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Direct Ultraviolet Spectrophotometric Determination of Total Sulfide and Iodide in Natural Waters

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A technique is described that allows the determination of total dissolved sulfide in natural waters using direct ultraviolet detection of the HS⁻ ion. The concentration of bisulfide is determined by measuring absorption from 214 to 300 nm and then deconvolution of the HS⁻ spectra from the complex spectrum of natural fluids. A nonlinear least-squares fitting approach is used for the deconvolution. At a pH near 8, where >95% of total sulfide is present as HS⁻, the results are indistinguishable from total sulfide measured using the methylene blue method in a wide range of sample types and matrixes including freshwater from groundwater wells, marine hydrothermal vent fluids, and marine sediment porewaters. The method allows simultaneous determination of other UV-absorbing ions, including nitrate, bromide, and iodide, in samples with low total sulfide concentrations. Bisulfide concentrations can be determined in samples with low background absorption, such as well water and hydrothermal fluids, with a detection limit of <1 μM. The detection limit for bisulfide in sediment porewaters that have a high organic loading, which produces background absorbances of ~0.5 A at 260 nm in a 1-cm cuvette, is 5 μM. The only chemical manipulation required is buffering acidic samples to pH >7 and filtration of particulate-rich samples.

Hydrogen sulfide and its ionization products bisulfide (HS⁻) and sulfide (S²⁻) are found in many natural waters.[1] They are formed in anoxic waters by heterotrophic, sulfate-reducing bacteria and as a result of geochemical processes in hydrothermal systems. Although toxic to many organisms, these sulfide species are also an energy source for chemosynthetic bacteria, where energy released during their oxidation to sulfate drives the phosphorylation of ADP to ATP. Determination of sulfide species concentration is important to a variety of studies including groundwater monitoring and assessment of biogeochemical processes in hydrothermal vent fluids and aquatic sediment porewaters. However, sulfides are not detected far from source areas, or long after collection, due to their reactivity with O_2, unless they are

preserved. Methods capable of rapid measurements in the field are desirable, therefore.

A number of techniques have been developed to measure total sulfide species (H_2S + HS⁻ + S²⁻ + reactive polysulfides) or hydrogen sulfide content in natural systems.[2] These include colorimetric methods with methylene blue,[3,4] nitroprusside,[5] and nitrilotriacetic acid and iron.[6] A variety of electrochemical methods using potentiometry,[7] voltammetry,[8] and amperometry[9] have been used to measure sulfide species, as well. Methods based on gas chromatography have been used to determine ultratrace concentrations of total sulfide.[10] This paper demonstrates the potential of direct ultraviolet spectrophotometric detection of the bisulfide ion in natural waters for the determination of total sulfide concentration. The advantages of this method include simplicity and speed of data acquisition.

Hydrogen sulfide solutions absorb light directly in the ultraviolet.[11,12] However, many naturally occurring inorganic ions[13,14] and a broad suite of organic compounds[11,15,16] also exhibit strong absorption at wavelengths below 300 nm. These interferences have prompted the development of several indirect methods for the determination of sulfide species in natural samples that involve chromatographic separation of the sulfide species[12] or extraction of hydrogen sulfide and measurement of the UV absorption signal in the gas phase.[17] We show that the direct ultraviolet determination of bisulfide ion in aqueous solutions at a pH near 8 yields accurate and precise estimates of total sulfide concentration in a variety of natural waters. The method involves measuring the

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(1) Schlesinger, W. H. *Biogeochemistry: An Analysis of Global Change*; Academic: San Diego, 1991.
(2) Kuhl, M.; Steuckart, C. In *In Situ Monitoring of Aquatic Systems: Chemical Analysis and Speciation*; Buffle, J., Horvai, G., Eds.; Wiley: Chichester, U.K., 2000; p 121.
(3) Cline, J. D. *Limnol. Oceanogr.* **1969**, *14*, 454−58.
(4) Sakamoto-Arnold, C. M.; Johnson, K. S.; Beehler, C. L. *Limnol. Oceanogr.* **1986**, *31*, 894−900.
(5) Kuban, V.; Dasgupta, P. K.; Marx, J. N. *Anal. Chem.* **1992**, *64*, 36−43.
(6) Kester, M. D.; Shiundu, P. M.; Wade, A. P. *Talanta* **1992**, *39*, 299−312.
(7) Berner, R. A. *Geochim. Cosmochim. Acta* **1963**, *27*, 563−75.
(8) Brendel, P. J.; Luther, G. W., III. *Environ. Sci. Technol.* **1995**, *29*, 751.
(9) Jeroschewski, P.; Steuckart, C.; Kuhl, M. *Anal. Chem.* **1996**, *68*, 4351.
(10) Cutter, G. A.; Oatts, T. J. *Anal. Chem.* **1987**, *59*, 717.
(11) Perkampus, H. H. *UV−Vis Atlas of Organic Compounds*; Plenum Press: New York, 1966; Vol. 5.
(12) Williams, R. J. *Anal. Chem.* **1983**, *55*, 851.
(13) di Noto, V.; Mecozzi, M. *Appl. Spectrosc.* **1997**, *51*, 1294.
(14) Collos, Y.; Mornet, F.; Sciandra, A.; Waser, N.; Larson, A.; Harrison, P. J. *J. Appl. Phycol.* **1999**, *11*, 179.
(15) Bricaud, A.; Morel, A.; Prieur. L. *Limnol. Oceanogr.* **1981**, *26*, 43.
(16) Green, S. A.; Blough, N. V. *Limnol. Oceanogr.* **1994**, *39*, 1903.
(17) Anwar, J.; Marr, I. L. *J. Chem. Soc. Pak.* **1986**, *8*, 67.

