

Evaluation of a lifetime-based optode to measure oxygen in aquatic systems

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Abstract

In this article, we evaluate the performance of a commercially available lifetime-based optode and compare it with data obtained by other methods. We performed a set of 10 different tests, including targeted laboratory evaluations and field studies, covering a wide range of situations from shallow coastal waters and wastewater treatment plants to abyssal depths. Our principal conclusion is that, owing to high accuracy ($\pm 2 \mu\text{M}$), long-term stability (more than 20 months), lack of pressure hysteresis, and limited cross-sensitivity, this method is overall more suitable for oxygen monitoring than other methods.

Introduction

Most chemical and biological processes are influenced by changes in dissolved oxygen concentrations. Oxygen is therefore a prime parameter to measure in a variety of applications ranging from industrial processes to environmental studies.

The standard method to analyze oxygen content in water is a 2-step wet chemistry precipitation of the dissolved oxygen

followed by a titration. The method was first described by Winkler (1888) and has since then remained the overall standard. Winkler titration is almost always performed in the laboratory on collected water samples. The collection and handling of water samples can induce errors, and the analytical work is time consuming and demands meticulous care. It is therefore not a suitable method to obtain in situ data with high spatial and temporal resolution.

For in situ measurements of oxygen, electrochemical sensors (often called Clark type sensors after a US patent, Clark, 1959; Kanwisher, 1959) are the most commonly used. Developed in a wide range of applications, they vary in size and design from micrometer-sized glass electrodes to more robust macro-electrodes with sensing tips of several centimeters (for a review, see Glud et al., 2000, and references therein). Performance studies of different types of electrochemical sensors have been presented in, e.g., Briggs and Viney (1964), Atwood et al. (1977), Hitchman (1978), Gneiger and Forstner (1983), Short and Shell (1984), Berntsson et al. (1997), Gun-

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dersen et al., (1998), and Glud et al. (2000). Regardless of the design, these studies have shown that the Clark sensor requires frequent (at least monthly) calibration to obtain accurate measurements of dissolved oxygen. Other shortcomings are irreversible pressure effects (hysteresis), cross-sensitivity (Berntsson et al., 1997), and contamination by hydrogen sulfide (H_2S).

Optodes (also called optrodes) may provide a more suitable method than electrochemical sensors for direct measurement of dissolved oxygen. Optode technology has been known for years (e.g., Kautsky, 1939), but it is relatively new to aquatic research (e.g., Klimant et al., 1995; Glud et al., 1999 Q1; Wenzhöffer et al., 2001). The fundamental principle is based on the ability of selected substances to act as dynamic luminescence quenchers. In the case of oxygen, if a ruthenium complex is illuminated with blue light, it will be excited and emit a red luminescent light with an intensity, or lifetime, that depends on the ambient oxygen concentration. It is important to distinguish between three different principles in detecting the red luminescence: intensity (how strong the luminescence is), lifetime (how quickly the luminescence dies out), and phase shift (in principle also a lifetime-based measurement, see "Measurement principle," below). Intensity-based measurements are technically easier to do, but they can drift over time. The different signal detection techniques are summarized by Wolfbeis (1991), Demas et al. (1999), and Glud et al. (2000) along with a wide range of applications. Klimant et al. (1995) and Stokes and Romero (1999) described intensity-based oxygen optodes and their use. The function and use of lifetime-based optodes were described by Holst et al. (1995) and Klimant et al. (1996).

Optode technology has an advantage over conventional sensors in that it can also be used to assess oxygen distributions in 2 dimensions (e.g., Holst et al., 1997, 1998; Glud et al., 1999 Q1, 2001, 2005) and to detect other substances (e.g., Klimant et al., 2000; Huber et al., 2000, 2001a, 2001b; Hulth et al., 2002; von Bültzingslöwen et al., 2002).

In this article, we evaluate a commercially available lifetime-based oxygen optode and compare its performance with different electrochemical sensors and oxygen concentrations obtained by Winkler titration. A novelty with this sensor, compared to the optodes used in other studies, is that it combines the benefits of using a platinum porphyrine luminescence dye with digital signal processing (DSP) electronics; we briefly describe the construction and working principles of this sensor. To evaluate its accuracy and precision in the laboratory, we tested the influence of simultaneous changes in oxygen, salinity, temperature, stirring, pressure, and pH using multivariate statistical methods. We present and discuss data from extended evaluations of pressure behavior as well as response time, and finally, we give a range of field application examples to demonstrate the performance of oxygen optodes in different field settings.

Materials and procedures

Measurement principle—The particular type of sensor used in this evaluation is commercially available from Aanderaa Data Instruments, Norway (Oxygen Optode models 3830 and 3930; Tengberg et al., 2003). The sensor is based on oxygen luminescence quenching of a platinum porphyrine complex. The lifetime measurement, and hence the oxygen measurement, is made by a so-called phase-shift detection of the returning, oxygen-quenched red luminescence. The relationship between oxygen concentration and the luminescent decay time can be described by the Stern-Volmer equation:

$$[O_2] = \frac{1}{K_{SV}} \left\{ \frac{\tau_0}{\tau} - 1 \right\}$$

where: τ = decay time, τ_0 = decay time in the absence of oxygen, and K_{SV} = Stern-Volmer constant (the quenching efficiency). The foil is excited with a blue-green light modulated at 5 kHz. The decay time is a direct function of the phase of the received red luminescent light, which is used directly for oxygen detection, without calculating the decay time. The basic working principles of dynamic luminescence quenching, lifetime-based optodes, and phase-shift detection can be found in, e.g., Klimant et al. (1996); Demas et al. (1999); Glud et al. (2000).

The sensor housing is made of titanium, rated to 600-bar pressure, with a diameter of 36 mm and a total length of 86 mm. This housing includes an optical part, a temperature sensor (Fig. 1), and the necessary electronics (a microprocessor with digital signal processing capacity) to process signals and output absolute temperature compensated oxygen readings (in μM or % saturation). An advantage of using digital signal processing, over analog technology, is enhanced possibilities of signal filtering and less risk of drift in the electronics over changes in temperature and time.

