol/L (*7*). In sediments, metal monosulfides (acid volatile sulfides or AVS) are determined via acidification and collection of the evolved hydrogen sulfide, which is then quantified by using spectrophotometric (*8*) or titrimetric (*9*) procedures. Two principal methods are used to determine pyrite. The technique of Lord (*10*) uses selective chemical leaching to remove all nonpyritic iron, followed by a nitric acid digestion to solubilize pyrite-bound iron; the resulting solution is subjected to atomic absorption analysis. This method requires substantial sample preparation efforts, and the removal of all nonpyritic iron is crucial to the method's accuracy. Pyrite can also be determined by using acidic Cr(II) reduction of pyritic sulfur to hydrogen sulfide, which is then determined via AVS methods (*11*). Pyrite determinations via Cr(II) reduction method are direct, but the available procedures are very time-consuming.

This paper describes a method for the determination of dissolved sulfide and sedimentary acid volatile sulfide, pyrite, and greigite which utilizes the selective generation of hydrogen sulfide and subsequent gas chromatography–photoionization detection. The use of this sensitive detection system and analytical protocols with minimal sample handling result in short analysis times, very low detection limits, freedom from chemical interference, and excellent precision. Moreover, the apparatus is relatively compact and sturdy, making determinations on-board research vessels possible. In combination with the independent determination of total sulfur using an elemental analyzer, the major speciation of sedimentary sulfur is almost completely elucidated.

EXPERIMENTAL SECTION

Apparatus. The hydrogen sulfide generation and trapping system is shown in Figure 1 and is similar to the apparatus used in metalloid determinations via hydride generation (*12*, *13*). The stripping vessel is made of borosilicate glass, has a 24/25 ground glass joint, and can hold ca. 40 mL of solution. This stripper is fitted with a Teflon bubbler, consisting of a 2-cm piece of Goretex microporous tubing (Anspec Co.) inserted into Teflon (TFE) tubing; the tip of the Goretex tubing is heat-sealed. The injection port consists of a Teflon Swagelok connector housing a Teflon-backed silicone rubber septum. A small magnetic stirrer is placed under the stripper for sediment analyses. The water vapor trap is a borosilicate glass U-tube (36 cm long, 14 mm i.d.) immersed in dry ice/2-propanol. The hydrogen sulfide trap/gas chromatographic column is a borosilicate glass U-tube (16 cm long, 6 mm o.d.) packed with 2.5 cm of 50/80 mesh Porapak QS (acetone washed, ref 14), and wrapped with Ni–Cr wire which is connected to a variable transformer. In order to reduce adsorptive losses, all glass surfaces are treated with dimethyldichlorosilane, and all tubing and Swagelok connectors are made of Teflon.

The detector is an HNU Systems photoionization unit and electrometer (Model PI-52) equipped with a 10.2-eV lamp. The detector output is processed with a digital plotter/integrator (Hewlett-Packard 3392A). An ultramicro balance (Cahn 29) is used for sample weighings. The following operating parameters are utilized: helium stripping/carrier gas, 60 cm^3 min^{-1}; detector temperature, 50 °C; Porapak column temperature, 50 °C; PID lamp intensity setting, 4. Total sedimentary sulfur is determined with a Carlo Erba ANA 1500 NCS analyzer.

Reagents and Standards. A standard solution of sodium sulfide (1–10 μg of S/mL) is prepared daily by using anhydrous Na_2S (Alfa Products) and nitrogen-purged, demineralized water which is adjusted to pH 8 with sodium hydroxide. Freshly synthesized greigite was prepared by J. Cornwell and J. Morse (Texas A&M University) using the method of Wada (*15*) and its identity verified by x-ray diffraction. This synthetic greigite is extremely

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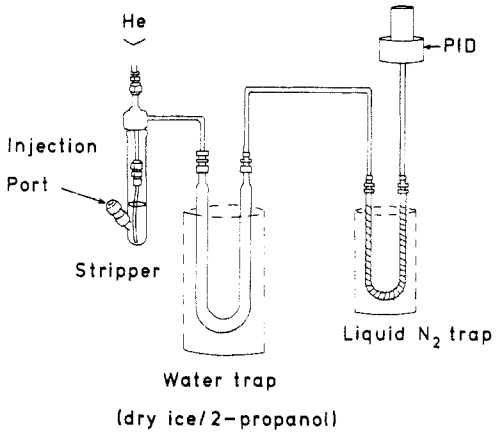

