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An Amperometric Microsensor for the Determination of H_2S in Aquatic Environments

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A new amperometric microsensor for detection of dissolved H_2S in aquatic environments was developed. The design of the microsensor is based on the same principle as the Clark-type oxygen microsensor. The sensor is equipped with a glass-coated platinum working electrode and a platinum guard electrode positioned in an outer glass casing (tip diameter 20−100 μm). Both working electrode and guard electrode were polarized at a fixed value in the range from +85 to + 150 mV with respect to a counter electrode. The outer casing is sealed with a thin silicone membrane and filled with a buffered electrolyte solution containing ferricyanide ($K_3[Fe(CN)_6]$) as redox mediator. Hydrogen sulfide penetrates the silicone membrane and is oxidized by $K_3[Fe(CN)_6]$, resulting in the formation of elemental sulfur and ferrocyanide ($K_4[Fe(CN)_6]$). The latter is electrochemically reoxidized at the exposed end of the platinum working electrode, thereby creating a current that is directly proportional to the dissolved H_2S concentration at the sensor tip. The sensor was characterized and calibrated in a flow-through cell combined with a coulometric sulfide generator. Difficult studies including the determination of H_2S with high spatial and temporal resolution seem to be possible.

Sulfide is an important component of aquatic environments. In aqueous solutions, total sulfide quantity is found as dissolved hydrogen sulfide (H_2S) and as HS^- and S^{2-} ions, depending on protolytic equilibria. Besides its high toxicity for most higher organisms, hydrogen sulfide plays an important role in biogeochemical processes at oxic−anoxic interfaces, such as in the formation of heavy metal precipitates and oxidation by phototrophic or chemolithotrophic bacteria, respectively.[1]

Investigation of these processes requires analytical systems of very fine scale, low detection limit, fast response, and the possibility for in situ measurements.

Most methods for trace determination of dissolved sulfide are based on the use of photometric techniques like the methylene blue method[2] and fluorescence analysis.[3] However, these methods are not suitable for in situ monitoring, although a modified methylene blue method was suggested for in situ measurements in the bulk.[4,5]

Direct monitoring of sulfide is possible by the combined use of a pH electrode and a Ag/Ag_2S ion-selective electrode.[6−9] The use of Ag/Ag_2S microelectrodes with pH microelectrodes has, for a long time, been the only possibility for measuring sulfide at high spatial resolution at the oxic−anoxic interface in aquatic sediments and biofilms, where sharp gradients of chemical and physical parameters exist.[10−12] There are, however, difficulties in using Ag/Ag_2S electrodes due to problems such as mixed potentials, deviation from ideal Nernstian response below 10^{-5} mol/L total sulfide, signal drift, long response time in low concentration range, and some problems with the electrolyte bridge to the reference electrode.[7,13]

A solid-state microsensor for detection of sulfide, oxygen, iron, and manganese using a fast-scan voltammetric method was recently described by Brendel and Luther.[14] The method needs, however, frequent reconditioning of the metal microelectrode surface.

An amperometric detection principle for dissolved hydrogen sulfide was described by Jeroschewski et al.[15] and has recently been used for a galvanic H_2S macrosensor[16] and in a flow-through detector system.[17] We have adapted this measuring principle for the development of an amperometric microsensor for dissolved H_2S. In this paper, we describe the construction of the new hydrogen sulfide microsensor and show data on the sensor performance with respect to stability, response time, and other measuring parameters.

EXPERIMENTAL SECTION

Materials and Methods. The microsensors were made of Pasteur pipets, AR glass and special highly resistive glass (Type 8513) from Schott-Rohrglas GmbH (Bayreuth, Germany) and 50 μm Pt wire from Goodfellow (Cambridge, UK). Silicone mem-

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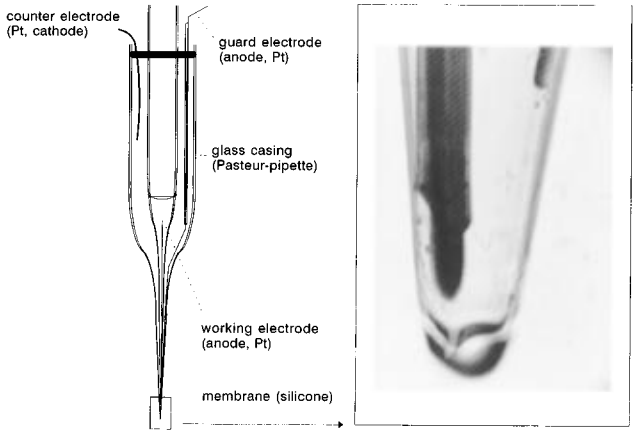


Figure 1. Amperometric microsensor.