The sensing foil is composed of an oxygen-sensitive luminescent substance (luminophore) embedded in a polymer layer that is coated onto a thin film of polyester support (Figure 1). The most commonly used oxygen luminophores have been ruthenium complexes (e.g., Klimant et al., 1996; Stokes and Romero, 1999), but for this sensor an oxygen-sensitive luminophore based on a platinum porphyrine complex, commercially available from PreSens GmbH (Regensburg, Germany), was used mainly because of its longer lifetime (about a factor of 5 longer than ruthenium's). A longer lifetime makes it easier to detect the signal and to obtain stable readings. Another advantage with platinum porphyrine is that it is less sensitive to photobleaching.

We tested 2 types of foils, with and without a gas-permeable protective black silicon layer (Fig. 1). The silicon layer also acts as an optical isolation layer to avoid potential influence from fluorescent/luminescent material in the surrounding water and/or direct incoming sunlight (when measuring in the photic zone). The disadvantage of this layer is that the sensor response time becomes longer.

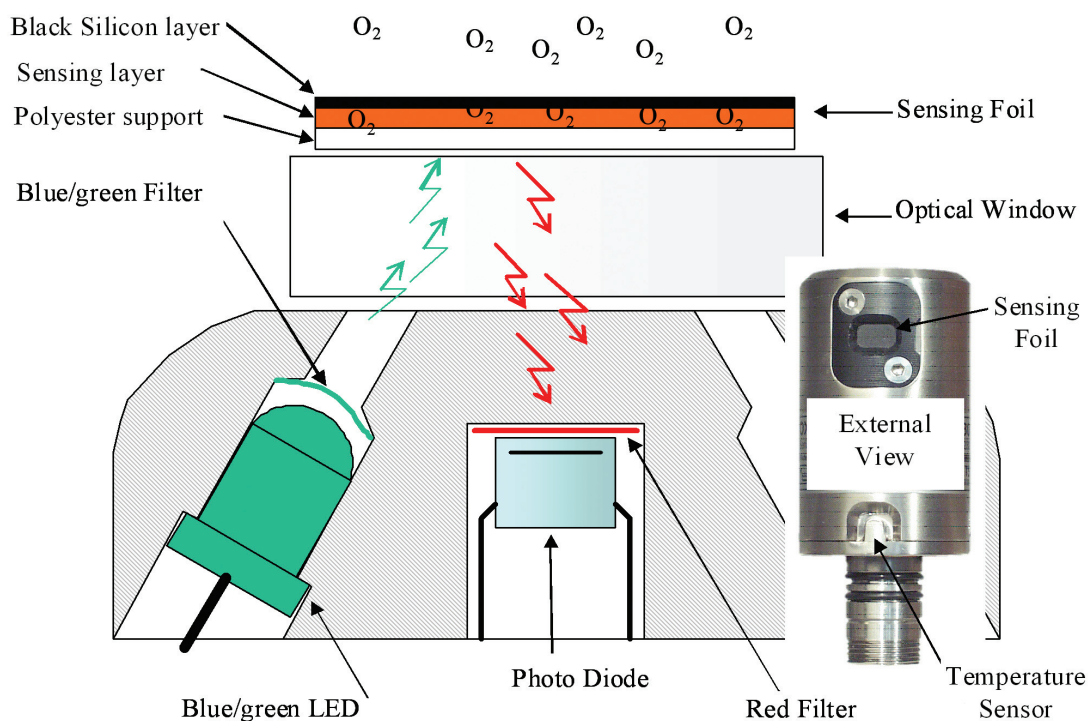


Fig. 1. Optical design and an outside view of the evaluated optode-based oxygen sensor.

Calibration performance—The response of an optode is such that it yields the highest sensitivity at low oxygen concentrations, following the Stern-Volmer equation (e.g., Demas et al., 1999). The response is also affected by temperature, which requires compensation in calibrations and measurements. To evaluate the effect of different calibration strategies on sensor accuracy, 2 different procedures were tested (Table 1). The first was a 30-point calibration (5 different temperatures and 6 different oxygen concentrations) of a batch of foils (normally produced in batches of 100) to obtain foil-specific calibration constants. These were stored in the sensor processor when the foil was mounted. Then a 2-point calibration was performed at 0% and 100% air saturation, taking into account the prevailing air pressure. The batch constants and the 2-point calibration were used together to fit the Stern-Volmer equation to the particularities of the foil and the sensor. This is the calibration procedure used when these sensors are produced.

A second set of calibrations were performed on 20 different sensors to assess if (and how much) the accuracy could be improved by making an individual sensor-specific 30-point calibration with the foil mounted from the start. This method is more time consuming, since every sensor has to go through an elaborate calibration procedure, but it is likely to better account for individualities of sensors and foils.

Cross-sensitivity, pressure hysteresis, and response time—The solubility of oxygen in water depends on salinity and temperature (e.g., Weiss, 1970; Garcia and Gordon, 1992). This means that in absolute concentration a seawater sample will contain

less oxygen than a freshwater sample at the same temperature, although the partial pressure is the same (e.g., 100% saturation). In theory, both electrochemical sensors and optodes measure partial pressure, which implies that salinity and temperature corrections have to be done to obtain absolute values. To validate if such relatively simple corrections are sufficient to get an accurate response or if other factors also can have an effect, multivariate statistical methods can be used (e.g., Francois et al., 2002; Bourget et al., 2003; Haus et al., 2003). In Bertsson et al. (1997), one type of electrochemical oxygen sensor was tested with such methods for simultaneous changes in oxygen concentration, temperature, salinity, pressure, stirring, and pH in 19 different experiments.

In this study we used the same methods as described in Bertsson et al. (1997) but with higher pressure levels of 1, 250, and 500 bar (Table 1). To perform these tests under controlled conditions, we constructed an experimental chamber that can be placed inside a pressure tank (Fig. 2).

A set of separate pressure tests were performed on the optodes, using the same equipment as described in Fig. 2, to evaluate the effects of high pressure and rapid pressure cycling. The pressure was varied in cycles from 3 to 405 bar. Pressurizing from 3 to 405 bar took approximately 4 minutes. The return to 3 bar was done by opening the valve of the pressure chamber and took less than 1 minute.

The response time was assessed with 2 different foils, one with and the other without optical isolation. It should be noted that there is no standard way of testing the response time, and

Table 1. Description of different optode tests and their major conclusions.

