White paper on dissolved oxygen measurements: scientific needs and sensors accuracy

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Introduction

The objective here is to review the practical accuracy and the precision of the existing oxygen sensors used in oceanography. The idea is to review all oxygen sensors mounted on fixed and lagrangian platforms (mooring, CTD profiler, glider, ARGO floats) used on coastal observatories. This report synthetizes the past experiences and recommendations for a better use of oxygen sensors in order to improve the quality of the oxygen data for scientific exploitations.

1-State-of-arts and scientific needs (accuracy, precision)

Oxygen is a key parameter for biogeochemical cycles and a major player in the carbon system of the ocean (Bopp et al., 2002) as well as the marine nitrogen cycle (Bange et al., 2005). The oxygen concentrations are very sensitive to physical processes as the air-sea fluxes and the interior ocean advection (Karstensen et al. 2008). Consequently, dissolved oxygen is an important parameter for understanding the ocean's role in climate (Joos et al., 2003).

Usually, the rapid exchange of oxygen with the atmosphere reduces the oxygen content of the surface water. A maximum of oxygen is observed when the biological production is present (near the Chl-a maximum depth). Regions with oxygen concentrations below about 10 μmol kg^{-1} are termed suboxic. In suboxic regions, nitrate (if present) becomes involved in respiration (Bange et al., 2005). Anoxic regions have no dissolved oxygen. At present, the intermediate-depth low-oxygen layers, here called the oxygen-minimum zone (OMZ), are suboxic in the eastern tropical Pacific Ocean and the northern reaches of the tropical Indian Ocean and are hypoxic in the tropical Atlantic Ocean (Paulmier et Ruiz-Pino 2009). Despite the important OMZ role for the origin of marine life and for the biogeochemical cycles of carbon and nitrogen, there are some key questions on the structure of OMZs at a global scale. Recently, a criterion has been proposed to characterize the OMZs (Fig.1). It corresponds to regions where O2 concentrations range from less than 20 μmol kg^{-1} to 1 μmol kg^{-1} (CRIO OMZ criterion). In this case, the total surface of the permanent OMZs has been evaluated to 30.4 millions of km^2 (8% of the total oceanic area) with two seasonal OMZs (the West Bering Sea and the Gulf of Alaska). OMZ is defined as being more intense when the O2 concentrations in its core are lower. In this case, our ability to measure accurately low dissolved oxygen concentrations in such regions is essential.
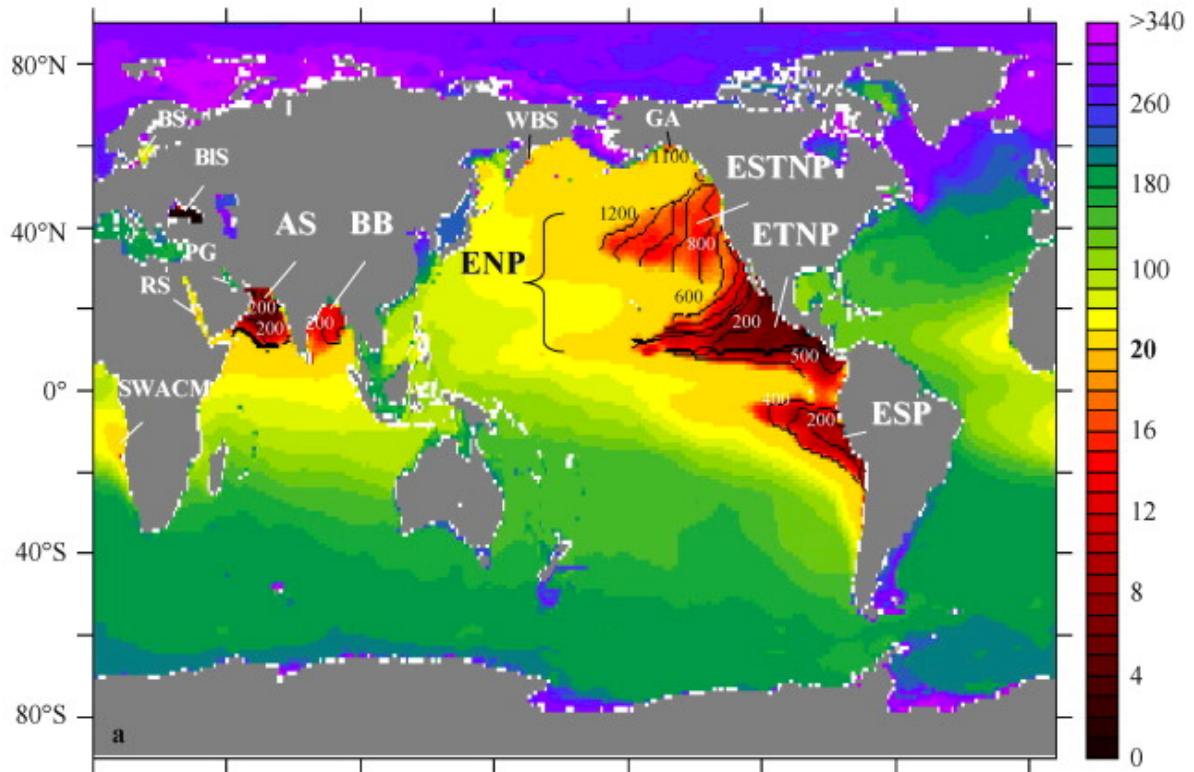
Fig 1. Level of O2 concentrations (µmol kg⁻¹) from the WOA 2005. The OMZs are represented in red (from Paulmier et Ruiz-Pino, 2009).

Dissolved oxygen (as well ass dissolved inorganic nutrients) may be used to trace water masses, to assess mixing processes, and to understand the biogeochemical conditions of their formation regions. An example of the usage of biogeochemical tracers has been given by Schroeder et al. (2008), who conducted an extended optimum multi-parametric analysis in order to quantify the spreading of the newly formed deep water from their formation region in the northern WMED (Fig.2). An increase of the oxygen concentrations in the deep waters have been observed from 2004 to 2006 illustrating the presence of a new deep water mass, richer in dissolved oxygen and coming from the Eastern basin through the Sicily Strait. Authors noticed that the dissolved oxygen concentrations had increased up to 0.2 ml/l (9 µmol kg⁻¹).