ultraviolet absorbance of the HS$^-$ ion over a range of wavelengths in aqueous samples without the addition of reagents, other than buffers for acidic solutions. The concentration of bisulfide in a sample can be determined by deconvolution of the HS$^-$ spectra from the complex spectrum of natural fluids using a nonlinear least-squares fitting approach.

EXPERIMENTAL SECTION

Reagents. All solutions were prepared from reagent grade chemicals and deionized water (DW; Millipore, Milli-Q water system, 18 MΩ cm^{-1}). Bisulfide standards were prepared by deoxygenating 250 mL of water in a 500-mL glass aspirator bottle with N$_2$ gas for 1 h. Na$_2$S· 9H$_2$O was rinsed with DW to remove any sodium sulfite and the crystals were wiped dry to remove any excess water before weighing 6 g, which were added to the deoxygenated water to produce a 100 mM solution. The glass aspirator bottle was sealed to prevent oxygen contamination. The bisulfide stock solution was standardized by iodometric titration.[4] If oxygen is excluded, the solution will be clear and the concentration should be stable for approximately 1−2 weeks.

Working standards were prepared daily by drawing portions of the stock primary standard into a syringe and micropipetting them into 100 mL of either DW or filtered seawater. Low-nitrate (<0.5 μM NO$_3^-$) surface seawater was used to prepare the standards for measurements in marine systems. Deionized water was used for all other standards. Absorption spectra of working standards were collected within 15 min of the preparation time to avoid changes in total sulfide concentration due to oxidation by O$_2$ in the standard solutions. The surface seawater used for the standards was filtered ($\leq$0.45 μm) prior to use to exclude sulfide-oxidizing bacteria and any particulate material.

The reagents used for the measurement of total sulfide species by the methylene blue technique were N,N-dimethyl-p-phenylene-diamine dihydrochloride ((CH$_3$)$_2$N·C$_6$H$_4$·NH$_2$·2HCl, Aldrich, 0.48 g dissolved in 100 mL of 6 M HCl) and ferric chloride (FeCl$_3$, Eastman Kodak Co., 1.6 g dissolved in 100 mL of 6 M HCl), and they were used as described previously.[4] Both reagents were stored in brown polyethylene bottles. These reagents should be stable for several months if protected from light and refrigerated.

Sample Collection and Preparation. *Well Water Samples.* Freshwater samples were collected from groundwater wells in Seaside, Monterey County, CA, in brown polyethylene bottles, which were filled completely and capped. Replicate samples were obtained from most of the wells and analyzed within a few hours. The samples were not filtered or diluted before analysis by the UV method. Well water samples were all within pH 7.7−8.0. Total sulfide was also determined by the methylene blue method, and nitrate was measured by colorimetry after reduction to nitrite.[18]

Hydrothermal Vent Fluid Samples. Samples were collected on the Juan de Fuca Ridge in September 1998 within the caldera of Axial Volcano[19,20] at a depth of 1500 m using the remotely operated vehicle *ROPOS*. Samples were drawn from the fluid sampler into

(18) Sakamoto, C. M.; Friederich, G. E.; Codispoti, L. A. MBARI Technical Report, No. 90-2, 1990.
(19) Baker, E. T.; McDuff, R. E.; Massoth, G. J. *J. Geophys. Res.* **1990**, *95*, 12, 843.
(20) Butterfield, D. A.; Massoth, G. J.; McDuff, R. E.; Lupton, J. E.; Lilley, M. D. *J. Geophys. Res.* **1990**, *95*, 12895.

plastic syringes on board ship. Some samples were filtered at depth during collection using in-line filters. One of the samples was filtered (0.5 μm Millipore Millex-LCR) in the laboratory to remove visible particulate material. The pH of each sample was determined with pH indicator strips (EM-Reagents) and values as low as 3 were found. Ammonium hydroxide (0.44 M) was added to samples with a pH <7 to raise the pH to ∼8.0. Gas-rich vent samples were diluted with deoxygenated seawater to prevent degassing in the spectrophotometer cell. No more than 60 μL of ammonium hydroxide was added to a volume of 5 mL of the sample. The ammonium hydroxide did not interfere with the detection of bisulfide in the samples. Total sulfide was also measured at sea in each sample by the methylene blue method.