Test (number of sensors used)	Test (test period)	Location; equipment	Main physical settings* O=O ₂ ; T=Temp pH=pH; P=Pres Sa=Salinity; St=Stirring	Comparisons with other methods	Major conclusions	Data in figure no.
1 (~20)	Accuracy of different calibration methods (5 days)	Lab; mass flow controllers, thermobath	O:0-500, T:2-40 pH:7 P:1 Sa:0 St:From gas mix	Concentration is known from the gas mix	Batch calibration: accuracy $\pm 5 \mu\text{M}$; individual calibration: accuracy $\pm 2 \mu\text{M}$; precision $\pm 1 \mu\text{M}$	Not shown
2 (3)	Multivariate calibration (10 days)	Lab; incubation device, pressure chamber	O:0, 115, 230; T:6,13,20 pH:5,6.5,8; P:1,250,500 Sa:0,17,34 St:0,25,50 RPM	Winkler	Salinity influence, corrected with standard equations; pressure effect 4% per 100 bar, linear; no sensor is individual	Figs. 2, 3A, 3B
3 (3)	Pressure cycling (1 day)	Lab; incubation device, pressure chamber	O:380; T:7 pH:7; P:3-405 Sa:0 St:0 RPM	No	Pressure effect 4% per 100 bar, linear, no remaining pressure effects (hysteresis); no sensor is individual	Figs. 2, 4
4 (3)	Response time of isolated and nonisolated foils (1 day)	Lab; air and N ₂ bubbled water	O:0, 284; T:20 pH:7; P:1 Sa:0 St:from bubbling	No	Isolation: $t_{67}=23 \text{ s}$, $t_{90}=47 \text{ s}$, $t_{99}=95 \text{ s}$; no isolation: $t_{67}=6 \text{ s}$, $t_{90}=10 \text{ s}$, $t_{99}=18 \text{ s}$	Not shown
5 (1)	Long-term stability (600 days)	Off Canada in Labrador Current; on Argo float	O:295; T:3 pH:ND; P:180 Sa:35 St:Natural circulation	Water horizon with constant oxygen concentration	No drift detected; average oxygen concentration = $295 \mu\text{M}$; SD = $0.7 \mu\text{M}$; values = 80 samples	Fig. 5
6 (1)	River fouling sensitivity (20 days)	Orge River (France); monitoring station	O:170-300; T:15-22 pH:ND; P:1 Sa:0 St:Natural circulation	Electrochemical sensor	Electrochemical sensor affected by fouling after 2 days; naked optode no influence of fouling within 20 days	Fig. 6
7 (2)	Waste water fouling sensitivity (90 days)	Various waste water treatment plants	O:0-150; T:10-25 pH:ND; P:1 Sa:0 St:Natural circulation	Several electrochemical sensors	Naked optode stable 14 days; copper plate has no effect; with water jet stable more than 90 days	Not shown
8 (1)	Slurry of livestock waste (2 hours)	Bioreactor	O:0-90; T:35 pH:ND; P:2 Sa:0 St:no	No	Above 6% total solids the mixing in the slurry is not sufficient to achieve good readings	Not shown
9 (1)	On-line ship system accuracy (35 days)	R/V <i>Meteor</i> expedition; Brazil-Africa; flowthrough	O:190-215; T:26-30 pH:ND; P:2 Sa:31-36 St:Throughflow	Winkler	50400 values, no spikes average difference Winkler-Optode $0.9 \mu\text{M}$; SD = $1.1 \mu\text{M}$; Winkler values = 72	Fig. 7
10 (1)	Profiling on CTD accuracy (10 hours)	Off Guinea; optode logger on CTD with bottles	O:17-233; T:2-28 pH:ND; P:1-550 Sa:33-26 St:Natural circulation	Winkler	High correlation Winkler and Optode Average difference = $2.1 \mu\text{M}$; SD = $5.1 \mu\text{M}$; Winkler values = 14	Fig. 8

*Oxygen concentrations in $\mu\text{mol/l}$; temperature in $^{\circ}\text{C}$; pressure in bar; and salinity in ppt.

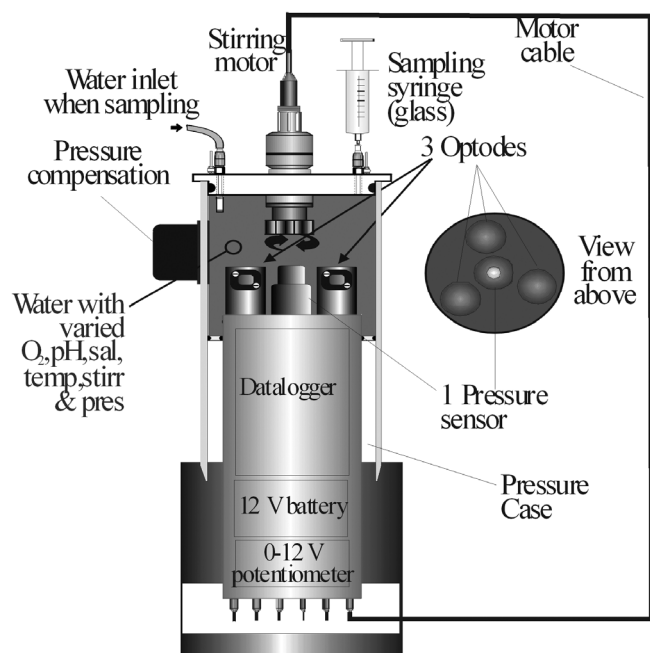


Fig. 2. Setup used for multivariate calibration and for pressure testing of 3 optodes in parallel. Temperature is measured by the optodes and pressure by a separate pressure sensor placed in the center of the top plate.

the results obtained depend to a large extent on how the tests are done. In our case, we simply moved the sensors, without wiping the water off, between 2 containers, one that was air saturated and the other depleted in oxygen through stripping with N_2 gas.

