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A Field Method for Sulfide Determination

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ABSTRACT

Hydrogen sulfide and sulfide salts are found throughout our environment from both natural and industrial sources. Many of these sulfides are soluble in water. Therefore, they end up in our aqueous environment. Since sulfides (H_2S , HS^- , and S^{2-}) undergo rapid oxidation by air (oxygen) to sulfates, it was essential that a simple and rapid method be developed which could determine the total sulfide concentration in water in the field.

Direct measurements were made using a silver/sulfide ion selective electrode in conjunction with a double junction reference electrode connected to an Orion Model 407A/F Specific Ion Meter. The method also made use of a sulfide anti-oxidant buffer (SAOBII) which consists of ascorbic acid, sodium hydroxide and disodium EDTA.

Prew weighed sodium sulfide crystals were sealed in air tight plastic volumetric flasks which were used in standardization process in the field. Field standards were prepared by adding SAOB. II to the flask containing the sulfide crystals and diluting it to the mark with deionized deaerated water. Serial dilutions of the standards were used to prepare standards of lower concentrations.

Concentrations as low as 6ppb were obtained on lake samples with a reproducibility better than $\pm 10\%$.

INTRODUCTION

Sources of hydrogen sulfide include a wide variety of natural and anthropogenic sources.(1). All versions of the sulfur cycle deduce the hydrogen sulfide source magnitude from the mass necessary to obtain a balanced cycle (2). No differentiation has been made between natural hydrogen sulfide sources and sources resulting from anaerobic metabolism of organic waste from man and his activities. No matter the origin or source of sulfides, anthropogenic or biogenic, they are usually associated with water pollution or generally speaking, environmental pollution.

Many sulfide salts are sparingly soluble in water and the solutions formed are toxic at certain concentrations. The safe concentration of sulfide in fresh water has been set at 0.002ppm(2).. Hence, it is essential that total sulfide concentration in the aqueous environment be known. Furthermore, the reaction of sulfide ions in water produces hydrogen sulfide gas. A detectable odor of this gas is a sufficient index of excessive concentration. A concentration of 0.2ppm in the air is known to produce a detectable odor and can become a potential health hazard. The production of excessive hydrogen sulfide in anaerobic waters usually entail extensive changes in the flora and fauna of the particular aquatic environment. Metals such as Cu, Fe, Ni, Al and Pd are known to be corroded by hydrogen sulfide(3).Corrosion rates of up to 140 μm / year for Cu have been measured near sources of hydrogen sulfide (4).

The purpose of this study was to determine total sulfide in the aqueous environment of the region surrounding Houston's first coal power electric power generating plant at the site of the sample.

The capability of a ion-selective electrode to monitor sulfide ion activity has been demonstrated (5-9). However, sulfide measurements at low levels are very difficult because of rapid oxidation of the sulfide ion by oxygen from the air. The field method presented in this paper should help to eliminate the problems associated with air oxidation.

EXPERIMENTAL

Apparatus. A field portable, Orion Model 407A/F specific ion meter was used for direct measurement of sulfide ion in water samples. A Beckman Selection 5000 Ion Analyzer was used to cross check the results in the laboratory which were obtained with the Orion Model 407A/F by titration of the sulfide ion with standard lead perchlorate. An Orion Model 90-02-00 double junction reference electrode and Orion Model 94-16-00 silver/sulfide electrode were used for all measurements. All samples and standards were magnetically stirred during the measuring process. Plastic ware was used at all times when handling the standards and samples.

Reagents. All chemicals used were reagent grade. Standard solutions of sodium sulfide were prepared with high purity Beckman Selection Reagent Sodium Sulfide Crystals (99.0% $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) purchased from Beckman Instruments, Inc. Deionized deaerated water was used in the preparation of all standards and samples. The sulfide antioxidant buffer was prepared by mixing disodium EDTA, ascorbic acid, and sodium hydroxide as described by Orion Research (10). The standard lead perchlorate solution (0.1M), which was used in the sulfide titrations, was obtained from Orion Research.

Procedure. The instruments to be used were first checked out for proper operation. The check methods used for the instruments were outlined in their respective instruction manuals. The reference electrode was filled with Orion inner chamber

