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

A. Tengberg[1,2*], J. Hovdenes[2], J. H. Andersson[3], O. Brocandel[4], R. Diaz[5], D. Hebert[6], T. Arnerich[7], C. Huber[8], A. Körtzinger[9], A. Khripounoff[10], F. Rey[11], C. Rönning[12], J. Schimanski[9], S. Sommer[9] and A. Stangelmayer[8]

[1]Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden
[2]Aanderaa Datainstruments, PO Box 160, Nesttunbrekken 97, NO-5852 Bergen, Norway.
[3]Netherlands Institute of Ecology (NIOO-KNAW), PO Box 140, NL-4400 AC Yerseke, The Netherlands
[4]Nereides, 4 avenue des Indes, FR-91 969 Courtaboeuf, Cedex, France
[5]College of William and Mary, Virginia Institute of Marine Science, P.O. Box 1346, Gloucester Pt., VA-23062, USA
[6]Univ. of Rhode Island, Graduate School of Oceanography, Narragansett, RI-02882, USA
[7]In-Situ Inc, 221 East Lincoln Avenue, Fort Collins, Colorado 80524, USA
[8]PreSens GmbH, Josef-Engert Str. 9, D-93053 Regensburg, Germany
[9]Leibniz-Institut für Meereswissenschaften (IFM-GEOMAR), Düsternbrooker Weg 20, D-24105 Kiel, Germany
[10]IFREMER, centre Brest, BP 70, F-29280 Plouzané, France
[11]Institute of Marine Research, Postboks 1870 Nordnes, N-5817 Bergen, Norway
[12]Department of Ecotechnics, Mid Sweden University, SE-831 45 Östersund, Sweden

*: Corresponding author : anderste@chem.gu.se

Abstract:

In this paper we evaluate the performance of a commercially available life-time based optode and compare it with data obtained with other methods. A set of 11 different tests including targeted laboratory evaluations and field studies were performed covering a wide range of situations from shallow coastal waters and waste water treatment plants to abyssal depths. The principal conclusion reached is that this method, due to high accuracy (±2 µM); long-term stability (more than 20 months); lower fouling sensitivity; no pressure hysteresis and limited cross sensitivity, is overall more suitable for oxygen monitoring than other methods.

Keywords: aquatic systems, oxygen, measure, lifetime-based optode

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In this paper we evaluate the performance of a commercially available life-time based optode and compare it with data obtained with other methods. A set of 11 different tests including targeted laboratory evaluations and field studies were performed covering a wide range of situations from shallow coastal waters and waste water treatment plants to abyssal depths. The principal conclusion reached is that this method, due to high accuracy (±2 μM); long-term stability (more than 20 months); lower fouling sensitivity; no pressure hysteresis and limited cross sensitivity, 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 two-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 the method which 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 common. Electrochemical sensors have been developed and used in a wide range of applications and therefore vary in size and design from micrometer sized glass electrodes to more robust macro electrodes with sensing tips of several centimeters (for a recent 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); Gundersen 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.

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 the aquatic research (e.g. Klimant et al., 1995; Glud et al., 1999; 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 a 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), life-time (how quickly the luminescence dies out) and phase shift (in principle also a life time based measurement, see below *Measurement Principle*). 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 was 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 two dimensions (e.g. Holst et al., 1997, 1998; Glud et al., 1999, 2001, 2005) as well as detection of other substances (e.g. Klimant et al., 2000; Huber et al., 2000, 2001a, 2001b; Hulth et al., 2002; Bültzingslöwen et al., 2002).

In this paper we evaluate a commercially available lifetime-based oxygen optode and compare its performance with different electrochemical sensors and Winkler titrations. 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 electronics (DSP). The construction and working principles of this sensor is described briefly and its accuracy and precision evaluated in the laboratory. The influence of simultaneous changes in oxygen, salinity, temperature, stirring, pressure and pH were tested by using multivariate statistical methods. Data from extended evaluations of pressure behavior as well as response time are presented and discussed. Finally a range of field application examples are given to demonstrate the ability and stability of oxygen optodes in different field settings.

Measurement principle

The particular type of sensor that has been used in this evaluation is commercially available from Aanderaa Instruments, Norway (Oxygen Optode model 3830 and model 3930, Tengberg et al., 2003). The sensor is based on oxygen luminescence quenching of a platinum porphyrine complex. The lifetime 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 with changes in temperature and over time.

The sensing foil is composed of an oxygen sensitive luminescent substance (luminophore) that is embedded in a polymer layer which is coated onto a thin film of polyester support (Fig. 1). The most commonly used oxygen lumniphores have been ruthenium complexes (e.g. Klimant et al., 1996; Stokes & Romero, 1999) but for this sensor an oxygen-sensitive luminophore based on a platinum porphyrine complex, commercial available from PreSens GmbH (Regensburg, Germany) was used mainly due to its longer lifetime (about a factor 5 longer than for ruthenium). 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 two 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.

Results from sensor tests and trials

To evaluate how suitable optodes are for measurements of dissolved oxygen, 11 different tests (see Table 1) using about 70 different sensors were selected from an initial set of 40 datasets.

a) Calibration performance

The response of an optode is giving highest sensitivity at low oxygen concentrations, and follows the Stern-Volmer equation (e.g. Demas et al., 1999). The response is also affected by temperature, which requires compensation in calibrations/measurements. To evaluate the effect of calibration on sensor accuracy two 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 are stored in the sensor processor when the foil is mounted. Then a two point calibration is performed at 0 % and 100 % air-saturation, taking into account the prevailing air pressure. The batch constants and the two-point calibration are together used to fit the Stern-Volmer equation to the particularities of the foil and the sensor. This is the calibration procedure that is presently used when sensors are produced.

A second set of calibrations were performed on 20 different sensors to assess if and by 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.

The individual 30 point sensor calibrations enhanced the accuracy by a factor of approximately 3 compared to a batch calibration with a subsequent two point calibration (Table 1). We have not been able to pinpoint the reason(s) for the improvements but we suspect that the lower accuracy from batch calibrations was caused by a combination of factors: 1. Individual temperature behavior of the foil; 2. Differences in the lifetime between foils, even though the foils are produced in batches of 100; 3. Differences in the electronic and optical properties between sensors, even if the sensors are produced in batches of 25. The obtained accuracy (±5µM) using a batch-calibrated sensor should be sufficient for most applications, especially in the coastal environment were 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 (± 0.5 µM) at lower oxygen concentrations. At the higher end (300-500 µM) precision was approximately ± 1 µM. A major advantage of the optode is that it is more accurate at lower concentrations for which Winkler titrations are more difficult, due to the risk of contamination.

b) Physical and chemical cross sensitivity

The solubility of oxygen in water is dependent 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 correction has to be done to obtain absolute values. To validate if such relatively simple corrections are sufficient to get an accurate response or if also other factors 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 Berntsson et al. (1997) electrochemical oxygen sensors were tested for simultaneous changes in oxygen concentration, temperature, salinity, pressure, stirring and pH in 19 different experiments. Only pH did not have an influence on the sensor response. All the other factors affected the sensor readings in a complex interrelated manner.

