Review

The Application of Electrochemical Tools for In Situ Measurements in Aquatic Systems

Martial Taillefert,[+] *George W. Luther III,*[*+] and *Donald B. Nuzzio*[++]

[+] College of Marine Studies, 700 Pilottown Road, University of Delaware, Lewes, DE 19958 USA; e-mail: luther@udel.edu
[++]Analytical Instrument Systems, Inc., P.O. Box 458, Flemington, NJ 08822–0458, USA

Received: September 30, 1999
Final version: November 22, 1999

Abstract
Since the 1970's, when the first in situ measurements of oxygen in the oceans were reported, the development of electrochemical sensors for in situ measurements in aquatic systems has significantly intensified. A synthesis of the progress made in limnology and oceanography to measure chemical species in situ is presented. From amperometric and potentiometric sensors that can measure a single analyte to voltammetric sensors that can measure several species during the same scan, a variety of electrodes have been used in situ to better understand the nature of the biogeochemical processes occurring in aquatic systems. The advantages and disadvantages of each technique, the technical improvements over the years, and some recommendations are presented together with representative data reported in the literature over the last two decades.

Keywords: In situ measurements, Aquatic systems, Electrochemical methods, Amperometric in situ measurements, Voltammetric in situ measurements

1. Introduction

Environmentally and geologically important chemical species need to be quantified in the dissolved phase of aquatic systems (groundwater, rivers, lakes, oceans, sediment porewaters) to provide relevant information on the processes that occur in these environments. In this prospect, electrochemical methods have been used extensively to determine salinities using conductimetry [1] and analyte concentrations using amperometric, potentiometric, or voltammetric techniques [e.g., 2–30].

Electrochemical techniques have been used over the last twenty years to analyze natural waters after sampling [e.g., 2–9] or using on-line measurements [10–20]. In the procedure for on-line measurements, a water column sample is pumped onboard ship into a flow cell, where the analysis is performed immediately. As the sample is not handled or exposed to the atmosphere, these analyses can be considered very close to in situ measurements. In addition, electrochemical techniques are more widely used to analyze porewaters directly (i.e., without extraction) after retrieving a sediment or a microbial mat core [e.g., 21–30]. As these analyses are performed in the laboratory, they cannot be considered in situ measurements.

Sampling and analysis of natural waters are not trivial because very often samples are difficult to access (e.g., sediment porewaters, groundwater), and contaminations (chemical changes) or perturbations (physical changes) may occur during sampling. Problems often encountered are oxygen contaminations when samples are exposed to the atmosphere, metal contaminations when processing samples onboard ship, pressure changes that affect the gaseous species when deep-sea samples are collected, and temperature changes that may modify the chemical speciation, especially when collecting samples from hydrothermal systems. These may result in systematic errors, which may be undetected, and ultimately in misinterpretation of the processes observed. In situ measurements are a good alternative to avoid artifacts due to sampling and handling of aquatic samples [31].

In the last decade, optical sensors and biosensors have been developed to measure environmentally important chemical species [32]. However, in situ measurements reported in the literature using these devices are still scarce [33], and most in situ determinations have been performed by electrochemical sensors. In addition, these sensors are generally limited to one species. The use of in situ electrochemical instruments in aquatic systems has several advantages: i) there is no need to collect samples, ii) a small amount of analyte is used, allowing multiple measurements, iii) microelectrodes can be used to obtain a high spatial resolution, iv) relatively high data acquisition in a short period of time is possible, and v) electrodes can be deployed in the water column, sediments, and microbial mats. However, like any analytical techniques, some limitations exist: i) the number of species detected depends on the electrode characteristics and may be limited ii) ion interferences may occur, iii) the detection limit can be high, and iv) the response may be operationally defined.

The goal of this review is to report the progress made in limnology and oceanography with the application of electrochemical techniques to measure in situ the distribution of analytes in aquatic systems. In situ implies that the electrochemical sensor has been inserted in the aquatic system with little perturbation and that the sample has not been removed from the aquatic system. On-line electrochemical measurements, though not truly in situ measurements, will be considered in this review when samples are not handled and exposed to the atmosphere. This review is structured in three different sections based on the chronological use of electrochemical techniques. The first section reports the different amperometric sensors used in situ for O_2 and on-line for H_2S measurements. The second section reports the different potentiometric sensors used in situ for pH, CO_2, H_2S, and trace metal measurements. Finally, the third section reports the recently deployed in situ voltammetric sensors for trace metals, H_2S, and O_2 measurements and the on-line voltammetric measurements of H_2S and trace metals. In each section, the sensors specifications, advantages, and disadvantages are

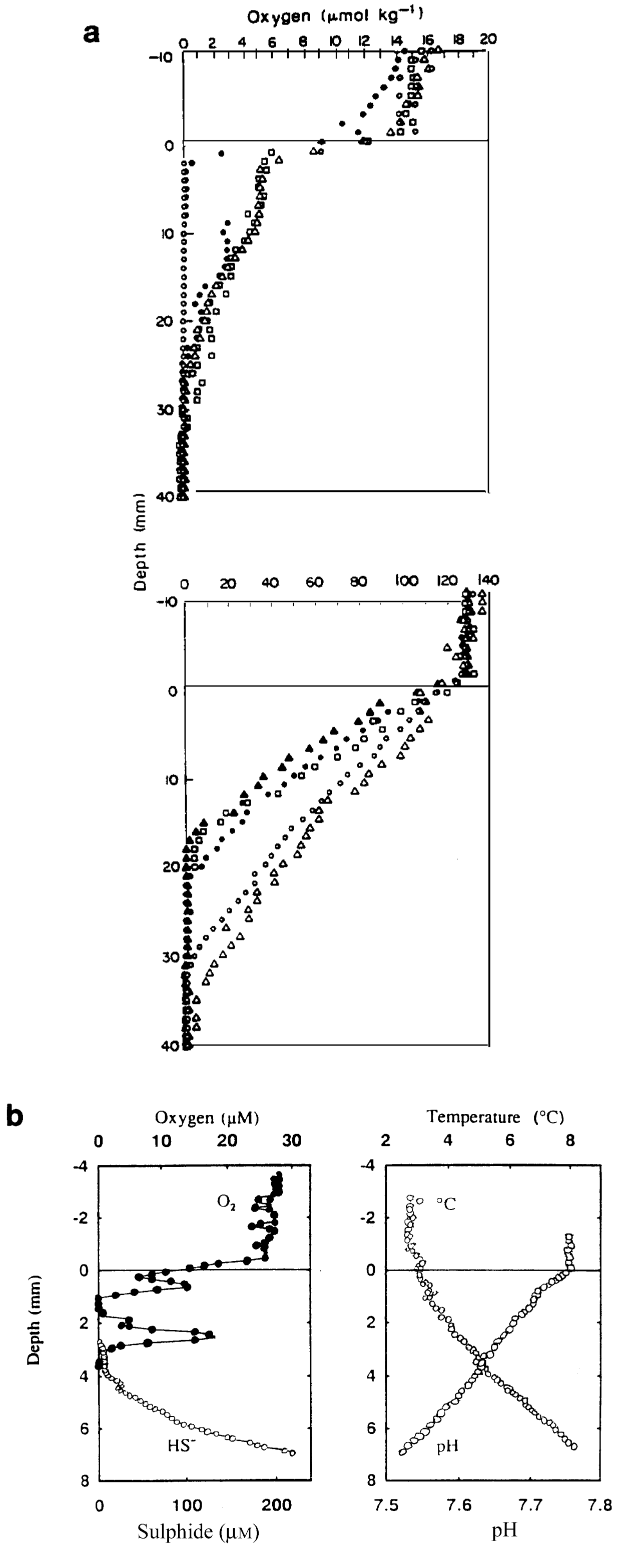

Fig. 1. a) In situ microprofiles of oxygen in deep sea sediments deployed on a benthic lander in the Santa Catalina Basin (top) and the Patton Escarpment (bottom). Each symbol designates a separate microelectrode record. Reprinted by permission from *Nature* [38], Copyright (1986) by Macmillan Magazines Ltd. b) In situ microprofiles of oxygen measured with a Clark electrode, sulfide measured with a Ag/Ag_2S potentiometric electrode, temperature measured with a thermistor probe, and pH measured with a glass membrane electrode. The microelectrodes were deployed on a lander from a submersible. Reprinted by permission from *Nature* [42], Copyright (1992) by Macmillan Magazines Ltd.

described, and recommendations for using these sensors in aquatic systems are discussed.

2. Amperometric In Situ Sensors

2.1. Oxygen

The most common amperometric sensor used in situ is the oxygen electrode, or Clark electrode [34–35], which has been routinely deployed to measure concentrations of oxygen in the water column [35–37], in sediment porewaters [38–46], and in microbial mats [24]. For sediment porewaters studies, these amperometric sensors have been used to measure fluxes of oxygen above the sediment-water interface using benthic chambers [43, 46 and references herein] and to measure profiles in the sediment using microprofilers [38–42, 44, 45]. Figure 1 provides two of the first in situ profiles of oxygen reported in deep sea sediments.