Long-term stability—The amplitude of the red luminescent signal (see Fig. 1) should not be of importance if a lifetime-based detection method is used. So if the foil is bleached/degraded over time (which it will be) or the optical properties of the system change, for example with changes in temperature, the response should not be affected. To evaluate long-term stability, we performed several laboratory and field evaluations. Data for one such evaluation that lasted for 580 days was collected by an optode mounted on a profiling Argo float. These floats are autonomous and freely drifting in the oceans. Today there are about 1900 units in operation (<http://www-argo.ucsd.edu/>, accessed Jan. 24, 2006). The floats can change their buoyancy and hence move up and down in the water column while collecting data (salinity, temperature, and more recently, also oxygen). When the float is at the surface, it transmits data back via satellite. For more information about these floats and their use with focus on oxygen measurements, see Körtzinger et al. (2004a, b).

Sensitivity to biofouling—Biofouling (and bacterial growth) is a major obstacle to long-term monitoring in the aquatic environment. The types of fouling that occur vary greatly from one environment to another, and so do the effects of fouling. To test the effects of biofouling on optodes, we did 3 different evaluations (Table 1).

A network of environmental on-line monitoring stations has been operational in rivers around Paris (River l'Orge) for many years. One of the most important parameters to monitor at these stations is oxygen, which is measured with electrochemical sensors. Oxygen has also been the most labor-demanding parameter, because drifting slime blocks the sensor membranes and rarely allows them to be operational for more than a week. Therefore, during weekly service intervals, the oxygen sensors are taken up, cleaned, and recalibrated (in 2 points). With the aim of prolonging the time between services, an oxygen optode was tested for 3 weeks in parallel with one of the electrochemical sensors. The electrochemical sensor was submitted to its regular weekly service and calibration, while the optode was left untouched for a 20-day test period.

City waste waters have a high content of organic material, microbiological activity is elevated, and the oxygen concentration is a critical element for proper processing. An accurate monitoring of oxygen in wastewater treatment plants is necessary to optimize the relation between cleaning efficiency and energy used for water aeration. Several comparative tests (Table 1) were made with optodes in 2 wastewater treatment plants (in Västerås, Sweden, and Attleboro, Providence, RI, USA). In the aeration basins, the residence time is relatively short (hours), and the bubbling ensures mixing of the water. The fouling consists of high organic content slime. Unprotected optodes were placed in parallel with special process-adapted electrochemical sensor systems with continuous cleaning.

A third and extreme test of the operational ability of the sensor to measure in high content of reactive organic matter (5%-12% weight) was performed in a bioreactor for livestock waste (e.g., Skjelhaugen, 1999). An optode was used in several studies measuring both in the headspace above the waste slurries and directly within them.

Other field applications—We selected two additional examples of data that were collected in the marine environment with the aim of covering a wide range of measuring situations from shallow depth to the deep sea (5500 m), from tropical surface waters with temperatures approaching 30°C to cold abyssal surroundings with temperatures around 2°C , and with oxygen levels ranging from 20 to $230\ \mu\text{M}$. In all cases, the data registered by the optodes were compared with independent measurements of oxygen obtained on collected water samples that were analyzed by Winkler titration.

One data set was collected from a shipboard underway seawater pumping system during a 35-day expedition to the tropical Atlantic Ocean. The other was obtained with a cable-operated profiling conductivity, temperature, and depth (CTD) instrument that was lowered to 5500 m off Guinea in the Equatorial Atlantic.

Assessment

Calibration performance—The individual 30-point sensor calibrations enhanced the accuracy ($\pm 2\ \mu\text{M}$) by approximately a factor of 3 compared to a batch calibration with a subse-

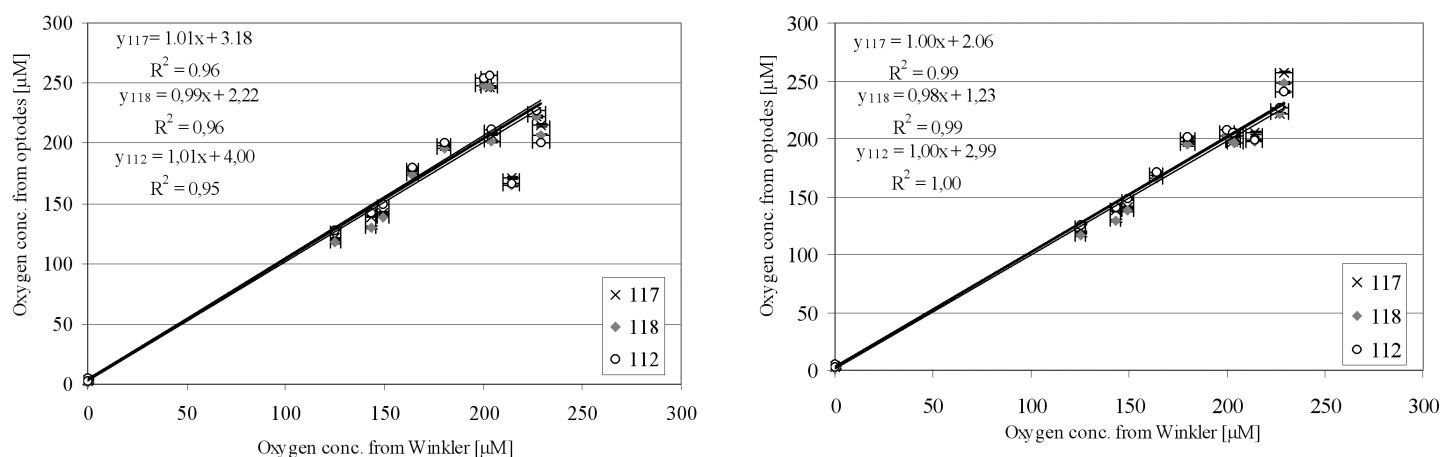


Fig. 3. Results from multivariate calibration experiments. Oxygen readings obtained with 3 parallel optodes plotted against oxygen readings obtained by Winkler titrations. Raw data (A) and data after compensation for pressure (4% per 100 bar) and salinity (according to Garcia and Gordon, 1992) (B).

quent 2-point calibration (Table 1). The reason for the better performance is still unclear and awaits further investigation. The obtained accuracy ($\pm 5 \mu\text{M}$) using a batch-calibrated sensor should be sufficient for most applications, especially in the coastal environment where variations in dissolved oxygen are often large. The absolute precision (resolution) of the sensors was the same regardless of the calibration method. As expected, the sensor performance was better ($\pm 0.5 \mu\text{M}$) at lower oxygen concentrations. At the higher end (300–500 μM), precision was approximately $\pm 1 \mu\text{M}$.