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

The outcome was that stirring had no effect, which was expected from earlier work by Klimant et al. (1995) and since the sensor is not consuming any oxygen. This is an advantage and also explains why optodes are less sensitive to fouling (see field data below) as compared to the oxygen consuming electrochemical sensors. Pressure had an effect (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 since 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 three different sensors that were run in parallel during the multivariate evaluations. Figure 3B shows the data after a general salinity (according to Garcia and Gordon, 1992) and pressure compensation.

A set of separate more detailed pressure tests were performed, using the same equipment as described in Fig. 2, to evaluate the effects of high pressure and rapid pressure changes. These evaluations confirmed the above described pressure effect of 4 % lower response per 100 bar and also demonstrated that rapid pressure cycling from 3 to 405 bar and back did not leave any remaining pressure effects (hysteresis) on the sensors (Fig. 4). Pressure hysteresis is a know problem for electrochemical sensors which limits the usefulness of this technology at high pressure (e.g. above 100 bar).

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 sensors can also be used in methanol- and ethanol-water mixtures as well as in pure methanol and ethanol. It is recommended to avoid other organic solvents, such as acetone, chloroform or dichloromethane, which may swell the sensor's foil matrix (data not shown).

c) Response time

A fast response time is a requirement for sensors that are used on profiling CTD instruments (typically descending/ascending at 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 90 % response time (t_{90}) of around 0.1 s (Glud et al., 2000). These sensor are however not rugged and difficult to handle and they 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 these have shown response times (t_{90}) of around 2 s. Larger electrodes are more rugged but the response times are generally longer. A typical electrochemical macro-sensor has a t_{90} of 30-120 s but this can be improved by using thinner membranes (which also makes the sensor more stirring sensitive and noisy). The response time of the optodes used in this study were tested with two different foils one which was optically isolated ($t_{90} = 47$ s) and one without optical isolation with a $t_{90} = 10$ s. It should be noted that there is no standard way of testing the response time and the results obtained are to a large extent dependent on how the tests were done. In our case we choose to simply move the sensors, without wiping the water off, between two containers one which was air saturated and the other depleted in oxygen, through stripping with N_2 gas. If the sensor is wiped off before being submerged into a new container the thin water film in contact with the foil is eliminated and the response time drops by approximately a factor 3. We have, however, chosen to use the conservative values here since we believe that this test method is more representative to what is happening in the field, e.g. when profiling through the water column. While a t_{90} of 10 s should be sufficient for most applications a t_{90} of 47 s is probably to slow for many profiling applications, especially when passing through sharp gradients in the water column. It is likely that the response time of these sensors could be improved by optimizing the foil and sensor design for this particular purpose.

d) Long-term stability

The amplitude of the red luminescent signal (see Fig. 1) should not be of importance if a life time 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 the long-term stability several laboratory and field evaluations were performed. Two are presented here each one which lasted for about 600 days (Table 1).

The first dataset was collected from an optode that was 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/). 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 they transmit data back via satellite. For more information about these floats and their use with focus on oxygen measurements see Körtzinger et al. (2004a,b).

Fig. 5 presents 580 days of oxygen and density data from one of these floats that was drifting off the east coast of Canada, most of the time in the Labrador Current. The data are collected every time the float is passing at 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 density and oxygen (295.0 ± 0.7 µmol L^{-1}) readings. No drift in the oxygen readings could be detected it is only at the end of the deployment (after about 400 days) when the float has moved out of the Labrador Current that there is a small and expected shift in oxygen and density values.

Another data set which also gives an indication of the long-term stability of this technology was collected by 37 so called Rafos floats (http://www.po.gso.uri.edu/rafos/). These floats are also free drifting but do not make profiles. They follow density layers and collect data every 12 h. The normal deployment time is 600 days and when this period is over the floats rice to the surface were they transmit data to the office via satellite. In the beginning of 2003 fifty optode equipped Rafos floats were launched at the south of the Canary Islands (east Atlantic). Thirty-seven of these floats were operating for 600 days and then returned to the surface. At the surface they were also collecting and transmitting data. The position of the oxygen optodes on these floats is about 2 m below the surface. Since all of these floats surfaced in an oligotrophic (nutrient depleted) area little primary production is expected and the oxygen saturation should be close to 100 %. The data in Fig. 6 are collected from 5 days of measurements in the surface layer just after the floats arrived to the surface. Although all the floats give readings not far from 100 % differences exist between them. These differences can depend on local variations since they are all drifting at different locations and/or on different calibrations of the float mounted optodes. This data set is not an absolute evidence that the sensors have not drifted over the 600 day deployment period but the results indicate that no or little (less than 5 %) drift has occurred.

Other data sets from continuous field measurements for periods of 10-16 months have also indicated no drift (not presented here) which give reason to believe that the stability of these sensors is at least 600 days and probably longer.

It should be noted that all the above presented stability data were collected in environment with low fouling. When fouling is affecting the sensor such long stabilities can not be expected (see below).

e) 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. It is well known that the electrochemical measuring principle is sensitive to fouling since oxygen is consumed during measurements. If the supply of oxygen is impeded this might results in a sensor drift. Various technical solutions such as wipers, pulsed sensors and slow response sensors with thicker membranes can improve the fouling resistance. Optical sensors are likely to be less sensitive to fouling since they do not consume any of the measured analyte. In order to test this, three different evaluations were done with the aim of covering a wide variety of fouling situations (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 since drifting slime blocks the membrane of the sensors and rarely allows them to be operational for more than one week. Therefore weekly service intervals are conducted. During service the oxygen sensors are taken up, cleaned and a recalibrated (in two points). With the aim of prolonging the time between services an oxygen optode was tested for three weeks in parallel with one of the electrochemical sensors in normal use. The electrochemical sensor was submitted to its regular weekly service intervals while the optode was left untouched for the 20 days test period. Measured oxygen concentrations in the river follow the daily variations in temperature (Fig. 7). When the water becomes colder during night the oxygen solubility increases leading to higher concentrations. During daytime the temperature increases and the oxygen level drops. In spite of becoming covered with slime only after 2-3 days the optode was stable for the whole test period. In general the electrochemical sensor started to drift towards lower values after 2-3 days. After cleaning and recalibration it returned to readings which were similar to the optode recordings (Fig. 7). In this particular case fouling did not have any detectable influence on the optode. There are, however, other river examples (data not shown here) in which the slime possibly contained more active microorganisms and the fouling started to affect the naked optode after 14 days (see also example from waste water treatment plants below).

