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Evaluation of the Aanderaa Oxygen Optode in continuous use in the NOC Portsmouth Bilbao FerryBox system 2005, 2006, with an assessment of the likely errors in the estimation of oxygen concentration anomalies

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ABSTRACT

An Aanderaa Oxygen Optode has been used as part of the "FerryBox" system on the P&O Ferries vessel the MV *Pride of Bilbao* since the beginning of 2005. This report covers data collected through 2005 and 2006. The accuracy, precision and stability of the Optode have been compared with (1) measurements of oxygen in water samples collected and processed on board the ship by Winkler titration and (2) estimates of the oxygen anomaly.

The comparison of the Winkler data with the output from the Optode suggests that the accuracy of the Optode in both years was close to 98% of the true value when compared to the Winkler measurements. The data suggest that the precision based on the comparison of the two data sets was equivalent to a standard deviation of 5 μM or 2% of the average value in 2005 and 2.9 or 1% of the average value in 2006. The resolution of the recorded a data is better than 1 μM.

Two sources of error in measurement of temperature which are significant for the calculation of the oxygen anomaly have been identified. Temperatures measured using sensors in board the ship are higher than "true" temperatures. The error changes through the year as the difference in temperature between inside the ship and the external water temperature changes. This error may be as large as 0.5 °C. The anomaly has to be calculated using temperature measurement in the water flowing past the Optode. This is because of delays and mixing in the water being pumped into the ship have smoothing effect on the data, and can enhance the difference between the internal and external temperature to being as high as 1.0 °C. Consequently to avoid this large error due to the timing of the measurements the oxygen anomaly should be calculated from the temperature measured in the pumped water stream adjusted by an offset to the "true" outside temperature.

KEYWORDS
Bay of Biscay, dissolved oxygen, English Channel, FerryBox, gas exchange, monitoring, Optode, productivity, seawater, Winkler titration

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Executive summary

This report is an evaluation of (1) the use of the Aanderaa Oxygen Optode (the Optode is a solid state device for measuring the concentration oxygen dissolved in water) and (2) the likely errors that will be present when it is used to determine the size of the anomaly in concentrations of oxygen present in sea water (the anomaly is the difference between the observed concentration and the equilibrium saturation concentration).

An Optode has been used as part of the "FerryBox" system on the P&O Ferries vessel the MV Pride of Bilbao since the beginning of 2005. This report covers data collected through 2005 and 2006. The accuracy, precision and stability of the Optode have been compared against measurement of oxygen in water samples collected and processed on board the ship by Winkler titration and estimates of the oxygen anomaly.

Part 1 of the report describes the scientific value of oxygen data, the basis of the Optode measurement, its installation and maintenance on the ship and availability of the data.

Oxygen is a key biogeochemical parameter. Changes in concentration of oxygen can be directly related to changes in biomass. For surface seawater where both data for oxygen and wind speed are available the flux of oxygen across the sea surface can calculated and related to net biological production. This was done successfully working from the Pride of Bilbao in 2004 using oxygen measurements made on collected water sample (Bargeron et al., 2006).

New solid state devices such as the Aanderaa Optode offer the possibility of autonomous measurement of oxygen and improvement in the assessment of productivity through measurement of concentration oxygen dissolved in seawater. In the Optode, oxygen is measured through its reaction with a sensing foil containing a platinum porphorine complex, the fluorescence of which is reduced by the presence of oxygen. An Optode was added to the "FerryBox" system on the Pride of Bilbao in 2005. Data has been recorded every 30 seconds since then.

PART 2 of the report describes operational experience with the Optode and its calibration and validation of relative to measurements of oxygen by Winkler Titration. The errors in the determination of oxygen anomaly prior to the calculation of sea to air fluxes of oxygen are then considered.

The comparison of the Winkler data with the output from the Optode suggests that the accuracy of the Optode in both years was close to 98% of the true value when compared to the Winkler measurements. The data suggest that the precision based on the comparison of the two data sets was equivalent to standard deviation of 5 μM or 2% of the average value in 2005 and 2.9 μM or 1% of the average value in 2006.

Comparison of data from the Optode to Winkler titration data probably underestimates the quality of the precision of the Optode measurements; this is because of the errors inherent in the application of Winkler procedure itself. Data records from use of the Optode in the FerryBox system indicates that the resolution of the Optode is better than 1 μM/L.

This level of precision is close to that of our knowledge of equilibrium solubility of oxygen at different temperatures and salinities (Garcia and Gordon, 1992). The Garcia and Gordon equation can be used to estimate errors in calculation of the oxygen saturation values associated with errors in the measurement of temperature and salinity. At temperature of 15 °C and a salinity of 35.0 an error in the temperature measurement of 0.2 °C will generate an error in the calculated saturation of about 1 μM/L. The same error in oxygen of 1 μM/L will be generated by an error in the measurement of salinity of 0.65.

Salinity data from the Portsmouth to Bilbao FerryBox has been shown to have an accuracy and precision of 0.1. This suggests that the errors in calculation of oxygen anomaly from errors in salinity are insignificant.

However we have identified two sources of error in measurement of temperature. These do produce significant errors in the estimation of oxygen anomaly values. Temperatures measured using sensors in board the ship are higher than “true” temperatures. The error changes through the year as the difference in temperature between inside the ship and the external water temperature changes. This error may be as large as 0.5 °C. The anomaly has to be calculated using temperature measurement in the water flowing past the Optode. This is because of delays and mixing in the water being pumped into the ship this has smoothing effect on the data, and can enhance the difference between the internal and external temperature to being as high as 1.0 °C. Consequently to avoid this large error due to the timing of the measurements the oxygen anomaly should be calculated from the temperature measured in the pumped water stream adjusted by an offset to the “true” outside temperature. Work is still being done to establish this offset and how it varies through the year. This being done by comparing data from the Seabird 48 hull mounted temperature sensor, the ISAR sea surface radiometer mounted on the above the bridge wing and data from monthly tow of temperature recorder fitted to the CPR (Continuous Plankton Recorder).

Further work is also needed to establish the relative size of errors in the estimation of oxygen anomaly as a result of:- (1) differences between the sea skin temperature which will change the partial pressure of oxygen at the sea surface and (2) changes in the actual concentration of oxygen through the day due to the diurnal cycle of production and respiration.

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PART 1 Background description of the instrument and installation

Background - Scientific Aims

Scientific Value

Oxygen is a key biogeochemical parameter which is evolved from photosynthesis and consumed by respiration. In observing systems its value lies in the simplicity of the measurement and the stoichiometric relationship of changes in concentration with of organic carbon (1.3:1). Fluorescence measurements are commonly used for rapid assessments of changes in biomass. Fluorescence is taken as a measure of chlorophyll but due to change in plankton type and photo-physiology of the plankton its ratio to concentrations of chlorophyll can vary widely. Mean ratios measured during calibration crossing varied by an order of magnitude between Portsmouth and Bilbao in 2003 and 2004 (see Qurban et al., 2004). In turn the ratio of chlorophyll to biomass carbon also can vary by an order of magnitude (Steele, 1964).

Use of measurements dissolved oxygen to estimate biological production

In 2004 the NOC Portsmouth Bilbao FerryBox was used to test the hypothesis that calculations of oxygen flux could be used successfully to estimate biological productivity (Najjar and Keeling, 2000; Bargeron et al., 2006). Regular measurements of oxygen concentrations were made from the Pride of Bilbao. Following the work of Najjar and Keeling (2000) and Garcia and Keeling (2001) the oxygen data were coupled with wind speed data to effectively estimate new production. Bargeron et al. (2006) showed that the resolution of the method was be sufficient to establish the magnitude of the contributions to the carbon cycle of the hydro-dynamically and bio-geo-chemically different region along the route.
In 2001, an oxygen Optode became available from the Norwegian Company Aanderaa. This had the potential to make continuous measurements of oxygen possible as a routine part of the FerryBox system. These continuous measurements were started in 2005. The functioning of this device has now been checked against oxygen concentrations measured by Winkler titrations during “calibration crossing” made on the ferry 2005, 2006. The sensor is described below and the installation on the ferry is shown in Figure 1.
Continuous measurements of oxygen offer the potential to improve the precision of the method developed by Bargeron et al (2006). That paper was an analysis of data collected at monthly intervals. The database that has been assembled from 2005 to 2007 should also enable a fuller analysis of the oxygen flux method to be carried out. The fuller data set will enable some of the sources of approximations made in the Bargeron et al (2006) paper to be examined more quantitatively. For example – (1) most obviously the variation in oxygen flux with in each month (2) diurnal variations in sea surface temperature which changes the oxygen solubility and hence anomaly (3) diurnal variation in the production respiration cycle which alter the concentration of oxygen in the water (4) errors resulting from higher wind speeds that result in wave activity that creates bubbles and so will tend to increase concentrations of oxygen in the seawater (5) the existing different parameterisations of gas exchange wind against wind speed may be testable against this extensive data set. Currently three different parameterisation of gas flux in relation to wind speed are commonly used to estimate gas exchange fluxes Wanninkhof (1992), Wanninkhof and McGillis, (1999) and

Nightingale and Liss (2003). There is some debate about which is the most appropriate to use in different circumstances (Wanninkhof et al., 2002; Nightingale and Liss, 2003).

Regional context - Quantification of the carbon cycle of ocean margins

The waters of the Northwest European shelf have been investigated for many years (e.g. Pingree et al., 1975; Puillat et al., 2004). Constraining estimates of seasonal primary production and respiration has proven difficult. Data sets tend to be sparse and incomplete (Frankignoulle and Borges, 2001) relative to the high temporal and spatial variability in the area (Wollast and Chou, 2001; Joint et al., 2001). Various methods have been utilised to estimate contributions of biological production and respiration to the carbon cycle, e.g. from bottle incubation experiments (Joiris et al., 1982) and radioisotope scavenged particle removal (Buesseler et al., 1992) to satellite remote sensing (Balkanski et al., 1999).
Estimates of seasonal primary production for whole shelf regions are usually extrapolated from sampling programmes of at best a few weeks in each of several years (Joint et al., 2001; Borges and Frankignoulle, 2003). Work to improve sampling frequency and geographical coverage is being done (Borges and Frankignoulle, 2003; Puillat et al., 2004, Hydes et al., 2004). Measurements are needed to asses the relative contributions of relatively small areas of high productivity, such as fronts, (Holligan, 1981 and 1989; Richardson & Pedersen, 1998) but which may make disproportionately large contributions to total production. The use of ships of opportunity (SOO) offers the required spatio-temporal resolution (Hydes et al., 2003) but this platform requires a complimentary method for measuring and assessing productivity and respiration.

Background to estimation of production from measurements of dissolved oxygen

Oxygen cycle studies have been also been used estimate production since Redfield (1948). A basic manual chemical measurement that is well understood (Winkler, 1888) has been used. Redfield (1948) reported observations of changes in oxygen concentration in seawater through the annual cycle of biological production and decay. Recent estimations of global new production have been made in the North Atlantic using oxygen fluxes to calculate biological Seasonal Net Out-gassing (SNO). These showed good agreement with site-specific new production and remineralisation estimates (Najjar and Keeling, 2000; Garcia and Keeling, 2001). The idea is that the flux of oxygen produced by photosynthetic biological production closely approximates new production within the mixed layer during the shoaling period - when the seasonal thermocline is strengthening (e.g. Jenkins and Goldman, 1985; Emerson, 1987; Keeling et al., 1993; Garcia and Keeling, 2001). The flow of oxygen across the air-sea surface is driven by the difference in oxygen concentration in the atmosphere and ocean. Equilibration will tend to occur in a few days to weeks following perturbations depending on the wind speed (Broecker and Peng, 1982). The physical and biological processes affect the concentration of oxygen at the sea surface. So that care has to be taken to work with data from period when the dominant process is biological production hence the choice of the shoaling period. Physical processes include air-sea gas exchange through surface turbulence and bubble breaking, solubility changes due to temperature and mixing of surface and deeper waters (Garcia and Keeling, 2001). Biochemical processes include production,

respiration and remineralisation of organic matter where photosynthesis produces oxygen and respiration consumes oxygen.
SNO is a measure of air-sea oxygen exchange and is defined as the spatially and temporally integrated oxygen flux over periods when the flux is positive i.e. sea to air in spring and summer. It is composed of biological and thermal components (Keeling and Shertz, 1992). The biological contribution, Biological Seasonal Net Out-gassing (SNO_B), can be separated from the thermal contribution (SNO_T) because changes in oxygen solubility due to changes in water temperature can be calculated. A key assumption of the method is that biological SNO, determined as the sum of positive oxygen fluxes, is approximately equivalent to net community production, NCP, the excess of gross primary production over total community respiration (Garcia and Keeling, 2001). NCP is considered almost equivalent to new production (Minas and Minas, 1992), the maximum exportable biomass that will preserve the long-term integrity of the system (Eppley and Peterson, 1979). Before the work of Bargeron et al. (2006) measurements have been tended to be too sparse to provide the kind of regional analysis that would distinguish the importance of features such as fronts. The use of the Optode (Tengberg et al., 2006) offers the possibility of enhancing the precision and accuracy of the approach taken by Bargeron et al., (2006) by enabling continuous autonomous measurements.

Background Description of the Oxygen Optode

Tengberg et al (2006) have described both the development of the oxygen Optode and its application in a number of environments including long-term deployments on mooring. Optode technology is based on the ability of selected substances to act as dynamic fluorescence quenchers. In the case of oxygen, if certain metal complexes are excited with a blue light they will emit a red luminescence. The intensity and lifetime, of the fluorescence depends on the ambient oxygen concentration. This can be followed in three ways:- (1) Intensity - how strong the return is (2) life-time - how quickly the return from a pulse of light dies out (3) phase shift between excitation and emmission. The different signal detection techniques are summarized by Wolfbeis (1991), Demas et al. (1999) and Glud et al. (2000).