Sediment Porewater Samples. Sediment samples were collected from Elkhorn Slough National Estuarine Research Reserve, Moss Landing, CA, and from the continental shelf in Monterey Bay. The Elkhorn Slough samples were collected by pushing 10-cm-diameter polycarbonate core tubes into a shallow mud flat (lat. 36°48′50″ N, long. 121°47′20″ W) at low tide. Core length was ∼30 cm. To ensure the presence of sulfide species, the Elkhorn Slough samples were left in the core tube at room temperature for 2 weeks prior to porewater extraction.

The Monterey Bay samples were collected on March 13, 1998 at 98 m (lat. 36°44′ N, long. 121°56′ W) and on April 12, 1999 at 85-m depth (lat. 36 42′ N, long. 121°55′ W) with a multicorer. The core collected on March 13 was left in the core tube for 2 weeks in the laboratory to allow bisulfide to develop within the core prior to porewater extraction. The mud from three cores collected on April 12 was left in the core tubes for either 1, 7, or 14 days prior to porewater extraction.

Each core was sectioned in an inflatable glovebag, which was filled with N$_2$ gas. Centrifuge tubes were filled with mud from each sediment section within the glovebag. The sealed tubes were centrifuged for ∼30 min at 2500 rpm to separate the porewater. The supernatant solution was filtered with a 0.45-μm filter under N$_2$ gas and was analyzed immediately by both the ultraviolet and the methylene blue methods. Some of the Elkhorn Slough samples had an extremely high baseline absorbance ($A_{260\ nm} > 0.5$) due to high concentrations of dissolved organic material. These samples were diluted with deoxygenated, filtered surface seawater from Monterey Bay.

Apparatus. A Hewlett-Packard HP 8452A diode array spectrophotometer with 2-nm resolution was used to collect absorbance data from 200 to 400 nm. Absorbance of well water and porewater samples was measured with a 1-cm square (Fisherbrand) quartz cuvette. Vent samples were measured in a 1-cm Hellma flow-through cuvette with Suprasil I windows. Four solenoid pumps (Lee LPLX0502100AA) were used to propel DW, seawater blank, bisulfide standard, and sample through the flow-through cuvette. The Lee pumps were controlled by a Metrabyte analog/digital interface, and the spectrophotometer was controlled through an HPIB (IEEE-488) interface bus using a Quick Basic 4.5 computer program. Each absorbance spectrum was saved along with the computer-generated estimate of the bisulfide concentration in the sample.

A Perkin-Elmer Elan 6000 IC MS was used to determine total iodine in Monterey Bay porewater solutions. Samples were diluted up to 250-fold with 1% ultrapure HNO$_3$ before analysis by ICPMS.
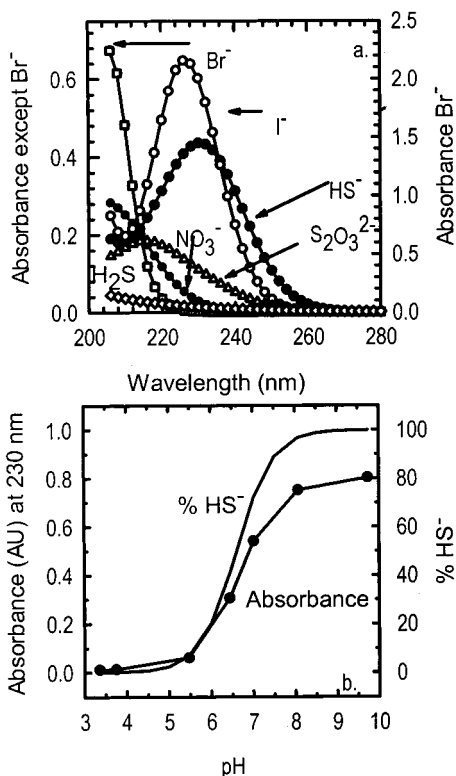
Figure 1. (a) Absorbance spectra for pure inorganic compounds in deionized water at typical concentrations found in seawater: (●) 50 μM HS⁻, (◇) 50 μM H$_2$S, (○) 50 μM I⁻, (□) 840 μM Br⁻, (△) 50 μM S$_2$O$_3^{2-}$, and (+) 30 μM NO$_3^-$. (b) Absorbance of a 115 μM total sulfide solution in seawater versus pH (solid circles) and percent of HS⁻ in the solution (solid line). Percent HS⁻ was calculated using a pK_1 value of 6.60 for seawater.

The pH of the samples was measured with a Corning model 130 pH meter, except as noted.