Concerning the organic matter export study, the role of dissolved oxygen is essential. It influences the degradation of sinking particles and in particular the final extent of degradation (Van Mooy et al., 2002). In this context, biological incubators have been recently developed (eg. IODA for In situ Oxygen Dynamics Auto-Sampler, D.Lefevre) to measure the high frequency signal of the *in situ* production and respiration rates (from the biology activity) and then to evaluate the importance of the remineralization process (due to the bacterial community) on the organic matter export.
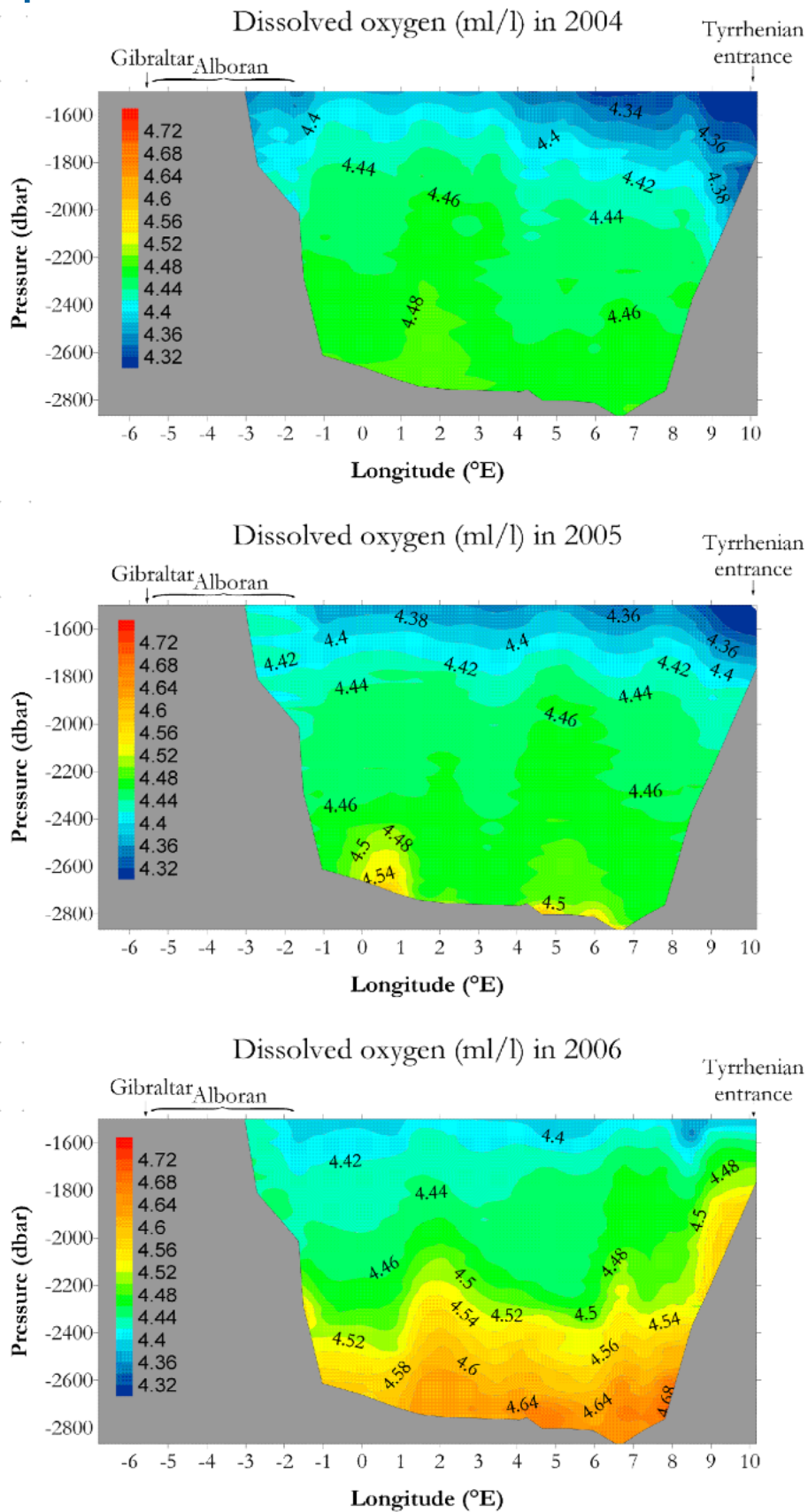
Fig.2 Vertical O2 distributions (ml/l) below 1500 m depth along an East-West transect in the NW Mediterranean Sea in 2004, 2005 and 2006 (from Schroeder et al. 2008). The increase of oxygen in the deep waters shows the presence of a new deep-water mass coming from the Eastern basin

Production and respiration rate are calculated from the dissolved oxygen concentrations measured directly inside the incubators. As the respiration rate is depending on the biological activity and the light intensity, it is highly variable between the day and night. A recent study has shown that daily change can modify the oxygen concentration up to 2 µmol kg^{-1} (Fig.3).
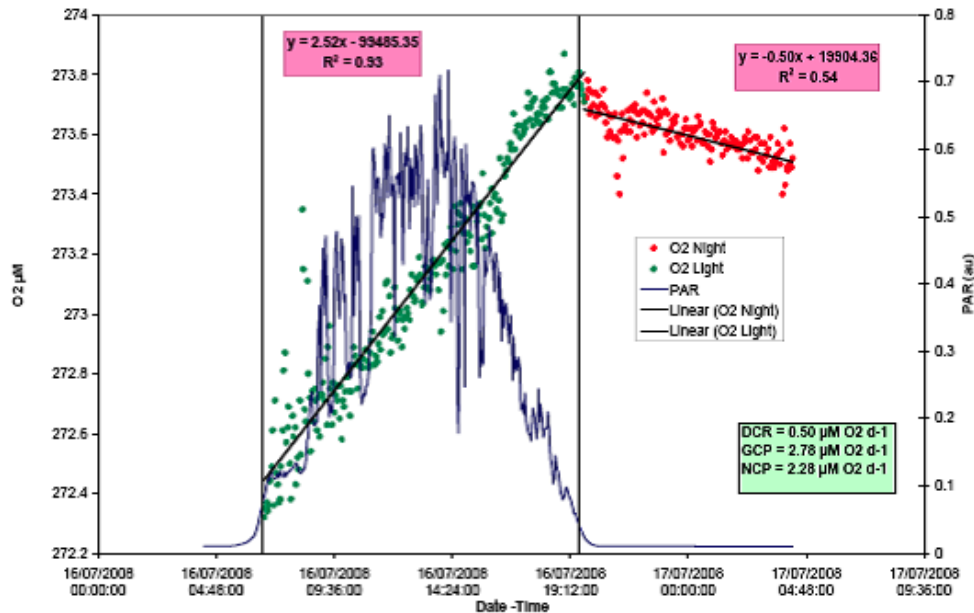

Fig.3 Biological activity measurements in surface from oxygen concentrations with an IODA (Robert et al.). In blue: daily light evolution. In green: oxygen production (during the day). In red: oxygen consumption (during the night).

2-Existing oxygen sensors: principle and practical performances

Oceanic dissolved oxygen concentration is one of the oldest oceanographic parameters observed in the global ocean. Nevertheless, the accuracy of the dissolved oxygen measurements that we can perform today is around 8 µmol kg^{-1} which is far away from the scientific needs (1 µmol kg^{-1}).

Dissolved oxygen in seawater is usually determined by using the Winkler's reaction scheme, a chemical titration method used for decades (Winkler, 1888). Nowadays, Winkler titration is a standard method used by many marine laboratories. It has the advantage to have a good precision and accuracy (± 2 µmol/l). Even when other methods are used, they are calibrated against this method (Emerson et al., 2002; Kuss et al., 2006). However, this method cannot be practically used for continuous measurements (ship cruises, autonomous platforms, deep moorings, coastal buoys) as laboratory equipment is needed. Nowadays, autonomous sensors are based on two techniques: an electrochemical method and an optical method.

2.1- Electrochemical sensors (eg. SBE43)

The SBE43, from Seabird Electronics, is an electrochemical sensor based on a Clark polarographic membrane (Clark et al. 1953) used mainly on Seabird shipboard CTD units. The SBE 43 sensor is adapted for autonomous measurements system, in particular for the CTD casts due to its very fast time response (< 1s). The initial accuracy is 2% of oxygen saturation and precision around 1 µmol kg^{-1}.

Even if this sensor has good specifications, an extensive calibration and maintenance work has to be done before its installation in order to reduce any electro-chemical drift for improving long-term data quality (Fig.4).