Measurement principle

The Aanderaa Instruments, Oxygen Optode is based on oxygen luminescence quenching of a platinum porphyrine complex. Oxygen measurement is made by phase shift detection of the returning, oxygen quenched red luminescence. The relationship between oxygen concentration and the luminescent decay time is described by the *Stern- Volmer* equation:-

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

Where: τ = decay time, τo = 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 light and can be used directly for oxygen detection, without calculating the decay time.

Description of the Aanderaa Oxygen Optode

The sensor housing is made of Titanium and Hostaform, rated to 300 dbar pressure, with a diameter of 36 mm and a total length of 86 mm. This housing includes an optical part (Figure 2), a temperature sensor 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). The sensing foil is composed of the oxygen sensitive fluorescent substance (luminophore) that is embedded in a polymer layer, which is coated onto a thin film of polyester support. 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) is used as its dynamic range is greater. Two types of foils, with and without, a gas permeable protective black silicon layer are available (Figure 2). The silicon layer provides an optical isolation layer to avoid interference from fluorescent material in the surrounding water or direct incoming sunlight, when measuring in the photic zone. The disadvantage of this layer is that the sensor response time is slowed. For the NOC FerryBox system the silicon coated type is used as it was expected to be more durable for long-term deployments.
The Optode has a single lead to take power to the sensor and return RS 232 based data output to a logging system. The data output string is the Optode temperature and the temperature compensated oxygen readings in μM/litre and % saturation. The unit essentially measures the partial pressure of oxygen in the atmosphere or solution in which the unit is immersed. Internal processing of the data assumes that the water sampled is zero salinity. It has to be post processed to calculate the true oxygen concentration at the temperature and salinity measured at the time of sampling.

Fitting in the NOC FerryBox system.

In late 2004 two Optodes were purchased from Aanderaa. One was fitted to test its use in December 2004. The photographs in Figure 1 show the installation on the Pride if Bilbao. While the ship was at refit in January 2005 the units was returned to Aanderaa for recalibration, and it was refitted to ferry on the 16 February. The same unit (Optode serial number 3835-34) was run continuously through 2005. The second unit (Optode serial number 3835-33) was used through 2006. [Note: The units were returned to Aanderaa for recalibration as we were wrongly advised by Aanderaa's UK agents to calibrate the units ourselves. This proved difficult to do because calibration has to be done using water, which is 100% saturated. Producing such water in the laboratory is difficult to achieve. User recalibration of the units would be relatively simple if a measured oxygen value could be entered into the sensor's memory through its software rather than telling it is in saturated water.]

Maintenance

In 2005 the Optode was not cleaned between installation and until the end of the second calibration crossing. From then on the Optode has been cleaned each time the FerryBox units have been serviced onboard the Pride of Bilbao. This has been at intervals of approximately 9 days. Cleaning consists of wiping the surfaces of the Optode an the inside of hosing with wet paper towel. The window of the Optode it

cleaned using a cotton wool bud. No jumps in sensor output have been detected in conjunction with cleaning the membrane.

Data Availability 2005 & 2006

There have been no problems with data availability from the Optodes themselves. Data was lost due to failures of other parts of the system. The success of the system in this respect is shown in Figure 3, which shows dot plots of the oxygen data from 2005 and 2006 plotted against latitude between Portsmouth and Bilbao and time.

PART 2 Operational experience

Calibration and validation of Optode data

Winkler Titrations

The reference point for all oxygen measurements is the "Winkler Method". The standard method to determine concentrations of oxygen in water is a two-step wet chemical procedure. Winkler first described the method in 1888. The Winkler titration is performed on collected water samples. The collection and handling of water samples can induce errors. The analytical work is time consuming and demands meticulous care. Details of the methods applied by NOC are described in the appendix. The appendix document is slight up data of IOS-JRC Internal Document 20 (1995).

Methods - Winkler

On certain crossing of the Pride of Bilbao between Portsmouth and Bilbao personnel from NOC sail with the ship to collect water samples, for calibration of the autonomous instruments and for other studies. Three people are involved when possible, so that samples can be collected 24 hours per day. These "calibration crossings" are planned to occur eight times a year 6 times in the most biologically active period between February and July and twice in the autumn. Samples for the determination of oxygen were collected on 8 crossings in 2005 and 4 crossings in 2006.
A pair of samples was collected (on most crossings at hourly intervals). The same procedures for samples collection and processing as described in IOS-JRC Report 20 (see Appendix) were followed, except that the sample bottles are filled from an in-board tap. The tap is mounted in the water supply line to the autonomous sensors at the point where water is taken off from the ships water supply being pumped through the ship for cooling of the ships refrigerated spaces. Samples are titrated when possible an hour after sampling. The IOS-JRC method uses a Metrohm Titrino and the potentiometric end point detection described in Grasshoff et al. (1983)
The thiosulphate solution used in the titration is standardised against an iodate solution prepared at NOC (and against the commercially available standard prepared and supplied OSI, Fareham, UK). A standardised work sheet is used and the results calculated in micro-moles per litre by entering the titration values the bottle volume and temperature of the water at sampling into an excel work sheet.

Methods - Optode

The data is output from the Optode at 30 second intervals. At this rate of measurement the power consumption of the Optode is sufficiently low for internal heating not to affect the stability of the data output from the sensor. Data is logged along with data for conductivity, temperature and fluorescence measured by a Chelsea Technologies Group MiniPack (which is mounted in a flow chamber adjacent to the Optode flow chamber), GPS position and time data. (The full data set is logged via purpose built PC based logger to a data card. The data card is changed each time the equipment is cleaned.) The internal firmware of the Optode outputs the temperature at which the Optode measurement is made and a value for the concentration of oxygen and the

oxygen saturation level. The default output (which is recorded in the NOC system) assumes that the salinity of the surrounding water is zero. Optode is detecting an "activity" of oxygen in the water, which is related to the partial pressure of oxygen in solution. The partial pressure varies with the solubility of oxygen at the in-situ temperature and pressure of the water. The output from the Optode therefore has to be corrected for the true salinity of the water.
The equation for the correction is
$O_2c = [O_2]*e^S(B_o+B_1T_s + B_2T_s^2 + B_3T_s^3) +C_oS^2$
Where
O_2c =corrected oxygen concentration (µM/L)
$[O_2]$= Optode output oxygen concentration (µM/L) were
S = in-situ salinity
T_s = is the adjusted temperature = LN((298.15-t)/(273.15+t)) were t is the observed temperature
B_o = -6.24*10^-3
B_1 = -6.93*10^-3
B_2 = -6.90*10^-3
B_3 = -4.29*10^-3
C_o = 3.1168*10^-7
At a temperature of 10° C and a salinity of 35.5 an Optode observation of 380 µM/L corrects to an in situ concentration of 303.3 µM/L. At 10.5° C the apparent oxygen concentration is 303.3 µM/L and at a salinity of 35 the apparent oxygen concentration is 304 µM/L.
For the calculation of in-situ oxygen concentration the salinity of the water needs to be known. A set of salinity data termed "Best Sal" is used for calculation of the in-situ oxygen concentration. To obtain "Best Sal" data "Raw salinity" is first calculated from the MiniPack conductivity and temperature data. The "Raw salinity" is corrected to "Best Sal" on the basis of salinity samples collected on the calibration crossings and when the system is serviced. The salinity of these samples is determined at NOC using and Guildline Salinometer and are standardised against OSI Standard Seawater.
The in-situ oxygen concentration is than calculated using the calibrated salinity data from the MiniPack and the temperature recorded by the Optode itself, as it is this temperature that has been used in the factory calibration of the instrument.
The output from the Optode is then further corrected on the basis of the comparison with the Winkler titration results samples. For this comparison data from the Optode averaged over periods of 5 minutes are used, an average of 10 readings. This may introduce some noise into the data but as the collection of the oxygen samples normally takes about 2 to 3 minutes a more precise match up would be difficult to achieve.

Results

(1) Variation over 5 minute intervals

To quantitatively validate the use data averaged over 5 minutes when assessing the accuracy of the Optode data relative to Winkler titrations - data for oxygen-Optode was extracted for the last four months of 2006 and in May and June 2007 from the web page data base. The median and standard deviation of the absolute changes over five minutes were calculated and the data is shown in Table 1.

The median change over a period of 5 minutes was about 0.3 µM in autumn and about 0.5 µM in spring. The standard deviation across the data sets about 0.6 and 1 µM respectively in autumn and spring. This suggests that some error will be introduced by not being able to a line the data sets accurately, but that the scale of the error is similar to that of the Winkler titrations. It will add to the spread of the data sets when compared but will not create a major source of noise. (The range of concentrations over which calibration data was collected was 230 to 340 µM/L.)

(2) Winkler Titration - precision

On the 8 calibration crossings carried out in 2005 and the 4 crossings in 2006 a total 562 pairs of Winkler titrations were successfully performed. The reproducibility of these duplicate measurements is summarised in Table 2.
The median difference between pairs of observations in 2005 was 1.5 µM with standard deviation of 2.2uM. In 2006 the corresponding values were 1.0 and 1.5 µM/L. As these errors are larger than the changes occurring over 5 minutes, this suggests that the main source of error is in the collection and processing of the samples rather than a true variation between the samples due to them not being collected at the same time.

(3) Winkler Titration - consistency

The consistency of the Winkler titration results from one set of calibration measurements to the next depends on the calibration of the thiosulphate solution used in the titration being accurately calibrated against a standard solution of potassium iodate (See Appendix). The standard iodate solution is prepared from dry salt at NOC. On occasions the standardisation of this solution is checked against an equivalent solution commercially available from OSI. In 2005 the standard deviation in the normality of the thiosulphate solution was 1.6 % in 2006 the range of values was 1.3 %.
Shifts the thiosulphate calibration due to inaccuracy in its standardisation will produce shift in the apparent calibrations of the Optode. Figure 4 shows a plot of the calibrated thiosulphate normalities against the derived Optode calibration constants. This plot suggests there is no obvious systematic error in the calibration of the Winkler titration that is consistent with the shift in the Optode calibrations.

(4) Comparison of Optode and Winkler results – individual crossings

The procedure to derive calibration information was to plot the Optode data corrected for the salinity of the sample against the lower Winkler titration result for each pair of samples. (The assumption is that as the deviation in the paired results is larger than the changes noted over 5 minute periods then the deviation is due to oxygen contamination of the samples. Therefore the lower value is the more accurate one.) This was done for each set of crossing data. The fit between the data sets was assumed to be linear. For each data set a calibration equation was calculated in Excel by (1) a least squares fit of the data forced through the origin and (2) without forcing the data through the origin.
The resulting plots for 2005 and 2006 are presented in Figures 5 and 6. In these plots the data for the individual crossings are shown in different colours. [The data for February and July 2005 and October 2006 are notably noisy. The data sets with the

better regression coefficients do correspond to those crossing during which the people collecting the samples were more experienced in working at sea.] The calculated fits are listed in Table 3.
Figures 5 & 6 show that there are apparent shifts in the calibrations from crossing to crossing. In Figure 7 the derived calibration constants are plotted against time. It shows no evidence of progressive drift. In Figure 7 the r^2 values are also plotted this high lights the noise seen in October 2006.
In 2005 the percent standard deviation of the calibration coefficient derived by forcing the data through the origin was 1.1% the level of variation. In 2006 variability seems to have been greater (see Table 3). When a free fit was applied to the different calibration crossings for the 2005 data, the standard deviation of the calibration constants rose to 2.9% reflecting the greater degree of freedom. When a free fit and forced fits were used for the all the 2005 data set the r^2 values were similar (Table 3).

(5) Comparison of Optode and Winkler results – annual summary

As above, for comparing the Optode and Winkler data the lower value of each pair of titrations was assumed to be the more correct. Starting with the data from 2005, the calibration coefficient calculated by a least squares fit forced through the origin is 1.017 with an r^2 value of 0.94. The data for 2006 gives a similar value of 1.022 and an r^2 of 0.96. In Figure 7 the calibration coefficients for the individual crossing are plotted against time. There is no sign in these plots of any consistent drift in the calibration of the Optode. The calibration coefficients suggest that the Optode data is reading about 2% low in both years. This level of accuracy is better than the value advertised by Aanderaa of "8 μM or 5%".
When a free fit is applied to the data for 2005 the resulting equation is

corrected (2005) O2 = Optode O2 *.9912 + 7.2.

In Figure 8 the residual difference between the Optode and Winkler values are plotted before and after correction using both the forced fit (equation 1) and the free fit (equation 2) coefficients. The effects on the median, mean and standard deviation of the difference is summarised in Table 4. The plots and summary suggest that there is no significant difference in 2005 between the two corrections. Both effectively reduce the median difference from 4.2 μM to -0.5 and -0.7 respectively. The standard deviation in the data is unaltered.
For the data from 2006 there is substantial difference in the equation resulting from free fit of the data

corrected (2006) O2 = Optode O2 *0.8807 + 35.6.

The effects of the two corrections are compared in Figure 9 and Table 4. These suggest that the equation derived from the free fit is the most appropriate one to apply. The linear fit reduces the median difference from 6.4 μM to 1.1 while applying the free fit reduces the median difference to -0.2 μM and also reduces the standard deviation in the data from 4.2 μM to 2.9 μM.

(6) Summary accuracy and precision based on Winkler comparison

The comparison of the Winkler data with the output from the Optode suggests that the accuracy of the Optode in both years was close to 98% of the true value when compared to the Winkler measurements. The data presented in Table 4 suggest that the precision based on the comparison of the two data sets was equivalent to standard

deviation of 5 µM or 2% of the average value in 2005 and 2.9 µM or 1% of the average value in 2006.