RESULTS AND DISCUSSION

The spectrum of a solution containing 50 μM total sulfide at pH 8 shows a well-defined peak at 230 nm (Figure 1a). The absorbance at 230 nm of a solution containing 115 μM total sulfide is shown at various pH values in Figure 1b. The absorbance has a strong pH dependence. The percent of the total sulfide present as HS⁻ in each sample, which was calculated with a pK_1 value of 6.60 for seawater at 25 °C (pK_1 = 6.98 in pure water),[21] is also shown. The similarity of the two lines demonstrates that the bisulfide ion is the primary species responsible for the UV absorption of hydrogen sulfide solutions. A much weaker spectrum is present in acidic solutions due to undissociated H$_2$S (Figure 1a). The dominance of HS⁻ in UV absorption dictates an optimal pH range for UV determination of total sulfide concentration in the range 8.0−9.0, where HS⁻ is >95% of total sulfide. The spectrum may be complicated above pH 9 by the absorbance of polysulfides, which are known to absorb in the UV.[21]

The UV absorbance spectra for some of the other compounds present in seawater are shown in Figure 1a at typical ocean concentrations. Bromide, nitrate, nitrite, and iodide have peak absorbances at approximately 204, 202, 210, and 226 nm, respectively.[11] Bromide dominates the absorption spectrum of nitrate-

(21) Millero, F. J. *Mar. Chem.* **1986**, *18*, 121.

free seawater at 210 nm, and other inorganic ions that comprise the major salt matrix contribute only weakly to the UV absorption spectrum.[14] For example, chloride, which is present in seawater at nearly 1000-fold higher concentrations than bromide, contributes less than 8% to the absorption at 210 nm. Other major ions such as bicarbonate and magnesium contribute less than 1% at typical seawater levels.[14] Nitrate makes significant contributions to the UV spectrum of seawater at wavelengths above 210 nm. Thiosulfate, which may be a significant shunt in the microbial sulfur cycle and which may form ~60% of the immediate sulfide oxidation product,[22] has a peak absorbance at 216 nm (Figure 1a). Sulfite and bisulfite have insignificant absorbance spectra at the wavelengths examined.

The peak in the spectrum of the bisulfide solution is generally well resolved from the spectra of the other ions except I⁻. Concentrations of total iodine are <1 μM in open ocean seawater,[23,24] which is not sufficient to interfere with bisulfide determinations at the micromolar level. However, appreciable concentrations of I⁻ (≫1 μM) may be found in marine sediment porewaters.[25] We show below that the peaks of HS⁻ and I⁻ can be resolved. Organic compounds will also absorb light in the UV. Studies have shown that the spectrum of natural dissolved organic matter can be modeled as an exponential function.[15,16]

The absorbance of a sample is given by the sum of the component absorbances:

$$A_\lambda / L = \epsilon_{HS,\lambda}[HS^-] + \sum_j (\epsilon_{j,\lambda}[j]) + \exp(a + b\lambda) + c \quad (1)$$

where (ϵ) is the molar absorptivity of the subscripted species at wavelength, λ and L is the path length. The sum over components (j) represents all possible combinations of inorganic ions other than HS⁻ that may be present in the sample. The exponential intercept (a) and the slope (b) represent the background absorption due to organic constituents in seawater.[15,16] The exponential baseline cannot fit spectra with negative absorbance values that may result from spectrophotometer drift. The term c may be added to allow spectral offsets to be included in the fitting process.

Equation 1 can, in principle, be used to determine HS⁻, NO$_3^-$, Br⁻, I⁻, and other components in a single sample. However, two factors may complicate the application of eq 1. Concentrations of HS⁻ in excess of 200 μM produce absorbances larger than 1.5A with a 1-cm cuvette. The low light transmission through these samples increases errors due to stray light and detector dark current. Response is not linear to concentration with the HP8452 under these conditions. High bisulfide absorbance may also preclude detection of inorganic species that absorb at lower wavelengths. Also, the background absorbance in samples with high dissolved organic carbon (DOC) concentration can deviate significantly from the exponential relationship in eq 1. The wavelength range used in the application of eq 1 must be carefully chosen to mitigate these factors. We normally used a range from 214 to 300 m. However, the lower wavelength range was limited to values with A < 1 to avoid nonlinear detector response. The