City waste waters have a high content of organic material, the microbiological activity is elevated and the oxygen concentration is a critical element for proper processing. An accurate monitoring of oxygen in waste water 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 two different waste water treatment plants (in Västerås, Sweden and at the Attleboro waste water treatment plant, Providence, 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. 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 had no effect, on the contrary the mounting of the plate made the particles accumulate faster. To solve this problem a spray nozzle (normally used to clean cars) was fitted and directed towards the sensor foil. The nozzle was connected to a freshwater garden hose. By turning on the water the sensor was sprayed/cleaned once every 1-2 days and it was continuously operated in this mode for 90 days (data not shown) without any visible fouling effects and without any drift.

To increase the agricultural reuse of livestock waste as fertilizers and to decrease the environmental effects when spreading these on the fields different types of bioreactors have been developed and studied (e.g. Skjelhaugen, 1999). In order to optimize the efficiency of the bioreactors and to study the ongoing processes it is desired to monitor the oxygen levels inside the 5-12 % (by weight) livestock waste / water slurries. Previously it has been difficult to use electrochemical sensors here since H_2S is often present and since these sensors are known to be stirring sensitive. An optode was used in several studies measuring both in the headspace above the slurries and directly in the slurries. Measurements in the headspace gave consistent results but when measuring in the slurries with waste concentrations above 6 % it was not possible to conclude anything on the efficiency of the aeration. When introduced into the slurry the sensor rapidly dropped to readings close to 0 and stayed at these levels in-spite of high levels of aeration. We think that the reason for this behavior is caused by an improper mixing of the slurry in front of the sensor. Since the content of organic materials is elevated the oxygen is rapidly consumed and if the aeration is not capable to achieve a proper mixing / aeration in front of the sensor it will measure to low values.

In the coastal marine environment the fouling is often a major impediment to monitoring. Unlike the cases described above (rivers and waste water) the fouling often consists of plants (e.g. algae, seaweed etc.) and/or animals (e.g. shell building barnacles). Several trials were done to prevent the effects of fouling on the here described sensor. The so far most efficient method was 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 7-10 days to 40-60 days. It is important to prevent the beryllium-copper net to enter into contact with 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 obtained by wrapping tape around the sensor before adding the alloy net. Other solutions such as a fixing a fine meshed copper plate in front of the foil has proven inefficient in most situations since the mesh was quickly clogged and prevented a proper circulation.

f) Other field applications

We selected two 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 30ºC to cold abyssal surroundings with temperatures around 2ºC and with oxygen levels ranging from 20 to 230 µM. In both cases the data registered by the optodes corresponded well (within the nominal limits of accuracy) with independent measurements of oxygen obtained through Winkler titration.

Figure 8 presents a subset of optode data that were collected from a shipboard underway seawater pumping system during a 35-day expedition of the German R/V *Meteor* to the tropical Atlantic Ocean. The two meridional sections along ~26.5°W (southbound) and ~24 °W (northbound) shows very similar oxygen concentrations at 5 m depth in the surface mixed layer. The corresponding saturation level is 101.5–104.5 %. The observed variability is mainly due to small-scale patchiness of phytoplankton (confirmed by separate samples) but also exhibits some diurnal cyclicity. Oxygen concentration from Winkler titration of samples taken regularly from 5 m hydro cast samples along the two transects are in good agreement with the optode data (offset = 0.9 µM, rms = 1.1 µM). 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).

On-line profiling with cable operated CTD (Conductivity, Temperature and Depth) instruments has been common practice in oceanography for several decades. The combination of real-time data access with the possibility of closing water sample bottles at depths of interest makes such instruments useful in many types of applications. CTDs have been equipped with a whole suite of sensors, e.g. to measure particles in the water, chlorophyll content, pH, current velocity etc. Oxygen, measured with electrochemical sensors, has also been one of the most common parameters to be included on CTD instruments. These sensors demand special attention and frequent recalibrations to be able to give reliable data. Furthermore, when making deep-sea profiles residual pressure effects (hysteresis) frequently causes these sensors to drift and to give unreliable readings.

Examples of data from one CTD mounted optode measurement, along with Winkler analyzed data from discrete samples, are presented in Fig. 9. This Figure shows an oxygen optode profile down to 5500 m off Guinea in the Equatorial Atlantic. Oxygen concentrations obtained by Winkler titrations on collected water samples are also included in the figure. The average difference between the Winkler values and the optode readings was 2.1 ± 5.1 µM. No remaining pressure effects (hysteresis) were discovered and the sensor was reading 252 µM in the air before the deployment and 253 µM after.

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 sensor specifications and performance can be summarized as follows:

- Precision (±1 µM) and accuracy (±2 µM) similar to what can be achieved by Winkler titration.
- Long-term stability for more than 600 days.
- No stirring sensitivity since the sensor does not consume any oxygen
- Temperature has an influence on the luminescence quenching and has to be corrected for. The sensors evaluated here had built-in temperature sensors. The corrections applied are adequate and performed internally and automatically.
- Salinity has to be corrected for by using standard formulas given in the literature (Garcia and Gordon, 1992).
- Pressure has an effect on the sensor response by lowering the signal with 4 % per 1000 m (100 bar) of water depth. This effect is fully and instantaneously reversible (no hysteresis).
- The 90 % response time (t_{90}) is 47 s for optically isolated and 10 s for non-isolated foils.

- This and other studies (Klimant et al., 1995) have demonstrated that there exists no cross sensitivity to, and the sensors do not get damaged by, hydrogen sulfide (H_2S), carbon dioxide (CO_2), ammonia (NH_3), pH, any ionic species like sulfide (S^{2-}), sulfate (SO_4^{2-}) or chloride (Cl^-). The sensors can also be used in methanol-water and ethanol-water mixtures as well as in pure methanol and ethanol.
- Interferences (cross-sensitivity) were found only for gaseous sulfur dioxide (SO_2) and gaseous chlorine (Cl_2).
- Biofouling resistance depends on the environment. In the marine environment longer deployment times (months) can be achieved by wrapping a beryllium-copper alloy net (used for domestic cleaning) around the sensor. In waste water flushing or a redesign of the sensor is needed to achieve longer deployment times.