(7) Other indications of precision

Aanderaa suggest that the Optode is capable of a resolution is better than 1 µM or 0.4% of saturation (See Appendix). The deviation between Optode and Winkler data suggests a lower level of precision is being achieved in practice. However we know that some of the error comes from errors in the Winkler determinations and from problems with matching up the data.
Above we noted that for the Winkler titrations the median difference between pairs of observations in 2005 was 1.5 µM with standard deviation of 2.2uM. In 2006 the corresponding values were 1.0 and 1.5 µM/L, and that in spring the variation over 5 minute periods was as high as 1 µM/L. This is sufficient to explain most of the larger than expected apparent noise in the Optode fit in 2006. For 2005, we suspect that the higher apparent level of noise relative to 2006 may also stem from errors in the Winkler work in 2005 as more titrations were carried out by less skilled people in 2005 than in 2006.
If the data that is being recorded is inspected a sense of the actual noise in the output from the Optode is gained. A typical plot of the oxygen data transmitted to shore (at 5-minute intervals and available for inspection via the NOC webs site http://www.soc.soton.ac.uk/ops/ferrybox_index.php) is presented in Figure 10 alongside with the corresponding data for temperature. Figure 10 indicates that the resolution of the Optode is better than 1 µM/L and that at this interval of sampling the Optode is responding to changes in the water at rate similar to temperature sensor on the CTG MiniPack.

Use of oxygen anomaly data and the errors associated with its calculation

As explained earlier, the purpose of making measurements of oxygen is to determine the oxygen anomaly and then using wind speed data to determine the flux of oxygen across the sea surface in order to estimate net primary biological production. The oxygen anomaly is the difference between the observed concentration of oxygen and the equilibrium/saturation value for water of the same salinity and temperature. For a given salinity and temperature the saturation concentration of a seawater can be determined using the equation in Garcia and Gordon (1992). They suggest this allows the oxygen concentration to be calculated to within a (route mean square) error of 0.23 µM/L compared to the data of Benson and Krause (1984). This would suggest that target level of accuracy and precision should be of the order of 1 µM/L. This limit in the precision of our knowledge of oxygen saturations is set by what can be achieved using the Winkler titration when used by skilled operators. The precision of the data out put from the Optode appears to match it.

(1) Saturation and therefore anomaly calculation errors

The Garcia and Gordon equation can be used to estimate errors in calculation of the oxygen saturation values associated with errors in the measurement of temperature and salinity. At temperature of 15° C and a salinity of 35.0 an error in the temperature measurement of 0.2° C will generate an error in the calculated saturation of about 1

μM/L. The same error in oxygen of 1 μM/L will be generated by an error in the measurement of salinity of 0.65.

(2) Relative size of differences in Optode and Winkler data to the size of the measured anomaly

In Figure 11 for 2005 data, for each of the collected calibration samples, the range of the difference between Winkler titration value and the Optode measurement, is compared to the range of values in the calculated oxygen anomalies. This plot suggests that the anomalies being observed are similar to or greater than the errors in the Optode data suggested by comparison with the Winkler data. The mean difference between the Optode and Winkler values was -0.2 and the mean of the absolute differences was 3.2 μM/L. The mean anomaly in the same samples was 16.5 μM/L.
Figure 12 shows the same data as Figure 11 for the error and anomaly plotted against the sample concentrations. The error between the Optode value and Winkler titration is independent of the concentration. At lower concentrations the errors and the anomaly are similar. At higher concentrations the anomalies are significantly higher than the errors. [Note: Concentrations of oxygen will tend to be highest at the time of the spring bloom because of the coincidence of (i) oxygen produced by the bloom (ii) waters which will have only warmed a little above winter minimum temperatures and will therefore tend to have higher concentrations because of the greater solubility of oxygen at lower temperatures.]

(3) Errors in calculation of oxygen saturation using different sources of data.

(3a) Salinity

An error of 1 μM/L in the calculation of the oxygen anomaly will be produced by a salinity error of 0.65. The FerryBox system on the Portsmouth-Bilbao ferry uses Chelsea Instruments “MiniPack” to measure conductivity and temperature from which from which the salinity is calculated (Hartman, 2007). The manufacturer’s claimed accuracy and precision data for the MiniPack are:- (i) conductivity accuracy 0.005 mmho/cm with a resolution of 0.001 mmho/cm and (ii) temperature accuracy 0.003° C and resolution 0.0005° C (See Appendix CTG MiniPack data sheet). This would suggest that salinity should be determinable to an accuracy and a precision better than 0.01. In practice because of distortion of the field round the conductivity head in the flow housing, variations in location of conductivity head in the housing and fouling of the sensor head the accuracy and precision of the measurements is approximately 0.1. This level of accuracy is achieved by calibration of the data with samples collected on the calibration crossings and inspection of the data sets for crossing to crossing drift. These procedures (Hartman, 2007) produce maps of the salinity variation in time and space which are oceanographically consistent to better 0.1 salinity. This error in salinity (0.1) is equivalent to an error in the calculated oxygen saturation of 0.16uM/L at 15° C. [Note: The measured salinity is also used to correct the output of the Optode. The software in the Optode calculates the concentration of oxygen from its internal measurement of temperature assuming a salinity of zero. The output of the Optode is then corrected to the true salinity. As both the saturation concentration of oxygen and the Optode-oxygen concentration are calculated using the same salinity value, the errors from the salinity measurement

should cancel out as the anomaly is the difference between these two concentrations of oxygen.]

(3b) Temperature

At 15° C and salinity 35.0 an error in the temperature measurement of 0.2° C will generate an error in the calculated saturation of about 1 µM/L. The Optode includes a temperature sensor which has an accuracy of ± 0.05° C (Aanderaa data see brochure in Appendix). The internal software of the Optode uses this temperature to calculate the measured concentration of oxygen. This potentially adds an error of ±0.25 µM/L to the oxygen measurement. **[Note: The calibration of Oxygen Optodes' temperature sensors have not been checked so the size of this error is unknown.]**
The anomaly which determines oxygen flux is the difference between the observed oxygen concentration and the oxygen solubility at the sea surface.
To determine the anomaly we make 3 assumptions:- (1) that the concentration measured at the Optode is the true concentration. [This assumption is probably good because the Optode is in closed system so the water cannot degas or become contaminated once it enters the ship. Data from the conductivity sensor is noise free suggesting that the ships water intakes are not entraining bubbles. Sampling of the water for Winkler titrations shows no evidence of bubbles in the water stream and the data achieved from the Winkler titrations is oceanographically consistent (Bargeron et al., 2006).] (2) that the water in the surface mixed layer is well mixed with respect to the concentration of oxygen and that it is only water from the mixed layer that is drawn into the ship's sea-chest. (3) that we have a measure of temperature that accurately represents the temperature of the sea surface.
It is this third assumption that is most problematic. We have a number of sources of temperature information. Each of which is measured to relatively high degree of precision ± 0.05° C or better. There are two problems that have been identified these are warming of the water above the in situ temperature by the ship and the different response times of the sensors. The amount of warming one sensor relative to another is:- (1) Optode temperature sensor typically reads 0.2 ºC higher than the MiniPack temperature (2) MiniPack temperature sensor tends to read a higher temperature than the Seabird 48 hull mounted temperature sensor but this relation changes as the seawater temperature changes and the relative degree of warming imposed by the ships internal temperature changes The size of the off set and its change with temperature can be gauged by plotting the two data sets against one another. This done in Figures 13 & 14 for the data used for the oxygen calibrations in 2005 and 2006. Fitting trend lines to these two data sets gives equations for the relationship between the MiniPack and Seabird 48 temperatures of -

Tminipack = Thull * 0.98 + 0.37 (in 2006) and
Tminipack = Thull * 0.96 + 0.77 (in 2005)

The offset this probably lower in 2006 due to the increased rate of flow of water through the system due to removal of a second fluorimeter from the FerryBox daisy chain. The discrepancy is greater at lower temperatures and at about 20 ºC the two temperatures agree more closely. The minimum temperature observed on the route was 5 ºC in 2005. The offset at 5 ºC was 0.3 and 0.6 ºC in 2006 and 2005 respectively equivalent to oxygen errors of 2.3 and 4.5 µM/L at 5 ºC. At hull temperature of 20 ºC in both years the MiniPack temperature would have started to read a lower temperature of 19.97 ºC.

This shows that neither the MiniPack nor the Seabird 48 is providing a true measure of the water temperature outside the ship. Temperature data is also available from two other sensor systems and the offsets relative to these systems needs to be considered in order to produce a "best correction" of the temperature data.

(3c) Further temperature corrections

Temperature data is also available from:- (1) The ISAR radiometer measurement made of sea surface temperature using the ISAR radiometer instrument mounted on the bridge wing of the Pride of Bilbao (www.noc.soton.ac.uk/lso/isar/). The ISAR unit provides ship-based *in situ* skin sea surface temperature (SST) measurements (to validate skin SST from similar instrument flown on satellites) for periods of up to six months with a SST measurement accuracy of ± 0.1 °C. (2) Monthly tows of a Continuous Plankton Recorder (CPR) are made once a month from the Pride of Bilbao for SAHFOS. Since mid 2005 the CPR on this route has been fitted with temperature recorder.
Data from these sources is still being worked up. Wrenfried Wimmer (pers comm. NOC PhD student working on the data) suggests that the CPR tow data suggest that the Hull temperature sensor may be 0.2 to 0.3 °C warmer than the true temperature. ISAR temperatures and CPR temperatures tend to agree to within 0.1 °C taking into account surface warming and cooling effects. [Note: In addition to the Seabird 48 Hull mounted temperature sensor two sets have 3 thermistors have also been attached inside the hull of the Pride of Bilbao. One adjacent to the Seabird sensor in the forward pump room where temperatures range between 20 and 40 °C and one the an adjoining store area which is "air conditioned" to a temperature between 20 and 25 °C. This latter set of sensors tend to read 0.1 °C lower than those in the pump room.]
This would suggest that assessment of the true surface temperature cannot be achieved to an accuracy of better than ± 0.1 °C, and to attain this level of accuracy corrections need to be made to the data collected by the FerryBox sensors on the basis of information that is available from the Hull mounted and CPR thermometers. Why the adjustment is to the FerryBox sensors is explained in the next paragraph. Notes about the consideration that needs to be given surface heating effects and the diurnal cycle in biological production and respiration follows.

(3d) Adjustments required for the different rates of response of the different temperature sensing devices

An additional problem in defining the "true" surface temperature to use for the calculation of gas fluxes are the different rates of response of the different sensors. Estimation of "true" temperature has to be done by adjustment of the MiniPack (or Optode) because these temperatures represent conditions in the water flowing past the Optode (or CO2 system). This water has been pumped into the ship, this and its passage through the sea-chest this generates a delay relative to the external sensors and some smoothing of the signal due to mixing in the sea-chest. The response time of the hull temperature sensor is quicker than that of the MiniPack temperature sensor this due to the residence time of water in the sea-chest which is of the order of ten minutes. This delay generates the noise between the two temperatures measurements. In Figures 15 & 16 the difference between the two measurements are mapped in time and space. These maps show:- (1) that the noise is coherent. Figures 15 and 16 are plots of south bound and north bound data. As fronts are crossed in different

directions the sign of the differences is reversed. This introduces errors approaching 1.0 ºC between the MiniPack and Hull temperature data sets. (2) that the relative temperature difference between the two sensors changes as the temperature of the water changes with time of year.
The scale of this error which is larger than the warming error suggest that the best temperature to use for the calculation of the in-situ saturation concentration of oxygen is the MiniPack temperature because it is measuring in water which has been sampled at the same time as the Optode. The good correlation of the Hull and MiniPack temperatures (Figure 13 & 14) suggests that the MiniPack temperature can be corrected to take account of the heating by linear correction factor. If a similarly good regression can be found with respect to adjustment to towards the true surface temperature represented by the ISAR and CPR measurements.

(3e) Summary

We have identified two sources of error in measurement of temperature. These do produce significant errors in the estimation of oxygen anomaly values. Temperatures measured using sensors in board the ship are higher than "true" temperatures. The error changes through the year as the difference in temperature between inside the ship and the external water temperature changes. This error may be as large as 0.5 °C. The anomaly has to be calculated using temperature measurement in the water flowing past the Optode. This is because of delays and mixing in the water being pumped into the ship this has smoothing effect on the data, and can enhance the difference between the internal and external temperature to being as high as 1.0 °C. Consequently to avoid this large error due to the timing of the measurements the oxygen anomaly should be calculated from the temperature measured in the pumped water stream adjusted by an offset to the "true" outside temperature. Work is still being done to establish this offset and how it varies through the year. This being done by comparing data from the Seabird 48 hull mounted temperature sensor, the ISAR sea surface radiometer mounted on the above the bridge wing and data from monthly tow of temperature recorder fitted to the CPR (Continuous Plankton Recorder).

Further work –

(1) Bulk surface layer true temperature.

At wind speeds above 6 m/s surface waters should be well mixed and the ISAR (skin temperature) and other temperature data (bulk surface layer) should be at their closest (Craig Donlon, *Pers. Comm.*). Under these conditions an assessment needs to be made of the offset between the CPR temperature data, MiniPack and Seabird Hull Temperature data through the annual cycle. It is hoped that this will show a linear variation similar to that seen between the MiniPack and Hull temperature sensor.

(2) Skin temperature effects

The ISAR data needs to be looked at to scale the variation on skin temperature relative to the bulk surface water temperatures measured by the other sensors, resulting from the generation of a diurnal thermocline and wind chill factors. The uppermost millimetre of the ocean, or skin, can be as much as 0.7 °C cooler than the water just below (Ewing and McAlister, 1960) due to evaporative or radiative cooling.