(22) Jorgenson, B. B. *Science* **1990**, *249*, 152.
(23) Luther, G. W., III; Swartz, C. B.; Ullman, W. J. *Anal. Chem.* **1988**, *60*, 1721.
(24) Nakayama, E.; Kimoto, T.; Isshiki, K.; Sohrin, Y.; Okazaki, S. *Mar. Chem.* **1989**, *27*, 105.
(25) Wakefield, S. J.; Elderfield, H. J. *Mar. Res.* **1985**, *43*, 951.
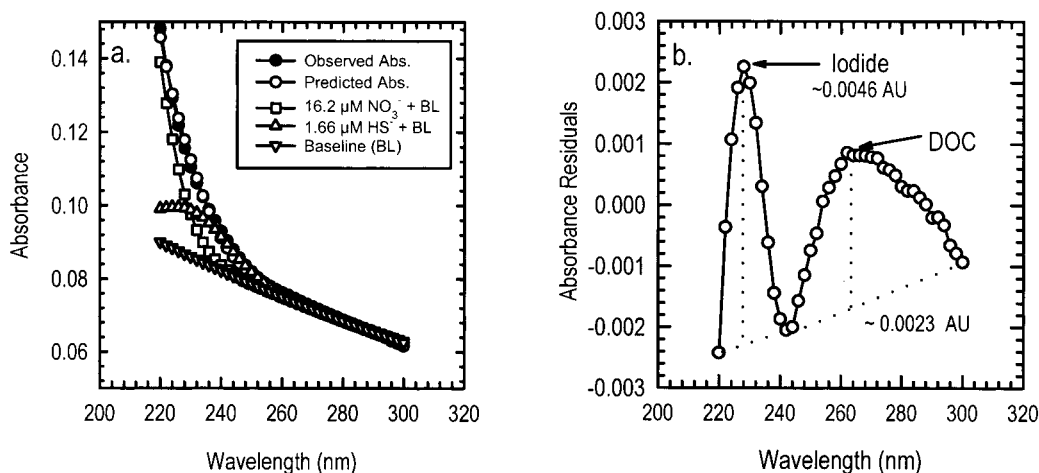
Figure 2. (a) Observed and calculated component absorbance spectra for a well water sample: (●) Observed spectra, (○) predicted spectra, (□) 16.2 μM NO$_3^-$ plus the exponential baseline, (△) 1.66 μM HS$^-$ plus the exponential baseline, and (▽) exponential baseline. Component spectra were determined from a nonlinear least-squares regression from 220 to 300 nm. The total sulfide concentration determined in the sample by the methylene blue method was 1.26 μM. (b) Absorbance residuals calculated for the spectra in (a).

upper wavelength limit was reduced to 278 nm to avoid the DOC peak if large baseline absorbances were found, as discussed below. We used the Systat 7.01 nonlinear equation fitting algorithm to fit eq 1 to the observed spectra. Curve fits using the Excel Solver function to minimize a nonlinear sum of square errors generally gave equivalent results but did not converge for some samples.

The array of molar absorptivities ($\epsilon_{j,\lambda}$) for each compound (j) was determined by calculating the slope of absorbance versus concentration at each wavelength for a series of standards of the compound of interest. To test the effect of salt on the molar absorptivity for bisulfide, standards were prepared in varying concentrations of NaCl, as well as seawater. Relative to deionized water, there is a weak increase of molar absorptivity (based on total sulfide concentration) at 230 nm in 1 M NaCl (∼5%), which is consistent with the change in HS$^-$ concentration that is created by the salt effect on the H$_2$S dissociation constant.[21] The molar absorptivity in seawater is suppressed by a similar amount (∼5%) relative to deionized water. The difference between molar absorptivities in NaCl and seawater may be caused by ion pairing of HS$^-$ with divalent cations in seawater, although we have no direct evidence for this.

Sulfide in Well Water. Samples of well water represent the simplest natural samples that we examined. These samples contain small amounts of halide ions. The absorbance in all samples was less than 1.0 at wavelengths greater than 214 nm. Equation 1 can be applied directly to the well water samples.

Figure 2a shows the absorption spectra of a sample and the component spectra that were determined by a multiple regression fit of eq 1 using a wavelength range from 220 to 300 nm. The detection limit (3 × standard deviation) for 15 repeated analyses of bisulfide in well water was 0.6 μM. Although an odor of hydrogen sulfide was present in most samples, concentrations of total sulfide above the detection limit were found in only one sample using either the ultraviolet (1.7 μM) or methylene blue (1.3 μM) technique (Figure 2). The absorbance residuals obtained across the spectrum after fitting eq 1 were distinctly nonrandom (Figure 2b). The residual peak at 228 nm (Figure 2b) may correspond to I$^-$ in this sample at a concentration of ∼0.3 μM. It produces the slight shift in the observed versus the predicted

absorbance for the well water sample (Figure 2a). Dissolved organic carbon probably accounts for the second residual peak at 260 nm. However, the impact on the calculated concentration of bisulfide due to the presence of these compounds in the samples is small.