Cross-sensitivity and pressure hysteresis—The outcome of the multivariate calibration was that stirring had no effect, which was expected from earlier work by Klimant et al. (1995), and because the sensor is not consuming any oxygen. Pressure had an influence (about 4% lower response per 100 bar of pressure) but was fully reversible and predictable (i.e., all sensors had the same response). Temperature also has an influence on the optical measurements, but because the optodes described here are equipped with temperature sensors this effect is automatically compensated for by the internal processor and no remaining influence of temperature could be distinguished (which also indicates that the temperature compensation was done correctly). Figure 3A gives raw data from the 3 different sensors that were run in parallel during the multivariate evaluations. Figure 3B shows the data after a general compensation for salinity (according to Garcia and Gordon, 1992) and pressure.

Repeated pressure cycling between 3 and 405 bar confirmed the pressure effect of 4% lower response per 100 bar and also demonstrated that rapid pressure cycling did not leave any remaining pressure effects (hysteresis) on the sensors (Fig. 4).

Potentially other substances present in natural waters could interfere with the oxygen measurements. Contamination by hydrogen sulfide (H_2S) is a major concern when using electrochemical sensors in oxygen-depleted environments. H_2S has no influence on the response of the optodes and it will not damage them in any way (Klimant et al., 1995). The only

interferences (cross-sensitivity) are found with gaseous sulfur dioxide (SO_2) and gaseous chlorine (Cl_2).

The 90% response time of the sensors was approximately 45 seconds for the optically isolated foils ($t_{90} = 45 \text{ s}$) and 10 seconds for the foils without optical isolation.

Long-term stability—Figure 5 presents 580 days of oxygen and density data from one of the Argo floats that was drifting off the east coast of Canada, most of the time in the Labrador Current. Data were collected every time the float passed 1800 m depth. At this depth and in this region, previous investigations have demonstrated that the density and oxygen conditions should be constant. This is confirmed by the collected data, which gave relatively constant readings for density and oxygen ($295.0 \pm 0.7 \mu\text{mol L}^{-1}$); no drift in the oxygen readings could be detected. Only at the end of the deployment (after about 400 days), when the float moved out of the Labrador Current, was there a small and expected shift in oxygen and density values.

Other data sets (not presented here) from continuous field measurements for periods of 10 to 20 months (e.g., RAFOS floats; <http://www.po.gso.uri.edu/rafos/>, accessed Jan. 24, 2006) have also indicated no drift, giving reason to believe that the stability of these sensors is at least 600 days and probably longer.

Sensitivity to biofouling—A direct side-by-side comparison of an electrochemical sensor with an optode at a river monitoring station demonstrated that in spite of becoming covered with slime only after 2 to 3 days, the optode was stable for the whole 20-day test period. In general, the electrochemical sensor started to drift toward lower values after 2 to 3 days. After cleaning and recalibration, it returned to readings similar to the optode recordings (Fig. 6). Measured oxygen concentrations in the river followed the daily variations in temperature. When the water became colder during night, the oxygen solubility increased, leading to higher concentrations. During daytime the temperature increased, and the oxygen level dropped. In this particular case, fouling did not have any detectable influence on the optode. There are other river examples (data

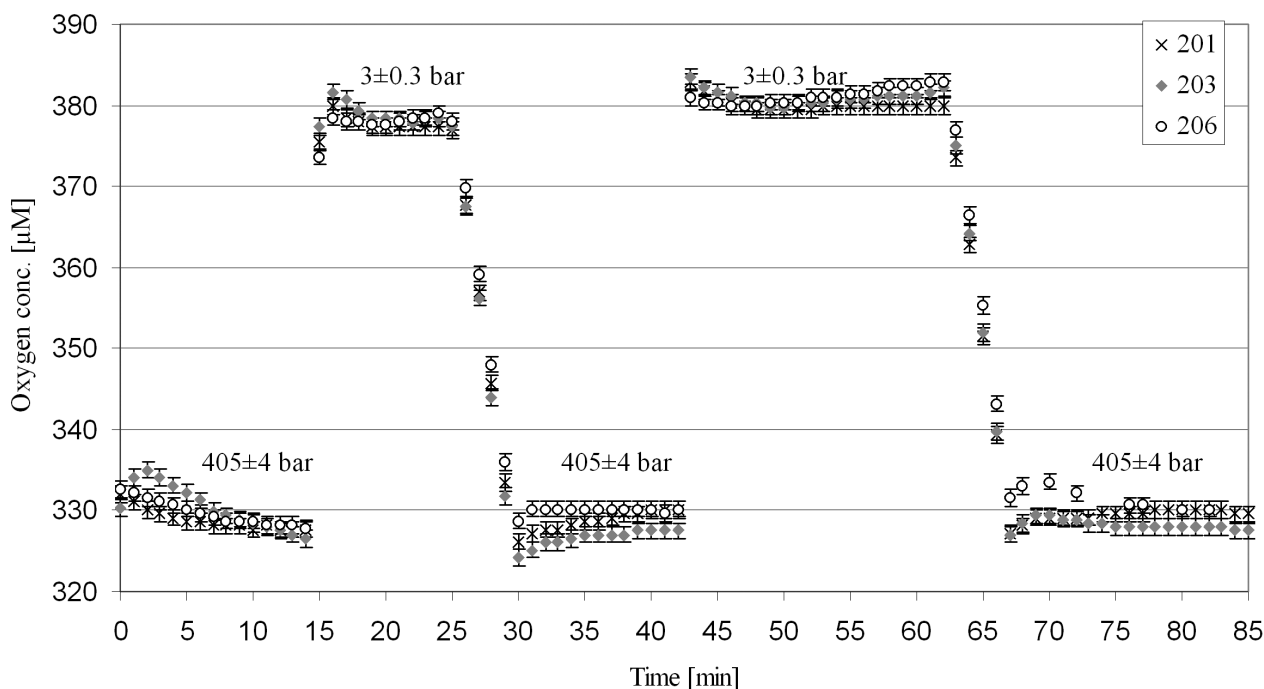


Fig. 4. Oxygen readings from 3 optodes during pressure cycling between 3 and 405 bar. The pressurization (from 3 to 405 bar) took approximately 4 minutes. The depressurization lasted approximately 1 minute.