The chemistry of the sensor electrolyte changes continuously as oxygen is measured, resulting in a slow but continuous loss of sensitivity that produces a continual, predictable drift in the sensor calibration with time. Membrane fouling also contributes to drift by altering the oxygen diffusion rate through the membrane, thus reducing sensitivity. Biological fouling, particularly on moorings, can be troublesome, because the living organisms either consume or create oxygen. Without protection and/or routine cleaning, a micro-environment around the sensor can produce oxygen levels that are different from the true ambient conditions. Usually Seabird recommends to clean meticulously the sensor after each cast (Triton and bleach) and to store the sensor in an anoxic (or near zero oxygen) condition (loop tubing from inlet to outlet). If the membrane is kept clean, the sensor's chemical stability yield demonstrated calibration drift rates of less than 2% over 1000 hours.
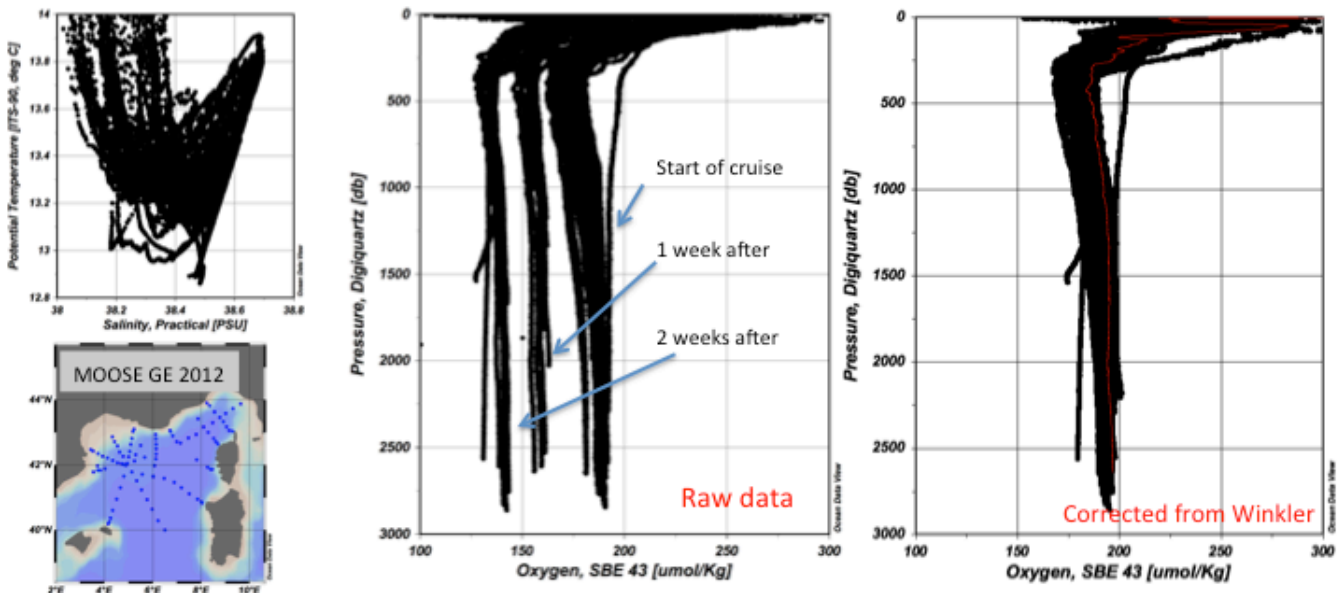

Fig.4 Example of SBE43 data drift during a two weeks cruise performed in the NW Mediterranean Sea in July-August 2012 (MOOSE-GE). Correction of O2 data has been possible from O2 Winkler measurements performed once per day (L.Coppola, personal communication)

2.2- Optical sensors (eg. optode 3835/4330, RINKO, SBE63)

Optical sensors operate on the principle of fluorescence quenching (Tengberg et al., 2006). Nowadays, the Aanderaa optodes 3835 & 4330 are the most used sensor implemented in Argo floats, gliders and on moorings.

2.2.1 The Aanderaa optode

Oxygen optodes are based on the oxygen luminescence quenching of a platinum porphyrin complex (fluorescent indicator) that is immobilized in a sensing foil. Optodes show a nonlinear decrease in luminescence decay time with increasing oxygen concentration. The signal can be linearized by means of the Stern–Volmer equation: $[O2] = (\tau 0/\tau – 1)/Ksv$, where [O2] is oxygen concentration in $\mu mol\ L^{-1}$, τ is luminescence decay time, $\tau 0$ is the decay time in the absence of [O2], and Ksv is the Stern–Volmer constant (Demas et al., 1999).

The advantages of the optical sensors appear to be its excellent long-term stability and high precision. It also appears to be accurate provided that it has sufficient time to come into equilibrium with the surrounding temperature and oxygen concentration and provided that its temperature response has been carefully calibrated (possibly by individual sensor factory-calibration plus in-situ calibration check/correction based on concomitant Winkler profile).

The main disadvantage of the Aanderaa optode sensor 3830-3835 is its relatively slow response time, which tends to lead to problems in the upper ocean, where vertical gradients in dissolved oxygen and temperature are greatest. A comprehensive evaluation of the optode 3830/3835 performance for long term in situ measurements was carried out by Tengberg et al. (2006). Up to 20 Aanderaa sensors were tested for their calibration performance, cross-sensitivity and pressure hysteresis, sensitivity to biofouling and long term stability. These sensors have a measuring range of 0-500 µM, a resolution of 1 µM and an accuracy of 5 µM as well as an operating depth of up to 6000 m. The optodes were deployed during test periods lasting from a few days to 600 days on an Argo float, and in different waters (estuarine, river, waste water, and ocean). 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. Biofouling is also an issue for the optode that have been deployed in coastal waters. Authors showed that wrapping the optode with a beryllium-copper alloy net around the sensor slowed down the fouling of the optode. In heavy fouling environments (Chesapeake Bay and Gulf of Mexico), this method prolonged the service interval from approximately 7 to 10 days to 40 to 60 days. But, such biofouling protection should not be used in calm water environment since copper ions induce bias on the dissolved oxygen concentration measurement.

Due to its small size and power requirement, the first generation of optode (3830/3835) have been also tested on profiling floats (Kortzinger et al. 2005). The first results in 2004 demonstrated that high quality long-term oxygen measurements from ARGO floats are feasible. While the optodes are very stable over times of several years, they are generally not completely well calibrated at the factory, and their offset from climatology can be quite large (Fig. 5). Consequently, Winkler oxygen measurements around the float deployment area are recommended as well as a better calibration lab experiment. Moreover, authors suggested that

the optode ability to measure in air should provide a means for identification of any drift problem and should be mounted at the top of the float.