Figure 1. Apparatus for the generation and detection of hydrogen sulfide.

unstable and must be stored and handled in an inert atmosphere (i.e., nitrogen-purged glovebox) to prevent oxidation. Two pyrite standards were used, a synthetic standard (Aesar) and a coarse mineral standard (Carolina Biological). Both of these pyrite standards were treated with concentrated hydrochloric acid and acetone to remove acid volatile and elemental sulfur, respectively (*16*). Iron monosulfide was synthesized by using the method described by Sweeney and Kaplan (*17*). Other standards used in methods development included cysteine, cystine, and methionine (Sigma).

All reagents and acids are reagent grade. The chromium(II) solution is prepared by passing 1 M chromium chloride (in 1 M HCl) through a Jones reductor column (*18*). This Cr(II) reagent is prepared daily and kept under a nitrogen atmosphere. The 4% (w/v) sodium tetrahydridoborate solution (in 0.08 M sodium hydroxide for stabilization) and 5% (w/v) potassium iodide solutions are also prepared daily.

Precedures. *Dissolved Sulfide Sampling.* Natural water samples should be obtained by using a nonmetallic water sampling bottle fitted with a rubber septum port. Immediately after the water is collected, an aliquot for field determination should be obtained by using a glass barrel syringe with Teflon plunger and Luer-lok tip and fitted with a platinum needle (Hamilton). If the sample cannot be analyzed immediately, a small glass bottle with ground glass stopper and known volume should be filled in a manner which does not introduce air bubbles. After the bottle is filled, 0.2 mL of 1 M zinc acetate is added (per 25 mL of sample) to fix the dissolved sulfide as ZnS, and the sample is capped and stored at 4 °C until analysis.

A similar procedure can be used for the acquisition of samples with nanomolar concentrations of dissolved sulfide. In this case, a larger glass-stoppered bottle (e.g., BOD bottle with ca. 300-mL volume) is carefully filled with sample, 2 mL of 1 M zinc acetate is added, and the bottle is stoppered and agitated. Within 1 h the contents of the bottle are passed through a 47 mm, 0.4-μm polycarbonate membrane filter (Nuclepore), followed by three 0.1 M zinc acetate rinses of the bottle. The filter is immediately frozen for later analysis.

Sediment Sampling and Preparation. Sediments are stored frozen between sampling and analysis. Samples for acid volatile sulfides and greigite determinations are quickly thawed with a microwave oven and used directly (wet-to-dry weight ratio determined on a separate aliquot). Sediments for pyrite and total sulfur determinations are dried slowly at 40 ° C, ground with an agate mortar and pestle, and sieved with a plastic mesh (150 μm openings). This powder is further treated prior to the determination of pyrite by a double extraction with carbon tetrachloride in a glass centrifuge tube (100–200 mg sediment, 10 mL of CCl_4, sonicated for 10 min, centrifuged, supernatant discarded) and drying at 80 °C.

Dissolved Sulfide Determination. Place 10 mL of 4 M HCl in the lower portion of the stripper, assemble, and purge with helium for at least 2 min. Immerse the trap/column in liquid nitrogen and inject up to 10 mL of sample into the stripper. For a 10–30 mL sample, the procedure is the same except 10 mL of 8 M HCl is added to the stripper. After 8 min of strip/trap time, begin heating the column and remove the trap from liquid nitrogen. Using the conditions stated above, hydrogen sulfide should elute at approximately 1.9 min. Additional samples can be analyzed without changing the 4 M HCl, until a total of 30 mL of sample have been added to the stripper. Between each determination the column should be heated an additional 3 min to remove other volatile compounds.

Zinc acetate preserved samples should be transferred to the lower portion of the stripper with rinsing. All of the dissolved sulfide procedures are followed, except 10 mL of 4 M HCl is added to the stripper *after* immersing the trap/column in liquid nitrogen. Filters for trace dissolved sulfide determinations are placed in the stripper and treated as acid volatile sulfide samples (as below).