The performance of this method in general and of this type of sensor in particular has been demonstrated here through numerous laboratory and field examples. When comparing to the general behavior of electrochemical sensors it is clear that the lifetime-based optical technology is superior in every aspect, except for the fast response time that has been demonstrated by electrochemical microelectrodes. With future development there is potential to improve the response time of the foils / sensors but probably not to the level achievable with microelectrodes (t_{90} = 0.1 s). Also when comparing this technology to intensity-based optodes, the lifetime-based measurements have advantages mainly in terms of stability.

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

A crucial point for the long-term stability of this type of sensors 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 chemistry dependent and the same stability can not automatically be assumed for other chemistries (e.g. ruthenium complexes or platinum porphyrine complexes with different ligands). Also for the electronics, the mechanical and optical systems differences between other makes of sensors should be expected.

Use of this sensor in waste water treatment plants and in live stock waste has demonstrated that this design, with the foil placed in a shallow depression, is not optimal for these types of applications. 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 environments since the accumulation of organic material would become lower.

In conclusion it has been demonstrated here that the lifetime-based sensor technology provides a new potential for accurate long-term measurements of oxygen. This opens new possibilities not only for environmental monitoring and research in lakes, rivers and the coastal environment where oxygen variations are in general large and rapid. It also gives the possibility to use oxygen as a tracer in oceanographic studies and to monitor the open ocean and deep sea environments where changes might take years/decades (e.g. Körtzinger et al., 2004a,b). 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, found in e.g. the Pacific Ocean and Arabian Sea. A slight change in the ambient oxygen level can make a drastic change in the benthic community, due too different tolerance levels for hypoxia (Levin, 2003).

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Table 1: Description of different 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 Fig #**
1 (about 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	Conc. is known from the gas mix	Batch calib:Accuracy ± 5µM Individual calib: Accuracy ± 2µM Precission ± 1µM	Not shown
2 (3)	Multivariate calibration (10 days)	Lab; Incubation device, press. chamb.	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	Sal influence, corrected with standard equations; Press effect 4% per 100 bar, linear; No sensor is individual	Fig.2 Fig.3A Fig.3B
3 (3)	Pressure Cycling (1 day)	Lab; Incubation device, press. chamb.	O:380; T:7 pH:7; P:3-405 Sa:0 St:0 RPM	No	Press effect 4% per 100 bar, linear, no remaining pressure effects (hysteresis). No sensor is individual.	Fig.2 Fig.4
4 (3)	Response time of isolated & non isolated foils (1 day)	Lab; Air & N_2 bubbled water	O:0,284; T:20 pH:7; P:1 Sa:0 St:from bubbling	No	Isolation:t_{67}=23s, t_{90}=47s, t_{99}=95s No isolation:t_{67}=6s, t_{90}=10s, t_{99}=18s	Not shown
5 (1)	Long term stability I (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 const. oxygen	No drift detected Average conc. = 295 µM Standard dev. = 0.7 µM values = 80 samples	Fig.5
6 (37)	Long term stability II (600 days)	Off Guinea in surface water; On Rafos floats	O:228-253; T:28 pH:ND; P:1 Sa:35 St:natural circulation	Surface zone close to 100 % sat	The floats are located at different positions. They give different saturation values 94-104 %. No indication of drift.	Fig.6
7 (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	Electro-chemical sensor	Electrochemical sensor affected by fouling after 2 days; Naked Optode no influence of fouling within 20 days	Fig.7
8 (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 Electro-chemical sensors	Naked optode stable 14 days. Copper plate has no effect. With water jet stable more than 90 days	Not shown
9 (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 sufficent to achieve good readings	Not shown
10 (1)	On-line ship system accuracy (35 days)	R/V Meteor expedition; Brasil-Africa; Flowthrough	O:190-215; T:26-30 pH:ND; P:2 Sa:31-36 St:throughflow	Winkler	50400 values, no spikes Aver. diff. Winkler-Optode 0.9 µM, Standard dev. = 1.1 µM Winkler values = 72	Fig.8
11 (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 corr. Winkler and Optode Average difference = 2.1 µM Standard dev. = 5.1 µM Winkler values = 14	Fig 9

* Oxygen Concentrations given in µmol/l; Temperature in degrees C; Pressure in bar and Salinity in ppt

Figure legends

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

Figure 2. Set-up that was used for multivariate calibration and for pressure testing of three optodes in parallel. Temperature is measured by the optodes and pressure by a separate pressure sensor placed in the center of the top plate.

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

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

Figure 5. Five hundred and eighty days of oxygen and density data collected from a free drifting Argo float off the east coast of Canada in the Labrador Current. The presented data shows oxygen readings as the float passes at 1800 m depth. As long as the float was in the Labrador Current (the first 400 days) it is considered that salinity and temperature and oxygen readings at this depth should be constant. The data demonstrates no drift over the given time period but as the float moves out of the Labrador Current the oxygen and density readings shift slightly. The average oxygen readings during the whole period were 295.0 ± 0.7 μmol L^{-1}.

Figure 6. Five day average of oxygen saturation values recorded with optodes mounted on 37 Rafos floats drifting at the surface at different locations off Guinea (East Atlantic). The data were recorded after each of the floats had accomplished a 600 day deployment in deeper layer. The optodes were mounted approximately 2 m below the surface. Since all

the floats are drifting in oligotrophic waters with low production/consumption oxygen saturation values around 100 % should be expected.

Figure 7. 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 never cleaned during this experiment.

Figure 8. Tropical 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 whereas Winkler titrations were made on water samples taken with Niskin bottles from regular hydrocasts.

Figure 9. Optode (continuous line) and Winkler data (dots) from CTD deployment to 5500 m depth in the equatorial Atlantic off Guinea.