The Clark electrode consists of a platinum disk cathodic working electrode embedded in a cylindrical insulator, usually glass. A ring-shaped silver anode is located around the lower end of the insulator. The electrodes and the insulator are placed inside a glass rod that contains an electrolyte (KCl 3M). An oxygen-permeable membrane of Teflon or polyethylene is fixed at the bottom of the outer glass rod usually with an O-ring. Oxygen diffuses through the membrane into the thin layer of electrolyte and is immediately reduced to water at the surface of the cathode at a fixed potential of -0.8V relative to a silver/silver chloride electrode [34]. The current resulting from the reduction reaction is then recorded with a picoammeter. For sediment porewaters, microelectrodes have been built in the same way, but usually with gold plated at the surface of the platinum wire [21] to increase the stability of the response. In addition, a silver wire guard cathode, partly recessed from the working electrode, can be added in the electrolyte solution to remove oxygen present in the electrolyte that could raise the background noise [47]. The membrane for these microsensors can be either cellulose nitrate [24], silicon rubber [47], collodion, polystyrene, zapon lacquer, or acrylic polymers [48]. These microelectrodes do not require stirring in the outside solution, because the current measured at the working cathode depends only on the diffusional supply of oxygen to the surface membrane, which is extremely efficient over small distances [47]. This is an advantage for work at the sediment-water interface, because it is necessary to use stirring-insensitive electrodes to measure oxygen at these locations, where changes from turbulent to laminar flow could affect the response of the sensor. This is realized by minimizing the distance between the electrode membrane and the working cathode, which further decreases the response time of these microelectrodes to less than a few seconds [47].

Because the current measured with the microelectrode is a function of temperature and salinity [49], calibrations should be carefully performed in a solution similar to that analyzed of known partial pressure of oxygen. Recently, it has been shown that when the dimensions of the electrode (i.e., diameter of the electrode tip, distance from the outer solution to the working cathode, and membrane permeability) are known, calibrations could be predicted as a function of salinity and temperature [50].

2.2. Nitrous Oxide

Another amperometric sensor has been built to detect nitrous oxide [51] in biofilms but has not been used in situ. The

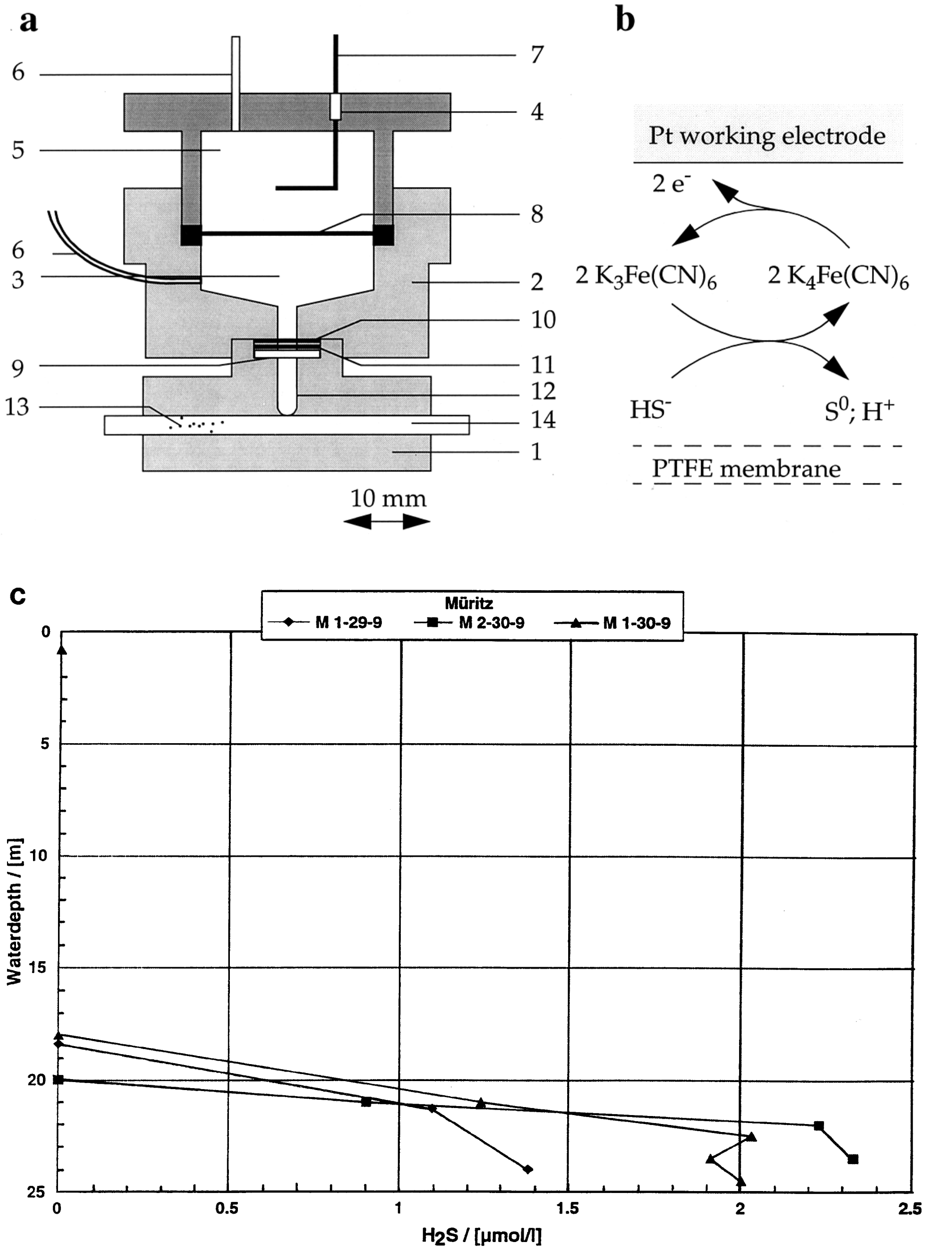

Fig. 2. a) Design of the H_2S amperometric flow-through microsensor. 1) sample side part; 2) anodic part containing electrolyte (3); 4) cathodic part containing electrolyte (5); 6) vent for pressure compensation; 7) Pt counter electrode; 8) Nafion membrane; 9) PTFE membrane; 10) Pt reference electrode; 11) Pt working electrode; 12) gas gap with conical gap end; 13) nitrogen bubble;14) sample (adapted from [54]). b) Mechanism of sulfide oxidation at the amperometric electrode. c) H_2S concentration profiles measured in situ with amperometric microelectrodes in the water column of Lake Fuchskuhle, Germany. Reprinted by permission from *Applied Geochemistry* [19], Copyright (1998) by Elsevier Science.

microelectrode designed for N_2O measurements contained an oxygen microelectrode and a guard cathode to remove any oxygen contamination as described previously. The N_2O sensor was made of a platinum wire plated with silver. The N_2O and O_2 sensors were encased with the recessed guard cathode in a glass electrode containing an electrolyte (a Ag_2SO_4/KCl/NaOH/Tris mixture). The tip of the electrode had a diameter of 20 µm and was filled with a silicon rubber membrane. The sensor was polarized at −1.175 V (vs. Ag/AgCl) to monitor N_2O diffusing through the membrane. It was found that an excess of sulfides could rapidly oxidize the silver layer and degrade the electrode. In addition, the presence of elevated concentrations of CO_2 could lead to the formation of H_2 and O_2 which interferes with the measurements [51]. Recently, this microsensor has been adapted in a biosensor to detect nitrate [52]. Denitrifying bacteria that do not contain N_2O reductase have been isolated and grown from soil and sediments and placed in a micro reaction chamber in the tip of the electrode. Because the bacteria were consuming oxygen before nitrate, an oxygen guard cathode was not used in this microsensor. This biosensor does not suffer from chloride interference and can be used in marine environments. The lowest detection limit of this biosensor is 1 µM, but its sensitivity depends on temperature. Unfortunately, the microbial activity stops below 5 °C [52], probably precluding its in situ application in cold environments such as deep sea sediments.

2.3. Hydrogen Sulfide

An amperometric microsensor for the determination of H_2S in aquatic systems has been developed (Fig. 2a, [19, 53–55]) and used for water column on-line measurements (Fig. 2b, [19]). This sensor is designed on the same principle as the Clark oxygen microsensor designed by Revsbech [47]. A silicon membrane allows diffusion of H_2S to an internal electrolyte solution made of $K_3Fe(CN)_6$ in a 0.5 M carbonate buffer (Fig. 2a). The alkaline buffer in the electrode modifies the sulfide equilibrium to generate bisulfide, which is immediately oxidized to elemental sulfur in the presence of ferricyanide, leading to ferrocyanide as a by product. The current of reoxidation of ferrocyanide is measured at a platinum counter electrode when a separate platinum working electrode potential is fixed between +85 and +150 mV. The advantage of this electrode is that oxygen does not interfere with H_2S, such as with potentiometric Ag/Ag_2S sensors, because it does not react with ferricyanide. However, the electrode is sensitive to temperature and salinity changes, and its sensitivity to H_2S and total sulfide is low at high pH.