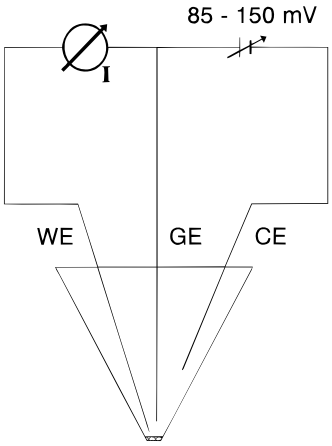


Figure 2. Circuit diagram of the amperometric microsensor.

branes were made of Medical Adhesive Silicone Type A from Dow Corning (Midland, MI). The various parts of the microsensor were fixed with a fast curing epoxy resin, "UHU sofortfest" from UHU (Bühl, Germany).

All materials which are in direct contact with the alkaline ferricyanide electrolyte solution have to be stable and nonoxidizing. A simple electrochemical test cell was used to check this requirement: two Pt electrodes immersed in the electrolyte solution were connected via a nanoammeter, and at the surface of one of the electrodes the material to be checked was placed for at least 2 weeks. A current increase during this period was indicative of an unsuitable material.

All techniques for preparation and handling of the various parts of the microsensor are analogous to previously described procedures for O_2 microsensor construction[10,18] and will only be briefly mentioned here. Essential equipment for the construction of microsensors are a dissection microscope, a compound microscope with large working distance objectives, one or more micromanipulators (Märtzhäuser, Wetzlar, Germany), and various heating loops connected to a variable power supply.

All chemicals and standards were obtained from Merck AG (Darmstadt, Germany) and VEB Laborchemie Apolda (Apolda, Germany) and were of purity grade "p.A." except for KCl which was of purity grade "suprapur". Nitrogen was obtained from Linde AG (Berlin, Germany) and possessed a purity of 99.9999%.

Microsensor Construction. The basic design of the H_2S microsensor was adapted from the Clark-type oxygen microelectrode described by Revsbech.[18] The microsensor consists of an outer glass casing, a working electrode (WE), a guard electrode (GE), and a counter electrode (Figure 1). The outer casing was made of a Pasteur pipet which was tapered to a thin capillary by use of a heating loop. The tip of the capillary was sealed with a thin silicone membrane. The WE was made of platinum wire, of which the tip was tapered by electroetching in a concentrated KCN solution, and was then covered with Schott 8513 glass. The special glass was used because of its good insulating characteristics and stability under the alkaline conditions used in the internal electrolyte. The platinum WE was subsequently exposed by carefully heating the tip with a small heating loop, thus removing the glass from the very end of the tip. The GE was made of a simple electroetched platinum wire, mounted in a thin glass capillary. The undermost 1−2 cm of the GE tip was exposed. The counter electrode was made of uncovered platinum wire (200 μm).

The microsensor was assembled by inserting first the WE and then the GE into the outer casing while observing the tip region under a microscope. When the WE position relative to the silicone membrane was suitable, the WE was fixed in position by a small drop of epoxy resin connecting the shaft of the WE and the outer casing. The same procedure was repeated with the GE. After the microsensor was assembled, the silicone and the epoxy were allowed to cure for at least 7 days before the outer casing was filled with electrolyte. The electrolyte consists of 0.05 M $K_3[Fe(CN)_6]$ in 0.5 M carbonate buffer (pH 10). Small glass beads (40−70 μm diameter) were added to the electrolyte and settled close to the sensor tip. The counter electrode was inserted into the electrolyte, and the microsensor was sealed with epoxy. The electrolyte should under no circumstances come into contact with the epoxy. After 1 day of curing the epoxy, the microsensor was ready for use. The geometric dimensions of the microsensor tip play an important role in the performance of the sensor and are described in the Results section.

Measuring Setup and Procedure. The H_2S microsensor was connected to a home-made picoammeter with an internal voltage source to polarize both WE and GE at a fixed value in the range from +85 to +150 mV vs the counter electrode, and the oxidation current was measured between WE and GE (Figure 2). Measuring signals from the picoammeter were recorded either on a strip chart recorder (Linseis, Germany) or with a multimeter (Conrad Electronic, Hirschau, Germany) connected to a computer (Commodore C286-LT).