Acid Volatile Sulfides and Greigite Determinations. Weigh 5–20 mg of wet sediment into a small tin or aluminum cup and place in the bottom portion of the stripper. Add 10 mL of deionized water and a magnetic stirring bar, assemble the stripper, and then stir and purge for 2 min. Immerse the trap/column in liquid nitrogen, inject 10 mL of 1 M HCl, and strip/trap for 15 min. At this time, begin heating the column and remove the trap from the liquid nitrogen. After hydrogen sulfide and any other compounds have completely eluted (ca. 5 min), reimmerse the trap/column in liquid nitrogen. Inject 1 mL of KI solution and then 2 mL of $NaBH_4$ reagent over 2 min. Strip/trap the greigite–sulfide fraction for 15 min and chromatograph as above.

Pyrite Determination. Weigh approximately 1 mg of CCl_4 extracted, dried sediment into a tin or aluminum cup, place in the stripper along with a magnetic stirring bar, and wet the sample with 10 mL of 0.5 M HCl. To remove any residual AVS or greigite, reassemble the stripper, begin stirring, and inject 1 mL of KI solution and 2 mL of $NaBH_4$ reagent. Strip the evolved H_2S from solution for 15 min, but *do not* immerse the trap in liquid nitrogen. After AVS/greigite removal, immerse the trap/column in liquid nitrogen and inject 4 mL of concentrated HCl followed by 10 mL of Cr(II) solution. After 22 min of stripping/trapping, chromatograph the generated H_2S as before.

RESULTS AND DISCUSSION

Sample Acquisition and Preparation. Samples for dissolved sulfide determinations (predominantly HS^- at the pH of most natural waters) must be taken in a manner which does not allow the loss of bisulfide ion through oxidation or by reaction with materials in the sampling devices (e.g., Fe(III)). Thus, nonreactive materials such as syringes with Teflon plungers and platinum needles should be utilized, and immediate determinations in the field are preferable.

If field determinations are not possible, samples can be preserved with a zinc acetate solution since zinc sulfide is very insoluble and stable to oxidation (*16*). This preservation technique can also be used as a preconcentration step for determining dissolved sulfide at the nanomolar level. In this application, the zinc sulfide precipitate is collected on a filter for later determination. Filtration is performed within an hour while the zinc sulfide is still dispersed in solution rather than adhered to the container walls. Precipitating ZnS in a 300 mL volume allows a 10-fold preconcentration over direct determination with the stripping apparatus (maximum sample volume of 30 mL).

Sediments are frozen immediately after sampling in order to minimize changes in sulfur speciation through oxidation or bacterial metabolism. Acid volatile sulfides (AVS) and greigite are determined on sediments thawed just prior to analysis, since these species may be affected by oxidation (*4*). Sediments for pyrite and total sulfur determinations are dried slowly at 40 °C, ground with an agate mortar and pestle, and sieved with a 150-μm mesh screen. In order to determine pyrite uniquely, elemental sulfur originally in the sediment or resulting from processing must be removed prior to analysis. While other investigators have used acetone (*11*, *16*) or carbon disulfide (*19*) to extract elemental sulfur, carbon tetrachloride was used in this study to avoid potential sulfur contamination from the solvent and as an attempt to find a more rapid

extraction procedure (e.g., existing methods extract for periods up to 16 h). To examine the efficiency of carbon tetrachloride extraction, S(0) was added to a coastal sediment (4.72 mg of S(0) added per gram of sediment) which had been dried, homogenized, and preextracted with acetone to remove any elemental sulfur (*11*). Pyrite determinations (described below) on the prepared sediment before S(0) addition yielded 7.2 ± 0.9 mg of S/g (n = 3). After two successive carbon tetrachloride treatments, 7.0 ± 0.8 mg of S/g (n = 3) was found in the spiked sediment. Thus, the extraction of sedimentary S(0) with carbon tetrachloride appears to be complete, with the procedure taking only about 1 h.