Recently, a new Aanderaa optode sensor has been launched on the market (4330) with a much faster response time, but few deployments have been performed so far preventing us from assessing its performance.
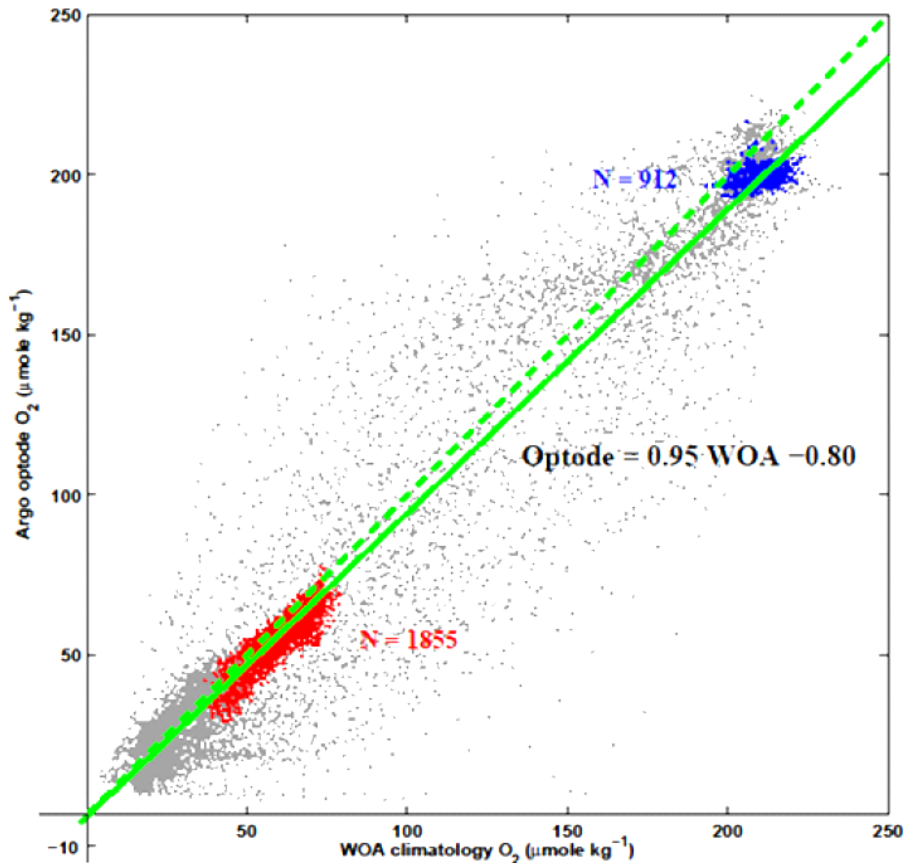

Fig.5 A plot of the dissolved oxygen measurements from University of Washington float 5089 (WMO 5901339) for the period 8/21/2006 to 5/17/2011, compared to the climatology from the World Ocean Atlas (WOA) 2009.

2.2.2 The RINKO-III optical oxygen sensor (D. Machoczek)

One of the main disadvantages of recent optical oxygen sensors has been their long response time of several seconds which does not fit the requirements of an oxygen sensor being used in profiling CTD-systems.

As the Federal Maritime and Hydrographic Agency (BSH) uses optical oxygen sensors (Aanderaa Oxygen Optode 3835 which is the shallow water (0 – 300 m) version of the 3830 optode) at all 11 stations of the Marine Environmental Network in the North and Baltic Seas (MARNET) in-situ calibration measurements are of great importance to guarantee the quality

of the real-time data. This is currently assured by taking water samples at the depths where oxygen sensors are mounted. The oxygen content of these water samples are determined by Winkler titration (Winkler, 1888, Carpenter, 1965). These measurements can only be carried out, if laboratory equipment and extra manpower can be provided during the maintenance cruises. As the extra ordinary amount of work cannot be carried out each maintenance cruise, there will be only a few calibration measurements by Winkler titration per station and year.

For MARNET-oxygen measurements, values of highest absolute accuracy do not have absolute priority, in fact producing reliable oxygen measurements over a long period without maintenance is much more favourable. Therefore the demand of high accuracy does not play such an important role as in deep sea oceanography. That is why greater deviations between Winkler-titration and optode values can be accepted.

To get additional calibration measurements a fast optical oxygen Sensor manufactured by JFE Advantech Co., Ltd, Kobe, Japan has been installed into a CTD90-System (Sea & Sun Technology GmbH, Trappenkamp, Germany). This Oxygen sensor is of Type RINKO-III Model ARO-CAV. Following specifications are given by the manufacturer: Accuracy: < +/- 2 %, resolution: 0.4 % and a response time (90 %) of ≤ 1 second.
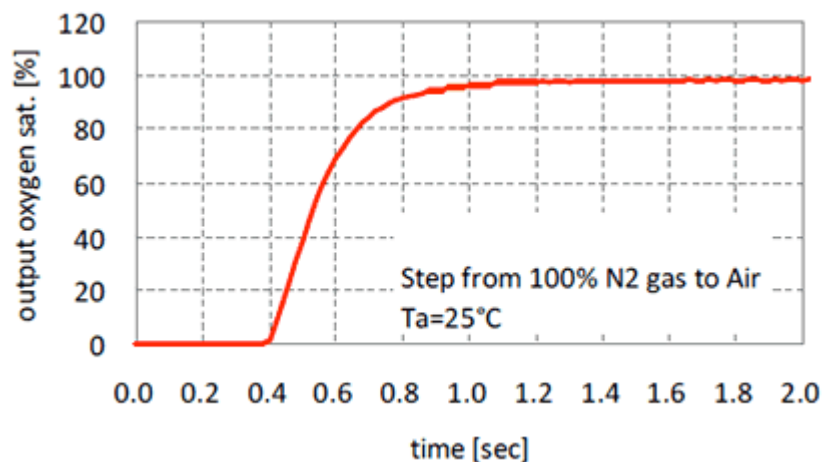

Fig.6. The response time of the RINKO-III sensor. This figure shows the response time which reaches 90 % value of oxygen in air within 1 second. (Fig. by JFE Advantech Co., Ltd)

As the CTD90-System is operated by a manually driven winch at stations with water depths of no more than 50 m, the heave down velocity varies from a few centimetres per second to half a meter per second the most. Together with the quick response time of the sensor (compared to the response time of the Aanderaa 3830/3835 sensors of less than 25 sec. (63 %)) it is ensured that usable oxygen data is delivered over the whole water column.

A 0 % and 100 % calibration of the RINKO-III ARO-CAV-Sensor according to the recommendations of the manufacturer was carried out at June 11th 2012. At June 12th 2012 in-situ calibration measurements were carried out at Lighthouse Kiel in the western Baltic Sea.

Unfortunately the conditions for these calibration measurements were not very favourable. Staring the measurements, the water column at the lighthouse showed a relatively homogeneous surface layer down to 9 m depth, starting an increase of the salinity from 13.25 at the surface to 13.64 PSU at 9 m together with a decrease in temperature starting from 13.72° C to 13.17° C, the oxygen saturation showing values of 101.93 % on the surface and 97.49 % at 8.18 m depth.

The water column at the position of the sensor at 13 m depth which is some 60 m north-west of the lighthouse showed a relatively homogeneous surface layer down to 8 m depth, then starting an increase of the salinity from 13.5 to 16.4 PSU at the bottom depth of 13.54 m together with a decrease in temperature starting from 13.5° C to 9.7° C at bottom depth during the measurements. The oxygen saturation varied from 102.94 % at the surface to 74.33 % at the bottom.

As the centre of the Niskin-bottle for taking the water samples is located 1.20 m above the lower end of the safety-frame of the CTD-System the water sample is actually taken at a depth of 12.34 m at bottom depth. Therefore the values of the Aanderraa optode in 13 m depth cannot be used for the comparison measurements. Taking the values at 8 m depth, the Aanderaa optode No. 1361 showed an oxygen saturation of 98 %, the average of the measurements of the RINKO-III ARO-CAV-Sensor was 100.50 % and the average of the Winkler-titration measurements was 99.9 %. The difference between the Winkler-titrations and the fast oxygen sensor is only 0.6 % and between the Winkler-titrations and the slow oxygen sensor 1.9 %. At 12.34 m depth the average of the Winkler-titrations is 82.9 % and the fast sensor shows a value of 82.11 %, the difference now negative and being a little bit exceeded to 0.79 %. One has to remark that at that depth, the oxygen saturation shows a change of 3 % between 12.20 m and 12.50 m depth. Having the length of the Niskin-bottle in mind, one easily recognizes that the water inside the bottle itself shows this stratification and the different measurements by Winkler titration show a relatively wide range of saturation values. Nevertheless both deviations from the Winkler-titration values lie well within the accuracy of the Aanderaa and the RINKO sensors. Three and a half months later on September the 27th another calibration measurement at Lighthouse Kiel was carried out. During the time between the measurements in June and in September the RINKO-sensor was not recalibrated.