The microsensor was tested in a flow-through system (Figure 3) consisting of a peristaltic pump (Ismatec, Wertheim-Mondfeld, Germany), a coulometric sulfide generator (AMT, Rostock, Germany), a PTFE switching valve (Rheodyne, Cotati, CA), and a glassy flow cell.

An important part of the flow system was the coulometric sulfide generator equipped with a mixing cell for preparation of sulfide standard solutions in the micromolar range. Hydrogen sulfide is generated by cathodic reduction at an electrode made of HgS, S, and C in an oxygen-free acid solution (0.005 M H_2SO_4) with 100% current yield. This was proven by the methylene blue method. The capacity of the generator electrode was found to be sufficiently high (350 mA·h for generation of H_2S) to guarantee 100% current yield over a long period of time allowing to generate standard solutions in the concentration range 0.09−2250 μM H_2S

(18) Revsbech, N. P. *Limnol. Oceanogr.* **1989**, *34*, 474−8.

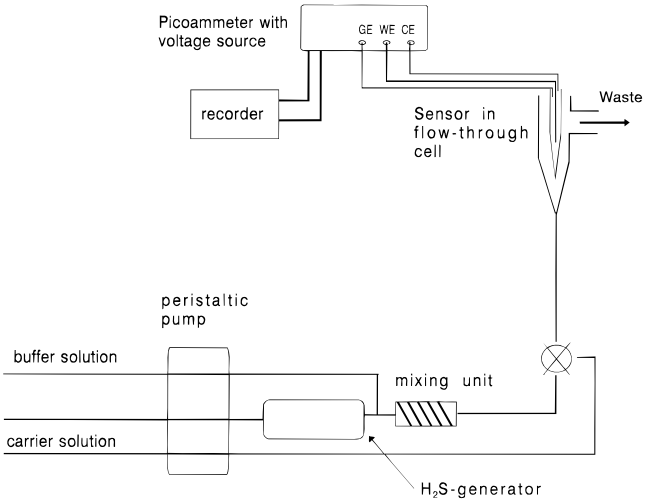


Figure 3. Flow scheme for testing and calibration of the amperometric microsensor.

(more details in ref 19). The sulfide concentration of the standard solution is precisely adjustable by simply varying the generator current and/or the flow rate of the pump. The pH of the acid standard solutions could be adjusted by pumping oxygen-free buffer solution into the mixing cell of the generator. This coulometric sulfide generator was used to prepare the sulfide test solutions.

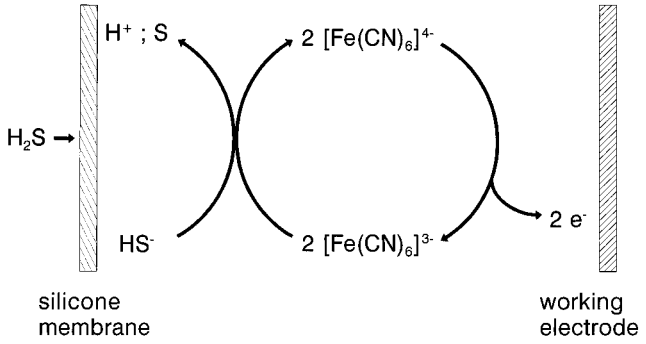
Because of rapid oxidation of sulfide at low concentrations, it was necessary to carefully prepare oxygen-free carrier solution and buffer. This was accomplished by flushing nitrogen gas through the solutions for at least 30 min. The solutions were then positioned in an ultrasonic bath, and a vacuum was applied for at least 15 min. Finally, the vacuum was terminated by readmission of nitrogen. To prevent oxygen diffusion into the solutions, a slight nitrogen overpressure was applied.

During measurements the microsensor was positioned into the flow-through cell using a micromanipulator, and the zero current was observed. After at least 30 min, the zero current signal decreased to 2−10 pA and was stable. A 30 μM H_2S test concentration was then applied, usually at 1 mL/min, and the sensor performance was observed. Showing a sensitivity higher than 1 pA/μM (down to 0.5 pA/μM for smaller membrane diameters) and a stable signal for at least 1 h, the microsensor was calibrated in the concentration range 1−300 μM using a flow rate of 1−2 mL/min. The microsensor was allowed to rest for 15 h, after which several (3−5) calibration curves were again recorded. The signal response time of the H_2S microsensor was determined by positioning the sensor—using the micromanipulator—slightly above the surface of the liquid and then quickly drawing it downward. The dependence of the measuring signal on the flow rate of the carrier was tested at 0.5, 1, and 2 mL/min, and finally by switching off the pump.