1 Fig. 1

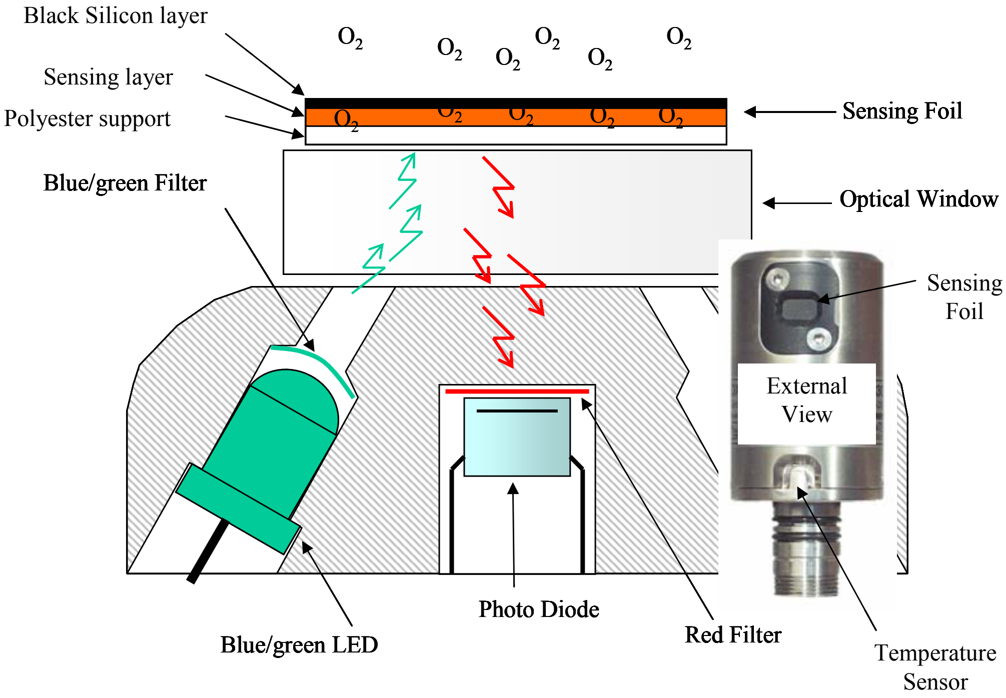

Black Silicon layer
Sensing layer
Polyester support
O_2
Sensing Foil
Blue/green Filter
Optical Window
Sensing
Foil
External
View
Photo Diode
Red Filter
Blue/green LED
Temperature
Sensor

Fig. 2

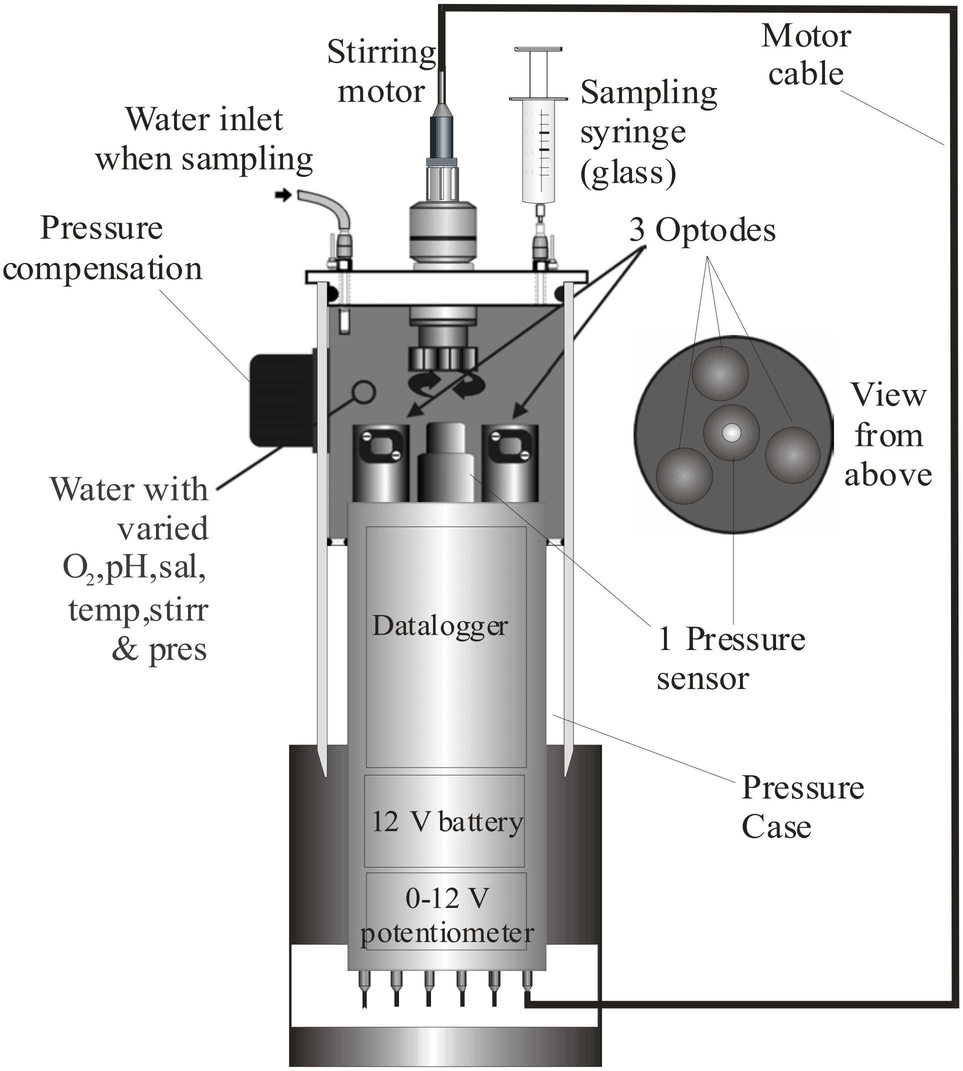
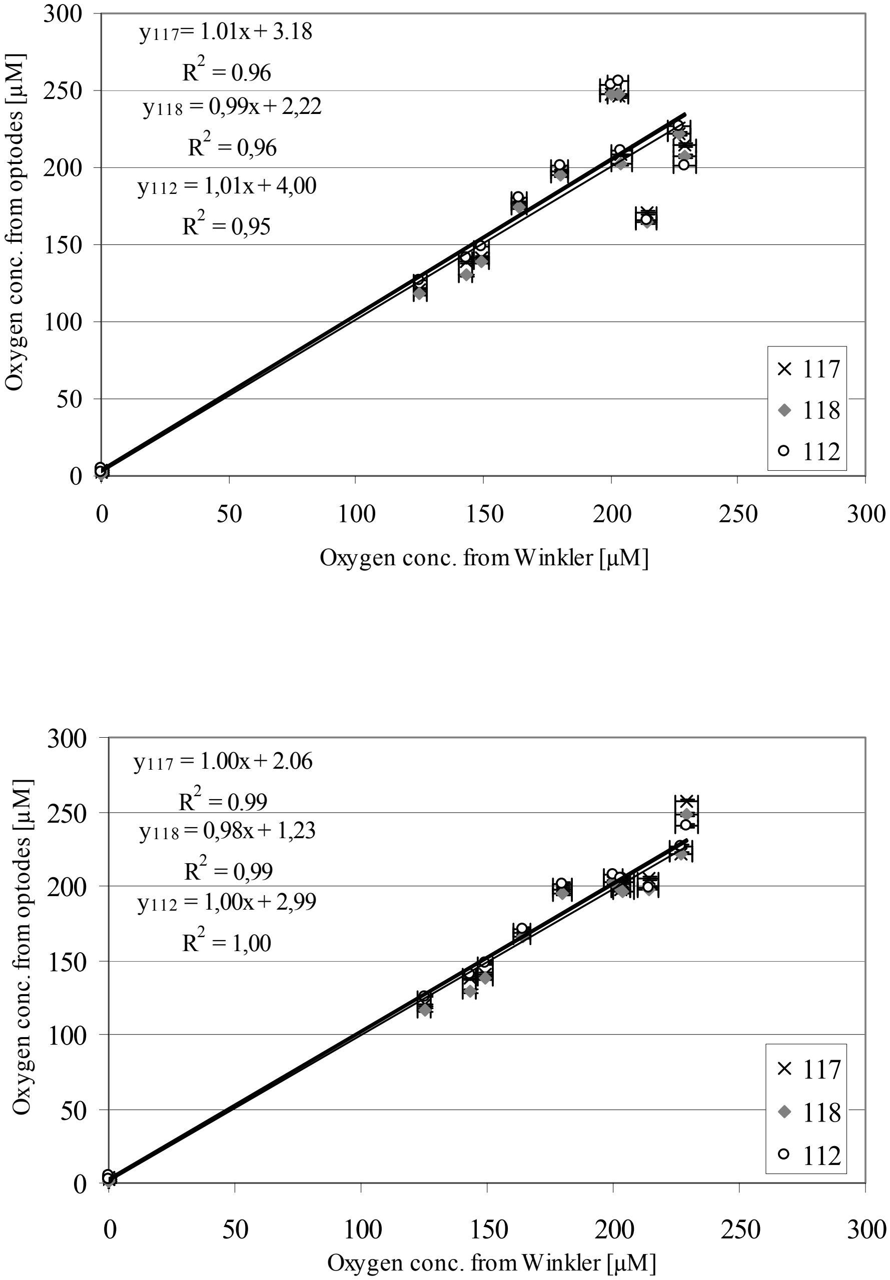