Dissolved Sulfide Determination. The generation, collection (via gas stripping of an aqueous solution), and determination of hydrogen sulfide are essentially the basis of most AVS and pyrite procedures. For this work the photoionization detector is employed because of its sensitivity, low cost, and simplicity (i.e., only a carrier gas is required). The PID utilizes the absorption of ultraviolet radiation to ionize molecules in the detector chamber whose ionization potentials are less than the energy of the UV source. In this manner, the PID is nonselective and hydrogen sulfide must be chromatographically separated from any coeluting compounds prior to entering the detector. The use of a liquid-nitrogen-cooled gas chromatographic column to trap hydrogen sulfide (similar to that used for antimony determinations, ref 13) greatly simplifies the required apparatus. However, such a column must be small for easy handling and capable of withstanding large temperature extremes. The porous polymer Porapak QS (acetone washed to remove monomers, ref 14) has been used by other investigators for the separation of different sulfur gases using relatively short columns and ambient temperatures (*14*). Additionally, this packing is silanized to minimize adsorptive loss, an important factor in trace sulfide determinations. Thus, the use of Porapak QS was investigated using hydrogen sulfide standards and glass U-tube columns with 2.5–14 cm of packing. These U-tubes are wrapped with nichrome wire and connected to a variable transformer for heating the column. To prevent clogging of the trap/column, water vapor in the stripping/carrier gas is removed with an open glass U-tube immersed in dry ice/2-propanol (*12*).

Using the shortest column, 2.5 cm, and heating to 50 °C after removal from liquid nitrogen (other operating parameters listed above), hydrogen sulfide has a retention time of 1.89 ± 0.03 min (n = 10). Furthermore, even at the low attenuation (high sensitivity) detector settings of ×10 and ×100, the hydrogen sulfide peak is completely separated from any other eluting compounds by at least 1 min. In the natural water and sediment samples (to be discussed below) thusfar analyzed, only one broad peak (retention time, ca. 3.2 min) elutes from the column in the vicinity of hydrogen sulfide. Through coinjection of various compounds to samples and comparison of retention times, this peak has been tentatively identified as methyl mercaptan, CH_3SH (coinjection was also used to identify the hydrogen sulfide peak). However, with the conditions given for hydrogen sulfide determination, the methyl mercaptan peak is too broad to be accurately quantified. The existence of sedimentary methyl mercaptan is not unprecedented since Guerin and Braman (*20*) have found this compound in coastal and estuarine sediments.

With the chromatographic conditions established, the major variables which affect the recovery of hydrogen sulfide from solution are the acidity and the strip/trap time. The use of 4 M HCl ensures that all dissolved sulfide is volatilized and allows several samples to be analyzed without changing the acid. With the described apparatus and flow rates, dissolved sulfide is quantitatively recovered after 7 min (Figure 2).

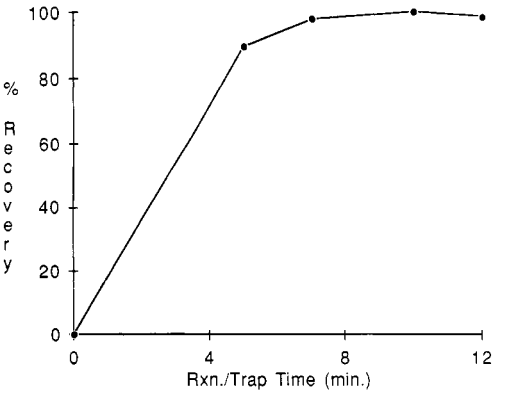

Figure 2. Recovery of hydrogen sulfide as a function of stripping time.

However, a strip/trap time of 8 min is used so that the determination is relatively time-independent. Since other compounds must be eluted from the column prior to the next determination (discussed above), the sample to sample time is 13 min.

The method's detection limit was evaluated by use of five determinations of a low concentration standard (0.11 μg of S as H_2S) since no hydrogen sulfide blank is present (i.e., the blank variability cannot be assessed). The absolute detection limit for hydrogen sulfide is 12.2 ng of S (3σ, detector at ×10). This corresponds to a relative detection limit for dissolved sulfide of 12.7 nmol/L using a 30-mL sample. For the zinc acetate/filtration method, 300-mL sample volumes are used. In combination with this preconcentration, the most sensitive detector setting (×1) lowers the detection limit to 0.13 nmol/L. However at the ×1 setting, base-line drift during column heating can become large and the time between samples consequently lengthened. Fortunately, most natural water samples do not require the most sensitive setting.