3. Potentiometric In Situ Sensors

Potentiometric sensors commonly used for in situ measurements include pH, pCO_2, and pS^{2-} electrodes. pH electrodes are widely used in both water column and sediment porewater studies [19, 40, 42, 44–46, 56, 58, 60, 61] (see also Fig. 1b), while pCO_2 electrodes have been usually deployed in sediment porewaters [44, 45]. pH_2S electrodes have been deployed in situ in sediment porewaters [42], in microbial mats [24, 57], and in water columns [59–61]. In addition, potentiometric stripping has been used to measure copper concentrations in seawater [62].

3.1. pH

pH is usually determined by measuring the difference of potential between a glass indicator electrode and a reference electrode, usually a silver/silver chloride or a saturated calomel electrode. The indicator electrode consists of a thin pH-sensitive glass membrane (usually a Corning 0150 glass made of 72 % SiO_2, 22 % Na_2O, and 6 % CaO) sealed onto one end of a heavy-walled glass or plastic capillary. A small volume of dilute hydrochloric acid saturated with silver chloride is contained in the capillary with a silver wire to make a silver/silver chloride reference electrode. The indicator and the reference electrodes are connected to a voltmeter. Depending on the activity of protons in the solution analyzed, the boundary potential, which is the difference between the potential of the external analyte solution and the fixed potential of the glass membrane, changes according to the Nernst equation [63].

For sediment porewater measurements, pH microelectrodes have been developed according to the same principles [21, 40, 44, 45, 56, 64, 65], mainly derived from the early work of Hinke [66] and Thomas [67] for physiological studies. A rapid response time, a stable reading with low noise, and a sensitivity close to the Nernst response slope (i.e., 59.2 mV/pH unit at 25 °C) are indicative of a good pH microelectrode [44]. Both the response time and the noise are controlled partly by the electrode resistance, which is inversely proportional to the surface area of the glass membrane. A high resistance electrode has a fast response time, accelerating measurements, thus minimizing drifting problems. However, a high resistance electrode may also increase potential noise problems and electrical leakage [44]. Recently, Zhao and Cai [68] built a new pH microelectrode with a polymeric membrane containing poly(vinyl chloride) (PVC) or carboxylated PVC. These microelectrodes are better suited for sediment porewater analyses because they have a stronger tip, a much longer lifetime (>1 month vs. few days), a lower resistance (1–4 10^9 vs. $10^{10}\,\Omega$), and a shorter response time ($t_{98} < 4$ s. vs. 2 min) than the classic liquid membrane microelectrodes [44]. This electrode has not been used for in situ measurements, but tests in the laboratory with sediments and microbial mats are promising.

3.2. Carbon Dioxide

pCO_2 electrodes (Fig. 3) are built by encasing a pH electrode in an outer glass capillary sealed at the tip with a silicon membrane [44, 65]. The pH electrode is positioned close to the silicon membrane to maximize response time (Fig. 3c). The solution between the pH electrode and the analyzed solution contains 1–10 mM $NaHCO_3$ (Fig. 3a). $CO_{2(aq)}$, diffusing through the silicon membrane, modifies the equilibrium of the internal solution and therefore the pH. The rate of the electrode response depends on the diffusion rate of CO_2 in the silicon membrane, hydration rate of CO_2, and distribution rate of the carbonate species to reach equilibrium in the internal solution [44]. Therefore, the response time of the electrode is a function of the length of the silicon membrane and the distance between the pH electrode and the silicon membrane. Figure 3d displays pH and $CO_{2(aq)}$ sediment profiles obtained in situ in San Diego Bay [44]. Recently, the response time of the electrode has been decreased from a few minutes to a few seconds by decreasing the travelling distance of the analyte [65], but this electrode has not been tested in situ at high pressure, which could damage the very thin membrane. Detection limits with these electrodes are smaller than 3 μM.

For in situ deployment of potentiometric membrane electrodes in natural waters, several potential problems need consideration. The first one is the effect of pressure and temperature, which can change the standard potential of the external and internal references [40, 69, 70]. The second problem is linked to a change in the liquid-junction potential between the analyzed solution and the external reference solution if ions migrate from the solution analyzed to the external reference solution [69]. This is generally avoided by using highly concentrated electrolytes which have nearly identical ion mobilities (e.g., $NaClO_4$, KCl_{sat}.). The third problem is related to the presence of colloids in the solution analyzed. Important liquid-junction potential changes can occur if the reference electrode is in contact with charged particles, the so-called suspension effect [71]. Therefore in sediment porewater measurements, the reference electrode has to be maintained in the overlying waters during deployment. In addition, the lifetime of these microelectrodes ranges between a couple of weeks [44] to a month [68], which prevents their deployment over long periods of time. General recommendations for using potentiometric membrane electrodes in situ in natural waters are the following: although the calibration slope of pH electrodes is not influenced by pressure as high as 1000 atm [72], calibrations for pH and CO_2 measurements should be performed in situ, by comparing readings of the electrodes to the pH calculated from alkalinity and total dissolved inorganic carbon measured in the same waters [44]. This approach avoids possible liquid-junction potential changes that

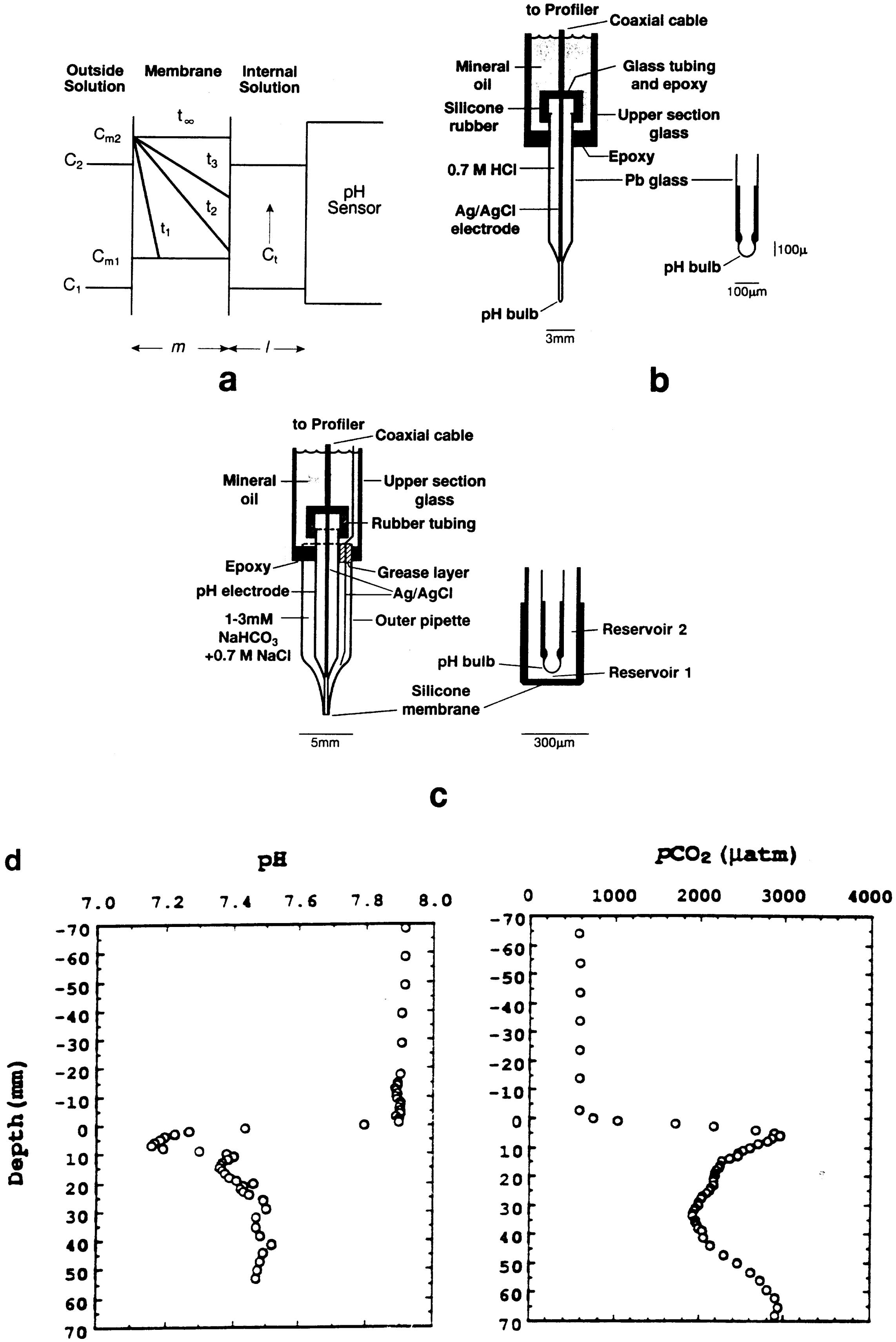

Fig. 3. Schematic representations of: a) the response of a pCO$_2$ electrode to CO$_{2(aq)}$ changes in the solution (at t_0, the concentration of CO$_{2(aq)}$ is increased from C_1 to C_2; at t_∞, the equilibrium is re-established, and the pCO$_2$ in the internal solution (C_t) increased from C_1 to C_2); b) the design of a pH microelectrode; and c) the design of a pCO$_2$ microelectrode. d) In situ microprofiles of pH and pCO$_2$ in the sediment porewaters of San Diego Bay Reprinted by permission from *Limnology & Oceanography* [44], Copyright (1993) by the American Society of Limnology and Oceanography, Inc.

may occur between buffer and sample solutions for pH calibration, and pressure effects that could occur during CO_2 measurements.