To analyze the dependence of the microsensor signal on temperature, the sensor was placed in a small flow-through cell and fully immersed in a thermostated water bath. The temperature was measured in the water bath near the sensor tip. After the sensor was cooled for about 30 min (stable and low zero signal), H_2S was applied and the signal observed.

To determine the influence of higher salt concentrations on the signal, the sensor had to be placed in a batch cell, because

Scheme 1



the KCl solution and the carrier solution do not mix sufficiently when combined in the flow-through system. The batch cell was rinsed for at least 10 min with Ar and then filled with 0.005 M H_2SO_4, 0.5 M KCl, 1 M KCl, and 2 M KCl (adjusted to pH 2.2). Using a Dosimat 665 (Metrohm AG, Filderstadt, Germany) with a 1 mL buret, aliquots of a Na_2S stock solution (about 0.5 M) which had been titrimetrically analyzed prior to use were added, and the signal was observed.

RESULTS

Using the amperometric measuring principle for the detection of H_2S[15] and construction principles for amperometric oxygen microsensors,[10,18] a microsensor was developed for fine scale determination of H_2S traces in aquatic environments. Dissolved hydrogen sulfide passes through the silicone membrane into the alkaline sensor solution, and the formed HS^- ions are immediatly oxidized by ferricyanide, leading to sulfur and ferrocyanide. The measuring signal is generated by reoxidation of ferrocyanide at the working electrode. This is shown in Scheme 1.

In this way there is no disturbance of the electrochemical oxidation of ferrocyanide by elemental sulfur. This has been proven by separate cyclic voltammetry experiments with a Pt microelectrode in ferricyanide solution. We measured identical I/U curves before and after sulfide exposure (at +0.4 V vs SCE) on the electrode. The current at the working electrode of the microsensor depends directly on the hydrogen sulfide concentration and can be used for quantitative determinations. More details, especially the function of the guard electrode, are given elsewhere.[16] The described measuring principle for hydrogen sulfide can be realized either as a galvanic sensor without an external polarization voltage[16] or as an amperometric sensor.[20] In the latter case, an external polarization voltage is necessary, but the measuring cell is undivided, with only one sensor electrolyte solution. This fact simplifies the sensor construction considerably, particularly in the case of an amperometric microsensor (Figures 1 and 2).

There is a high dependence of the performance of the H_2S microsensor on the geometry and dimensions of the sensor tip and, above all, on the distances between working electrode/membrane ($R_{WE/mem}$) and working electrode/guard electrode ($R_{WE/GE}$), on the diameter of the membrane ($\varnothing_{mem}$), and on the outer casing of the sensor tip (Figure 4). Best results were obtained with small diameters of the WE (<5 μm), with $R_{WE/mem}$ 10−30 μm, $R_{WE/GE}$ = 100−200 μm, and relative wide outer casings (inner diameter about 30−50 μm). Microsensors with narrow tip

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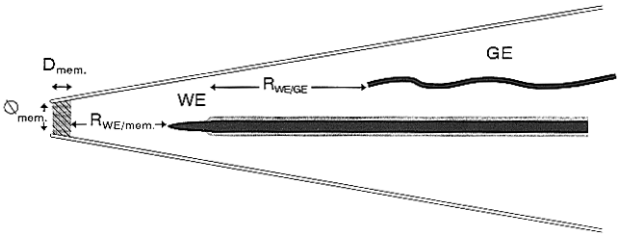

Figure 4. Schematic description of the sensor tip.

Table 1. Features of H_2S Microsensor

zero current	2−40 ± 0.5 pA, depending on sensor age
zero current drift	<5% for 3 days
sensitivity	1.2−0.6 pA/μM H_2S (Figure 5) depending on sensor age, tested for 2−300 μM H_2S
sensitivity drift	−40% after first contact with H_2S, <5%/day (Figure 6)
limit of detection	≈2 μM
rel. S. D.	≈2.5%
signal drift	≈5% for 2 h, for permanent contact with 30, 60, or 90 μM H_2S
response time	<100 ms

diameters (<30 μm) had a short lifetime and exhibited drifting signal currents. With $R_{WE/mem}$ > 40 μm or with $R_{WE/GE}$ > 200 μm, microsensors generally exhibited a low signal-to-noise ratio and oscillations of both baseline and signal current. Sensor sensitivity and flow dependence of the current signal are strongly determined by the diameter and thickness of the silicone membrane. For $\varnothing_{mem}$ < 5 μm, the sensor sensitivity is about 1 pA/μM without measurable flow dependence of the sensor signal according to the properties of microelectrodes.[21] Larger membrane diameters (5−15 μm) result in a doubling of the sensitivity but in a significant influence of stirring on the sensor current (about 8% decrease when the solution flow was stopped).