In addition to having low detection limits, the dissolved sulfide method is also highly precise, with a relative standard deviation of 0.5% at 1.0 μmol/L (n = 7). The corresponding precision for the zinc acetate/filtration technique is 6.2% at 0.7 nmol/L (n = 8). Finally, the detector's response is linear from 0.03 to 7 μg of S (as hydrogen sulfide, r = 0.9999, n = 7). By variation of the volume injected into the stripper (i.e., 0.1–30 mL), this linear range would correspond from 31 nmol/L to 2.2 mmol/L. Overall, the GC/PID determination of dissolved sulfide has distinct advantages over the commonly used methylene blue spectrophotometric technique (*7*). In particular, the GC/PID determination is faster (13 vs. 20 min), has lower detection limits (spectrophotometric, 0.1 μmol/L), better precision (0.5 vs. 3%), and a wider linear working range (spectrophotometric, 1–1000 μmol/L).

Acid Volatile Sulfides Determination. In sediments there are many monosulfide compounds with divalent metal ions, including iron, nickel, and copper (*21*). Upon acidification, hydrogen sulfide is released from these monosulfides, leading to the term "acid volatile sulfides" (AVS) for this sedimentary sulfur fraction. Since the GC/PID apparatus has low detection limits for H_2S, only 5–50 mg sediment (wet weight) are required for AVS determinations. In comparison, existing AVS techniques use 0.5–2.0 g of wet sediment (*8*, *9*). The principal advantage of this small sample size will be discussed below.

The recovery of AVS as a function of strip/trap (i.e., reaction) time was examined by use of an iron sulfide standard (recovery calculated by comparison with theoretical yield), a marine sediment sample (recovery calculated by a comparison with the maximum yield of H_2S), and two HCl concentrations, 0.5 M and 3.0 M. For both acid concentrations, a strip/trap time of 15 min gives complete AVS recovery (Fe standard, 99 ± 5%, n = 5). However for reasons to be dis-

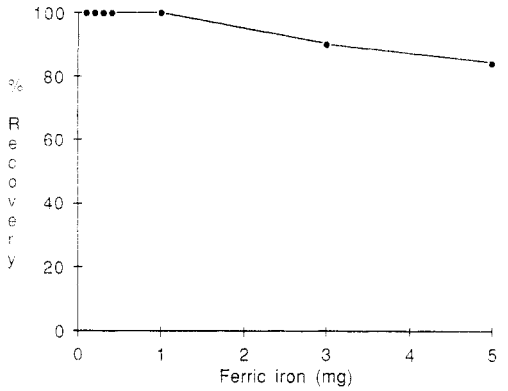

Figure 3. Effect of Fe(III) on the recovery of hydrogen sulfide.

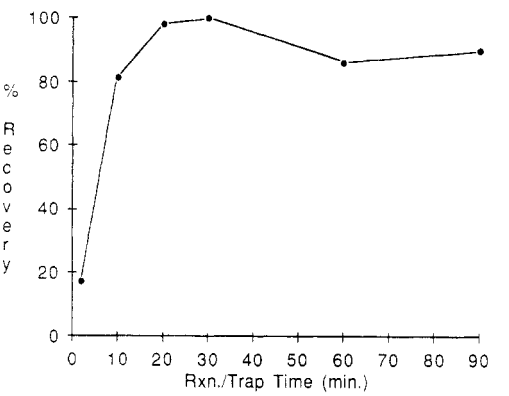

Figure 4. Recovery of pyritic sulfur (as hydrogen sulfide) with increasing Cr(II) reaction time.

cussed momentarily, only the lower acid concentration is used. Allowing for the elution of other compounds from the column (e.g., methyl mercaptan as above), the sample to sample analysis time is 20 min, considerably shorter than the 40 min of Zhabina and Volkov (*11*) or 18 h used by Munsen (*9*). Since the absolute detection limit for the GC/PID is 12.2 ng of S (as hydrogen sulfide), with a 2-mg sediment sample (dry weight), the AVS detection limit is 6.1 μg of S/g. The precision for AVS determinations is 3.4% (relative standard deviation) at 0.44 mg of S/g (n = 6). The need to analyze wet sediments is the greatest cause of analytical imprecision with this method.

Cornwell and Morse (*22*) have reported that greigite (Fe_3S_4) may be partially recovered by acid volatile sulfides methods. In order to avoid such "contamination" of the AVS fraction, the effect of HCl concentration on the recovery of AVS and greigite was examined by using iron sulfide and greigite standards. A 15-min strip/trap time (as above) was used and the HCl concentration varied from 0.5 to 3.0 M. At 0.5 M HCl, hydrogen sulfide generated from greigite is nondetectable, but AVS–sulfide is completely recovered. Raising the HCl concentrations to 3.0 M causes hydrogen sulfide production from greigite (10% recovery, n = 4). Thus, 0.5 M HCl is used for the determination of AVS specifically.