3.3. Ag/Ag_2S (pS^{2-}) Electrodes

pS^{2-} potentiometric sensors are electrodes of the second kind that contain a crystalline membrane of silver sulfide immersed in the solution analyzed [63]. Dissolution of a tiny amount of silver sulfide quickly saturates the film of liquid adjacent to the electrode. The solubility, and thus the silver ion concentration, depends on the sulfide concentration of the analyte. The potential change, due to the creation of a variation in electrical charge at the membrane surface, is recorded with respect to a reference electrode [69]. For high spatial resolution in sediments or microbial mats, a similar potentiometric sensor has been built [21, 24]. For in situ application in water columns (Fig. 4), the Ag/Ag_2S electrode has been improved [59–61] by using a solidified internal membrane of Ag_2S on a silver ring with an internal reference made of a silver/silver iodide in 0.2 M HI. The working electrode was used with a sodium glass electrode as external reference to avoid artifacts from hydrostatic pressure and temperature changes (see below). This system guarantees highly reproducible readings, but is limited to natural systems where the sodium ion activity is constant [61]. Because potentiometric pS^{2-} electrodes are sensitive to S^{2-}, pH measurements need to be performed in parallel during in situ deployments. Both electrodes have to be deployed very close to each other in sediments and microbial mats because these environments are heterogeneous. In addition, these electrodes are sensitive to silver ions [73], which may preclude their use in some silver polluted areas. Finally, nonideal responses, signal drifts, and long response time may occur at low sulfide levels, and coprecipitation at the surface of the membrane may cause drifts in the potential [53, 74].

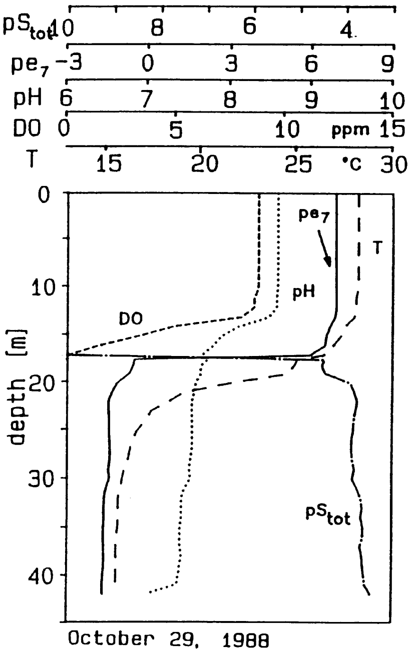

Fig. 4. In situ profiles of total sulfide (pS_{tot}), redox intensity normalized to pH 7 (pe_7), pH, dissolved oxygen (DO), and temperature (*T*) in the stratified water column of Lake Kinneret. Reprinted by permission from *Biogeochemistry* [61], Copyright (1993) by Kluwer Academic Publishers.

3.4. Potentiometric Stripping

Potentiometric stripping has been used with a gold microelectrode to measure in situ trace concentrations of copper in the marine environment [62]. The probe used consists of a three electrode assembly: a gold working microelectrode, an Ag/AgCl reference electrode, and a platinum counter electrode. These electrodes are housed in a weighted PVC tube connected to a 50 foot long shielded communication cable [75]. Potentiometric stripping was used by depositing the metal at a negative potential (i.e., −0.4 V) for 1–2 min without stirring. The small diameter of the working electrode (i.e., 100 μm) results in a nonlinear diffusional flux which does not require stirring of the solution. The potentiogram is recorded by applying a constant oxidation current (usually of 1–2 μA). To ensure complete regeneration of the gold electrode, a conditioning step at +0.8 V was applied for 1 min before each measurement. This technique requires a background correction to eliminate the interference of oxygen in natural waters. Figure 5 presents some of the typical stripping potentiometric peaks and the corresponding copper concentrations recorded in San Diego Bay as a function of time.

Wang and co-workers have described a potentiometric stripping sensor contained in a small flow-through cell [76]. The inlet solution is filtered through a dialysis membrane, and reactants can be simultaneously added to the analyzed solution. With such a device, remote stripping analysis may be extended to metals that are not readily electroplated (e.g., Ni, U). Wang and co-workers have also constructed remote electrochemical sensors for the monitoring of phenolic [77] and peroxide [78] compounds. They have tested them with natural waters, but have not used them in situ. These sensors are based on the technology presented in [75], except that the working electrode differs from a tyrosinase carbon paste electrode, for phenol detection, to a horseradish peroxidase electrode, for peroxide detection. The tyrosinase electrode catalyzes the *o*-hydroxylation of phenolic compounds to catechols, with subsequent dehydrogenation to *o*-quinones [77]. The peroxidase electrode catalyzes the reduction of the peroxide group with a ferrocene derivative as electron donor for the regeneration of the peroxidase [78].

3.5. Nitrogen Species

Other potentiometric microsensors have been built to measure nitrate [23, 79, 80], nitrite [81], and ammonium [82] in sediment porewaters, but they have not been used in situ in limnology or oceanography. Sediment cores were collected and brought back to the laboratory where measurements were performed by lowering the microelectrodes in the sediment with a micromanipulator. These sensors contain a liquid ion exchanger (LIX) membrane in their tips. The solvents used are hydrophobic, and the microelectrodes are previously silanized, usually with a solution of trimethylchlorosilane in carbon tetrachloride [79]. The shaft of the nitrate electrodes was filled with filtered and degassed potassium nitrate solution. Concentrations as low as 1 μM were accurately measured with these microelectrodes, but a high chloride interference, as for commercially available macroelectrodes, prevents their use in marine environments [79, 80]. The nitrite electrodes use the hydrophobic ion-carrier aquocyanocobalt(III)-hepta(2-phenylethyl)-cobrynate in a polyvinyl chloride (PVC)-gelled liquid membrane [81]. These sensors can reach detection limits of 1 μM in freshwater and 10 μM in seawater. Finally, the ammonium electrodes contain the neutral carrier nonactin. Their detection limit is 10 μM in freshwater, but suffers

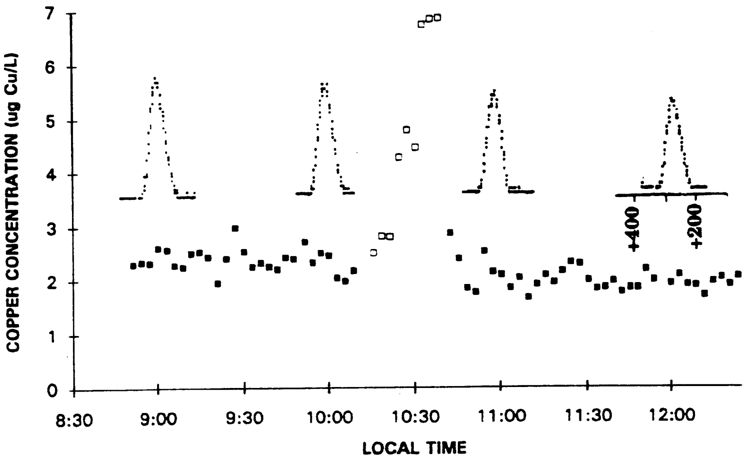

Fig. 5. Copper concentrations recorded in situ in San Diego Bay over three hours (dark squares), along with the values for an intermittent shipboard calibration. The calibration involved triplicate runs for the collected sample and two standard additions (open squares). Also shown, typical stripping potentiometric peaks as a function of potential from this series, obtained in 30 min intervals. Reprinted by permission from *Analytica Chimica Acta* [62], Copyright (1995) by Elsevier Science.

from a low selectivity with respect to Na^+ and K^+ which limits their application to low salt environments [82].