The oxygen saturation values show a first decrease at 6 m depth down to 8 m depth and a second decrease starting from 9 m depth on. Besides this vertical gradient there is a distinct variation of the saturation values at 8 m depth in time. In a period of only 20 sec. the oxygen saturation changes from 85.45 % to 75.04 %. The difference of 10.41 % is exceptionally great, displaying unfavourable conditions for calibration measurements. However the comparison between oxygen-saturation values by Winkler-titration and the saturation values by the RINKO-sensor show a good agreement, the Winkler- value being 85.85 % and the RINKO-value being 85.45 %. The difference of 0.4 % is a factor 2 smaller than the accuracy of the sensor itself.

These measurements give no hint to a drift of the senor during the period of three and a half months. Between November 30th and December 2nd 2012 some more calibration measurements were carried out at three stations (German Bight, Ems and North Sea Buoy III) in the German Bight. This time the conditions for the measurements were much more favourable compared with the measurements taken at Lighthouse Kiel in June and September. At all stations no distinct gradient in temperature, salinity and oxygen content was present. At Station German Bight the water temperature changed from 9,10° C at the surface to 9,46° C at the bottom, the salinity from 33,26 PSU to 33,66 PSU and the oxygen saturation from 95,4 % to 94,8 %. At station Ems the values are: temperature from 9,96° C at the surface and 9,97° C at the bottom, salinity from 34,65 PSU to 34,69 PSU and oxygen saturation from 95,6 % to 95,7 %. At station North Sea Buoy III the temperature changed from 9,80° C at the surface to 10,27° C at the bottom, salinity from 34,34 PSU to 34,67 PSU and oxygen saturation from 95,4 % to 95,1 %.
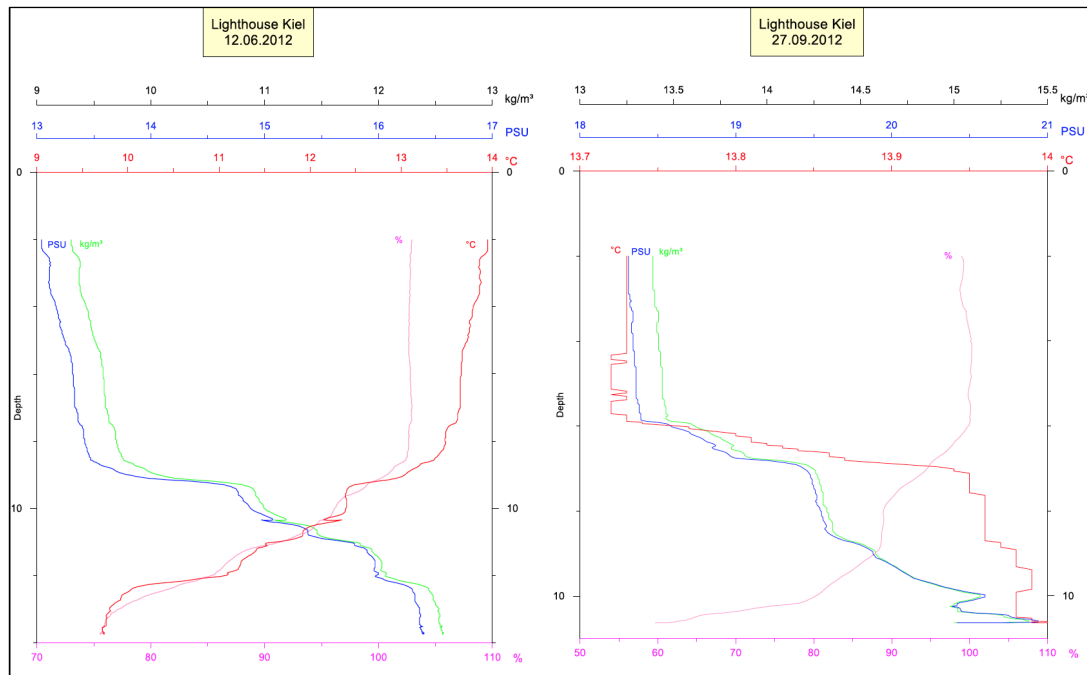
Fig. 7 CTD-Profiles at Lighthouse Kiel, left: 12. 06. 2012, right: 27. 09. 2012, temperature: red, salinity: blue, density: green and oxygen saturation: pink

Following table shows the results of the calibration measurements between the Winkler-Titration and the RINKO-oxygen sensor values:

Station	Depth	Oxygen-Winkler saturation [%]	Oxygen-RINKO saturation [%]	Diffference saturation [%]
North Sea Buoy III	6 m	97,5	95,3	2,2
30.11.2012	35 m	97,4	95,2	2,2
Ems	6 m	98,5	95,8	2,7
01.12.2012	35 m	98,55	95,8	2,75
German Bight	6 m	97,25	94,9	2,35
02.12.2012	30 m	97,15	94,8	2,35

At the time of these measurements the RINKO-Sensor has not been calibrated since June 11th 2012, a period of 171 day, nearly half a year. The measurements clearly show a deviation of the RINKO-values from those obtained by Winkler-Titration. The sensor seems to underestimate the oxygen values proceeding with time. After half a year the difference lies somewhat around 2,3 %, the higher values at Ems are based on the fact that the time gap between the Winkler-Titration and the RINKO-measurements is two hours in which a slight change of the oxygen saturation has occurred.

As the measurements cover only a range of oxygen saturation values from 80 % to 100 % no evidence can be given if the deviation found is steady over the whole measuring range. Therefore a calibration of the RINKO-Sensor over the whole measuring range is necessary.

For the purpose of checking the saturation values of the Aanderaa-optodes, the deviation of the RINKO-Sensor after half a year without calibration is just acceptable as it is still only half the size of the accuracy of the optodes, using the sensor for obtaining oxygen-saturation-profiles where absolute precise saturation values are preferable, the sensor should be calibrated every three month to guarantee that the error in the measurements is still smaller than the accuracy of the sensor itself.

Deviation of the RINKO-Oxygen-Sensor compared to reference measurements from 11. 06. 2012 until 30. 01. 2013