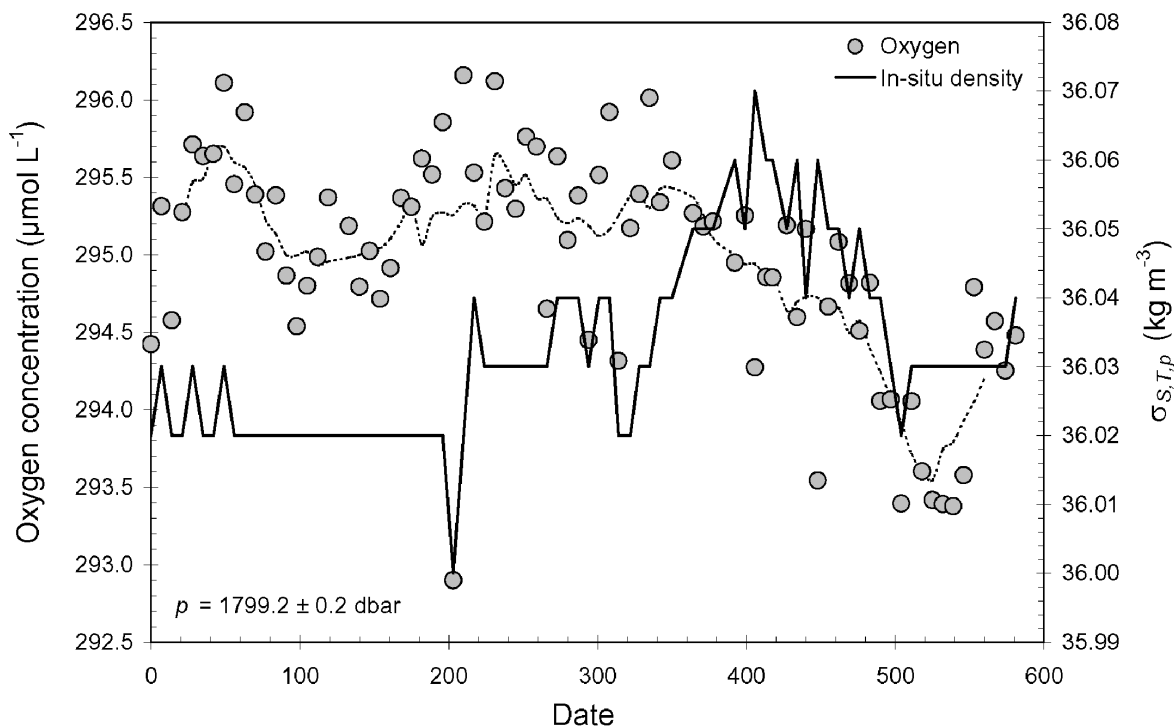


Fig. 5. Oxygen and density data collected over 580 days from a free-drifting Argo float off the east coast of Canada in the Labrador Current; oxygen readings as the float passed at 1800 m depth. As long as the float was in the Labrador Current (the first 400 days), salinity, temperature and oxygen readings at this depth should be constant; the data demonstrate no drift over the given time period. As the float moved out of the Labrador Current, the oxygen and density readings shifted slightly. The average oxygen readings during the whole period were $295.0 \pm 0.7 \mu\text{mol L}^{-1}$. The dotted line is a 7-point centered running mean of the measured oxygen concentrations.

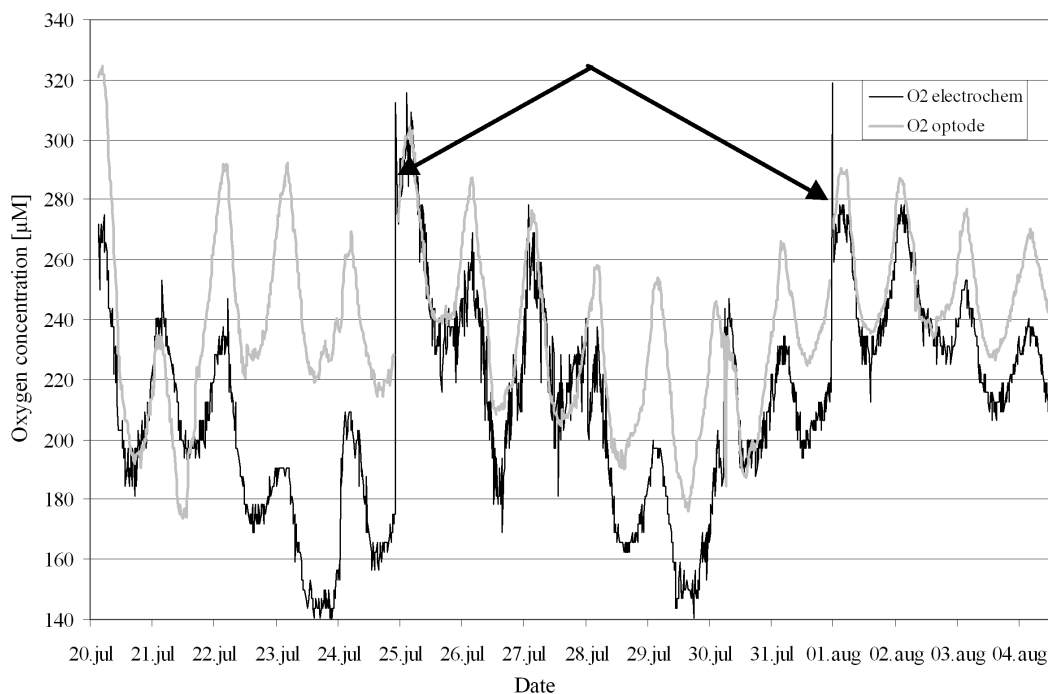


Fig. 6. Oxygen data from a comparison between an optode and an electrochemical sensor at a monitoring station in the River l'Orge (France). Two occasions when the electrochemical sensor was taken up, cleaned, and recalibrated are marked with arrows in the figure. The optode was not cleaned during this experiment.

not shown here), however, in which the slime possibly contained more active microorganisms and the fouling started to affect the naked optode after 14 days (see also examples from wastewater-treatment plants below).