The microsensor has a maximum lifetime of about 6 weeks, depending on the sensor construction and H_2S exposure. Expiration of the microsensor is indicated by instability of measured signals and/or by an increase in noise of both zero current and analyte signal. These effects can be observed more readily with small sensor tips. Increasing the polarization voltage up to +150 mV results in disappearance of the noise so that the microsensor can further be used.

As was expected, the response time of the microsensor is rather short (<100 ms) due to the very small dimensions, in the micrometer range.

Considering the above-mentioned geometric prerequisites, we succeeded in constructing a H_2S microsensor with the parameters given in Table 1.

Analysis of the dependence of the sensor signal on pH gave a correlation as theoretically predicted by the protolytic equilibria of H_2S (Figure 7):

$$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+ \quad (1)$$

$$K_1 = [HS^-][H_3O^+]/[H_2S] \quad (2)$$

and

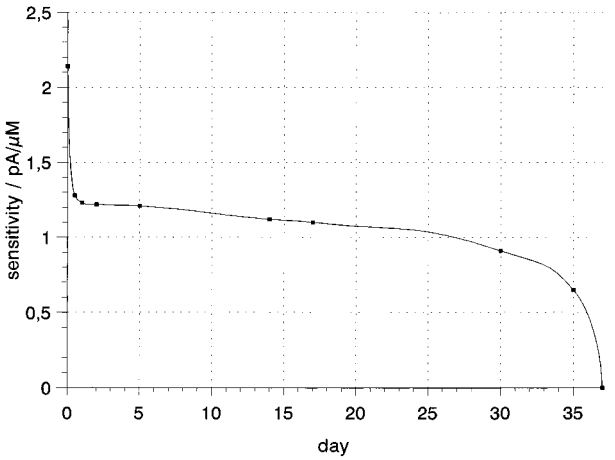

Figure 5. Temporal changing of performance (pH 2.2, 1 mL/min).

$$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+ \quad (3)$$

$$K_2 = [S^{2-}][H_3O^+]/[HS^-] \quad (4)$$

with

$$[S^{2-}_{tot}] = [H_2S] + [HS^-] + [S^{2-}] \quad (5)$$

leads to

$$[H_2S] = [S^{2-}_{tot}]/\left(1 + \frac{K_1}{[H_3O^+]} + \frac{K_1K_2}{[H_3O^+]^2}\right) \quad (6)$$

For pH > 5, the pH value has to be taken into account to determine $[S^{2-}_{tot}]$. At pH > 9, the H_2S concentration decreases to such low values (<1%) that the amperometric microsensor can only be used in the case of very high S^{2-}_{tot} concentrations. In the relevant pH range (pH < 9), the second protolytic equilibrium can be neglected, and eq 6 is simplified to

$$[H_2S] = [S^{2-}_{tot}]/\left(1 + \frac{K_1}{[H_3O^+]}\right) \quad pK_1 = 6.919 \quad \text{(ref 22)} \quad (7)$$

Varying the temperature (tested in the range 9−23 °C) leads to a nonlinear behavior of the analyte signal, while the zero current is only slightly changed (Figure 8). When 23 °C is used as the reference (100%), the signal decrease is 15% at 9 °C.

Salt concentrations of 1 M KCl increase the sensor signal by about 5%. Applying higher salt concentrations (for example, 2 M KCl) results in a further rise in the sensor signal (about 20%, Figure 9). Simultaneously, a larger spread in single measuring values was observed at the same H_2S concentration.

There is no influence of oxygen on the mode of sensor operation because sulfide is immedeately oxidized by ferricyanide. Due to the dense silicone membrane, the microsensor is only sensitive to H_2S but not HS^- or S^{2-}. Only a few uncharged molecules can pass the membrane and may give interferences. The most important interfering substances are SO_2 (300-fold smaller signal at pH 2, no response for pH > 6.5) and ethanethiol (about 20-fold smaller signal at pH 2). Ammonia (≤2 M),

(21) Heinze, J. *Angew. Chem.* **1993**, *105*, 1327−49.