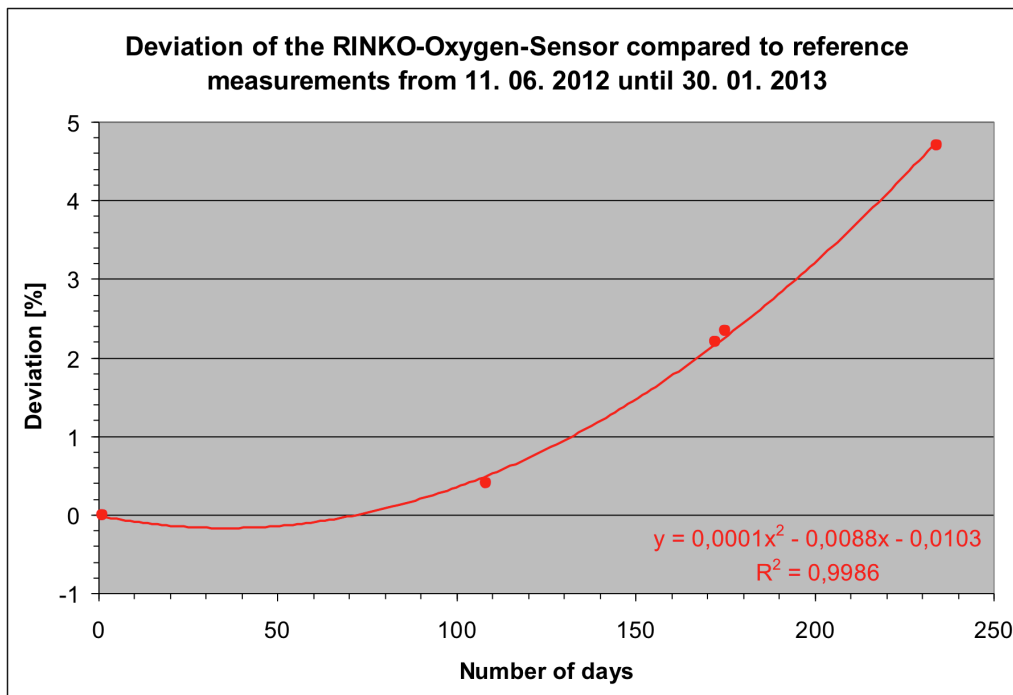$y = 0,0001x^2 - 0,0088x - 0,0103$
$R^2 = 0,9986$

Fig.8 The figure shows clearly that there is a slight nonlinearity in the increase of the deviation of the sensor with increasing time. The coefficient of determination is almost 1 (0.9986).

As the measurements cover only a range of oxygen saturation values from 80 % to 100 % no evidence can be given if the deviation found is steady over the whole measuring range. Therefore a calibration of the RINKO-Sensor over the whole measuring range is necessary. As BSH is operating three CTD-Systems with RINKO-sensors and only one sensor has been tested (CTD No. 512), a final assessment about the quality characteristics of this sensor-type can only be made after testing the two other sensors.

Preliminary results based on the experience with the RINKO-Sensor of CTD-System No. 512 are:

- The sensor is suitable for continuous profiling measurements as the response time is lesser than 1 s (90 % value) and as long as the heave down velocity is not to high.
- The sensor has a tendency to underestimate the existing saturation values.

- Deviations from the existing saturation values are highest at high oxygen saturation values and decrease when the oxygen values diminishing.
- The sensor shows a slight nonlinearity in the increase of the deviation of the sensor with increasing time.

Further tests of the two other systems have to follow, especially testing if an increasing deviation is not only nonlinear in time but also in saturation and temperature.

2.2.3 The SBE63 sensor

The SBE 63 is a new optical D.O. sensor set for moorings and Argo floats. The SBE63 is designed for use in the CTD's pumped flow path. Water does not freely flow through the plumbing between samples, allowing anti-foul concentration inside the system to maintain saturation and eliminating exposure of the sensor to light, maximizing bio-fouling protection. The elapsed time between the CTD and associated oxygen measurement is easily quantified, and corrected for in post-processing.

The SBE63 initial accuracy proposed by Seabird is around ±3 µmol/kg and resolution of 0.2 µmol/kg. The response time is lower than 6s. Each SBE 63 is calibrated individually in a temperature-controlled bath. Bath temperatures are varied at each of 4 oxygen values, providing a comprehensive 24-point calibration. Two reference sensors in each bath are standardized against Winkler titrations.

A SBE63 sensor has been mounted on SBE floats (NAVIS floats) but few experiences have been gained in the field to discuss further about the SBE63 accuracy and limits (http://navis.sea-birdscientific.com) .

3- Oxygen measurements on existing platforms: results, experiences and recommendations

3.1 Argo floats experiences (V.Thierry)

In the ARGO community the Aanderaa optode 3830 is the most widely-used sensor for measuring oxygen concentrations (Körtzinger et al. 2004, 2005). Over 130 sensors of this type have been deployed on Argo floats. The sensor is popular due to its demonstrated long-term stability. Aanderaa proposes now a new version of this sensor, the optode 4330, with a faster time response but experiences are too recent to be debated here.

The ARGO-O2 community published in 2007 a white paper dedicated to the oxygen measurements implementation on Argo floats in order to determine seasonal to decadal-time variability in sub-surface ocean oxygen storage and transport on a global scale (Gruber et al. 2007). From this paper they underlined some O2 measurements issues mostly operated by an optode sensor. For the application on Argo floats, an accuracy threshold of 5 µmol kg^{-1} has been defined for the data to be of useful quality to address scientific objectives, whereas the accuracy target for the desired data quality has been set to 1 µmol kg^{-1} (Gruber et al. 2010). Kobayashi et al. (2006), however, reported large discrepancies (up to 40 umol kg^{-1}) between

the oxygen concentrations measured with profiling floats equipped with optode sensors 3830/3835 and oxygen concentrations in discrete water samples obtained from nearby shipboard hydrographic casts (Winkler method). It appears that the response of the sensing foil of the optode is one the cause that explained this discrepancy (Uchida et al. 2008). The response of the foil decreases with increasing ambient pressure, and this pressure effect was found to decrease the response by 3.2% (1000 dbar).

Between Argo floats deployments, several observations that processes yet unidentified lead to a change in the sensor response, e.g., between factory calibration and in-situ data (Takeshita et al. 2010, Bittig et al. 2013). To solve this issue, the ARGO community proposed to use a new calibration equation for the optode sensors by using 7 coefficients instead of 20 (Uchida et al. 2008). A re-adjustment of these 7 coefficients is also possible by using a best-fitting set of calibration coefficients based on in situ oxygen concentrations (Uchida et al. 2010). Concerning the calibration technique, Bittig et al. (2013) proposed recently a new laboratory calibration setup for the individual multi-point calibration of oxygen sensors based on the electrochemical generation of oxygen in an electrolytic carrier solution. This new calibration method should facilitate accurate oxygen measurements on a large scale, and its small size makes it possible to configure as a mobile, sea-going, Winkler-free system for oxygen sensor calibrations (Fiedler et al. 2013).

While the optode stability is attractive compared to the SBE43 sensor, measurement errors of the order of 12 µmol/kg are unacceptable in most quantitative biogeochemical studies. Scientists agreed that errors in oxygen of 1 µmol/kg or less should be the goal of any DO sensors measurement. While this would seem to be a difficult goal, there was a general consensus that several steps could be taken immediately to reduce the present errors significantly and to move towards an accuracy of 1 µmol/kg. These steps are summarized here:

- Calibrate all DO sensors to an accuracy of 1 µmol/kg in a laboratory setting prior to deployment.

- Collect concomitant Winkler oxygen samples at DO sensor deployments whenever possible

- Decrease the response time of the sensor (presently near 30 seconds) without sacrificing accuracy

- Explore methods to use the temperature from the CTD unit for the oxygen calculation instead of the temperature sensor itself (optode).

- Transmit the raw data from the DO sensor (B-phase for optode) instead of computed oxygen values. This will make it easier to adjust the data from Winkler titration and explore new calibration methods

- Employ a new calibration equation based on the physics of the oxygen-sensing process (the Stern-Volmer equation) instead of the arbitrary polynomial now used

- Continue to explore issues such as self-heating and sunlight bleaching of Optode sensors.