In the aeration tanks of city waste water, unprotected optodes were placed in parallel with special process-adapted electrochemical sensor systems with continuous cleaning. Unprotected optodes gave correct readings on average for 14 days. After that, the microbiological oxygen consumption of the organic material that had accumulated in the small depression in front of the foil (see Fig. 1) resulted in signal drift. The use of a protective copper plate did not help—on the contrary, the mounting of the plate made the particles accumulate faster. To solve the problem, a spray nozzle (normally used to clean cars) connected to a fresh-water garden hose was fitted and directed toward the sensor foil. By turning on the water, the sensor was sprayed/cleaned once every 1 to 2 days and it was continuously operated in this mode for 90 days (data not shown) without any visible fouling effects and without any drift.

After evaluation of an optode in a bioreactor containing slurries of livestock waste, we concluded that in organic waste concentrations below 6% (weight) the sensor was functioning well for time periods of up to 1 week. When introduced into the slurries with concentrations above 6%, the response rapidly dropped to readings close to 0 and stayed at these levels in spite of high levels of aeration. We believe this artifact is caused by an improper mixing of the slurry in the depression just in front of the sensor.

Other field applications—Figure 7 presents a subset of optode data that were collected from a shipboard underway seawater pumping system during a 35-day expedition to the tropical Atlantic Ocean. The two meridional sections along $\sim 26.5^\circ\text{W}$ (southbound) and $\sim 24^\circ\text{W}$ (northbound) show similar oxygen concentrations at 5 m depth in the surface mixed layer. The corresponding saturation level is 101.5% to 104.5%. The observed variability is mainly due to small-scale patchiness of phytoplankton (confirmed by separate samples) but also exhibits some diurnal cyclicity. Oxygen concentrations from Winkler titration of samples taken regularly from 5-m depth hydrocasts along the 2 transects are in good agreement with the optode data (offset = $0.9\ \mu\text{M}$, rms = $1.1\ \mu\text{M}$). Winkler samples were also taken regularly from the underway pumping system, but these discrete samples show frequent contamination by small air bubbles and are therefore of inferior quality (data not shown).

Examples of data from the upcast of a CTD-mounted optode, along with Winkler-analyzed data from discrete samples, are presented in Fig. 8. The average difference between the Winkler values and the optode readings was $2.1 \pm 5.1\ \mu\text{M}$. No indications of remaining pressure effects (hysteresis) were discovered, and the sensor was reading $252\ \mu\text{M}$ in the air before the deployment and $253\ \mu\text{M}$ after. Absence of pressure hysteresis was better demonstrated in the pressure cycling test presented above (Fig. 4) and has also been confirmed through numerous other field deployments on profiling CTD instruments (data not shown).

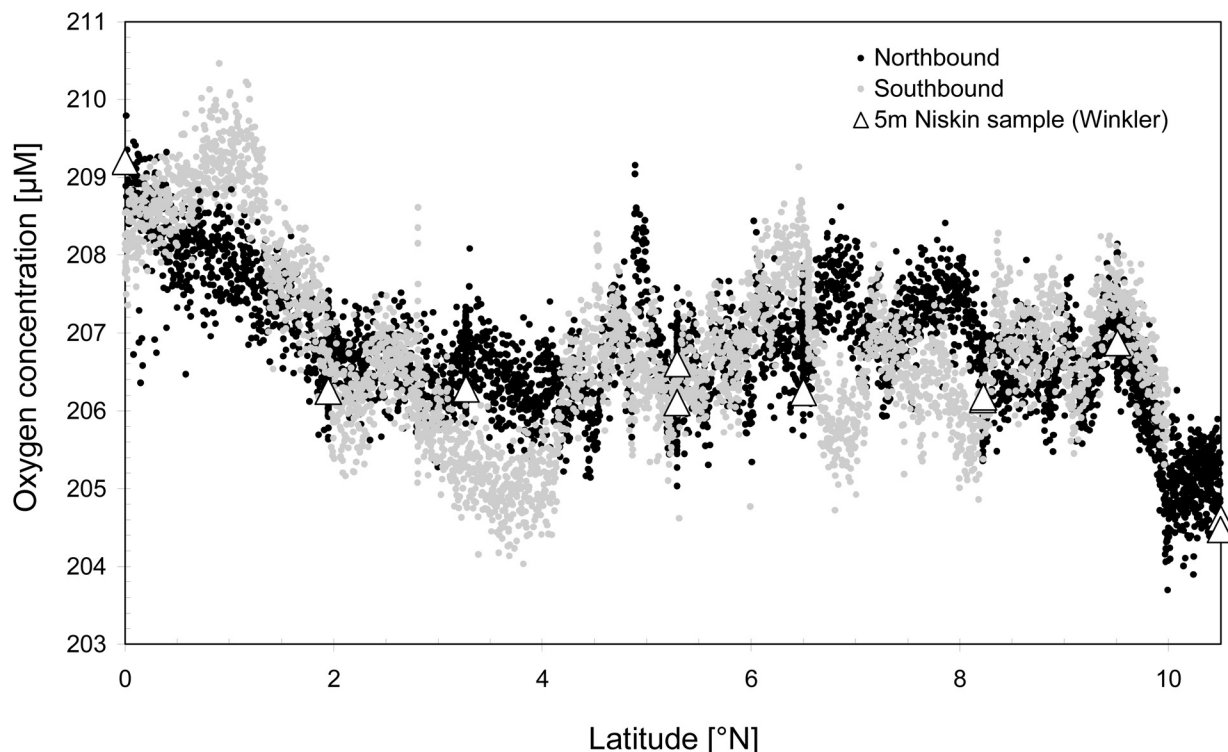


Fig. 7. Surface ocean oxygen data collected during a cruise to the tropical Atlantic Ocean. Optode measurements were made on seawater provided by an underway pumping system; Winkler titrations were made on water samples taken with Niskin bottles from regular hydrocasts from the same depth as the water intake of the pumping system.