(22) Broderius, S. J.; Smith, L. L. *Anal. Chem* **1977**, *49*, 424.

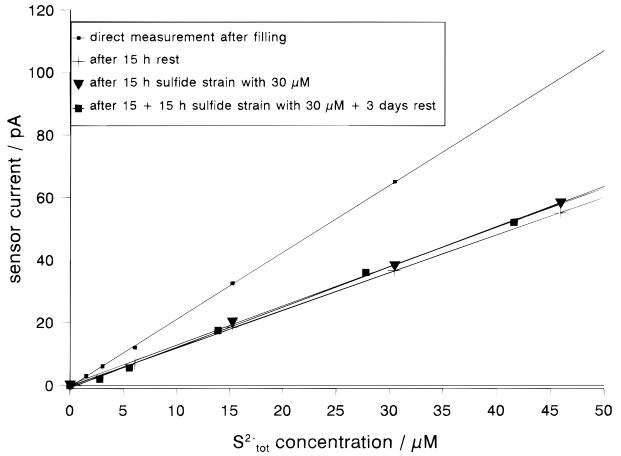

Figure 6. Long time test of a microsensor (conditions as in Figure 5).

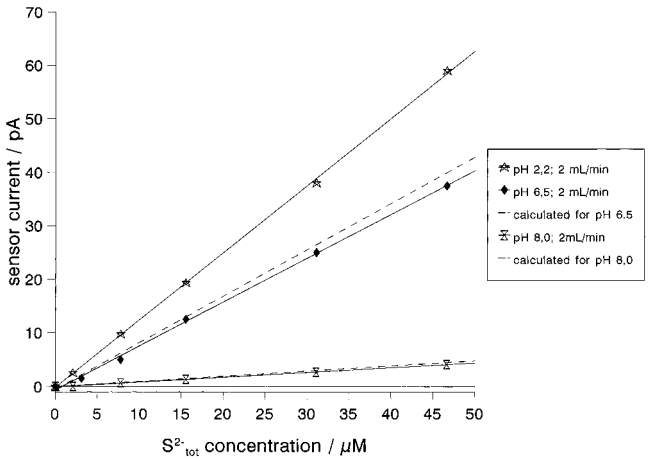

Figure 7. Comparison of measured and calculated H_2S concentrations according to protolytic equilibria for different pH.

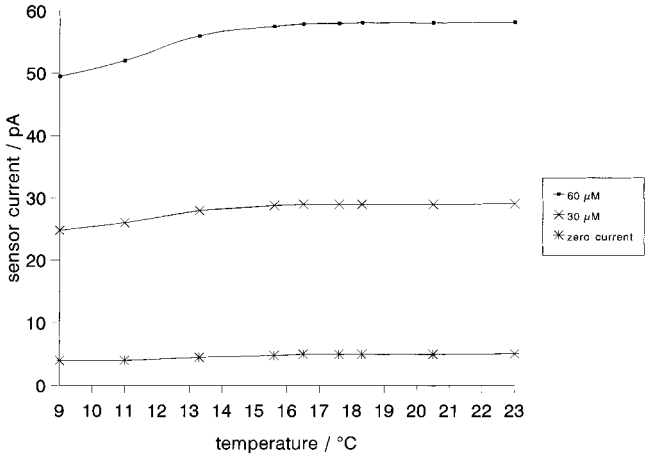

Figure 8. Influence of temperature on the sensor current.

methylamine (≤6 M), and acetic acid (≤1 M) do not affect either the zero signal or the measuring signal.

DISCUSSION

Hydrogen sulfide as an important environmental parameter can now be observed in the same way as dissolved oxygen. There is a close analogy between the amperometric microsensors for hydrogen sulfide and oxygen with respect to the construction, but the performance of the H_2S microsensor is substantially more influenced by the geometric parameters of the sensor tip. This