Zeng et al (1999) found that the diurnal amplitude of skin temperature reaches its maximum of about 2.8 °C for daily averaged wind speed between 1–2 m/s and skin temperature between 20°–21_°C and decreases with greater wind speeds. The most frequent amplitude is about 0.5 °C, the average amplitude is 0.65 °C, and the accumulated frequency for amplitudes greater than 1 °C is 10% within the parameter space of daily averaged wind speed between 1 and 15 m_s^{-1} and daily averaged skin temperature between 18° and 34_°C.
[Notes: (quote from Met Office modelling web page. Two physical processes contribute to the discrepancy between skin and bulk SSTs. The first is the skin effect, which arises as a result of conductive heat loss from the ocean, and generally results in a skin temperature up to 0.4 ºC cooler than the bulk temperature, depending on the net heat flux and wind speed. The second is the development of the diurnal thermocline, a thermally-stratified layer which builds up under conditions of strong insulation and low wind speed. This can result in a skin temperature up to 3 °C warmer than the bulk temperature. We (*MetOffice FOAM model*) currently employ a skin to bulk conversion scheme which uses NWP model fluxes to predict the temperature difference resulting from the skin effect, and the likelihood of diurnal thermocline development. It also includes a number of quality control checks, which assign flags to the final bulk SST product indicating the confidence that can be placed in each temperature measurement.]

(3) Diurnal cycle in concentrations of oxygen resulting from the cycle in biological production and respiration.

The track of the Pride of Bilbao is such that the out and return journeys cover some sections of the track at similar time of day and other areas particularly the central English Channel and the southern Bay of Biscay are sampled in the night and afternoon. If diurnal biological cycle has significant effect on concentrations it should be discernable as a consistent difference the data from the out and return tracks are compared for these areas. Data is currently being processed for this comparison.

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Tables

Table 1.
Median change and the standard deviation in concentration of oxygen between consecutive oxygen samples when the data is reported at five minute intervals. Data calculated for different period in in 2006 and 2007, including data extracted during the calibration crossing in October and December 2006.

date	sept-dec 06	oct 06	dec 06	may-jun 07
median	0.33	0.33	0.30	0.47
stdev	0.54	0.75	0.59	0.97

Table 2.
Summary of the reproducibility of the Winkler titration data in 2005 and 2006. Lost samples are those where the titration difference was greater than 10 µMol or one of the samples was spilt.

year	2005	2006
Count (pairs)	348	214
lost	29	9
Max (µMol)	10.7	10.3
Min (µMol)	0.0	0.0
Median (µMol)	**1.5**	**1.0**
Stdev (µMol)	**2.2**	**1.5**

Table 3.
Summary of the calibration data from the individual crossings and for the data sets for each year. N = numbers of pairs of duplicate samples on each crossing, Nthio = normality of thiosulphate solution used in the Winkler titration, b = linear fit forced through the origin calibration constant, r2 =corresponding linear regression coefficient, b' calibration constant linear fit not forced through the origin, c = corresponding intercept, r'2 = corresponding linear regression coefficient.

2005	N	**Nthio**	b	r2	b'	c	r'2
feb	61	**0.1047**	1.026	0.922	0.976	14.4	0.925
mar	60	**0.1015**	1.005	0.963	0.995	3.1	0.964
apr	61	**0.1017**	1.017	0.919	0.994	6.8	0.920
may	47	**0.0996**	1.033	0.929	0.920	31.1	0.944
jun	52	**0.1004**	1.023	0.936	0.948	20.0	0.942
jul	35	**0.1000**	1.000	0.932	0.935	17.2	0.937
sep	8	**0.1018**	1.017	0.943	0.960	14.6	0.946
dec	41	**0.1002**	1.013	0.959	0.940	19.1	0.965
mean		**0.1012**	**1.017**		**0.958**	**15.8**	
stdev		**0.0016**	0.011		0.028	8.5	
%dev		**1.6**	**1.1**		**2.9**	**54.0**	
all data			**1.017**	0.943	1.0	7.3	0.944
2006	n	**Nthio**	b	r2	b'	c	r2
apr	57	**0.1004**	1.003	0.988	0.946	17.3	0.992
jun	43	**0.1000**	1.021	0.958	0.935	23.3	0.966
oct	58	**0.1002**	1.037	0.720	0.896	33.7	0.738
dec	62	**0.1013**	1.030	0.888	0.970	15.5	0.892
mean		**0.1005**	**1.023**				
all data			**1.021**	0.964	0.889	35.6	0.986
2007							
apr	57	**0.0995**	1.0219	0.940	0.941	21.9	0.947

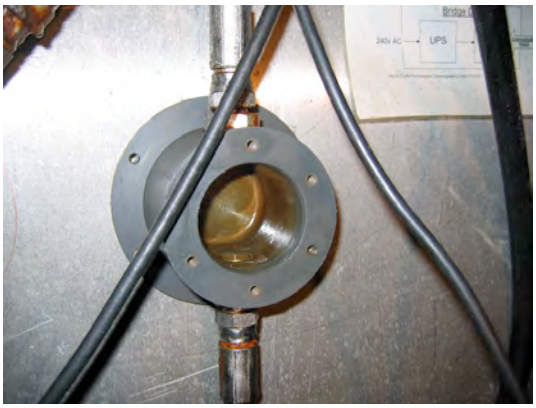
Table 4.
Summary of data on differences between Optode and Winkler data before and after correcting the data on the basis of the calibration equations derived from the whole year data sets for 2005 and 2006. All values are in µM/L.

	Opt 2005	W 2005	W-Opt 2005
n	361		
median	273.9	279.5	4.2
mean	276.6	281.4	4.9
max	337.0	341.4	29.8
min	235.3	240.4	-8.9
stdev	20.5	20.9	5.0
dif 1			
median	278.5		-0.5
mean	281.3		0.2
max	342.8		25.3
min	239.3		-13.5
stdev	20.8		5.0
dif 2			
median	278.7		-0.7
mean	281.4		0.0
max	341.3		24.9
min	240.5		-13.8
stdev	20.3		5.0

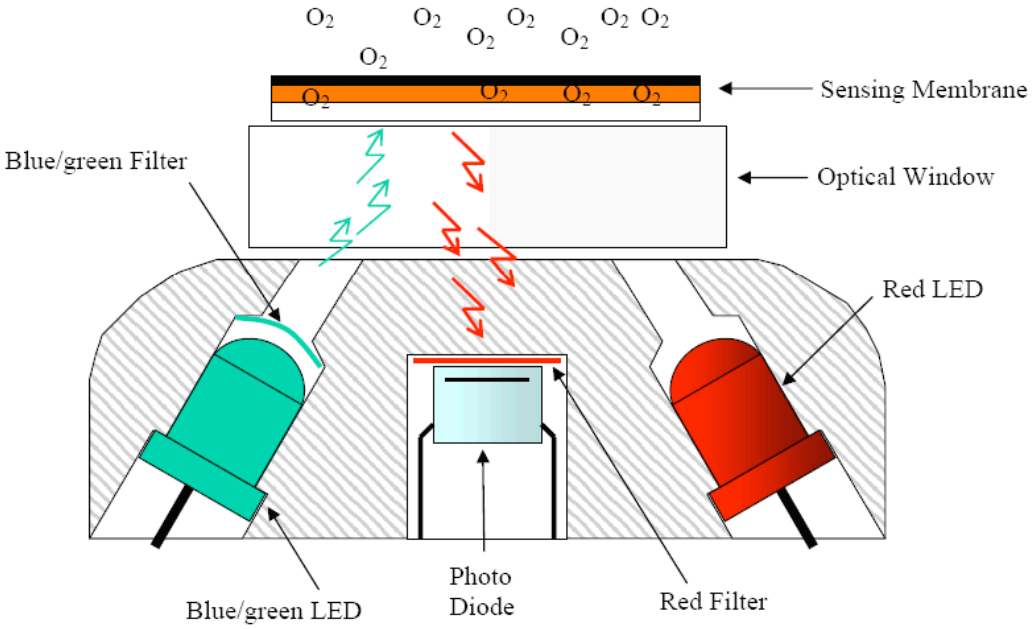
	Opt 2006	W 2006	W-Opt 2006
n	219		
median	261.1	268.0	6.4
mean	266.8	272.7	5.9
max	346.0	348.2	20.0
min	229.1	236.6	-5.0
stdev	27.5	24.6	4.2
dif 1			
median	266.5		1.1
mean	272.4		0.4
max	353.1		15.1
min	233.8		-12.1
stdev	28.0		4.7
dif 2			
median	267.6		-0.2
mean	272.7		0.0
max	343.1		10.8
min	239.2		-10.8
stdev	24.4		2.9

Figures

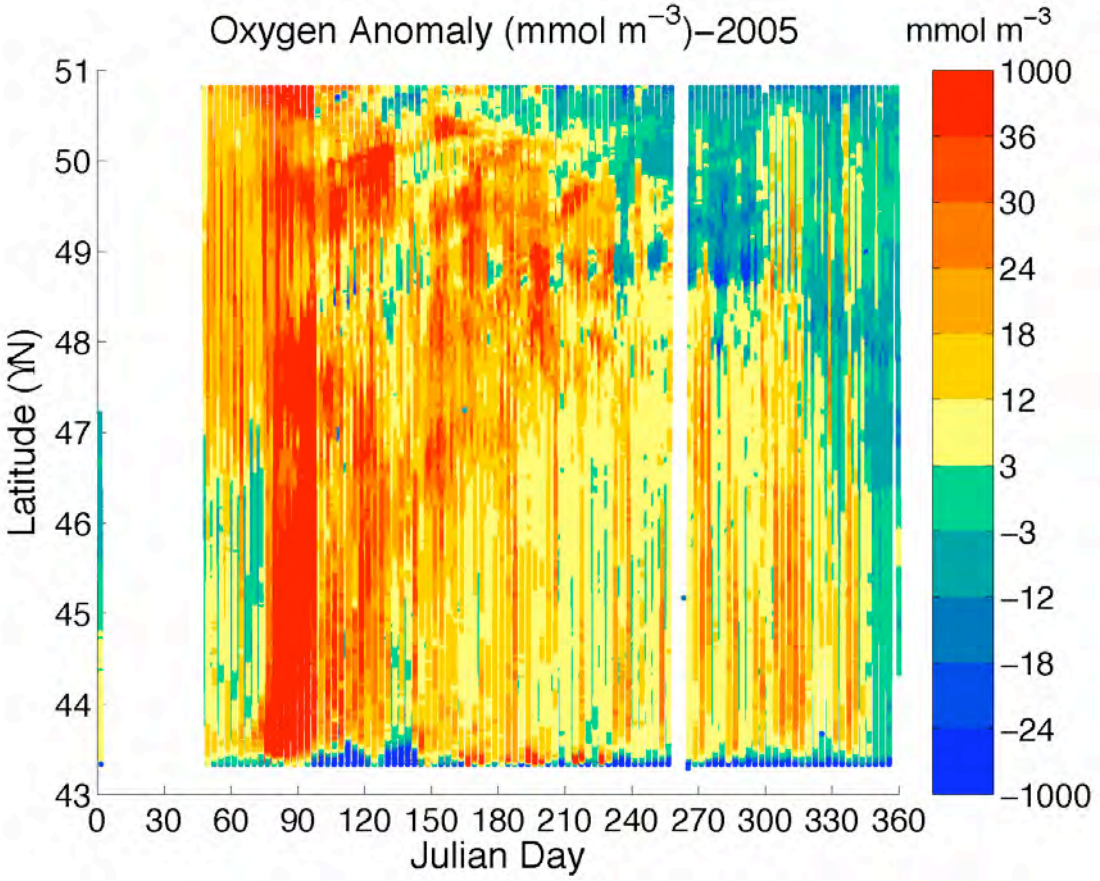
1. Photograph of the installation of the optode housing on the Pride of Bilbao and Optode removed from hosing for cleaning -s shows the high levels of fouling in summer 2005.