Stirring motor
Water inlet when sampling
Sampling syringe (glass)
Motor cable
Pressure compensation
3 Optodes
View from above
Water with varied O_2,pH,sal, temp,stirr & pres
Datalogger
1 Pressure sensor
Pressure Case
12 V battery
0-12 V potentiometer

Fig. 3A & 3B


y117= 1.01x + 3.18
R2 = 0.96
y118 = 0,99x + 2,22
R2 = 0,96
y112 = 1,01x + 4,00
R2 = 0,95
Oxygen conc. from optodes [µM]
Oxygen conc. from Winkler [µM]
0
50
100
150
200
250
300
× 117
◆ 118
○ 112
y117 = 1.00x + 2.06
R2 = 0.99
y118 = 0,98x + 1,23
R2 = 0,99
y112 = 1,00x + 2,99
R2 = 1,00
Oxygen conc. from optodes [µM]
Oxygen conc. from Winkler [µM]
× 117
◆ 118
○ 112

1 Fig. 4

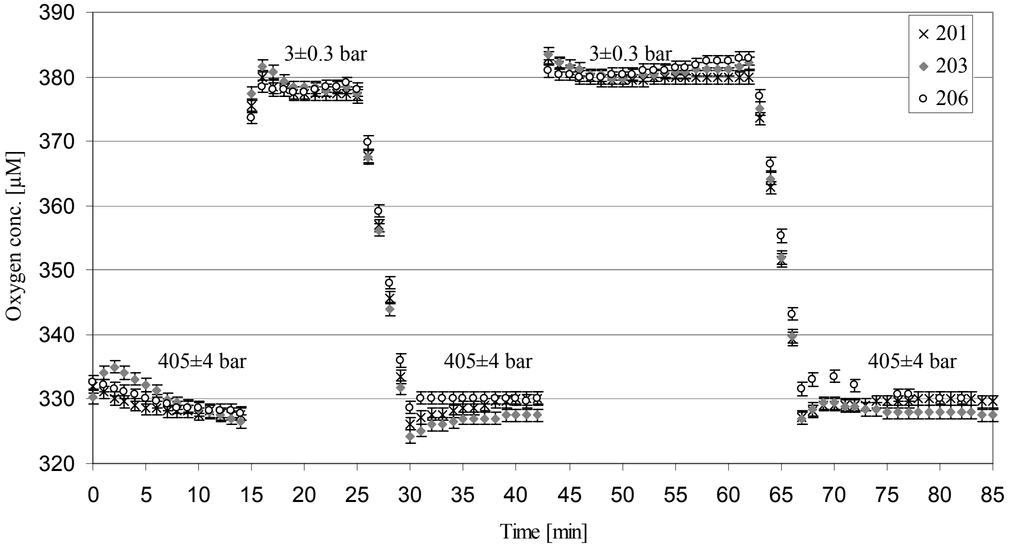
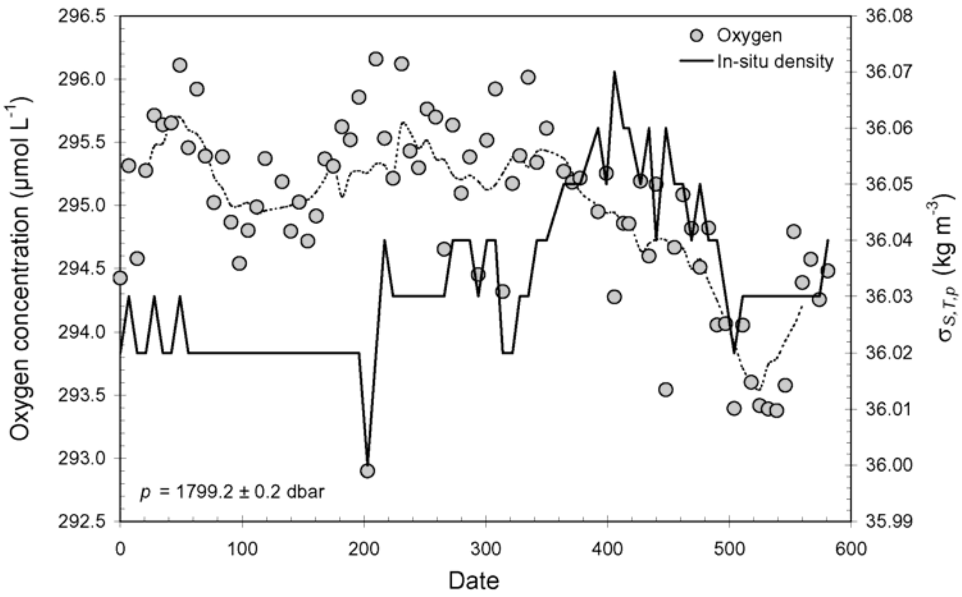