Sulfide, Nitrate, and Bromide in Hydrothermal Vent Fluids. The spectra of vent fluid samples were more complex than those of well water. The high bromide concentration in seawater (∼850 μM) and high total sulfide concentrations in the samples resulted in absorbances above 1.0. The vent fluid samples were divided into two groups, those containing low total sulfide concentrations ($A < 1.0$ at $\lambda = 230$ nm and pH 8) and those with high total sulfide concentrations ($A \geq 1.0$ at $\lambda = 230$ nm and pH 8). Equation 1 was applied directly to samples with a low bisulfide concentration. This allowed bromide, nitrate, and a semiquantitative estimate of DOC to be determined, as well as HS$^-$. The high bisulfide samples were modeled with bisulfide and DOC as the only constituents.

Figure 3a shows the absorbance spectra of a low total sulfide vent sample and the component spectra that were determined by multiple regression of the sample spectrum from 214 to 300 nm. The absorbance spectrum for a high total sulfide vent sample and the component spectra that were determined by nonlinear regression fit of eq 1 from 246 to 300 nm are shown in Figure 3b. The lower wavelength limit (246 nm) was chosen because all lower wavelengths had $A > 1.0$. Deviations of the predicted spectra from the observed value at wavelengths of <246 nm are probably due to nonlinear response of the spectrophotometer at high absorbance.

Bisulfide concentrations in vent fluids predicted by the ultraviolet method are compared with total sulfide determinations by methylene blue analysis in Figure 4. There is good agreement across the concentration range, which indicates that the UV method can accurately predict total sulfide concentrations in samples adjusted to pH near 8, where bisulfide accounts for >95% of the total sulfide concentration.

It is not necessary to include the absorbance peak in model curve fits to obtain accurate concentration estimates. High-concentration samples can be analyzed by the UV method without
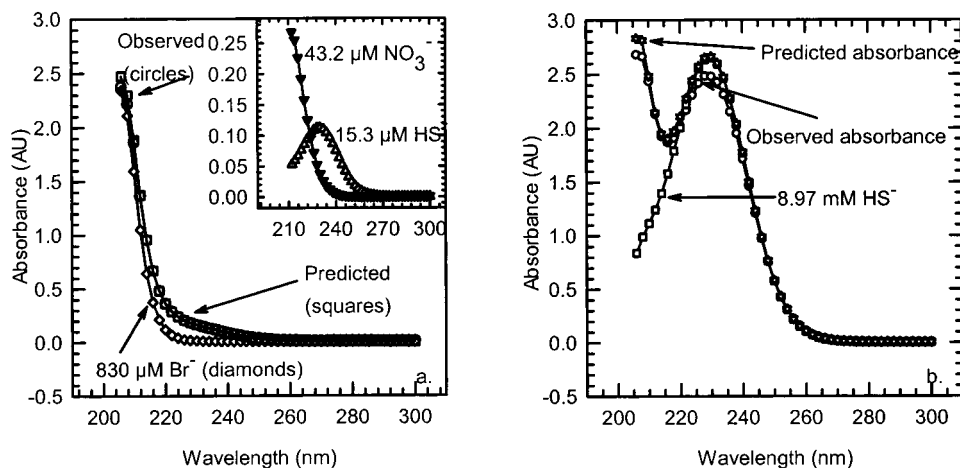
Figure 3. (a) Observed and predicted absorbance spectra for a low total sulfide vent sample. The component spectra for bisulfide and nitrate (inset) and bromide are also shown. Component spectra were determined using a nonlinear least-squares regression analysis from 214 to 300 nm. (b) Observed and predicted absorbance spectra for a high total sulfide vent sample. The component spectrum for bisulfide is also shown. Data from a least-squares nonlinear regression from 246 to 300 nm.
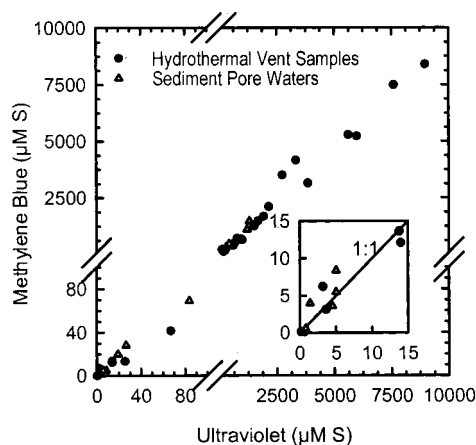

Figure 4. Total sulfide concentration measured by the methylene blue method versus bisulfide concentrations determined at pH $\cong$ 8 using the ultraviolet method for hydrothermal vent fluid samples (●) and Elkhorn Slough sediment porewaters (△). Regression lines fit to the two sets of data: vent samples − MB = 0.95UV − 10 (R^2 = 0.983), Porewaters − MB = 1.04UV − 0.52 (R^2 = 0.988). The inset shows the low-sulfide values and a 1:1 line.