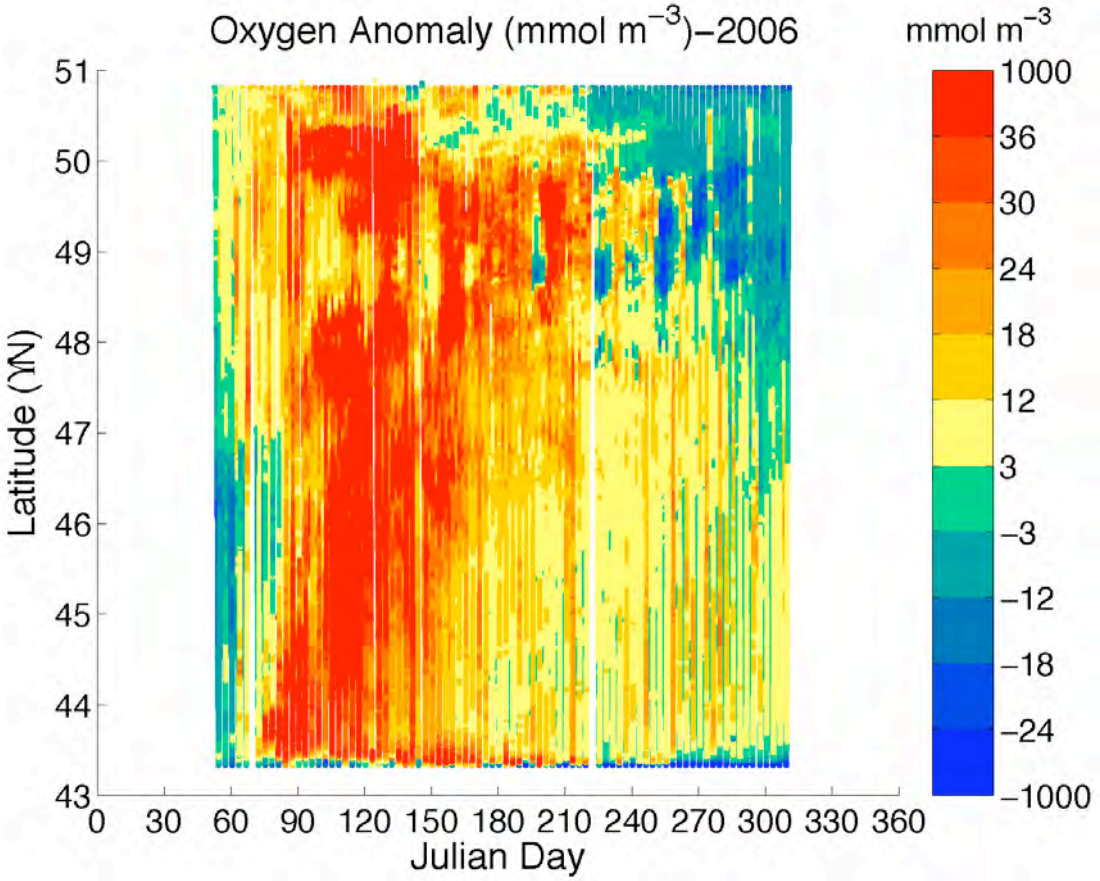


2. Diagram of the working parts of the Aanderaa Oxygen Optode (taken from Aanderaa brochure see Appendix 3)

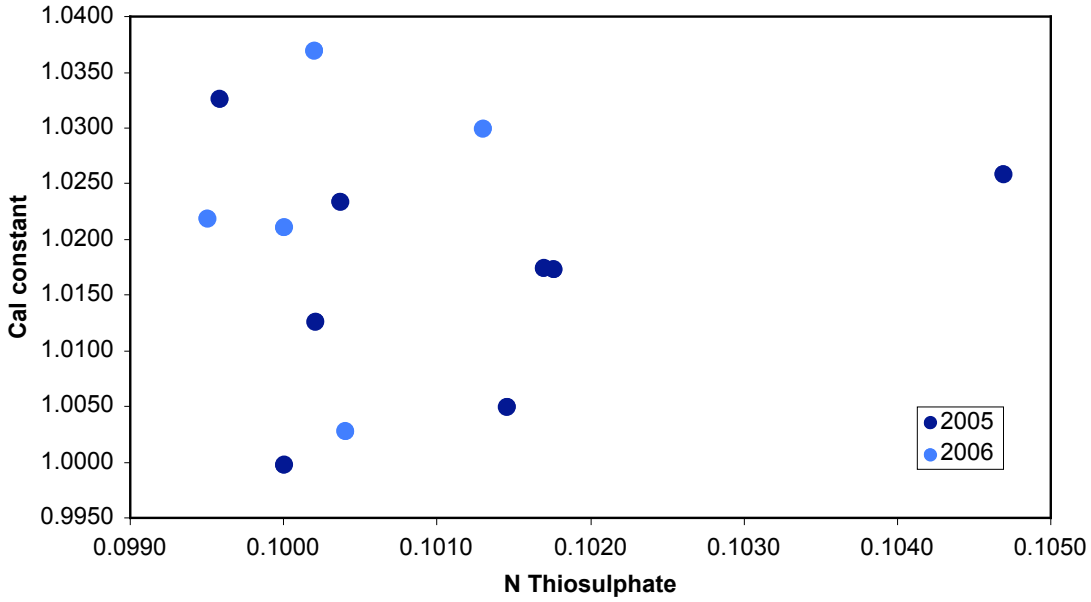


3. Maps of the 5 minute data for calculated oxygen anomaly in 2005 and 2006 based on measurements using the Aanderaa Optode.

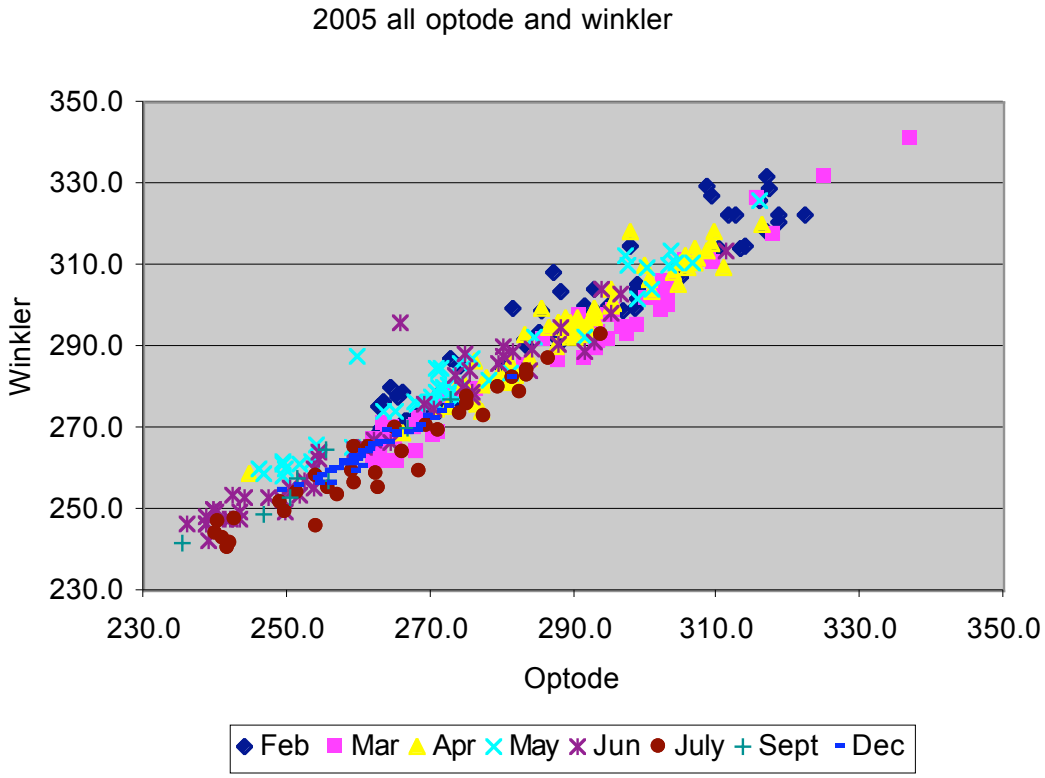




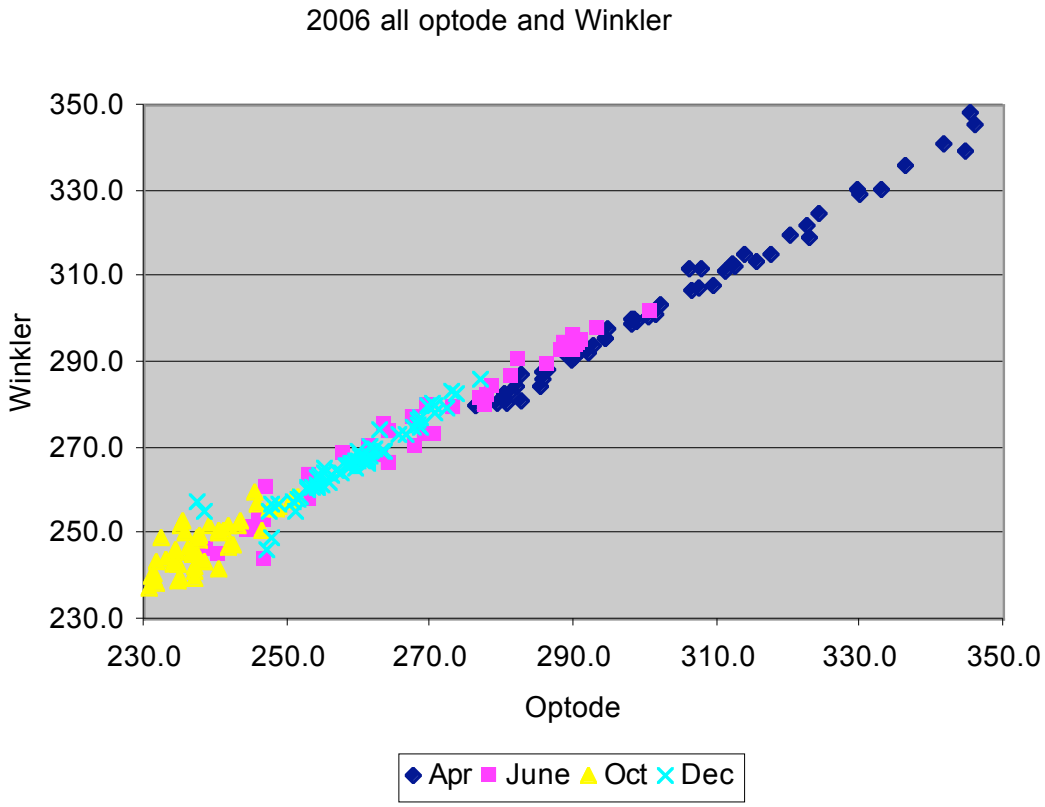
4. Plot of the thiosulphate normalities against the derived calibration constants for each of the calibrations crossing on the Pride of Bilbao in 2005 and 2006



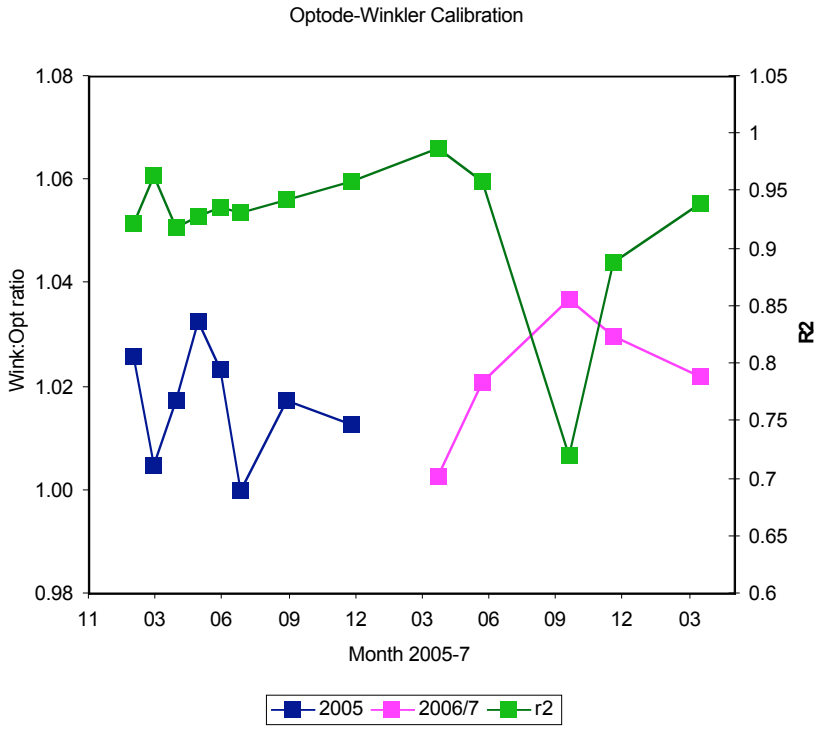
5. Plot of the Winkler data against the optode data (after correction for the salinity of the water) with each of the calibration data sets in 2005 distinguished. Optode data is plotted on the x-axis so the fitting a trend line calculates the required calibration equation.



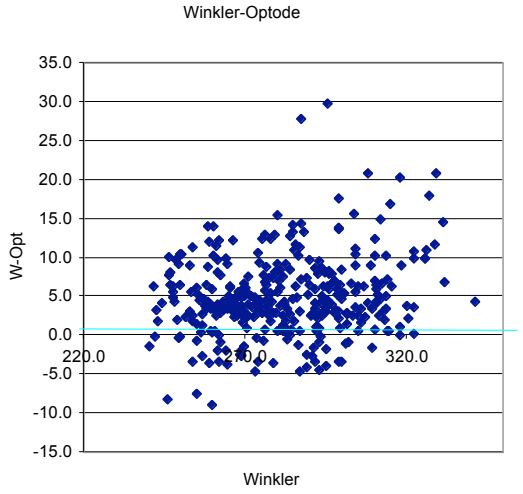
6. Plot of the Winkler data against the optode data (after correction for the salinity of the water) with each of the calibration data sets in 2006 distinguished.

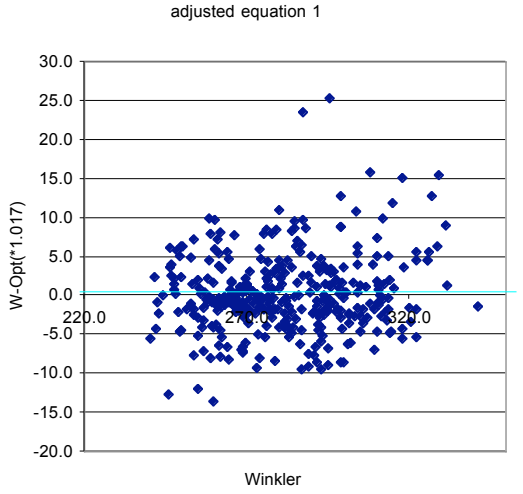


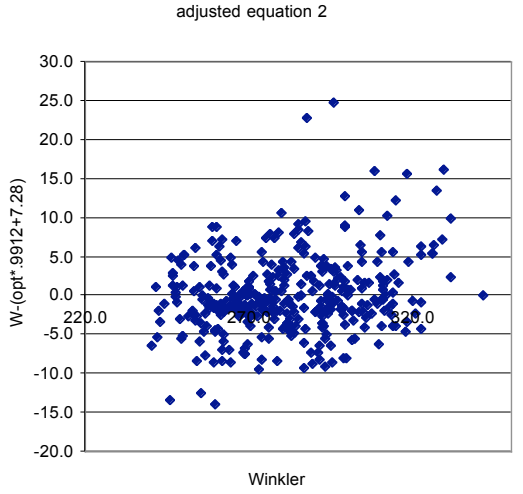
7. Plot the derived calibration constants and the corresponding R2 values against the date of the calibration crossings in 2005 and 2006.