390
380
370
360
350
340
330
320
Oxygen conc. [µM]
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
Time [min]
3±0.3 bar
3±0.3 bar
405±4 bar
405±4 bar
405±4 bar
× 201
◆ 203
○ 206

Fig. 5


Oxygen
In-situ density
Oxygen concentration (μmol L^{-1})
$\sigma_{S,T,p}$ (kg m^{-3})
Date
p = 1799.2 ± 0.2 dbar
296.5
296.0
295.5
295.0
294.5
294.0
293.5
293.0
292.5
36.08
36.07
36.06
36.05
36.04
36.03
36.02
36.01
36.00
35.99
0
100
200
300
400
500
600

1 Fig. 6

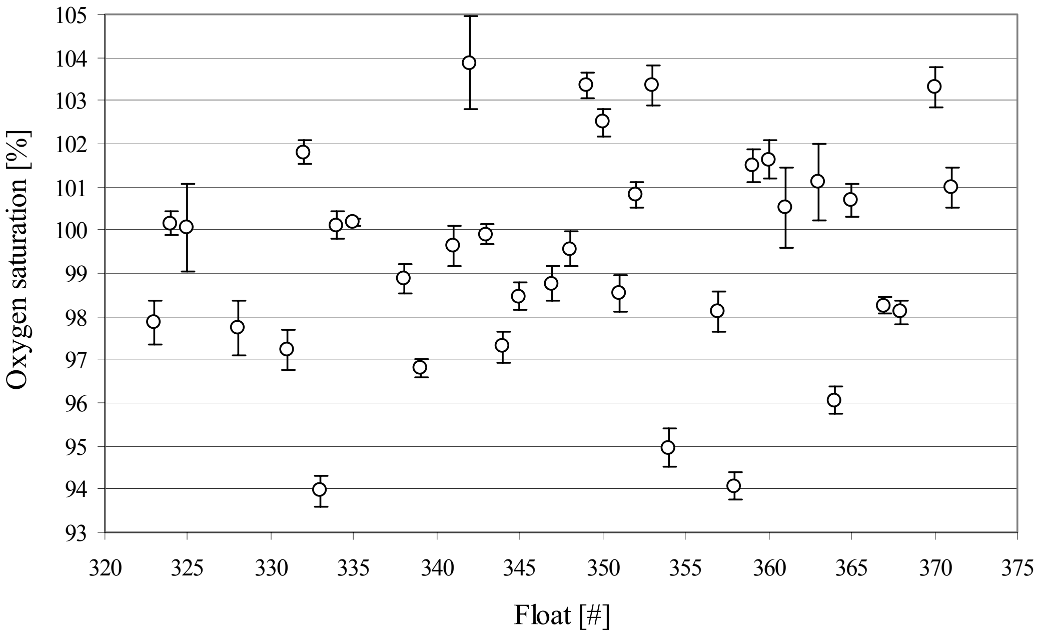
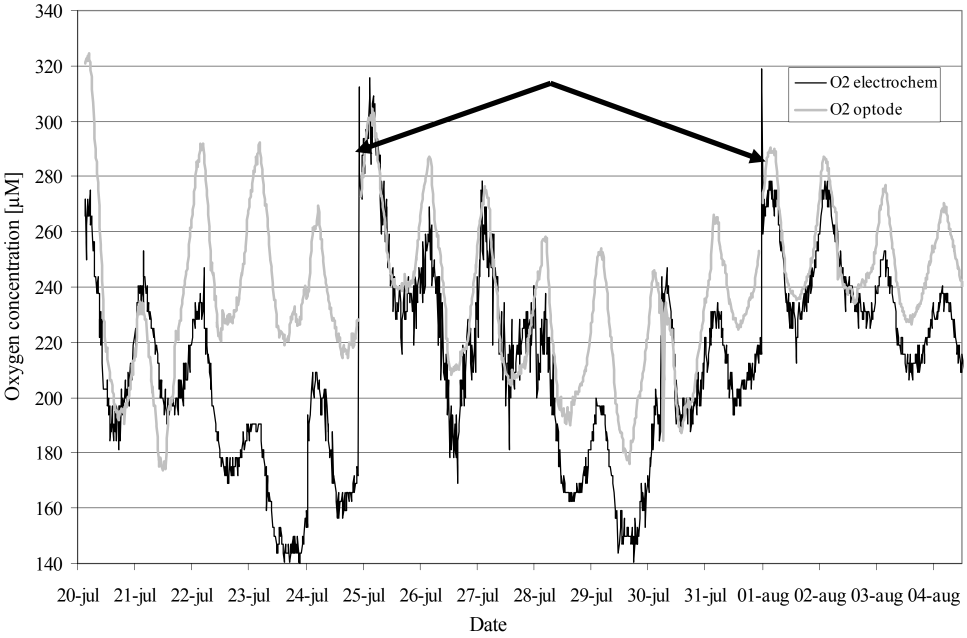
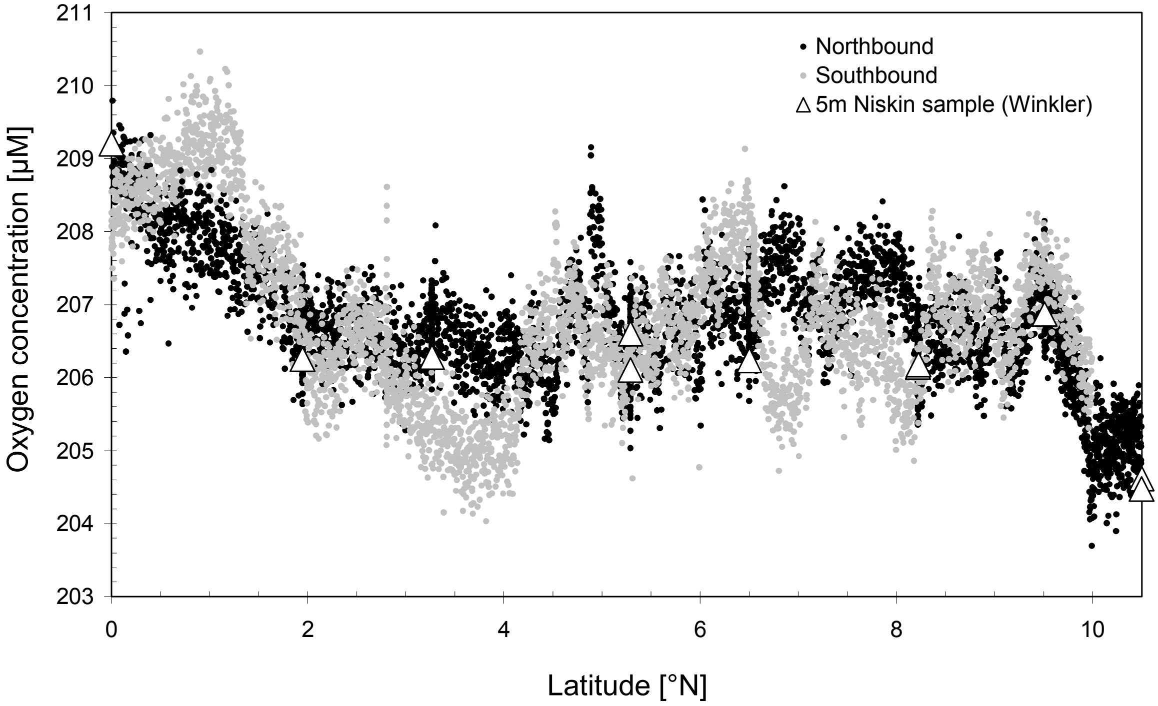