Several investigators (*23*, *24*) have noted that Fe(III) in sediments can oxidize hydrogen sulfide to S(0), thus leading to an underestimation of AVS concentrations. Typically, stannous chloride is added to remove ferric iron interference (*24*). However, the selectivity of the AVS treatment is compromised due to the inclusion of greigite and pyrite when reductants such as stannous chloride are used (*22*, *24*). Consequently, the effect of Fe(III) on the AVS determination was reexamined by using the GC/PID apparatus. The amount of sulfide in the stripper was held at 13.9 μg of S (2 mg of sediment, dry weight), 0–5 mg of Fe(III) as ferric chloride solution (6.2 mM) was added, and the AVS procedure (.5 M HCl, 15 min strip/trap) followed; stannous chloride was not used. The results of this experiment (Figure 3) show a decrease in the recovery of sulfide after 3 mg of Fe(III) is added. Since only 2–3 mg of sediment (dry weight) is needed for the AVS determination, Fe(III) does not appear to be an interferent using this apparatus. The small sample size and rapid stripping of hydrogen sulfide from solution may account for this behavior.

Pyrite Determination. By use of an acidic Cr(II) solution, sulfur in pyrite is reduced to hydrogen sulfide (*11*). The use of the PID system can allow small samples to be treated and can simplify the determination of pyrite compared to existing methods by combining the hydrogen sulfide generation and determination steps. The recovery of pyrite vs. stripping/reaction time was first investigated. For this work mineral and synthetic pyrite standards (elemental sulfur, AVS, and greigite removed, refer to appropriate discussions) were utilized. In order to simplify the procedure, heating of the reaction mixture (*11*) was not performed. The data in Figure 4 show that pyrite is quantitatively recovered after 20 min of reaction time; 22 min is used to make the determination relatively time independent. This reaction time is considerably less than that used in other pyrite methods (ca. 1 h, ref 11) and is likely due to the small sample size used (ca. 1 mg of dry sediment compared to 1 g).

Cr(II) is reported to also reduce elemental sulfur to hydrogen sulfide, but not to react with organic sulfides (*11*). In order to accurately speciate sedimentary sulfur, the selectivity of Cr(II) reduction was reinvestigated. Amino acids (0.2 mg) containing labile sulfide (methionine, cystine, cysteine) were subjected to the pyrite procedure above. In agreement with previously reported results (*11*), no detectable sulfide was recovered in these experiments. Sediments, to which a known quantity of elemental sulfur was added (as described in the sample preparation section), were also subjected to pyrite analysis. In these experiments the recovery of elemental sulfur was poor (30%, n = 3), and may be due to the lack of heating which is used in other pyrite methods. Since this nonquantitative recovery would hamper the determination of pyrite, S(0) is removed by using carbon tetrachloride extraction prior to Cr(II) reduction (described in the sample preparation section). Moreover, before pyrite can be determined, AVS and greigite must be removed by using the methods detailed above. This processing lengthens the sample-to-sample analysis time to 45 min. The pyrite detection limit is equivalent to that for AVS (6.1 μg of S/g; 2-mg sample), and the precision (as relative standard deviation) is 4.1% at 2.3 mg of S/g (n = 5).

Greigite Determination. Existing methods for the identification of greigite (Fe_3S_4) are only semiquantitative (*17*). In view of the possible role of greigite as an intermediate in pyrite formation (*4*, *17*), a method for greigite determination was developed. The formal oxidation state of greigite sulfur is intermediate between S(-II) and S(0), and reduction is necessary to produce hydrogen sulfide quantitatively. However, the reducing conditions must be sufficiently mild to prevent pyrite–sulfur reduction. Cornwell and Morse (*22*) observed partial recoveries of greigite using HCl, as confirmed in the AVS experiments above. While complete recovery of greigite occurs with acidic stannous chloride (*22*), this reagent also reduces pyritic sulfur (*22*, *24*).