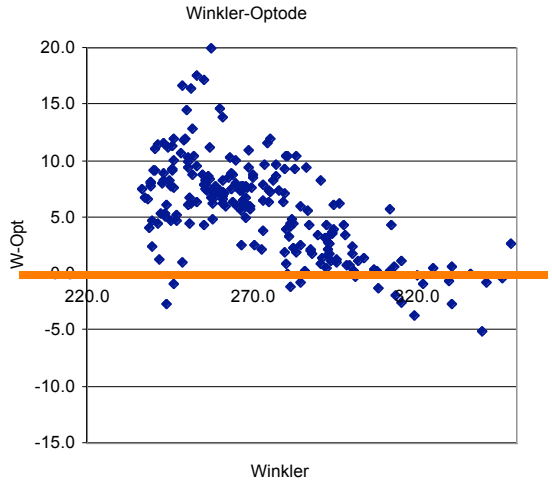
8. Plots of the residual differences between the Optode and Winkler values and the concentrations of oxygen in the samples determined by the Winkler method. (A) Before adjustment of the optode concentration for the calibration adjustment taken over the data for all the calibration sin 2005 (B) after adjustment by factor of 1.017 (C) after adjustment by factor 0.9912 and a constant +7.28

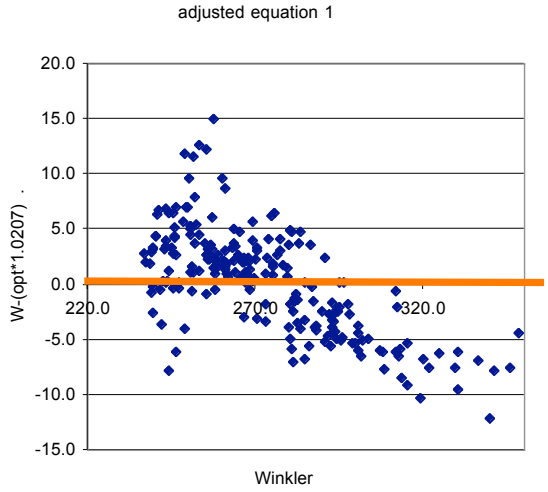


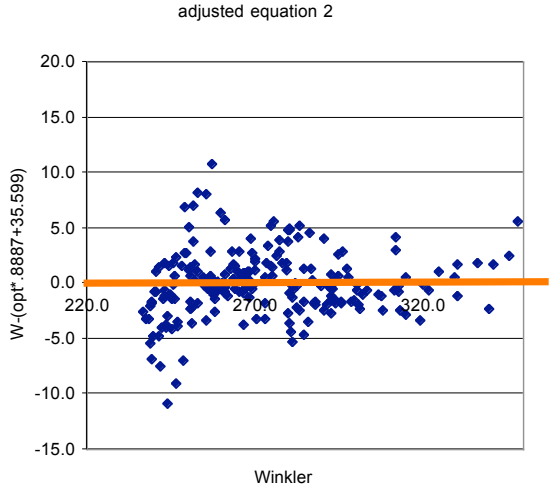




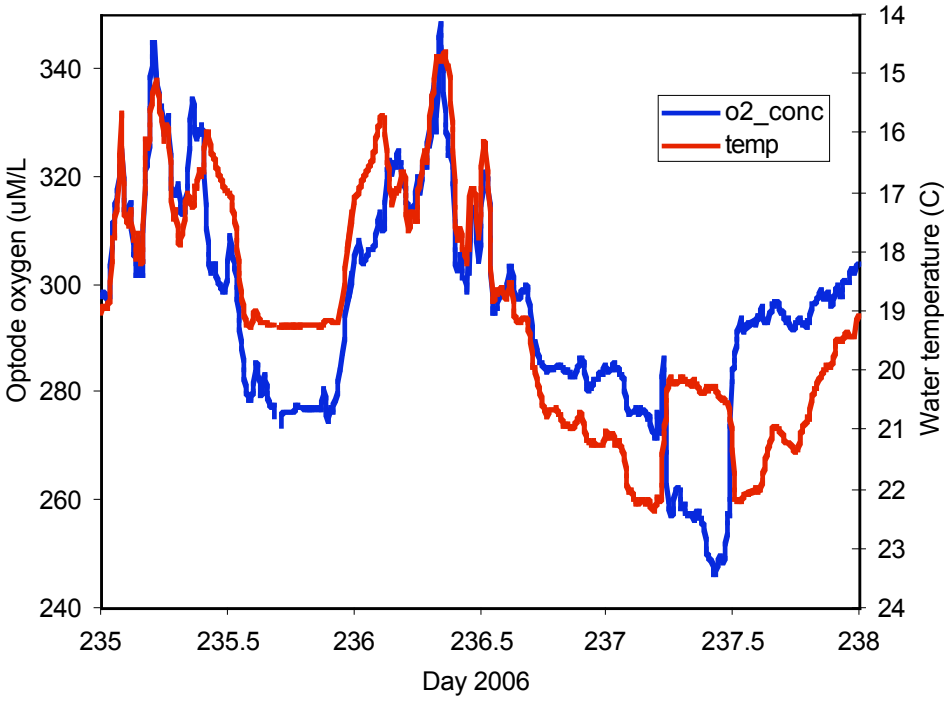
9. Plots of the residual differences between the Optode and Winkler values and the concentrations of oxygen in the samples determined by the Winkler method. (A) Before adjustment of the optode concentration for the calibration adjustment taken over the data for all the calibration sin 2006 (B) after adjustment by factor of 1.0207 (C) after adjustment by factor 0.8887 and a constant +35.599.



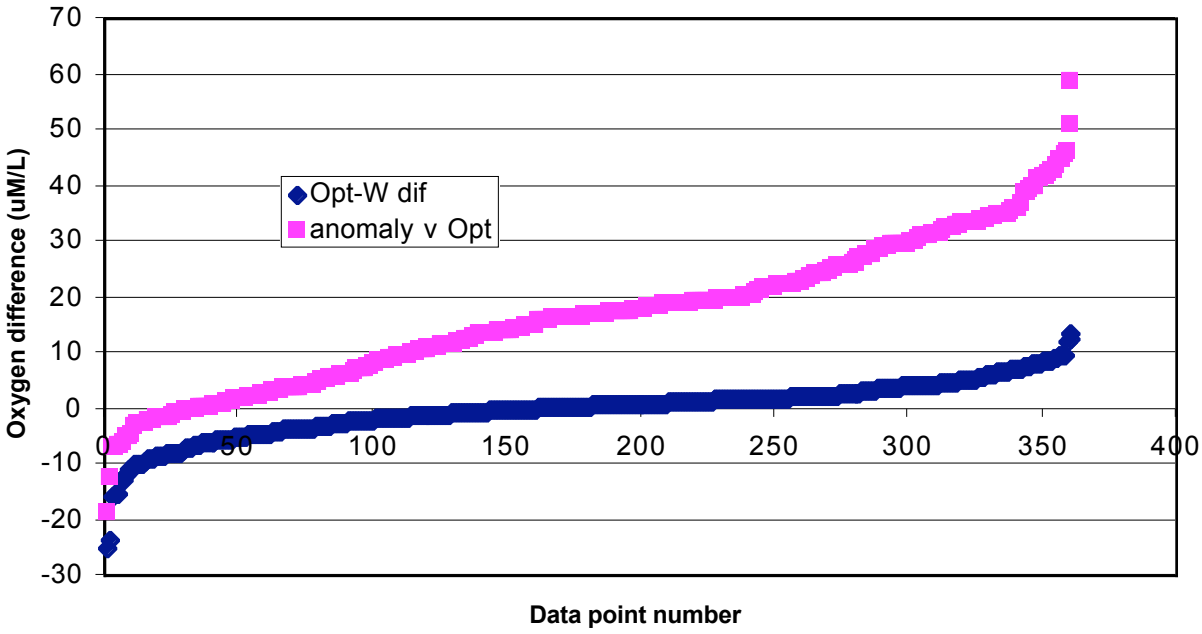




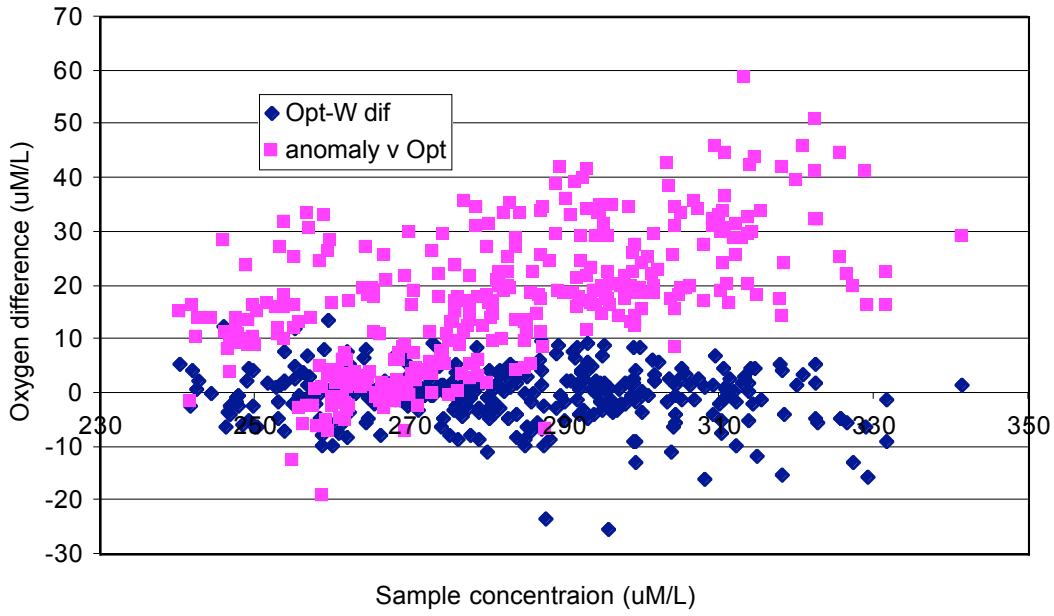
10. Representative data from 2006 to demonstrate the resolution of the Optode. Data at a resolution of one un-averaged data point every 5 minutes taken from the data archive attached to the NOC FerryBox webpages. www.soc.soton.ac.uk/ops/ferrybox_index.php



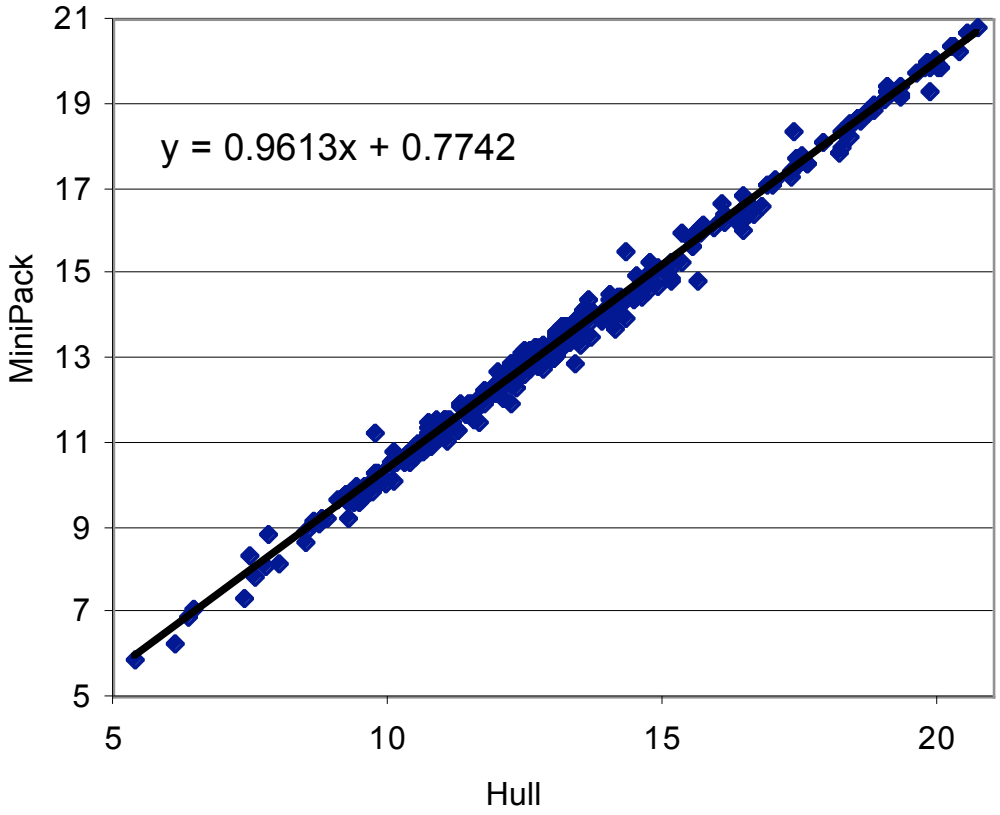
11. Winkler and optode titration data difference compared to the size of the calculated oxygen anomaly. Both sets of data sorted independently into size order



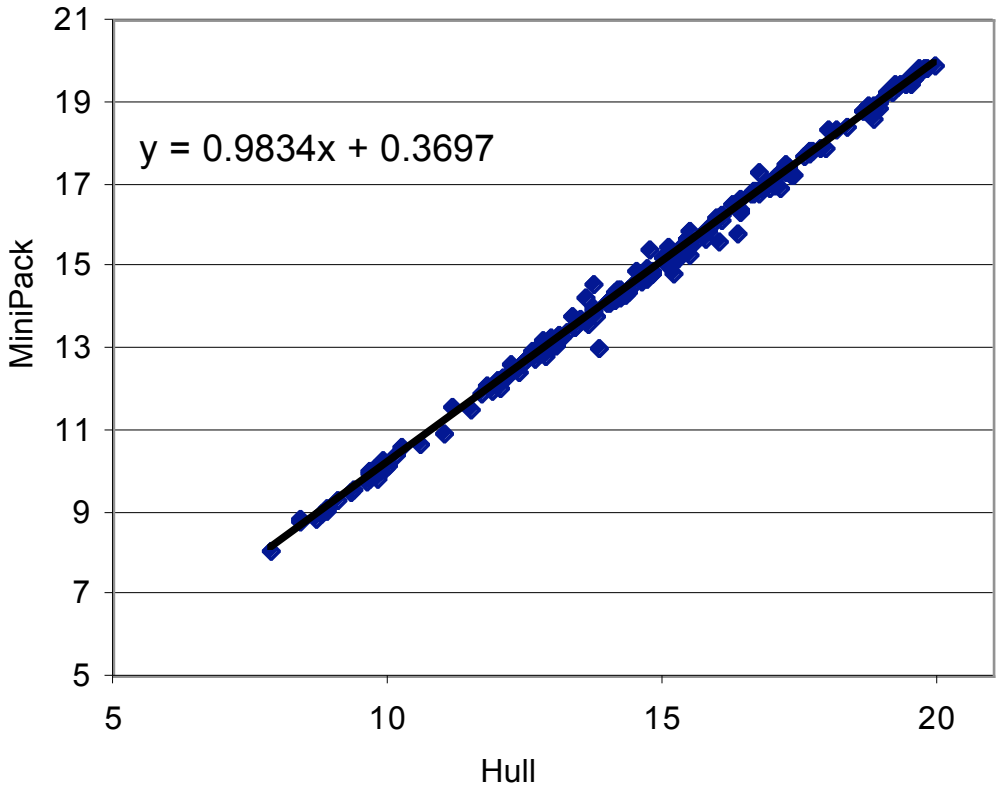
12. Winkler and optode titration data difference compared to the size of the calculated oxygen anomaly and plotted against the measured concentration of the sample.