3.2 FerryBox system experiences (M.Haller, D.Hydes)

An autonomous measurement system (FerryBox) equipped with optodes has been tested on a ferry operating between Portsmouth (UK) and Bilbao (Spain) in 2005-2006. The optode outputs were compared to dissolved oxygen measurements from Winkler titrations. The results revealed that optodes maintained good stability with no evidence of instrumental drift during the course of a year. Over the observed concentration range (230–330 mMm^{-3}) the optode data were approximately 2% low in both years which was better than the value advertised by Aanderaa (5% or 8uM). By fitting the optode data to the Winkler data the median difference between the optode and Winkler measurements was reduced to less than 1 mMm^{-3} (0.3%) in both years (Hydes et al. 2009).

However the optode accuracy can be improved by user calibration, as it was observed from the Argo floats. Ideally this should be done both in the laboratory and the field to take into account the change in the optode output with oxygen concentration and temperature.

3.3 Glider experiences (J.Karstensen)

Oxygen data from optodes mounted on a glider (optode 3830) have been obtained in the Southeast Pacific oxygen minimum zone (OMZ) to test the calibration of the optodes. OMZ are interesting for such test because one can find regions with rather constant and known oxygen concentrations over a wide temperature, pressure and salinity range. Measurements recorded in these regions can be used to recalibrate the optodes with a very low oxygen concentration (about 2µmol/kg) and saturation at surface (OMZ is consider as a "natural calibration laboratory" for oxygen). These points have been used to fit the optode data. In addition, pressure and salinity observations can also be introduced in the correction polynom (Karstensen et al. 2011).

From this experience, the optode mounted on glider should follow these recommendations:

Before Deployment:
- Always record Dphase
- Do at least a 0% & 100% saturation calibration before deployment
- After 0% & 100% calibration read out ALL calibration from optode before deployment

Deployment (Glider specific):
- Sample 1 sec (SLOCUM glider software > V7.0)
- Record data (at least at some) up and downcasts

After Deployment:
Always use calibrated CTD temperature and salinity for conversion Dphase that are used to calculate oxygen concentrations.

3.4 Experience on CTD profiler (R. Nair & S. Sparnocchia)

Modular DO sensors are standard elements in most profiling CTD packages. The suitability of a DO sensor for profiling is essentially determined by its ability to provide reliable

measurements notwithstanding potentially rapid changes in ambient oxygen concentrations (strong gradients) and the relatively high rate of sample turnover required to ensure adequate spatial resolution with depth. In other words, to be effective, the sensor has to be fast and stable during the typical CTD duty cycle (the down and up casts), while continuing to maintain accuracy.

Currently, electrochemical Clark-type polarographic sensors still remain the best choice for DO profiling, provided certain dynamic effects on performance are adequately addressed either in-line or during data processing. Possible sources of such effects include transient polarization delays (during power-up), alignment geometry, sensitivity to flow rate, poor internal temperature compensation, pressure dependency, and response time mismatches with respect to the CTD temperature and conductivity (salinity) sensors. Polarographic sensors are also notoriously subject to drift that can be caused by changes in membrane structure and tension, the depletion of electrolyte and deterioration/alteration of the condition/s of the anode or/and cathode. Fouling must also be watched out for as it can directly affect membrane thickness, and proper cleaning of the sensor between casts is recommended. Note that closed-path, pumped (well-ventilated, with a controlled flow-rate) CTD configurations are intrinsically more suited for mitigating many of the dynamic effects affecting polarographic DO sensors, and therefore are to be preferred when using such sensors. From the point of view of accuracy, regular multiple-point laboratory calibration at possibly more than one temperature is a prerequisite, and adjustments of *in situ* output values over deployment intervals using DO measurements obtained utilizing the Winkler method on field samples specifically collected for this purpose is mandatory.

Optical DO sensors are coming to be considered as an attractive alternative to polarographic sensors because of their insensitivity to stirring and the compactness of the underlying sensing technology. But these sensors too are sensitive to temperature and pressure, and employ membrane coverings to make them more robust and deal with interference. It is to be expected that this will make them susceptible to many of the same problems affecting their electrochemical counterpart, with the difference that the possible effects on performance are more poorly known, less well-characterized, and hence harder to compensate for at the present time.

4- Calibration recommendations (F. Salvetat)

The calibration (and the adjustment, if needed) of dissolved oxygen sensors is essential to collect quality DO data. The calibration will estimate the trueness and the uncertainty of the sensor but it will also check the potential influence parameters on the data. Indeed, up to now, we still don't master all the influence parameters that can affect the measurement of optical sensor for instance. That is why it is extremely important to carefully control all DO sensors. It will also give a better understanding of the behavior of DO sensors.

The calibration will be carried out over the range of dissolved oxygen measured *in situ*. Depending on the width of this range, several calibration concentrations will be done (including the extreme points of the range) at different temperatures corresponding to the range of temperature measured at sea.

If needed, a specific expertise of the sensor response with regard to pressure could be done (for instance, if there is a lack of agreement of the oxygen concentration measured by two sensors).

We remind that all measurements have to be done in conformity with Good Laboratory Practice.

Reference devices recommendations

To avoid any issues, the reference measurements should be Winkler titration.
No device recommendations are proposed, except that the calibration device must perform different DO concentrations.
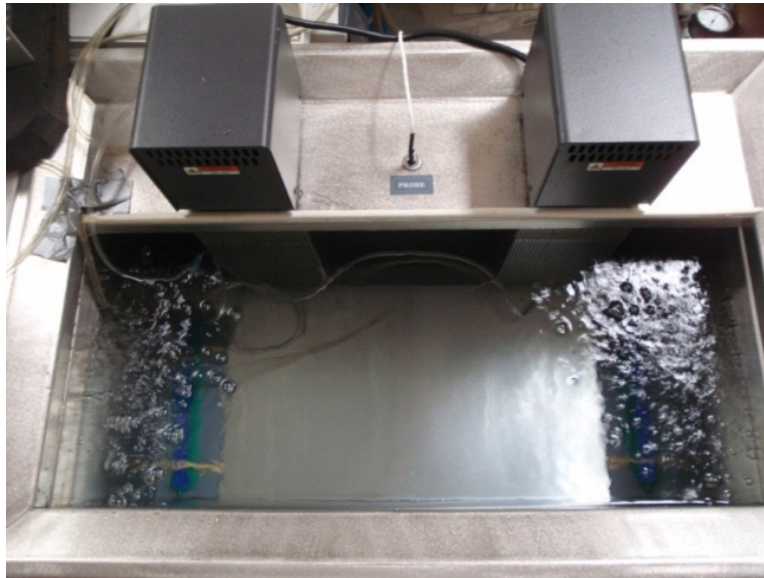
Fig. 9. Example of a dissolved oxygen bench with bubbling system
(Photo, courtesy of Ifremer – Florence Salvetat)

Specific protocol recommendations

Due to the difficulty of the Winkler method (sampling, reagents, …), the calibration laboratory should implement some trials to ensure the quality of its Winkler titration (eg. inter-laboratory comparisons).

Calibration laboratory in the field of oxygen (non exhaustive):

- CSIRO (Australia). Contact person: Craig Neill
- GEOMAR (Germany). Contact person: Henry Bittig
- IFREMER (France). Contact person: Florence Salvetat
- CNRS-M.I.O. (France). Contact person : Dominique Lefevre

5- Biofouling protection for oxygen sensors

The marine biofouling development on *in situ* sensors affect the measurements produced. The measurements got out of tolerance and then data are unworkable. Commonly, the drift observed due to biofouling is a slow decrease. But, other effects can be observed like decrease in the response time of the sensor or a signal that get noisy.

Biofouling protection for oceanographic oxygen sensors is a difficult task where the specifications should be driven by three important characteristics:

- It should not affect the measurement or the environment

- It should not consume too much energy, in order to preserve the endurance of the autonomous monitoring system

- It should be reliable even in aggressive conditions (seawater corrosion, sediments, hydrostatic pressure, …).