and Orion outer chamber filling solutions. Since all sulfide standard solutions and samples have to be buffered, a sulfide anti-oxidant buffer (SAOB II) was prepared by mixing together in a one liter volumetric flask the following reagents: 200ml of 10M sodium hydroxide, 35g ascorbic acid, 67g disodium EDTA and about 600ml deaerated water. The mixture was dissolved and diluted to one liter with deaerated water. Orion 0.1M lead perchlorate solution was serially diluted down to $1 \times 10^{-4}M$ for titration of sulfide solution of different concentrations. A saturated solution of sodium sulfide was prepared by dissolving approximately 100g reagent-grade $Na_2S \cdot 9H_2O$ in 100ml deaerated water. This stock sulfide solution was stored overnight in a tightly capped bottle. Weekly sulfide standard solutions were prepared by pipeting 10ml of the stock solution into a one liter volumetric flask and diluting it to one liter by adding 500ml of SAOB-II and deaerated water. The exact concentration of the weekly sulfide standard was determined by titration with standard lead perchlorate. This titration procedure was later eliminated by using ACS reagent grade sodium sulfide crystal, which has a minimum purity of 99.0%. A calculated amount of the $Na_2S \cdot 9H_2O$ was accurately weighed out and dissolved in 500 ml water and 500ml SAOB-II to make sulfide solutions of whatever molarity that was required. For field determinations calculated amounts (approximately 2.4112g) of the sodium sulfide crystals were accurately weighed and sealed in air tight plastic 100ml volumetric flasks. On arrival in the field, standard solutions were prepared by adding

50ml of the SAOB II to the flask and diluting to the 100ml mark with deaerated water. Serial dilutions of the weekly sulfide solutions were made to provide solutions for instrument calibrations/standardization and for titration. Before using the electrodes, a daily electrode stop check was done. Depending on which instrument was being used for the check, the procedure varies(11).

Direct Measurements Using the 407A Specific Ion Meter. First, serial dilutions of the weekly sulfide standard solution was made for meter calibrations. The dilute solutions made should contain SAOB-II in a 1:1 ratio. Any two of these dilute standard solutions bracketing the sample concentration could be used. Pipet 50ml of the more dilute standard into a 150ml beaker, connect the electrodes to the meter and immerse in the solution. Set the function switch on the 407A meter to X^{2-} and stir magnetically. Adjust the meter needle to "1" with the calibration control. Now pipet 50ml of the more concentrated standard into a 50ml beaker. Stir gently and immerse electrodes into the solution. Turn the temperature compensator knob until the meter needle reads "10". Rinse electrodes, blot dry, and place in sample buffered 1:1 with SAOB-II. To obtain total sulfide concentration of the sample, multiply meter reading by the concentration of the more dilute standard sulfide solution. Other samples could then be measured simply by repeating the procedure of rinsing electrodes, immersing in buffered sample and reading the concentration.

RESULTS AND DISCUSSION

Experimental results obtained for concentration of sulfides in various aqueous samples have revealed that the silver/sulfide electrode is both sensitive and selective and is well suited for such determinations. Hseu and Rechnitz, who carried out an analytical study of a sulfide ion-selective membrane electrode in alkaline solution, found same to true (12). All potentiometric electrodes sense activity (A) of an ion rather than concentration. Activity is defined as active concentration of free ion in solution which the electrode senses and it is related to concentration (C) by the activity coefficient (γ).

$$A = \gamma(C)$$

By calibrating an instrument with standard solutions or with standard in a sample, the difference becomes insignificant and the activity sensed by the electrode can be related to concentration. Total ionic strength of a sample affects the activity coefficient and the electrode response, and therefore the results (11). Mixing the samples with buffers bring the ionic strength of all samples to relatively the same level. In very low ionic strength samples, the measurement was unstable due to low conductivity, high sample resistance and large reference junction potential. The solid electrode sensitivity is usually a function of solubility of the sensing membrane and in the case, the sensing membrane was a solid silver/sulfide membrane which allows silver ions to pass between the sample solution and the internal reference solution which is

kept at a fixed silver concentration (12). A potential develops from the mixing of silver ions between the two solutions and this potential depends on the silver ion activity in the sample solution.

Measurement of Samples. Samples were collected from nearby lakes in Missouri City and Sugar Land, Fort Bend County, Texas (see Figure 1). These samples were buffered with SAOB-II. Buffering these samples with alkaline buffers raised the pH to approximately 13. Hydrogen ion (H^+) complexes S^{2-} to form HS^- and H_2S . The lower the pH, the larger the amount of S^{2-} complexed. In low pH solutions, sulfide is chiefly in the form of H_2S ; in the intermediate pH range (up to about pH12), about all the sulfides are in the form HS^- . Only in very basic solutions does the sulfide exist primarily as free ions (S^{2-}). Therefore, the use of SAOB-II in all samples and standards maintain a fixed level of S^{2-} . Measurements were carried out using procedures outlined in the instruction manual. The time response of the electrode, that is the time required to reach 99% of the stable reading varied from several seconds in solutions of high concentrations to several minutes in solutions whose concentrations were near the electrode detection limit. Off scale readings to the left of the specific ion meter was often experienced. Such readings indicated that the sample concentration was too low compared to concentration of standards used in calibrating the meter. To correct this, a weaker standard was used to recalibrate the meter without going beyond the electrode's lower limit. In some of the samples collected,

Figure 8

Index Map

This figure shows a portion of the Houston, 1:250,000, quadrangle map. The W.A. Parish electric generating plant is located near the center of the map, at Smithers Lake. Lakes sampled in this study and sample numbers used (e.g. ST-1) are shown.

no sulfide was determined. If any sulfides did exist in such samples, the concentration must be less than 1×10^{-7} moles/liter or 3×10^{-3} ppm which is the electrodes's lower limit.