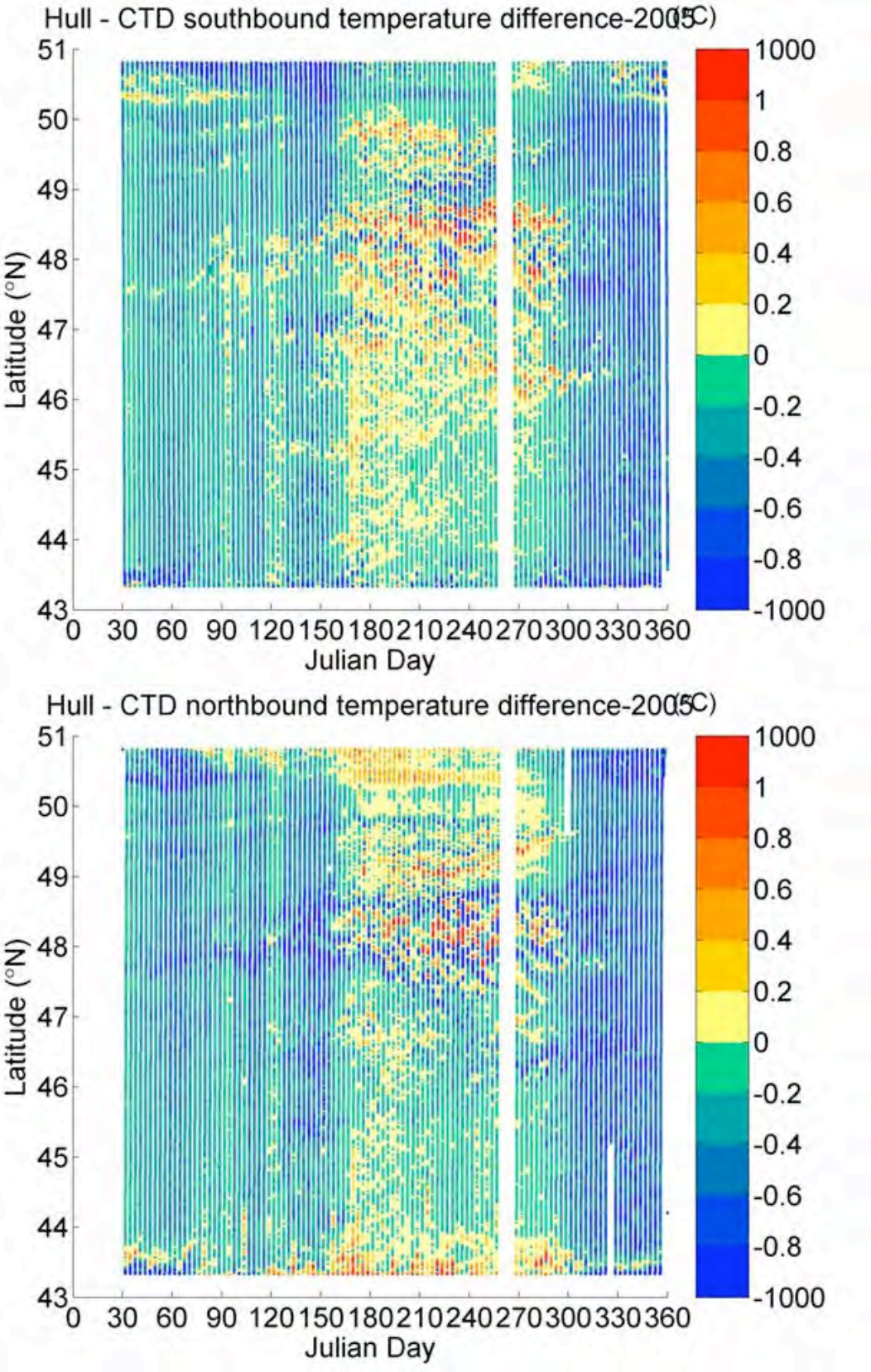
13. MiniPack temperature data plotted against Hull temperature data for the oxygen sample set for 2005



14. MiniPack temperature data plotted against Hull temperature data for the oxygen sample set for 2006



15. Plots by latitude and time of the difference in recorded temperature between the hull mounted Seabird 48 and the MiniPack temperature sensor



Procedures For The Determination Of Dissolved Oxygen In Seawater.
As used as part of the NOC FerryBox project

S E Holley and D J Hydes

Revised 2007

ABSTRACT

WOCE requires an accuracy of <1% and precision of 0.1% for dissolved oxygen measurements. The present IOS equipment used to achieve these aims includes a Metrohm Titrino, with amperometric end point detection.
In order to achieve a high quality data set consistent procedures must be followed at every stage from sampling, through to reporting the data.
The procedures used in the analysis of dissolved oxygen have been documented. Possible sources of error that may affect the precision of the final results are discussed.
The Excel work sheet used for calculation is included in the electronic version of this document.

Contents

1. PROCEDURE RECOMMENDATIONS

These procedures will be followed in order to achieve the WOCE criteria for accuracy and precision. An accuracy of <1% is required, with a precision of 0.1%. The end point of the standard Winkler Titration will be measured amperometrically by a dead stop titration.

2. BRIEF PROCEDURE OUTLINE

The basic outline of the procedure is as follows:

1) Collect a bubble free sample of seawater.

2) React oxygen in the sample with a mixture of manganous chloride and alkaline iodide, immediately sealing the bottle, at a known temperature.

3) Shake bottle vigorously to mix sample and reagents for at least 60 seconds.

4) After 30 minutes shake again.

5) After another 30 minutes add acid and titrate the liberated iodine against sodium thiosulphate, using an amperometric dead stop titration.

3. REAGENTS

All the reagents follow the WOCE recommended use of the Carpenter (1965) solutions. In this document concentrations are expressed both in terms of molarity and normality. The old chemical term normality is retained for consistency with earlier documentation, and because of its convenience for use in titration calculations. The molarity (M) is defined as the number of gram molecular weights (moles) of solute in 1L of the final solution. The normality (N) is defined as the number of gram-equivalent weights of the reactant in 1L of solution.

3.1 Reagent 1: Manganous Chloride 3M

Dissolve 600g of Analar grade $MnCl2.4H2O$ in 600 ml of distilled water in a beaker. Filter through a GF/F grade filter, to minimise blank readings, before making up to 1L. Dedicated glassware should be used in the preparation to avoid manganese contamination in other reagents.

3.2 Reagent 2: Alkaline iodide - sodium hydroxide (8M) and sodium iodide (4M)

Dissolve 600g of Analar grade NaI in 600 ml distilled water and then slowly add 320g NaOH. Care should be taken as the reactions are exothermic. Discard the solution if, at any stage it is cloudy or a yellow-brown colour develops. Filter through GF/F filter papers before making up to 1L.

3.3 Reagent 3: Sulphuric acid 10N(5M)

Slowly add 280 ml concentrated acid to 600 ml of distilled water then allow the solution to cool before dilution to 1 L

3.4 Sodium Thiosulphate 0.02N (0.01M)

Dissolve 25g of $Na2S2O3.5H2O$ in 1L of distilled water to be used with the 5 ml Metrohm burette exchange unit. Bulk quantities can be prepared onboard and stored in Winchesters. The solution is stable if kept in a dark, sealed bottle.

3.5 Potassium Iodate Standard 0.01N (0.0016M)
Potassium iodate (KIO3) is dried overnight at 110°C, cooled in a dessicator then weighed out to five decimal places and the weight recorded. For a 0.01N solution 0.3567g is dissolved in a calibrated 1L volumetric flask at a recorded temperature. The weight does not have to be exactly 0.3567g but the weight must be precisely recorded to 5 decimal places. The solution is stable indefinitely.

Note:
It is required that sodium hydroxide and sulphuric acid should be taken to sea in 2.5L Winchester bottles, in dangerous goods packaging. Manganous chloride is also taken in liquid form but as it is not classed as a dangerous chemical it can be taken to sea in 'Safepak' containers. These reagents are prepared on shore to minimise the risk involved in handling caustic exothermic solutions at sea. Bulk quantities should be made up, sufficient for the proposed cruise campaign.

4. CHEMISTRY OF THE METHOD

4.1 Equations of the Winkler titration
The equations involved in the Winkler Titration (Grasshoff et al. 1983) are as follows:

1) Precipitation of manganous hydroxide.

$$Mn^{2+} + 2OH^- = Mn(OH)_2$$

2) Uptake of oxygen by conversion of Mn(II) to Mn(III). Dissolved oxygen becomes chemically bound by manganese (II) hydroxide in a strongly alkaline medium. This is the key reaction of the Winkler method. The oxidation results in a mixed precipitate of manganese (II) and (III) hydroxides.

$$2Mn(OH)_2 + 1/2O_2 + H_2O = 2Mn(OH)_3$$

3) Acidic oxidation of iodide to iodine when acidified to a pH of 1.0 - 2.5. The precipitated hydroxides dissolve and Mn (III) ions are liberated.

$$2Mn(OH)_2 + 2I^- + 6H^+ = 2Mn^{2+} + I_2 + 6H_2O$$

4) Complexing of iodine with excess iodide to form a less volatile ionic species.

$$I_2 + I^- = I_3^-$$

5) Iodine is titrated with thiosulphate resulting in the reduction of iodine by the thiosulphate to iodide, in turn the thiosulphate is reduced to the tetrathionate ion.

$$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}$$

6) In the standardisation of thiosulphate, using the primary potassium iodate standard, iodate oxidises iodide to titratable iodine (then equations 4 and 5 above).

$$IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O$$

4.2 Titration equivalences

The endpoint of the titration is given when the number of equivalents of thiosulphate added and the number of equivalents of iodate balance and the fraction of iodate neutralised reaches unity. One mole of iodate is equivalent to six moles of thiosulphate and one mole of oxygen is equivalent to four moles of thiosulphate. The oxygen concentration in the sample is calculated by proportion.

4.3 Basis of the endpoint detection

In the dead stop titration two bright platinum electrodes with small surface areas are used as indicator electrodes. A dc voltage of 200 mV is applied to the electrodes. The cathode is depolarised by the reaction shown below:

$$I_3^- = I^- + I_2$$
$$I_3^- + 2e^- = 3I^-$$

The anode is depolarised by the reverse reaction. A current flows only if iodine and iodide coexist in the solution. The oxidation of thiosulphate is irreversible and cannot depolarise the electrodes.

$$2S_2O_3^{2-} = S_4O_6^{2-} + 2e^-$$

With decreasing iodine concentration during the titration the initial current drops until it is almost zero when all the iodine is reduced at the end-point of the titration. If the stirring of the solution is constant the decrease in the current is directly proportional to the decrease in iodine concentration. The small remaining current after the end-point is caused by minor components of the solution.

5.0 EQUIPMENT

5.1 Equipment calibration

All volumetric apparatus must be calibrated on shore before a cruise, this includes the following equipment:

- 10 ml pipette, for dispensing iodate standard (spares must also be calibrated);
- 1 ml fixed volume Eppendorf pipette, for iodate when measuring blanks although the precision is more important than the accuracy in this case;
- piston burette in the exchange unit;
- Repeat dispensing pipettes used for sulphuric acid, manganous chloride and alkaline iodide;
- 1L volumetric flask for iodate standard preparation.

The calibration is done by finding the mean weight of pure water contained in, or delivered by, the apparatus at the calibration temperature Adjustments are made to take account of buoyancy correction and the density of pure water at this temperature. The buoyancy correction factor is necessary as the weight of an object is less in air than in a vacuum. Calibration is normally done at 20°C.. The calibration equations whereby buoyancy, temperature and density corrections are made to arrive at the true volume at 20°C are given by Culberson in the WOCE operations manual. Even if a

class A flask is used it must still be checked as the calibrations are only certified to 0.3%.

5.2 Equipment descriptions and set-up

5.2.1 Sample bottles

Wide neck borosilicate glass bottles with an approximate volume of 100ml. The elongated bottle stoppers are unique to each bottle and have the same number engraved onto them. They have been produced to have a sloping surface to break the water tension of the solution. The bottles are supplied by HGL, Hampshire, ready calibrated to three decimal places.

A box of 24 bottles should be taken to sea. They should be stored for transport with tissue or paper between the stopper and the neck of the bottle to prevent them locking in the bottles. Checks should be made onboard for cracks and chips in the bottles and stoppers.

5.2.2 Dispensers

Repeat dispensers supplied by Bibby-Sterilin Pressmatic (part no. 307816604 from VWR International) for 500 ml amber Safebreak glass bottles. They are used for sulphuric acid, manganous chloride and sodium hydroxide/iodide, set and pre calibrated to dispense 1 ml. A reproducibility of 0.1% is quoted by the manufactures. The Pressmatic dispenser can be made bubble free by rotating the wheel on the side of the unit and viewing the liquid through the window and pumping several times until the bubbles have disappeared and then rotating the wheel back.