4. Voltammetric In Situ Sensors

Voltammetric techniques are attractive to measure chemical species in situ because they can detect several analytes in the same potential scan, they have low detection limits, and generally do not suffer from matrix problems (e.g., high salinity). Different methods are available to measure oxygen, sulfide species, Fe(II), Mn(II), thiosulfate, iodide, and other trace metals (usually Zn, Cd, Pb, and Cu) in situ [83–89] or on-line [10–18]. Measurements of other species (e.g., Cr, Co, Ni) can be conducted with chemically modified samples, usually performed on-line [16–18]. Reports of in situ measurements using voltammetric sensors are still relatively scarce, so on-line measurements aboard ship using flow cell systems will be considered here as well.

The mercury thin film electrode (MTFE) is preferred for on-line measurements [10–13], in situ deployments in water column [83–85], groundwater [86], and sediment [87–89]. However, some on-line measurements have been performed with the hanging mercury drop electrode (HMDE) [14–18].

4.1. On-Line Measurements

On-line total measurements of trace metal concentrations in marine waters have been performed using a mercury thin film electrode (MTFE) by anodic stripping voltammetry (ASV) [10–13] or a hanging mercury drop electrode (HMDE) with pretreatments of the waters and subsequent cathodic stripping voltammetry (CSV) [16–18]. In addition, Mn(II), Fe(II), ΣH_2S, and $FeS_{(aq)}$ were measured with a HMDE by cathodic differential pulse polarography (DPP) in the water column of a lake [14–15]. All these measurements involve a step where the solution is degassed with nitrogen to eliminate the oxygen interference that is nonnegligible with these electrodes. A titration unit was used with HMDEs to determine the concentration of the trace metal by standard addition [16–18]. When used, the mercury thin film was plated in situ before each analysis [10, 12] or once before analysis [11, 13]. Table 1 presents the electrochemical methods and the chemical treatments used on-line to monitor the concentrations of different metals and sulfide.

4.2. In Situ Measurements in the Water Column

Tercier and co-workers have manufactured a voltammetric in situ profiling (VIP) system that is now commercially available

Table 1. Electrochemical methods and chemical treatments used for on-line dissolved trace metal and sulfide detection (ASV and CSV: anodic and cathodic stripping voltammetry; MTFE: mercury thin film electrode; HMDE: hanging mercury drop electrode; DME: dropping mercury electrode).

Species	*Environment*	*Method*	*Electrode*	*Treatment*	*References*
Zn	River	ASV	MTFE on glassy carbon	Ammonium Acetate (pH 6.4)	[13]
Zn, Pb, Cu	Seawater	ASV	MTFE in tubular graphite	None	[10, 12]
total Cr	Seawater	CSV	HMDE	UV oxidation to Cr(VI)	[16]
total Cu	Seawater	CSV	HMDE	Tropolone	[16]
total Cu and total Zn	Seawater	CSV	HMDE	8-Hydroxyquinoline	[17, 18]
total Ni	Seawater	CSV	HMDE	Dimethyl glyoxime (DMG)	[17, 20, 18]
Fe^{2+}, Mn^{2+}, ΣH_2S, FeS	Lake	Cathodic DPP	DME	None	[14, 15]
ΣH_2S	Lake	Amperometric Pt		Redox mediator: $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	[19]

]

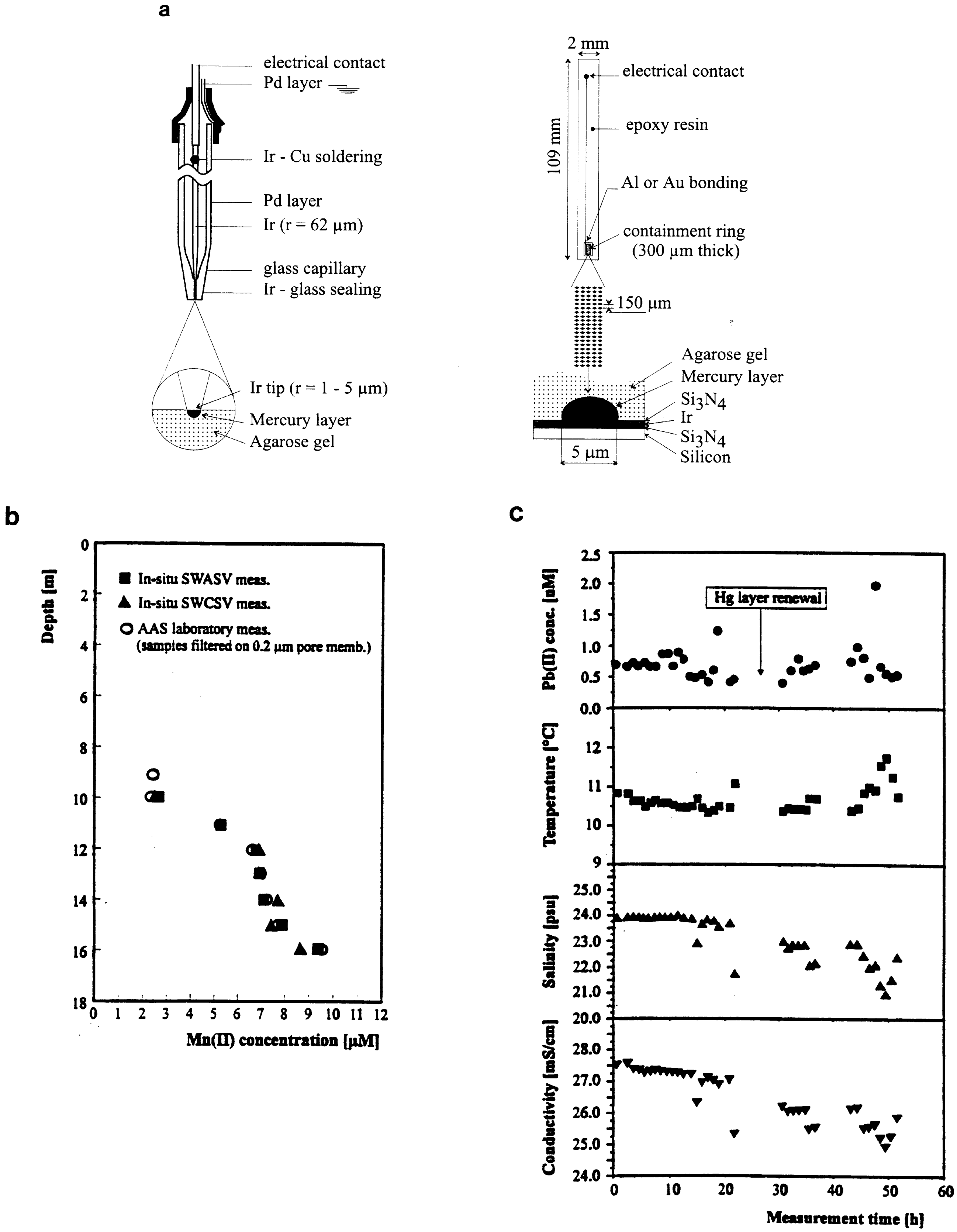

Fig. 6. a) Schematic representation of the agarose membrane-covered mercury-plated Ir-based single electrode (μ-AMMIE, left) and of the agarose membrane-covered mercury-plated Ir-based electrode arrays (μ-AMMIA, right). Reprinted by permission from *Environmental Science & Technology* [84]. Copyright (1998) by the American Chemical Society. b) In situ profile of Mn(II) in the water column of Lake Brêt (Switzerland) obtained with the VIP. c) Unattended autonomous in situ monitoring of Pb, temperature, salinity, and conductivity performed with the VIP at Kristineberg Marine Station (entrance of Kullmar Fjord, Sweden). Reprinted by permission from *Electroanalysis* [85], Copyright (1998) by Wiley-VCH, Weinheim, Germany.

and uses a mercury plated solid state iridium microelectrode (diameter = 2–10 μm) [90]. They also developed a system that can support an array of 100 interconnected iridium microelectrodes to increase the sensor's sensitivity [91, 92]. Fig. 6a presents the two different electrode configurations. The probe contains a pressure resistant housing (up to 150 bar) for the electronics, a flow-through voltammetric cell, a pressure case, and a submersible peristaltic pump. As the flow-through cell is lowered in the water column, this system performs in situ measurements. The data are transferred by telemetry to the surface deck unit where they can be visualized after the profile measurements are completed. Tercier el al. [84, 85] used square wave voltammetry (SWV) in both anodic and cathodic modes to determine profiles of Mn in the water column of a lake (Fig. 6b), and square-wave anodic stripping voltammetry (SWASV) to monitor over time trace concentrations of Cd, Pb, and Cu in a marine environment. Figure 6c presents the in situ data for Pb, along with temperature, salinity, and conductivity measurements. For Cd, Pb, and Cu measurements, depositions at potentials ranging between −1 and −1.3 V for 15 minutes were necessary to reduce and preconcentrate the metal studied on the mercury film. This procedure allows measurements of low metal concentrations (subnanomolar level), but diffusion and adsorption of large inorganic colloids and natural organic matter onto the electrode surface generally occurs during the deposition [5]. This electrode fouling may modify or suppress the metal voltammetric signals. To overcome this problem, Tercier and co-workers embed their electrodes in a 300–600 μm thick agarose gel membrane [93]. This membrane is also useful to protect the electrodes for long time deployment and from ill-controlled hydrodynamic currents that occur in a water column. However, a drawback of such a membrane is that species diffusing into the gel layer are still not well-defined, and in situ measurements need to be compared to total analyses of filtered and unfiltered waters to determine the metal speciation performed by voltammetry [90, 92].