Oxygen saturation [%]
105
104
103
102
101
100
99
98
97
96
95
94
93
320
325
330
335
340
345
350
355
360
365
370
375
Float [#]

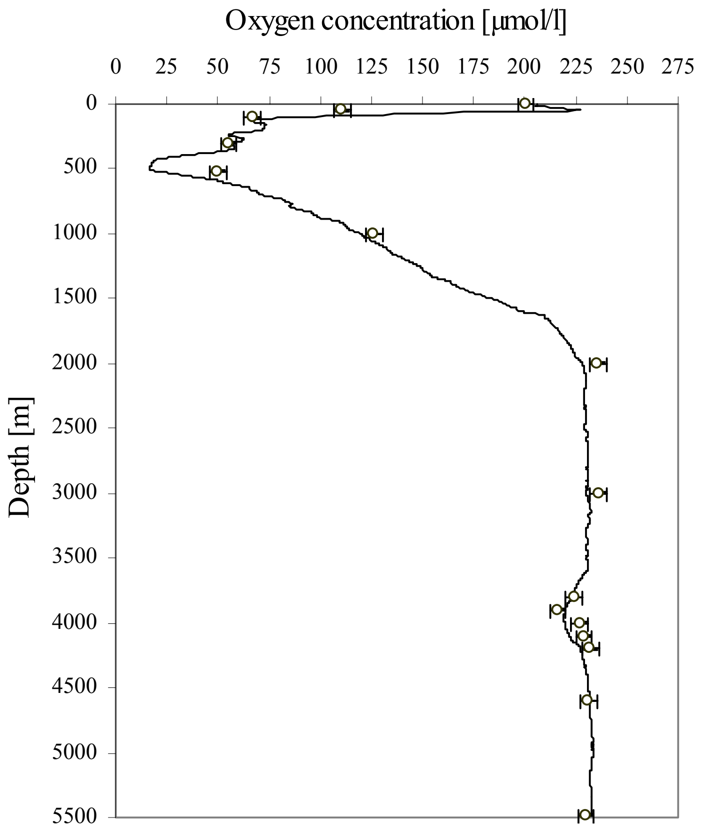
Fig. 7


340
320
300
280
260
240
220
200
180
160
140
Oxygen concentration [µM]
O2 electrochem
O2 optode
20-jul
21-jul
22-jul
23-jul
24-jul
25-jul
26-jul
27-jul
28-jul
29-jul
30-jul
31-jul
01-aug
02-aug
03-aug
04-aug
Date

1 Fig. 8


211
210
209
208
207
206
205
204
203
0
2
4
6
8
10
Oxygen concentration [µM]
Latitude [°N]
● Northbound
● Southbound
△ 5m Niskin sample (Winkler)

1 Fig. 9


Oxygen concentration [µmol/l]
0
25
50
75
100
125
150
175
200
225
250
275
Depth [m]
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500

Appendix 1

Salinity compensation of oxygen readings from optode and calculation of % saturation at a given salinity and temperature (Garcia and Gordon, 1992).

Input variables:

$[O_2]$ = O_2 concentration in µM, from the optode

t = Temperature in degrees Celsius, from the optode temperature sensor

S = Salinity in ppt, from a parallel salinity measurement

Empirical constants:

A_0 = 2.00856

A_1 = 3.22400

A_2 = 3.99063

A_3 = 4.80299

A_4 = 9.78188e-1

A_5 = 1.71069

B_0 = -6.24097e-3

B_1 = -6.93498e-3

B_2 = -6.90358e-3

B_3 = -4.29155e-3

C_0 = -3.11680e-7

Intermediate calculations:

T_s = Scaled Temperature = $\ln\left[\dfrac{298.15-t}{273.15+t}\right]$

$$\alpha = S\left(B_0 + B_1 \cdot T_s + B_2 \cdot T_s^2 + B_3 \cdot T_s^3\right) + C_0 S^2$$

$$\beta = A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 + A_4 T_s^4 + A_5 T_s^5$$

Final results:

Salinity compensated oxygen concentration

O_2 [μM] = *[O_2]* * e^{α}

100 % oxygen saturation with air at a pressure of 1013 mbar:

$O_{2,100\%\ sat}$ [μM] = $e^{(\beta + \alpha)}$ / 2.2414

percent saturation in the given water

$O_{2,sat}$ [%] = O_2[μM] / $O_{2,100\%\ sat}$ [μM]