Discussion, comments and recommendations

The data presented above strongly suggest that the lifetime-based methodology and the oxygen optode sensors evaluated here are well suited for measurements of dissolved oxygen in the aquatic environment. The performance of this method in general and of this type of sensor in particular has been demonstrated through numerous laboratory and field examples. Compared to the general behavior of electrochemical sensors, the lifetime-based optical technology is superior in all aspects, except for the fast response time that has been demonstrated by electrochemical microelectrodes.

A fast response time is desirable for sensors that are used on profiling CTD instruments (typical descent/ascent rates of 0.5 m/s), on towed vehicles (often towed at 2-5 m/s), and when high-frequency sampling is required to resolve rapid oxygen fluctuations, for example, close to the bottom (e.g., Berg et al., 2003). Electrochemical microelectrodes (e.g., Revsbech, 1989) are unmatched with regard to fast response time, and a well-designed sensor can have a t_{90} of around 0.1 s (Glud et al., 2000). These sensors, however, are not rugged, are difficult to handle, and suffer from the typical limitations of electrochemical sensors (except possibly stirring sensitivity, since the oxygen consumption is low). Microoptodes are easier to

make and more robust than the electrochemical microelectrodes and have shown t_{90} values of around 2 s. Larger electrodes are more rugged but the response times are generally longer. A typical electrochemical macrosensor has a t_{90} of 30 to 120 s, but this can be improved by using thinner membranes (which also makes the sensor more stirring sensitive and noisy). With future development there is potential to improve the response time of the optode foils/sensors, but most likely not to the level achievable with microelectrodes ($t_{90} = 0.1$ s).

In the coastal marine environment, fouling is often a major impediment to monitoring. Unlike the cases described above (rivers and wastewater), the fouling often consists of plants (algae, seaweed, etc.) or animals (e.g., shell-building barnacles). Several trials were done to prevent the effects of fouling on the sensors. The most efficient method developed so far has been to wrap a beryllium-copper alloy net (used for domestic cleaning) around the sensor. In environments with heavy fouling (shallow coastal waters in Chesapeake Bay and the Gulf of Mexico) this method prolonged the service interval from approximately 7 to 10 days to 40 to 60 days. It is important to prevent the beryllium-copper net from contacting the metal of the sensor, since this will create a galvanic element which makes the mesh disappear faster. (It also makes it significantly less efficient in preventing fouling.) Electronic isolation was

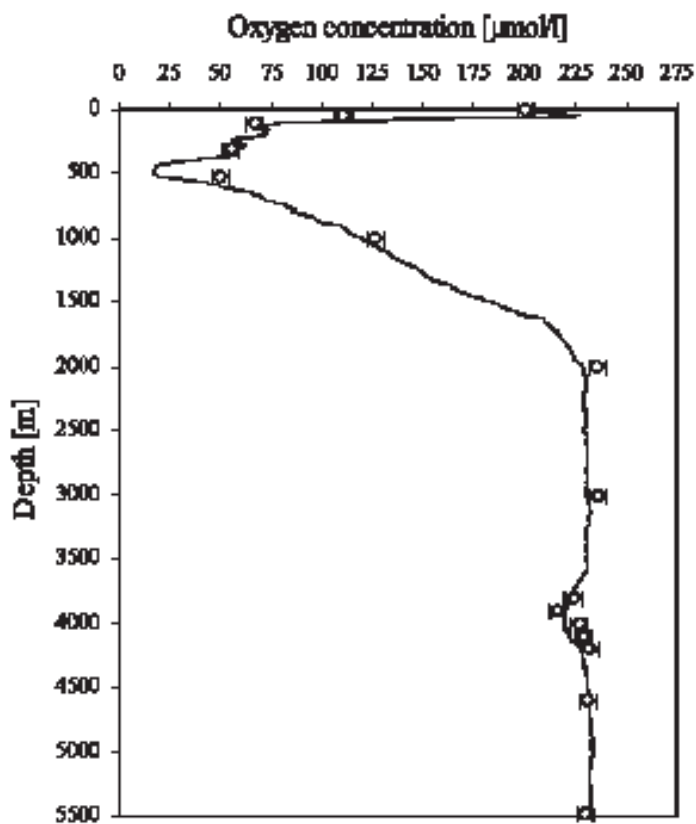


Fig. 8. Optode (continuous line) and Winkler data (dots) from CTD deployment to 5500 m depth in the Equatorial Atlantic off Guinea.

obtained by wrapping tape around the sensor before adding the alloy net. Other solutions, such as fixing a fine-meshed copper plate in front of the foil, have proven inefficient in most situations because the mesh was quickly clogged and prevented a proper water exchange.

It should be noted that all the long-term (1- to 2-year) stability data presented above were collected in environments with low fouling. When fouling is affecting the sensor, such long stability cannot be expected.

The active chemical compound used on this sensor is a platinum porphyrine complex, which yields a longer and more easily detectable lifetime than the more commonly used ruthenium complexes (e.g., Klimant et al., 1996; Stokes and Romero, 1999). Ruthenium-based sensors will likely perform similarly to the sensors tested here, but their accuracy and precision are expected to be lower, due to the shorter lifetime of ruthenium. The pressure behavior might also be different.

A crucial point for the long-term stability of this type of sensor is how strongly the sensing compounds are bound to the support layer and how rapidly they bleach with time (number of excitations). If the sensing substance dissolves with time or if it bleaches rapidly, the long-term stability will be compromised. The technology presented here appears to be stable for years (not yet fully demonstrated) but this is chem-

istry dependent, and the same stability cannot automatically be assumed for other chemistries (e.g., ruthenium complexes or platinum porphyrine complexes with different ligands). Also, the design of the electronic, mechanical, and optical systems differs between sensor makes, and differences in performance should be expected.

This design, with the foil placed in a shallow depression, is not optimal for use in wastewater treatment plants or livestock waste. Organic material accumulates in the depression, the response time becomes longer, and the bacteria change the local oxygen conditions. A leveled mounting of the foil would most likely improve the ability of the sensor in this type of environment, since the accumulation of organic material would become lower.

The oxygen response of an optode is exponential, yielding highest sensitivity at low concentrations. A high sensitivity at low concentrations is important in environments such as ocean oxygen minimum zones, for instance, in the Pacific Ocean and Arabian Sea. A slight change in the ambient oxygen level can make a drastic change in the benthic community, due to different tolerance levels of hypoxia (Levin, 2003).

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