Figure 5. Absorbance spectra for two sediment porewater samples from Elkhorn Slough. A peak near 260 nm in the sample with 20.8 μM total sulfide causes a significant deviation from the exponential background curve used to model DOC spectra and negative estimates of bisulfide if the regression is extended to 300 nm. This peak is absent in the sample with 26.5 μM total sulfide.

dilution, therefore, simply by using wavelengths off the spectral peak. Analysis without dilution is not possible with the methylene blue method.[3] The detection limit for total sulfide in the vent fluids using the UV method was determined by 11 replicate analyses of a low-bisulfide sample. The standard deviation (SD) of the measurements for bisulfide was 0.26 μM, which gives a detection limit (3 SD) of 0.8 μM. The calculated absorbance residuals for spectra of both low- and high-bisulfide vent samples showed the possible absorbance of dissolved organic material at 260−280 nm. These signals were much lower than found in well water, however, and DOC did not bias the determination of bisulfide in the vent samples.

Sulfide and Iodide in Sediment Porewater. Determination of bisulfide in sediment porewater samples presents a stringent test of the ultraviolet method for several reasons. Some of the samples had high baselines (>0.5A at 260 nm) after filtration. We believe that this is due to the high concentration of dissolved organic carbon in these samples. Additional inorganic interferences such as I⁻ are also present at significant concentrations.
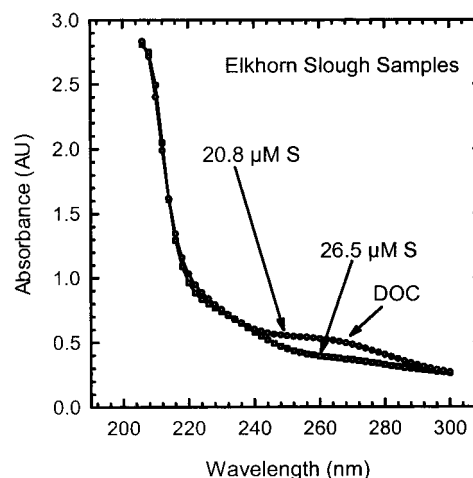
Elkhorn Slough Sediment Porewaters. High background absorbances and the presence of a peak near 260 nm (Figure 5) characterize many of these samples. This background absorbance is likely due to concentrations of DOC greater than 950 μM, estimated from the DOC concentration to absorbance at 280 nm relationship reported by Krom and Sholkovitz.[26] The peak at 260 nm in porewater will bias the exponential baseline at 230 nm to higher absorbance values in a least-squares curve fit. This forces an underestimate of HS⁻ concentrations and negative estimates of HS⁻ if concentrations are near zero.

One potential approach to solve this problem would be the use of hybrid linear analysis (HLA)[27] to model the dissolved organic spectrum. An assessment of the general applicability of HLA would probably require a larger data set than we have. We therefore used an alternative approach to avoid the upward bias of the baseline that is driven by the 260-nm peak. The upper

(26) Krom, M. D.; Sholkovitz, E. R. *Geochim. Cosmochim. Acta* **1977**, *41*, 1565.
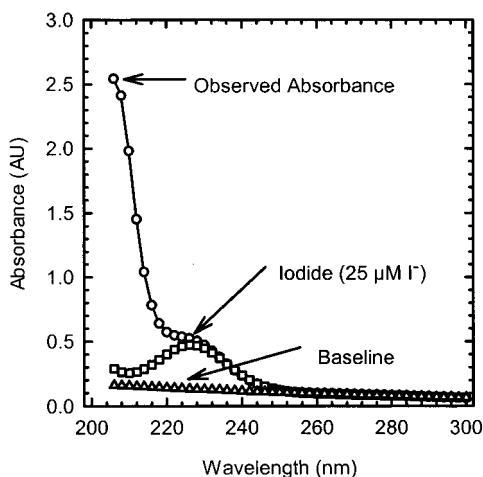(27) Berger, A. J.; Koo, T. W.; Itzkan, I.; Feld, M. S. *Anal. Chem.* **1998**, *70*, 623.

Figure 6. Absorbance spectrum from a sediment porewater sample from a sediment core collected at 85-m depth in Monterey Bay, April 1999 (○). Component spectra for 25 μM I$^-$ plus the baseline (□) and the baseline alone (△), which were obtained with a least-squares nonlinear regression from 234 to 300 nm, are also shown.

Figure 7. Iodide concentrations calculated from the UV method (○) and total iodine measurements by ICPMS (●) n versus depth in a core collected in Monterey Bay, April 1999. The core was extracted and analyzed on the day after collection. This core had <1 μM total sulfide detected by the methylene blue method, or by the UV method if I$^-$ was included in the regression.

wavelength limit of the regression was reduced to 278 nm, which limits the background spectra primarily to the flat region that just includes the peak due to DOC (Figure 5). The wavelength limit of the regression was not reduced for those samples where a peak at 260 nm was not apparent (peak height at 260 nm less than 0.05A). Some of the samples with high baseline absorbances were diluted with surface seawater in order to decrease the effect of the high concentrations of DOC in the samples.