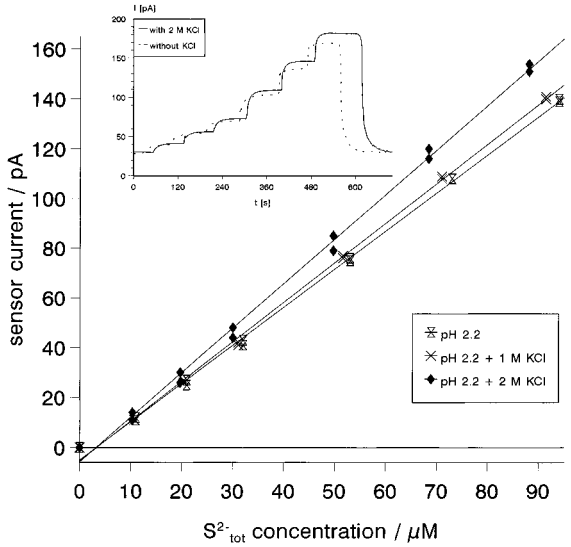

Figure 9. Influence of neutral salt concentrations on the sensor current and typical current/signal curves at the chosen S^{2-}_{tot} concentrations. The inset corresponds to the seven S^{2-}_{tot} concentrations chosen; the temporal differences between the two curves are unimportant artifacts.

is probably caused by the presence of the redox mediator ferricyanide/ferrocyanide.

At the electrodes of amperometric sensors, electrochemical transformation of substances always occurs, which results in changes in their chemical composition. The degree of this change at the electrodes depends on the current density and on the electrolyte volume. Such changes occur particularly in the case of microsensors due to their very small geometric dimensions and can be the reason for signal drift and limitation of lifetime. Such effects have, e.g., been observed with oxygen microsensors with a very narrow tip geometry.[23] This can also be expected for amperometric H_2S microsensors.

Reaction of H_2S with the inner electrolyte of the sensor gives rise not only to changes in the pH but also to precipitation of sulfur, and finally in the brutto reaction for the sensor (eq 11) to a reduction of ferricyanide and to a decrease in pH:

anode

$$H_2S + 2K_3[Fe(CN)_6] \rightleftharpoons 2K_4[Fe(CN)_6] + S + 2H^+$$

chemical step (8)

$$2K_4[Fe(CN)_6] \rightleftharpoons 2K_3[Fe(CN)_6] + 2e^-$$

electrochemical step (9)

cathode

$$2K_3[Fe(CN)_6] + 2e^- \rightleftharpoons 2K_4[Fe(CN)_6]$$

electrochemical step (10)

brutto reaction

$$H_2S + 2K_3[Fe(CN)_6] \rightleftharpoons 2K_4[Fe(CN)_6] + S + 2H^+ \quad (11)$$

Using an excess of $K_3[Fe(CN)_6]$ and buffer, these changes will not be observed directly but actually may cause in the case of microsensors remarkable local changes (for example, changing of pH and decrease in the ratio $[K_3[Fe(CN)_6]]/[K_4[Fe(CN)_6]]$).

(23) Kühl, M. Unpublished results.

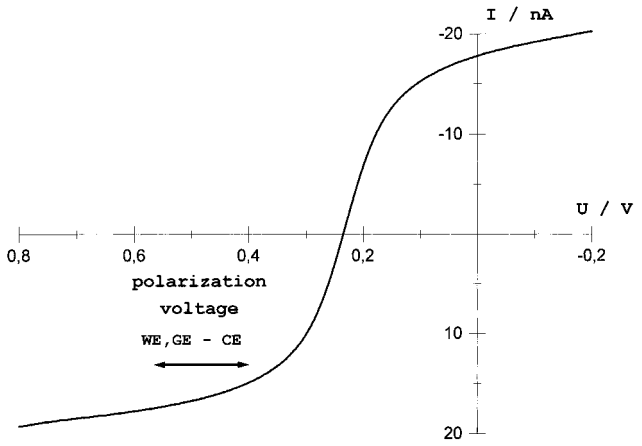

Figure 10. Polarization voltage with respect to the I/U curve (vs SCE) for the redox mediator $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (0.05 M/0.05 M) in 0.5 M carbonate buffer, Pt microelectrode (5 μm).