The reductant for greigite has to be relatively selective and a rapid reaction is preferable. Sodium tetrahydridoborate was examined as a reductant for greigite sulfur because of its use in reducing metalloids to their corresponding hydrides. To examine the recovery of greigite sulfur, a synthetic greigite standard was used; the theoretical yield of sulfur was determined by using the pyrite procedure. In the analytical scheme, greigite must be determined after AVS but before pyrite.

Table I. Dissolved Sulfide and Sedimentary Sulfur in Natural Waters

A. Water Samples (μmol/L, except as noted)

location	total H_2S
mid-Chesapeake Bay, 34 m, 8/2/85	1.11 ± 0.06
sediment porewater, mid-Chesapeake Bay, 8/3/85	1410 ± 60.0
Hyco Reservoir, NC, 11 m, 8/13/85	120 ± 10.0
North Atlantic Ocean 37°12′N, 75°4′W, 32 m, 7/15/86	0.51 ± 0.07 nmol/L

B. Sediments (mg of S/g, dry weight)

location	AVS	greigite	pyrite	total S[a]
mid-Chesapeake Bay, 8/3/85	0.07 ± 0.01	0.02 ± 0.005	9.71 ± 0.39[b]	ND[c]
Great Marsh, DE, 3/26/86				
2.7–5.5 cm	0.03 ± 0.002	ND	0.85 ± 0.02	6.97 ± 0.03
10.9–13.7 cm	0.05 ± 0.02	0.19 ± 0.03	1.86 ± 0.10	8.88 ± 0.11
15–17.5 cm	0.53 ± 0.003	0.51 ± 0.04	10.2 ± 0.71	15.0 ± 0.05
Hyco Reservoir, NC, 8/13/85	1.27 ± 0.12	ND	0.36 ± 0.03	1.55 ± 0.03

[a] Determined with a Carlo Erba ANA 1500 NCS analyzer. [b] Pyrite concentration determined by the Lord method (ref 10) is 9.29 ± 0.18 mg of S/g. [c] ND is not determined. All samples were analyzed in triplicate (n = 3).

Thus, initial experiments involved the addition of 1–6 mL of borohydride solution to 0.5 M HCl (i.e., used in AVS determinations). The recovery of greigite sulfur was incomplete and ranged from 50 to 75%. In order to strengthen the reducing conditions, potassium iodide (0.01 M in the reaction solution) was added to the stripper. With this modification the recovery of greigite sulfur was 101 ± 3% (n = 4) using a 15-min reaction/stripping time.

Selectivity of the greigite procedure was examined by subjecting two pyrite standards to the greigite procedure. Coarse-grained, mineral pyrite and a commercially synthesized pyrite did not show detectable reduction to hydrogen sulfide using the greigite procedure. However, experiments performed by J. Cornwell (personal communication) show that a microcrystalline pyrite synthesized in the laboratory is completely reduced by the borohydride/iodide reductant solution. Although it is unclear whether such a form of pyrite exists in sediments, the greigite determination should also be considered to include microcrystalline pyrite. The greigite determination itself takes 20 min (sample to sample), possesses the same detection limits as pyrite and AVS (6.1 μg of S/g), and has a precision of 7% (relative standard deviation) at 0.51 mg of S/g (n = 4).

Application to Field Samples. A large variety of marine and freshwater sediments and water samples have been subjected to the dissolved and sedimentary sulfur procedures; some of the results are presented in Table I. The dissolved sulfide data show that the procedures can be used to determine widely different concentrations. It is also particularly interesting to note that dissolved sulfide can be detected in oxygenated seawater. The sediment results show that very good precision is obtained even though only milligrams of sample are used. In marine sediments, AVS and greigite are minor sulfur components, while AVS is the dominant sulfur species in the freshwater sediments of Hyco Reservoir. In order to check the recovery of pyrite in field samples, the Chesapeake Bay sediment was subjected to the Cr(II) method described here and the selective leach procedure of Lord (*10*); good agreement between the two methods is shown (Table I). If total sulfur is determined (using an elemental analyzer such as the Carlo Erba ANA 1500) along with AVS, greigite, and pyrite, the speciation of sedimentary sulfur is almost completely revealed. Presumably the difference between total sulfur and the other sulfur species is the concentration of elemental and organic sulfur in a sediment. By use of the Great Marsh data as an example, the amount of organic and elemental sulfur decreases with depth, and pyrite becomes the dominant form of sulfur.

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