The bisulfide concentrations obtained by the ultraviolet method in samples at pH near 8 compare favorably with the total sulfide concentrations measured in all of the samples (Figure 4). The slope of the regression line fit to the UV and methylene blue data is not significantly different from 1.0 (Figure 4). The largest standard error of the regression fitted to the UV spectra for these samples was on the order of 0.016A, and most sample regressions had errors that were <0.005A. The samples with the highest regression error all had high (>0.3A) baselines, which suggests that the exponential baseline is less accurate in these samples. A detection limit (3SD) of 5 μM HS$^-$ was obtained from 15 replicate analyses of an Elkhorn Slough sample.

Monterey Bay Sediment Porewaters. The spectra of porewater samples from Monterey Bay had lower baselines at 260 nm (<0.1A) than did the Elkhorn Slough samples. The observed absorbance spectrum of a sample collected from 85-m depth in Monterey Bay on April 12, 1999 is shown in Figure 6. A peak with a maximum at 226 nm is present. This peak does not appear to be HS$^-$ for several reasons. The standard error of the regression for a model spectrum based on HS$^-$ and DOC in these samples (0.005−0.02A) was larger than typical (~0.003A) for other pore-water samples with low background absorbance, which indicates that a model with HS$^-$ did not fit the spectra well. The 226-nm peak also decreased with depth in the cores. Total sulfide would show the opposite behavior, increasing with depth. The peak was also much less discernible in porewater samples that were processed after cores were left at room temperature for 7−14 days in sealed core tubes, which should promote sulfide formation.

The peak present in the Monterey Bay porewater samples appeared to be caused by large iodide concentrations. Iodide has
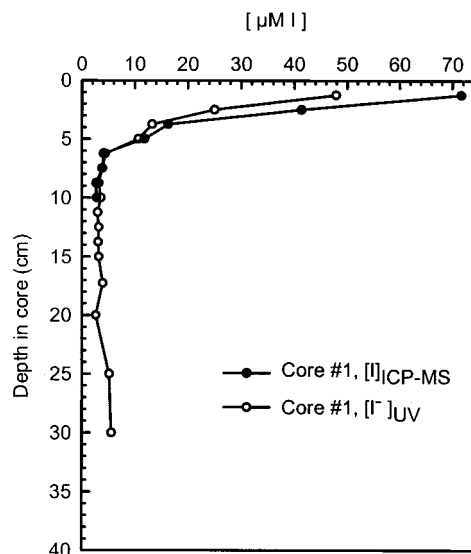
a peak absorbance at 226 nm (Figure 1a). Iodide concentrations would generally decrease with depth in the sediment, unlike sulfide.[25] Fitting the observed absorbance spectra with HS$^-$ and I$^-$ components, or I$^-$ alone, results in a considerably smaller standard error of the regression (<0.003A) than was observed when the core was fit for HS$^-$ alone.

Iodide concentrations up to 50 μM were calculated from the spectra of the Monterey Bay core that was sampled after 1 day (Figure 7). The presence of dissolved iodine at these concentrations was confirmed by ICPMS analysis of the pore fluids for this core (Figure 7). The total dissolved iodine concentrations measured by ICPMS in the core top sample parallels the UV results, but the ICPMS values are larger by ~33%. This suggests that one-third of the total iodine was present as iodate or organic iodine compounds[28] that were not detected by the UV method. The detection limit for bisulfide in sediment pore fluids is 5 μM. All of these Monterey Bay porewater samples were below the detection limit for bisulfide when I$^-$ was included in the regression model. This is in agreement with the methylene blue total sulfide measurements, which had a highest concentration of 2.3 μM. Negative concentrations, which lie within the bounds of the detection limit, were obtained by the UV method for some samples.

The ultraviolet method has proven applicable for monitoring bisulfide in some of the most complex natural systems. The predictions of bisulfide concentration by the UV method are in satisfactory agreement with the methylene blue technique, and the errors (<±2.0 μM HS$^-$, 1 SD) are comparable. Complexation of bisulfide by trace metal ions is unlikely to impact estimates of total sulfide as trace metal ion concentrations are generally orders of magnitude less than total sulfide levels in anoxic systems.[20,29]

(28) Luther, G. W., III; Ferdelman, T.; Culberson, C. H.; Kostka, J.; Wu, J. *Estuarine Coastal Shelf Sci.* **1991**, *32*, 267.

(29) Jacobs, L.; Emerson, S. *Geochim. Cosmochim. Acta* **1985**, *49*, 1433.

Nitrate, bromide, and iodide concentrations can also be measured by the ultraviolet method. An indication of the amount of dissolved organic carbon in the samples could be inferred as well by examining the absorbance spectrum of the nonlinear baseline in each sample. Monitoring the standard error of the regression for unusually large values allowed the presence of interfering compounds such as I^- to be detected, identified, and quantified.