Tables 1, 2, and 3 show concentrations of sulfides in some samples measured in the Fall of 1979, Winter of 1979 and Spring of 1980 respectively. Sulfide concentrations were found to be highest in the samples with pH between 8-9. The exact reason for this is unknown but it is suspected that it has something to do with reduced oxidation rate of the sulfides in the lakes. Chen and Morris, who attempted kinetic study of oxidation of aqueous sulfide by oxygen, found that variations of rate parameter with pH showed a very complex pattern (13). In acid solutions, pH 6, where hydrogen sulfide is the predominating sulfide species, the rate is very slow. The specific rate increases greatly as pH increases through 7 to a maximum at pH 8.0, then decreases to a minimum near pH 9. In our winter samples, all the pH measured were between 8.0 and 8.8. Based on Chen and Morris pH dependency findings, this may be part of the reason for the slow oxidation and high concentration of sulfide in the sampled lakes. They confirmed this unusual pH dependence of sulfide oxidation rate by the manometric measurement of oxygen uptake. No attempt was made at this time to investigate this concentration differences any further. Other factors which retard and enhance sulfide oxidation include initial dissolved sulfide:oxygen ratio. The larger this initial ratio is, the slower the oxidation rate (13). The presence or absence of the cations Ni^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+} , Fe^{2+} , Ca^{2+} , or Mg^{2+} affects the oxidation rate in the order written

TABLE I

Measurements of sulfide concentration and p^H of lake samples collected in the Fall of 1979 (October 22, 1979)¹

Samples	Conc. (ppm)	p^H
*MC-1-6	0.045	8.4
*MC-8-3	0.064	8.5
*MC-15-5	0.049	7.4
*MC-5-5	0.010	7.9
C-1-3	0.064	8.3
SL-2-5	0.042	8.4
MC-16-3	0.044	8.1
MC-17-2	0.051	8.3
MC-3-4	0.014	7.5
SL-3-4	0.042	9.0

Note: All samples were buffered 1:1 with SAOB-II before concentration measurements.

*Samples from the same lake.

¹Date samples were collected.

TABLE 2

Measurements of sulfide concentration and p^H of lake sample collected in the Winter of 1979 (December 2, 1979)¹

Samples	Conc. (ppm)	p^H
*MC - 1 - 7	0.077	8.8
*MC - 5 - 6	0.067	8.6
*MC - 8 - 4	0.082	8.3
*MC -15 - 6	0.056	8.5
MC -16 - 4a	0.077	8.7
MC -16 - 4b	0.073	8.5
MC -17 - 3	0.051	8.5
MC - 3 - 5	0.056	8.0
C - 1 - 4	0.061	8.4
SL - 2 - 6	0.072	8.5

Note: All samples were buffered 1:1 before concentration measurements.

*Samples from the same lake.

¹Date samples were collected.

TABLE 3

Measurements of sulfide concentration and p^H of lake samples collected in the Spring of 1980 (March 21, 1980).¹

Samples	Conc. (ppm)	p^H
*MC - 5 - 8	0.026	8.2
*MC - 1 - 9	0.029	8.3
*MC -15 - 8	0.017	8.3
MC -17 - 5	0.012	8.4
MC -16 - 5	0.008	8.3
MC - 3 - 6	0.032	7.8
SL - 1 - 6	0.010	8.2
SL - 4 - 6	0.003	9.2
C - 1 -12	0.011	8.1
C - 3 - 3	0.002	8.6
C - 2 - 2	0.000	7.9
LG - 1 - 4	0.026	8.5

Note: All samples were buffered 1:1 with SAOB-II before concentration measurements.

*Samples collected from the same lake.

¹Date samples were collected.

and in the pH range of 7 to 9. Organic compounds, impurities and the number of intermediates and their products formed also influence the oxidation of aqueous sulfides. Thus, any one of the factors or all of them may have influenced the sulfide oxidation in the lakes where the samples were collected and hence the concentrations of sulfides in the lakes at the time of measurement. Figure 2 shows graphs of seasonal variations in sulfide concentration and pH of some lakes sampled at three different seasons (Fall, Winter and Spring). Sulfide concentration in these lakes were highest in the Winter while pH values stayed approximately the same during all three seasons. At this time, there is no detailed explanation for the variations is being planned. One explanation is that the lakes were diluted by rain prior to some of the measurements.

It has been shown that even with the use of SAOB II to retard air oxidation of sulfide ions in solution the retardation is less than 100% and a slight decrease in sulfide is observed over time (9). However, results have shown that sulfide concentrations as low as 6 ppb can be measured with a reproducibility of better than $\pm 10\%$ (14).

Figure 1. Graphs of seasonal changes in pH and sulfide concentration of four lake samples.

Figure Graphs of seasonal changes in p^H and sulfide concentrations of some lake samples.

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