According to the Nernstian equation, a decrease in the ratio $[K_3[Fe(CN)_6]]/[K_4[Fe(CN)_6]]$ shifts the redox potential of the mediator to more negative values. Although a redox potential lower than 0 V (vs SCE) is sufficient for oxidation of sulfide, it should not be <0.4 V. It is obvious from the current/potential curve (Figure 10) that, in the steep part, already a very small change of the potential results in a considerable current. If the potential of the WE is not far enough from this region, the sensor shows a remarkable noise of both zero current and signal current as previously observed for the galvanic H_2S sensor.[16] In the case of the amperometric H_2S sensor, the potential of the WE can be shifted to more positive potential values in the anodic current/potential region (Figure 10) simply by increasing the polarization voltage. So, the noise can be avoided completely. However, after a prolonged use, when the ferricyanide concentration in the sensor has been decreased below some limiting value, according to the brutto reaction (eq 11), a further increase of the polarization voltage is not helpful. This fact is mainly limiting the sensor lifetime, whereas a possible decomposition of the ferricyanide solution does not have to be taken into consideration. In diluted alkaline solution, ferricyanide is sufficiently stable.[24]

The zero current is mainly influenced by oxidation of dirt particles in the very sensor tip by generating ferrocyanide. Such particles can be kept away from the sensor tip by adding small glass beads to the electrolyte solution.

The use of platinum as working electrode is due to its mechanical strength in construction of the microsensor. Gold wire is unsuitable for this purpose. Despite the problems with Pt electrodes in connection with sulfide,[25] in our case it is possible to employ platinum because there could not be found any poisoning effects on the redox reaction of the mediator.

Changes of the pH of the sensor solution as well as the build-up of elemental sulfur, which perhaps influences transport conditions of H_3O^+ and ferricyanide/ferrocyanide, may affect the sensor performance. A detailed discussion of these phenomena is outside the scope of this paper and would require a more systematic investigation.

Geometric parameters, especially of the sensor tip, are very important for the sensor characteristics. Above all, the membrane diameter (entry of the sensor) has to be less than 5 μm. Thereby, a hemispherical diffusion layer is formed, resulting in a fast response and a complete independence of the electrode signal on flow rate of the surrounding solution.[21] Only a very small amount of H_2S is consumed by the microsensor, so that no disturbance of equilibria is given. This was proven experimentally for the protolytic equilibrium in eq 1 (Figure 7). The property of the microsensor not to disturb equilibria is of considerable importance for direct investigation of sensitive environmental processes and may offer a contribution to solving such fundamental problems concerning hydrogen sulfide/metal sulfide equilibria as discussed in ref 26. In addition, the tiny amount of reacting H_2S has a favorable effect on the lifetime of the sensor. On the other hand, the small measured signal in the range of picoamperes requires a sensitive measuring system.

The distances $R_{WE/mem}$ and $R_{WE/GE}$ are other important parameters of the sensor tip. The position of the reaction layer (eq 8), which depends on the amount of H_2S that has passed the silicone membrane, is located within the distance $R_{WE/mem}$. Thereby, the diffusion path of the ferrocyanide to the WE is determined by the distance reaction layer−WE. Acceptable results can be obtained only if a certain distance $R_{WE/mem}$ is kept (optimally 20−30 μm). $R_{WE/GE}$ is responsible for a low zero current and has to be kept as low as possible.

The rate of the H_2S transport through the silicone membrane, which is of importance to the signal current, is rather high and, in the case of the contact with two gas phases, already known for the membrane used in our study.[27] Unfortunately, these results cannot simply be applied to our specific situation, because the properties of the membrane are strongly influenced by the activity of the water in the aqueous solutions. Therefore, determination of the rate of H_2S transport concerning the membrane of our probe is outside the scope of this paper.

The influence of the temperature on the zero current in the range applied is remarkably low (Figure 8). This is probably due to the fact that, at all electrodes (WE, GE, and CE), the same redox process takes place, so that the temperature effect may be compensated. It may be assumed that the signal current is mainly affected by the temperature dependence of the permeability of the silicone membrane to H_2S.

In comparison to the Clark sensor, the influence of the salt concentration —as expected—follows the same trend, i.e., raising sensor signal with increasing ionic strength[28] due to the increase in partial pressure of the analyte. Investigations of the solubility of H_2S in pure water and NaCl brine solutions at different ionic strengths show significant influence on the activity coefficient of molecular H_2S.[29]

CONCLUSIONS

The new amperometric microsensor may have important applications in the field of trace analysis in aquatic environments, especially for studies of the oxic−anoxic interfaces in sediments, biofilms, and stratified water columns. The direct determination of dissolved H_2S enables measurements with high spatial and temporal resolution in both abiotic and biotic systems. The

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amperometric sensor is particularly useful under acidic conditions and may also be utilized under moderate alkaline conditions (pH < 8.5) limited by the protolytic equilibrium (eqs 1 and 2). At higher pH, the quantity of H_2S decreases so much that it becomes more advantageous to use the traditional sulfide ISE method.

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