Kounaves and co-workers have constructed an array of twenty interconnected mercury coated iridium microelectrodes (diameter 10 μm) [86, 94]. The electrochemical sensor system built consists of a 5 cm diameter PVC tube with flow through holes at one extremity and which contains the reference, counter, and working electrodes [86]. This lower unit is connected to another PCV tubing which encapsulates a homemade potentiostat and a microcontroller. The potentiostat is connected to a laptop computer through a 33 m shielded cable. The whole system is run by four 9 V batteries. The simple design of this system is an advantage, but the authors indicate that the in situ measurements provide only "reasonable representations of heavy metal contaminations for initial, rapid, order-of-magnitude, field screening". It is not clear why traditional sampling and analytical methods in this study gave significantly different total metal concentrations from some of the in situ analyses.

4.3. In Situ Measurements in the Sediment and at the Sediment-Water Interface

The first in situ measurements in sediment porewaters have been reported by Luther and co-workers [87–89] who have mounted a gold microelectrode plated with mercury [26] on a remotely operated vehicle (ROV). The electrode was connected to the shipboard voltammetric analyzer with a 30 m long shielded cable which had receiver-transmitter transducers on each end to preserve the quality of the signal. The sensor was positioned and manipulated with a microprofiler controlled in real time from the research vessel anchored at the site. Cameras on the ROV allowed for continuous visual monitoring of the electrode system. Luther and co-workers successfully measured O_2, ΣH_2S, Mn^{2+}, and Fe^{2+} on a (sub)millimeter scale down to 5 cm in the sediment (e.g., Fig. 7). In addition, in situ measurements of oxygen profiles with a Clark microelectrode [39] were similar to the profiles obtained with the Au/Hg voltammetric microelectrode [89]. These authors condition the solid state electrode between scans to remove organic material, metals, and sulfides that may interact with the mercury surface. Finally, these authors have simultaneously recorded pH and resistivity changes with depth to understand the physical, biological, and chemical factors that affect the mineralization of organic matter in sediments [89].

4.4. In Situ Measurements in Deep-Sea Waters

Recently, Luther and co-workers (in preparation) performed the first voltammetric measurements near deep sea hydrothermal vents (2500 m depth at 9° 49–52′ N East Pacific Rise) using mercury-gold amalgam electrodes encased in PEEK tubing to resist the high pressure and temperature at these locations. An electrochemical analyzer (DLK-SUB–1, Analytical Instrument Systems, Inc.) was placed into an aluminum pressure housing and set up to run from DSV Alvin DC power. The analyzer was cabled through the hull of the submersible to a portable computer

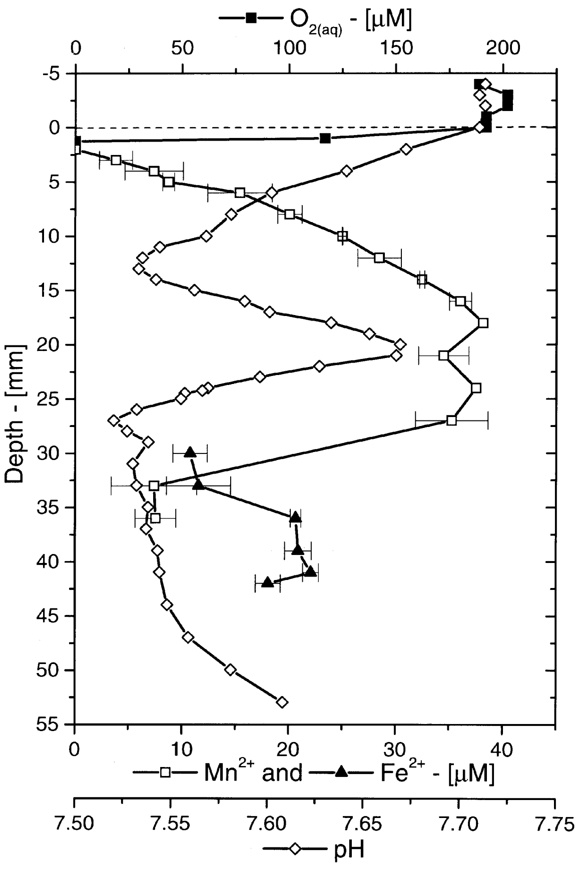

Fig. 7. First voltammetric in situ profiles of O_2, Mn(II), Fe(II) in a marine sediment (Raritan Bay, New York City) obtained with a remotely operated vehicle (ROV). A pH profile was recorded simultaneously with a potentiometric membrane microelectrode [88].

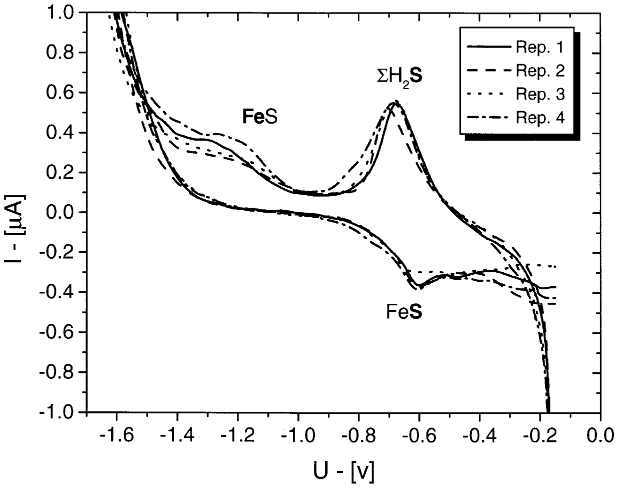

Fig. 8. First voltammetric in situ measurements of Fe(II), ΣH_2S, and FeS in diffuse flow areas near hydrothermal vents located at the East Pacific Rise (9° 49–52′ N). The PEEK Hg/Au electrodes were positioned with the arm of DSV Alvin 0.5 m above a black smoker chimney. The temperature was 24 °C at 0.5 m above the chimney orifice and 365 °C at the orifice. The cyclic voltammogram was acquired at 1000 mV/s from −0.1 to −1.8 V (vs. Ag/AgCl). A cleaning step was performed for 10 s at −0.9 V.

which controlled the analyzer. Four electrodes were connected to the analyzer and housed in a wand that was moved by the robotic arms of the submersible. This system allowed the operator to perform real time measurements and experiments. Measurements of H_2S, Fe(II), and FeS were performed in situ in diffusive flow environments and in the plume of black smoker hydrothermal vents. Figure 8 displays four consecutive cyclic voltammograms recorded in the plume above a vent. A wave for ΣH_2S ($E_{1/2} \approx -0.7$ V) is measured cathodically. In addition, the cathodic ($E_{1/2} \approx -1.1$ V) and anodic ($E_{1/2} \approx -0.6$ V) waves for $FeS_{(aq)}$ are measured, corresponding to the reduction of Fe(II) in FeS and the consecutive electrochemical oxidation of Hg^0 to form HgS, respectively [95], confirming the presence of $FeS_{(aq)}$ in this extreme environment.

4.5. New Voltammetric Systems

New in situ voltammetric technologies have been developed in the laboratory, but have not yet been tested in the field. Wang and co-workers have constructed remote voltammetric sensors for the monitoring of silver [96] and TNT [97]. These sensors are based on the technology presented in [75], except that the working

Table 2. Summary of the dissolved chemical species determined in situ in aquatic systems and the electrochemical techniques employed (MTFE: mercury thin film electrode).