For optical or membrane based oxygen sensors, the interface between the measurement medium and the sensor sensitive area must remain intact. Moreover, antifouling paints cannot be used to protect sensors sensitive area.

For oxygen sensors, 3 methods has been commonly used, TBT leaching (Seabird), copper ion production, and chlorination by seawater electrolysis.

Protection based on **TBT** (Tributyl-tin) leaching should no longer be considered as a solution for biofouling protection. Despite the fact that this chemical has proved to be extremely efficient, tributyl-tin compounds have been shown to have deleterious effects upon the environment. TBT was banned for antifouling paints from 2003 and should not be used on ships hulls from 2008 (Champ, 2003; Evans, 1999). Nevertheless one company still uses this biocide for sensor biofouling protection. This American company, "Seabird", has obtained from the U.S. Environmental Protection Agency (E.P.A.) the authorization to use TBT rings in a pumping device coupled to sensors. When the oxygen sensor is performing a measurement the pumping device is on, consequently the TBT is flushed and its concentration becomes very low. Therefore there is no danger for the TBT to disturb the measurement. When the sensor is idle, the pump is off, the TBT concentration can rise inside the measurement cell, which protects it from biofouling.

Copper is known for it's biocide properties, and is currently used to protect oxygen sensors against biofouling in a variety of ways. The released bivalent Cu^{2+} interferes with enzymes on cell membranes and prevents cell division (Breur, 2001). For the last five years, some manufacturers have used this protection technique. Some of them build the sensor head totally in copper and add a wiper system to scrape the optics (YSI 6-Series Anti-Fouling Kits[1] or Wet Labs/Sea-Birds WQM's sensors[2]).

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[1] See https://www.ysi.com/portal/page/portal/YSI_Environmental/Products/Product_Family/Product?productID=EMS_ANTIFOULING_KIT accessed on 09/09/2009

[2] See http://www.wetlabs.com/products/wqm/wqm.htm accessed on 09/09/2009

A specific item of equipment can be found that allows the user to equip any sensor with a copper cell system, more commonly named a "Copper shutter". A motor drives the mechanism with shutters that open for measurements and close for biofouling protection over the optical windows. It keeps the sensor very close to the copper shutter and when closed the sensor surface is in darkness, which reduces biofouling, and also allow biocide concentration to increase.

Such protection is not easy to implement on an oxygen sensor. The copper screen with the stepper motor needs to be placed on the sensor in such a way that the copper screen catches a small volume of water over the sensor measurement interface. An example of such system can be found on a fluorometer (Delauney *et al.*, 2006), figure below. In order to maximize the effectiveness of the protection, it was necessary to build up a copper cell and to coat the entire sensor head with copper.
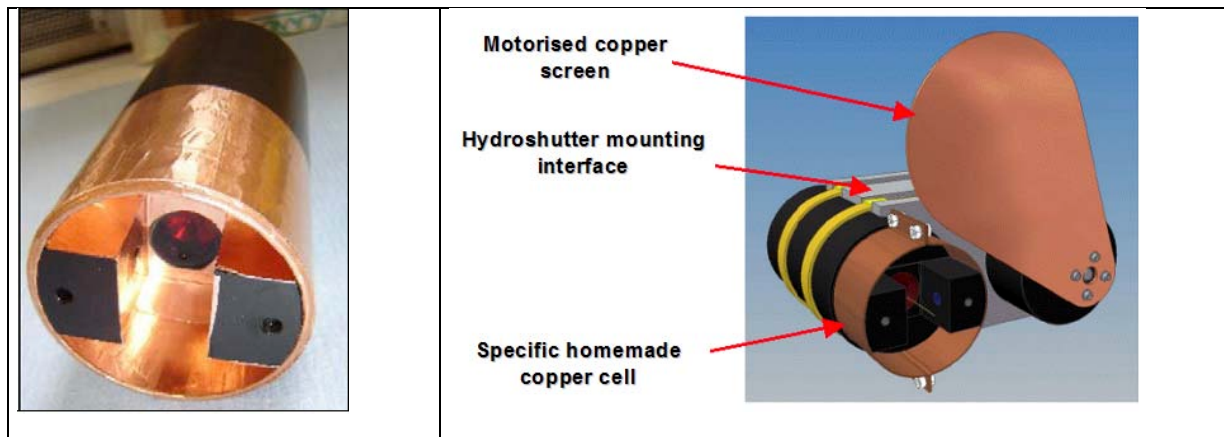

Fig. 10. Biofouling protection with a motorized copper shutter
(Photos and schematic, courtesy of Ifremer – Laurent Delauney)

Results obtained with such a system, when the implementation made exactly as described above, are quite satisfactory. Similar results were obtained with copper tubing and a copper shutter during experiments on optical instruments by Manov *et al.* (2004).

For oxygen sensors, copper protection should be implement with great care. If no mechanical or natural flushing is operated with such biofouling protection, there is a great risk of adverse effect on the measurement since copper corrosion process is involved which can affect oxygen concentration in the medium.

Chlorination has long been used in industrial applications to protect systems from biofouling. Recently it has been used for biofouling protection of *in-situ* oceanographic instruments. Two modes of action are used, bleach injection and electrolysis chlorination. These two modes of action are still not widely used by manufacturers.

Bleach injection methods can be found on fresh water monitoring stations and very recently on autonomous monitoring instruments such as the Wet Labs/Sea-Bird WQM's instrument. This scheme requires a reservoir for the chlorine solution and a pump.

The electrolysis chlorination system can be found on monitoring stations (Woerther and Grouhel, 1998; Woerther, 1999) and "Ferry Box" instruments that use pumping circuitry, the protection is known as a "global chlorination" scheme (Hengelke *et al.*, 2005). In this way the whole measurement circuitry is protected at the same time as the sensors.

An other electrolysis chlorination scheme can be found on few autonomous sensors, it consists of protecting only the sensing area of the sensor. Thus the electrolysis is performed on a very restricted area and consequently the energy needed is very low and compatible with autonomous deployment. Very few commercial instruments are equipped with such a scheme (Delauney and Compere, 2009). But, local chlorination has been used on oxygen sensor. By the way, it must be known that hypochlorous acid generated by the sea water electrolysis affects the oxygen measurement, but, as soon as the electrolysis is stopped, the bias on the measurement disappears. As an example, a one-year deployment on a seabed observatory is shown below with an Aanderaa optode protected by local chlorination. The Aanderaa optode was deployed in 2005 and then recovered during the Momareto cruise in 2006.

Fig. 11 Aanderaa oxygen sensor, equipped with the electrolysis antifouling system. A) Deployment "Exomar" 2005. B) recovering "Momareto" 2006. (Photos, courtesy of Ifremer)

The Aanderaa optode recovery allowed for the first time to demonstrate efficiency of the antifouling method in hydrothermal environment and showed validity of this sensor in hostile and dynamic environment. Indeed, the following figures show that only the sensor part of the module remained protected against biofouling and macrofouling.

Fig. 12 A) Global view of macro fouling after 12 months.
B) Detailed view of local protection efficiency.
(Photos, courtesy of Ifremer)

As a conclusion on biofouling protection for oxygen sensor, these technics must be applied very carefully in order not to disturb the measurement. In medium where water current can flush the sensor, there is less risk of disturbance, but in calm water, extreme care should be taken about biofouling protection which use a biocide generation and above all with a uncontrolled biocide generation scheme (TBT and copper).

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