Species	*Environment*	*Instrument*	*Electrode(s)*	*Treatment*	*References*
O_2	Lake	Depth probe	Clark	None	[35]
	Marine plankton productivity	Bell Jar Respirometer	Clark	None	[35]
	Benthic respiration	Grab Respirometer	Clark	None	[35]
	Deep-sea sediment	Profiling lander	Clark	None	[38, 39]
	Shallow marine sediment	Profiling lander	Clark	None	[41]
	Deep-sea sediment	Benthic chamber	Clark	None	[43]
O_2, pH	Deep-sea sediment	Profiling lander	Clark and potentiometric	None	[40]
	Shallow and deep-sea sediment, lake sediment	Benthic chamber	Clark and potentiometric	None	[46]
O_2, pS^{2-}	Microbial Mats	Profiling lander	Clark and potentiometric	None	[24, 57]
	Lake	Depth probe	Clark and potentiometric	None	[59]
O_2, pH, pS^{2-}	Lake	Depth probe	Clark and potentiometric	None	[60, 61]
	Deep-sea sediment	Profiling lander	Clark and potentiometric	None	[42]
O_2, pH, pCO_2	Shallow and deep-sea sediment	Profiling lander	Clark and potentiometric	pCO_2:pH change measured in $NaHCO_3$	[44,45]
O_2, pH	Lake	Towed probe	Clark and potentiometric	None	[19]
pH	Deep-sea sediment	Profiling lander	Potentiometric	None	[56]
	Microbial mats	Profiling lander	Potentiometric	None	[58]
Cu	Seawater	Depth probe	Au potentiometric stripping	None	[62]
Mn	Lake	Depth probe	Voltammetric MTFE/Ir (single and arrays)	None	[84, 85]
Cd, Pb, Cu	Seawater	Depth probe	Single voltammetric MTFE/Ir	Agarose gel membrane	[83, 85]
Cd, Pb, Cu, Zn	Groundwater	Depth probe	Votammetric MTFE/Ir arrays	None	[86]
O_2, ΣH_2S, Mn^{2+}, Fe^{2+}	Shallow marine sediment	Profiling lander	Votammetric MTFE/Au	None	[87–89]
O_2, ΣH_2S, FeS, Fe^{2+}	Deep-sea hydrothermal vents	Holder mounted on submersible arm	Voltammetric MTFE/Au	None	[see text]

electrode is a multiple carbon fiber electrode. Silver is detected by ASV [96], while TNT is measured by square-wave voltammetry (SWV) [97].

5. Summary and Future Directions

In situ measurements in aquatic systems are needed to minimize artifacts that occur during sampling. As a result, electrochemical techniques have been used extensively in a variety of freshwater or marine environments (e.g., water columns, microbial mats, salt marshes, and sediments). Table 2 summarizes the measurements performed in situ in different aquatic systems, the instrument used, the electrochemical technique applied and the characteristics of the sensors, and the physical and chemical treatments eventually used.

Potentiometric and amperometric techniques have been preferred, mainly because the sensors are easy to build and at low cost. However, these techniques can only detect one species per electrode, which can be a drawback when spatial and temporal resolution of analytes is needed. Thus, a complete picture of microbial and/or geochemical processes occurring in a specific system requires the use of several electrodes. In addition, their selectivity is very often poor, which limits their use to a few environments.

Voltammetry is an alternate method that can provide concentrations of several species on the same electrode. Mercury electrodes have been preferred because of their high capacity for in situ regeneration via conditioning potentials, and their broad analytical window to measure several species in one voltage scan. In turn, they are sometimes limited by the operational definition of element speciation.

Future improvements of electrochemical sensors are to be expected since they are used in numerous research areas and in a variety of environments. In addition, the development of instruments that could be deployed over time in aquatic systems should be expected. These instruments should be able to monitor the concentration of chemical species over time to determine the dynamics of environmental systems influenced by physical, biological, and chemical changes. Finally, instruments that incorporate as many sensors as possible to collect a variety of relevant data in a specific aquatic system are needed to identify the relevant biogeochemical processes that regulate the fate of pollutants and the cycling of essential elements.

6. Acknowledgements

This work was supported by grants from NOAA office of Sea Grant (NA16RG0162-03) and NSF (OCE-9714302).

7. References

[1] T.R.S. Wilson, in *Marine Electrochemistry* (Eds: M. Whitfield, D. Jagner), Wiley, Chichester **1981**, pp. 146–185.

[2] G.E. Batley, D. Gardner, *Estuarine Coastal Mar. Sci.* **1978**, *7*, 59.

[3] S.R. Piotrowicz, M. Springer-Young, J.A. Puig, M. J. Spencer, *Anal. Chem.* **1982**, *54*, 1367.

[4] C.M.G. van den Berg, *Mar. Chem.* **1984**, *15*, 1.

[5] T.M. Florence, *Analyst* **1986**, *111*, 489.

[6] G. Capodaglio, K.H. Coale, K.W. Bruland, *Mar. Chem.* **1990**, *29*, 221.

[7] E. Henneke, G.W. Luther III, G. J. de Lange, *Mar. Geol.* **1991**, *100*, 115.

[8] H. Xue, D. Kistler, L. Sigg, *Limnol. Oceanogr.* **1995**, *40*, 1142.

[9] F.L.L. Muller, *Marine Chem.* **1996**, *52*, 245.

[10] A. Zirino, S.H. Lieberman, C. Clavell, *Environ. Sci. Technol.* **1978**, *12*, 73.

[11] J. Wang, M. Ariel, *Anal. Chim. Acta* **1978**, *99*, 89.

[12] A. Zirino, in *Marine Electrochemistry* (Eds: M. Whitfield, D. Jagner), Wiley **1981**, pp. 421–503.

[13] J. Wang, B. Greene, *Wat. Res.* **1983**, *17*, 1635.

[14] R.R. De Vitre, J. Buffle, D. Perret, R. Baudat, *Geochem. Cosmochim. Acta* **1988**, *52*, 1601.

[15] W. Davison, J. Buffle, R. De Vitre, *Pure Appl. Chem.* **1988**, *60*, 1535.

[16] E.P. Achterberg, C.M.G. van den Berg, *Anal. Chim. Acta.* **1994**, *284*, 463.

[17] E.P. Achterberg, C. M. G van den Berg, *Marine Poll. Bull.* **1996**, *32*, 471.

[18] C. Braungardt, E. P. Achterberg, M. Nimmo, *Anal. Chim. Acta.* **1998**, *377*, 205.

[19] D. Stüben, S. Braun, P. Jeroschewski, P. Haushahn, *App. Geochem.* **1998**, *13*, 379.

[20] D. Whitworth, E. P. Achterberg, M. Nimmo, P. J. Worsfold, *Anal. Chim. Acta* **1998**, *371*, 235.

[21] N.P. Revsbech, B.B. Jorgensen, T.H. Blackburn, Y. Cohen, *Limnol. Oceanogr.* **1983**, *28*, 1062.

[22] T. Frevert, *Arch. Hydrobiol.* **1987**, *109*, 1.

[23] J-P. R.A. Sweerts, D. de Beer, *App. Environ. Microb.* **1989**, *55*, 754.

[24] P.T. Visscher, J. Beukema, H. van Gemerden, *Limnol. Oceanogr.* **1991**, *36*, 1476.

[25] K. Jensen, N.P. Revsbech, L.P. Nielsen, *App. Environ. Microb.* **1993**, *59*, 3287.

[26] P.J. Brendel, G.W. Luther III, *Environ. Sci. Technol.* **1995**, *29*, 751.

[27] L. R. Damgaard, N. P. Revsbech, *Anal. Chem.* **1997**, *69*, 2262.

[28] D. de Beer, A. Glud, E. Epping, M. Kühl, *Limnol. Oceanogr.* **1997**, *42*, 1590.

[29] G.W. Luther III, B. Sundby, B.L. Lewis, P.J. Brendel, N. Silverberg, *Geochem. Cosmochim. Acta* **1997**, *61*, 4043.

[30] G.W. Luther III, B.L. Lewis, P.J. Brendel, B. Sundby, L. Lefrançois, N. Silverberg, D. B. Nuzzio, *Limnol. Oceanogr.* **1998**, *43*, 325.

[31] M.-L. Tercier, J. Buffle, *Electroanal.* **1993**, *5*, 187.

[32] O.S. Wolfbeis, *Fiber Optic Chemical Sensors and Biosensors*, Vol.1, CRC Press, Boca Raton, FL **1986**.

[33] R.N. Glud, I. Klimant, G. Holst, O. Kohls, V. Meyer, M. Kühl, J.K. Gundersen, *Deep-Sea Res.* **1999**, *46*, 171.

[34] M.L. Hitchman, *Measurement of Dissolved Oxygen*, a Wiley-Interscience publication **1978**.

[35] E. Gnaiger, H. Forstner, *Polarographic Oxygen Sensors: Aquatic and Physiological Applications*, Springer, Berlin **1983**.

[36] D R. Kester, in *Chemical Oceanography, Vol. 1* (Eds: J.P. Riley, G. Skirrow), Academic Press, New York **1975**, pp. 497–556.

[37] F.J. Millero, M.L. Sohn, *Chemical Oceanography*, CRC Press, Boca Raton, FL **1992**.

[38] C.E. Reimers, K.M. Fischer, R. Merewether, K.L. Smith Jr., R.A. Jahnke, *Nature* **1986**, *320*, 741.

[39] C.E. Reimers, *Deep-Sea Res.* **1987**, *34*, 2017.

[40] D. Archer, S. Emerson, C. Reimers, *Geochim. Cosmochim. Acta* **1989**, *53*, 2831.

[41] J.K. Gundersen, B.B. Jorgensen, *Nature* **1990**, *345*, 604.

[42] J.K. Gundersen, B.B. Jorgensen, E. Larsen, H.W. Jannasch, *Nature* **1992**, *360*, 454.

[43] R.N. Glud, J.K. Gundersen, B.B. Jorgensen, N.P. Revsbech, H.D. Schulz, *Deep-Sea Res.* **1994**, *41*, 1767.

[44] W-J. Cai, C.E. Reimers, *Limnol. Oceanogr.* **1993**, *38*, 1762.

[45] W-J.Cai, C.E. Reimers, T. Shaw, *Geochim. Cosmochim. Acta* **1995**, *59*, 497.

[46] A. Tengberg, F. De Bovee, P. Hall, W. Berelson, D. Chadwick, G. Ciceri, P. Crassous, A. Devol, S. Emerson, J. Gage, R. Glud, F. Graziottini, J. Gundersen, D. Hammond, W. Helder, K. Hinga, O. Holby, R. Jahnke, A. Khripounoff, S. Lieberman, V. Nuppenau, O. Pfannkuche, C. Reimers, G. Rowe, A. Sahami, F. Sayles, M. Schurter, D. Smallman, B. Wehrli, P. De Wilde, *Prog. Oceanog.* **1995**, *35*, 253.

[47] N.P. Revsbech, *Limnol. Oceanogr.* **1989**, *34*, 474.

[48] H. Baumgärtl, D.W. Lübbers in *Polarographic Oxygen Sensors: Aquatic and Physiological Applications* (Eds: E. Gnaiger, H. Forstner), Springer, Berlin **1983**, pp. 37–65.

[49] M.L. Hitchman, in *Polarographic Oxygen Sensors: Aquatic and Physiological applications* (Eds: E. Gnaiger, H. Forstner), Springer, Berlin **1983**, pp. 18–30.

[50] J.K. Gundersen, N.B. Ramsing, R.N. Glud, *Limnol. Oceanogr.* **1998**, *43*, 1932.

[51] N.P. Revsbech, L.P. Nielsen, P.B. Christensen, J. Sorensen, *App. Environ. Microb.* **1988**, *54*, 2245.

[52] L.H. Larsen, T. Kjaer, N.P. Revsbech, *Anal. Chem.* **1997**, *69*, 3527.

[53] P. Jeroschewski, C. Steuckart, M.Kühl, *Anal. Chem.* **1996**, *68*, 4351.

[54] P. Jeroschewski, S. Braun, *Fresenius J. Anal. Chem*. **1996**, *354*, 169.

[55] M. Kühl, C. Steuckart, G. Eickert, P. Jeroschewski, *Aquat. Microb. Ecol.* **1998**, *15*, 201.

[56] T.R. S. Wilson, S.D. McPhail, A.C. Braithwaite, B. Koch, A. Dogan, A. Disteche, *Deep-Sea Res.* **1988**, *36*, 315.

[57] P.T. Visscher, P. Quist, H. van Gemerden, *App. Environ. Microbiol.* **1991**, *57*, 1758.

[58] P.T. Visscher, H. van Gemerden, *App. Environ. Microbiol.* **1991**, *57*, 3237.

[59] W. Eckert, T. Frevert in *4th Symposium on Ion-Selective Electrodes*, Mátrafüred **1984**.

[60] W. Eckert, T. Frevert, H.G. Trüper, *Wat. Res.* **1990**, *24*, 1341.

[61] W. Eckert, H.G. Trüper, *Biogeochem.* **1993**, *21*, 1.

[62] J. Wang, N. Foster, S. Armalis, D. Larson, A. Zirino, K. Olsen, *Anal. Chim. Acta.* **1995**, *310*, 223.

[63] D.A. Skoog, J.J. Leary, *Principles of Instrumental Analysis*, 4th ed., Saunders College Publishing, **1992**.

[64] S.A. Jong, P.A.G. Hofman, A.J.J. Sandee, *Mar. Ecol. Prog. Ser.* **1988**, *45*, 187.

[65] D. de Beer, A. Glud, E. Epping, M. Kühl, *Limnol. Oceanogr.* **1997**, *42*, 1590.

[66] J.A.M. Hinke in *Glass Electrodes for Hydrogen and Other Cations* (Ed: G. Heiseman), Marcel Dekker, New York **1967**, pp. 464–477.

[67] R.C. Thomas, *Ion-Sensitive Intracellular Microelectrodes, How to Make Them and Use Them*, Academic Press, New York **1978**.

[68] P. Zhao, W-J. Cai, *Anal. Chim. Acta* **1999**, *395*, 285.

[69] J. Buffle, *Complexation Reactions in Aquatic Systems an Analytical Approach*, Halsted Press, New York **1988**.

[70] C.H. Culberson, in *Marine Electrochemistry* (Eds: M. Whitfield, D. Jagner), Wiley, Chichester **1981**, pp. 188–261.

[71] J.T G. Overbeek, *J. Colloid Sci.* **1953**, *8*, 593.

[72] A. Distèche, *Rev. Sci. Instrum.* **1959**, *30*, 474.

[73] N.W.H. Adams, J.R. Kramer, *Aquatic Geochem.* **1999**, *5*, 1.

[74] N.P. Revsbech, B.B. Jorgensen, in *Advances in Microbial Ecology* (Ed: K.C. Marshall), Vol. 9, Plenum Press, New York **1986**, pp. 293–352.

[75] J. Wang, D. Larson, N. Foster, S. Armalis, J. Lu, X. Rongrong, K. Olsen. A. Zirino, *Anal. Chem.* **1995**, *67*, 1481.

[76] J. Wang, J. Lu, D. Luo, J. Wang, M. Jiang, B. Tian, K. Olsen, *Anal. Chem.* **1997**, *69*, 2640.

[77] J. Wang, Q. Chen, *Anal. Chim. Acta* **1995**, *312*, 39.

[78] J. Wang, G. Cepria, Q. Chen, *Electroanal.* **1996**, *8*, 124.

[79] D. De Beer, J-P. Sweerts, *Anal. Chim. Acta* **1989**, *219*, 351.

[80] K. Jensen, N.P. Revsbech, L.P. Nielsen, *App. Environ. Microb.* **1993**, *59*, 3287.

[81] D. De Beer, A. Schramm, C.M. Santegoeds, M. Kühl, *App. Environ. Microb.* **1997**, *63*, 973.

[82] D. De Beer, J.C. Van den Heuvel, *Talanta* **1988**, *35*, 728.

[83] M.-L. Tercier, J. Buffle, A. Zirino, *Anal. Chim. Acta* **1990**, *237*, 429.

[84] M.-L. Tercier-Waeber, C. Belmont-Hebert, J. Buffle, *Environ. Sci. Technol.* **1998**, *32*, 1515.

[85] M.-L. Tercier, J. Buffle, F. Graziottin, *Electroanal.* **1998**, *10*, 355.

[86] J. Herdan, R. Feeney, S.P. Kounaves, A.F. Flannery, C.W. Storment, G.T.A. Kovacs, R.B. Darling, *Environ. Sci. Technol.* **1998**, *32*, 131.

[87] G.W. Luther III, M. Taillefert, A.B. Bono, P.J. Brendel, B. Sundby, C.E. Reimers, D.B. Nuzzio, D. Lovalvo, *Miner. Magaz.* **1998**, *62(A)*, 921.

[88] G.W. Luther III, C.E. Reimers, D.B. Nuzzio, D. Lovalvo, *Sea. Technol.* **1999**, *40*, 10.

[89] G.W. Luther III, C.E. Reimers, D.B. Nuzzio, D. Lovalvo, *Environ. Sci. Technol.*, **1999**, *33*, 4352.

[90] M.-L. Tercier, N. Parthasarathy, J. Buffle, *Electroanal.* **1995**, *7*, 55.

[91] C. Belmont, M.-L. Tercier, J. Buffle, G.C. Fiaccabrino, M. Koudelka-Hep, *Anal. Chim. Acta* **1996**, *329*, 203.

[92] C. Belmont, M.-L. Tercier, J. Buffle, G.C. Fiaccabrino, M. Koudelka-Hep, *Anal. Chem.* **1998**, *70*, 2949.

[93] M.-L. Tercier, J. Buffle, *Anal. Chem.* **1996**, *68*, 3670.

[94] S.P. Kounaves, W. Deng, P.R. Hallock, G.T.A. Kovacs, C. Storment, *Anal. Chem.* **1994**, *66*, 418.

[95] S.M. Theberge, G.W. Luther III, *Aquatic Geochem.* **1997**, *3*, 191.

[96] J. Wang, J. Lu, P.A.M. Farias, *Anal. Chim. Acta* **1996**, *318*, 151.

[97] J. Wang, R.K. Bhada, J. Lu, D. MacDonald, *Anal. Chim. Acta* **1998**, *361*, 85.