5.2.3 Temperature

On the FerryBox the temperature of fixing is recorded as the water temperature at the time of sampling.

5.2.4 Tubing

A 15 cm length of silicon tubing is attached the sampling tap to transfer water to the oxygen sample bottle.

5.2.5 Automatic burette

A 5 ml automatic burette, or exchange unit, supplied by Metrohm. The exchange units includes: a 1L titrant reservoir bottle which is to be filled with thiosulphate (includes a lid with air outlet); a stand for the reservoir bottle and piston which locks onto the top of the Titrino unit; three pieces of tubing which must be connected up; and the piston body. All of these parts are removable for transport.

When connecting the unit up after transport the piston unit is screwed into place first and the bottle, filled up with thiosulphate, is put into its stand. The lid, with a straw attached which goes to the base of the reagent bottle, must be screwed on and then the three tubes can be attached to the unit. The small piece of tubing connects from the front to the piston; the medium piece connects from the front left to the top of the 1L reservoir bottle; the large piece connects from the front right to the aspirator tip.

The fittings must all be tightened with the plastic spanner provided. The whole unit is then lined up in front of the Titrino and pushed along the runner until it locks in place

on top of the unit. Once the Titrino has been powered up an error message will result on the Titrino screen if the exchange unit is not correctly in place.

5.2.6 Titrino unit

A diagram representing the 716 DMS Titrino unit is shown in Figure 1. The front panel consists of a screen and three press buttons. When the DOS button is pressed the reservoir empties for as long as the button is pressed, when the FILL button is pressed the unit will fill up ready to dispense up to its full capacity of 5 ml.

When the reservoir bottle is first topped up with thiosulphate the burette must be fully filled and emptied on a high speed (to help remove bubbles) at least four times, until the lines are bubble free. The speed can be adjusted back to setting 3 on the dV/dt control. If the burette has not been used for several it should be flushed once (checking for bubbles while flushing). This is necessary as the thiosulphate may be diluted by the solution in which the dispensing tip is standing or bubbles may form at the top of the piston, as the unit is left standing.

In Figure 1 is a diagram of the back of the Titrino unit. When setting up the equipment the leads connect from the back of the Titrino to the other units as described below:

1) Power lead into the power socket;
2) Printer lead to socket 'A';
3) Electrode lead into 'pol';
4) Stirrer lead into 'E';
5) Keyboard lead into 'C'.

There is also an on/off button on the back of the Titrino unit.

5.2.7 Printer

A printer is not used in the FerryBox system

5.2.8 Stirrer

The stirrer unit (Metrohm 649) connects to the Titrino as described above. The unit has a speed setting which is usually set to 3.

The stand is held in the back of the stirrer by a screw fitting, this can be removed for transportation. The aspirator tip and electrode fit into the same holder on the top of the stand.

The position of the aspirator tip with respect to the electrode is important. The aspirator is placed slightly below the electrode tip in the stand so that when the unit is lowered into the solution the thiosulphate will be immediately drawn into the stirrer vortex. The stand can be adjusted so that it can always be lowered to the same height to avoid damage to the electrode by the stir bar.

5.2.9 Electrode

The electrode (Metrohm, part number 6.0341.100) connects to the Titrino unit by a lead running from the 'pol' socket at the back of the Titrino, which attaches to the top of the electrode. The electrode has a plastic cover used for transportation but when it

is in place in the stand the electrode is kept in a conical flask of distilled water to keep it clean.

5.2.10 Keypad

The 716 DMS Titrino keypad is attached by a lead to the Titrino. The titration is controlled through this keypad by using the STOP and START keys. The parameters can be set-up in the unit using the PARAMETERS key, this is a rolling function key so that the parameter menu is explored by continuing to press the key. At any time the menu is left by pressing QUIT and the last variable keyed in will be stored provided that the ENTER key had been pressed after each entry. For example, when changing the start volume from 0.5 ml to 0 ml for blank measurements: key down to the start volume (Start V) prompt and ENTER the new volume, then QUIT.

Figure 1
Equipment set-up

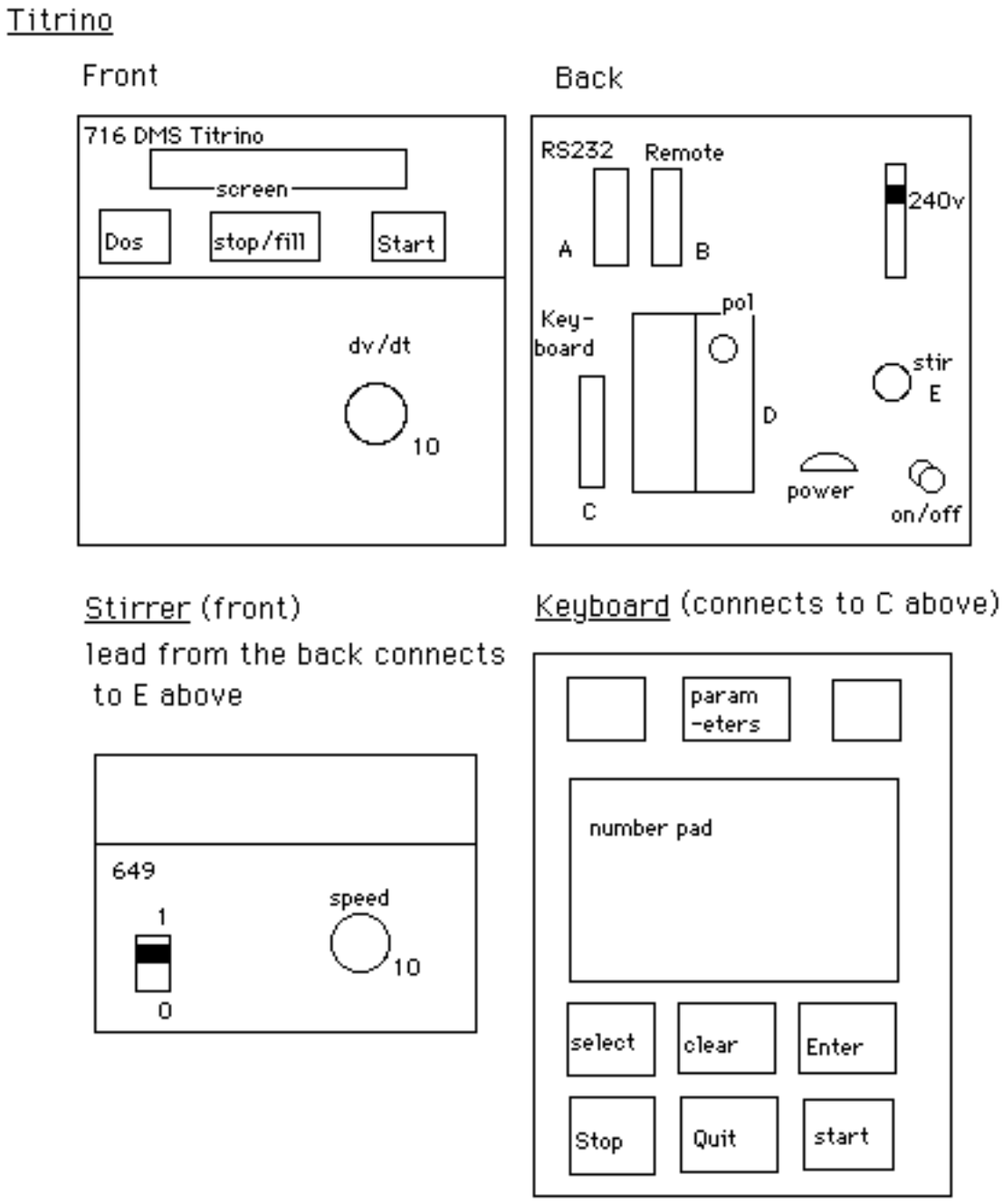


Table 1
Parameter listing as programmed into the Titrino keyboard.

Parameter:	Setting:	Description:
>SET1		Parameters for first endpoint (only one end point in this case)
EP at I	0.1 uA	End point set to 0.1 uA
dynamics	10 uA	distance from end point where controlled additions begin.
max.rate	1 ml/min	maximum rate of dosing
min.rate	2 ul/min	
stop.crit	drift	type of stop criteria
stop drift	2 ul/min	titration stops if stop drift reached.
>SET 2		
EP at I	OFF	no second end point.
>titration parameters		
titration direction	(-)	direction towards lower current
start V:	abs.	absolute start volume used
start V	(0.3 ml)	or 0ml Primary shot for standards and samples. NB: change to 0 ml for blank measurements
dos.rate	max. ml/min	Dosing rate for start volume
pause	10s	wait time following addition of start volume.
U (pol)	200 mV	polarisation of the electrode
electrode test	ON	
temperature	20.0°C	
>stop conditions		
stop V:	abs.	type of stop volume is absolute
stop V	5 ml	set to 5 ml for 5 ml exchange unit
filling rate		max.ml/min burette fills after titration
>statistics		
status	OFF	calculations mode off
>presentations		
conditioning	OFF	All other parameters off

6.0 SAMPLING

6.1 Worksheets

Prior to sample collection prepare an oxygen worksheet for crossing to include the following information:- sample number; oxygen sampling bottle number (each has a different three place calibrated volume with an identifying number on the stopper and bottle); bottle temperature and the titration volume.

Sample worksheets should be signed and dated, any notes on which pipettes were used on deck to add the fixing reagents and when new batches of reagents were used should be detailed on this form. Other notes to be recorded here during analysis include: the weight of iodate used to prepare the primary standard; the volumetric flask used in its preparation and the pipette used to dispense it; any bubbles noted in the system; and any other problems which may arise. Sample titration volumes are recorded on this form, a template is shown in the Appendix A.

6.2 Procedure

Oxygen samples are taken along with the other calibrations samples.

1. Oxygen samples are collected in duplicate
2. Take 2 oxygen bottles and the check list (and containers for other samples being collected) to the sampling point.
3. The repeat dispensers for manganous chloride and alkaline iodide are normally left at the sampling point
4. Empty the sampling bucket and run in new water to depth of about 15 cm. Immerse the oxygen bottles in this water to bring them to sample temperature.
5. Collect the other samples being collected at this time
6. To collect oxygen samples adjust flow from sampling tap so an oxygen bottle is filled in 5 to 10 seconds. Make sure there are no air bubbles stuck in the tube
7. Fill oxygen bottles with the tube on sampling tap at the base of the bottle. Rotate the bottle slowly making sure any bubble leave the bottle. Allow at least 500ml of water to flow through the bottle.
8. Place first bottle by reagent dispensers and then fill second bottle in same manner as first.
9. Check there are no bubble in the end of reagent dispensers (if there are dispense reagent a spare container until bubble free – this should be one shot).
10. Place tip if manganous chloride dispenser below surface of oxygen sample. Dispense 1 ml. Repeat for alkaline iodide.
11. Add reagent o second sample.
12. Now insert stoppers into sample bottles. Stoppers should be wet as they should have been in the bucket. Insert stopper at an angle to minimise risk of trapping an air bubble.
13. Put stopper in second bottle. Tighten stoppers and shake bottles vigorously for at leas 6o seconds.
14. Check there are no air bubbles in the sample. If there are reject the sample and resample. Wast sample should be emptied into an oxygen waste container (a heavy duty 20-30 L plastic carboy).
15. Return samples to lab.
16. After 30 minutes shake samples again for at least 15 seconds.

17. After 60 minutes samples should be titrated.

7.0 ANALYSIS

7.1 Reagent blank measurements

The reagent blank should be determined at the start of each crossing. It may change whenever a new batch of manganous chloride, sulphuric acid or sodium iodide-hydroxide is opened. It must be checked when the repeat dispensers are topped up in case of contamination of the reagents. Carpenters' (1965) method of reverse 1 ml reagent addition is used.

1. When the Titrino unit is first switched on the exchange unit burette is flushed out using the DOS and FILL keys on the Titrino unit. This is done at least four times and until the piston burette is bubble free.

2. Make sure that the Titrino keypad PARAMETERS are set-up so that the start volume is set to zero ml addition for blank measurements.

3. Blank measurements are made in oxygen sample bottles These must be thoroughly washed in tap water three times then in distilled water before being filled to about 100 ml with distilled water. Put a stir bar into the flask then add 1 ml of sulphuric acid and place the conical flask on the stirrer.

4. Add 1 ml of sodium hydroxide-sodium iodide and stir, check the solution is clear before adding 1 ml of manganous chloride. If the solution is not clear wash the flask and start again, as some manganese contamination may be present . If clear, carefully add 1 ml of the iodate standard. Note on the worksheet the pipette used to add the standard material. The same dispensers must be used for the manganous chloride and alkaline iodide as used when collecting samples. Make sure that the iodate standard is dispensed into the solution and any left of the walls of the conical flask must be washed down into the solution using distilled water.

5. Titrate to a dead stop (use the keypad START key, this will automatically fill up the burette with thiosulphate for each titration). Note the result on the worksheet.

6. Add a second 1 ml aliquot of iodate and titrate to a dead stop, then a third aliquot and titrate again to a dead stop. Record each result on the worksheet.

7. The values are written on the worksheet then typed into the spreadsheet with the sample values, to calculate the blank value. The blank measurement is calculated from the first reading minus the mean of the second and third reading; the blank reading is calculated from the mean of the blank measurements made for each conical flask. This whole procedure should be repeated for a minimum of three readings which must be consistent to within 0.002 ml. A 0.002 ml difference in blank measurements results in a 0.0334% change in the oxygen result calculated.

7.2 Standardisation of the thiosulphate titrant

The thiosulphate normality is checked against an iodate standard of known normality. The normality of the titrant should be checked every time the thiosulphate reservoir is topped up, it is also checked when a new batch of iodate standard is prepared. The volumetric flask used to prepare the iodate, the weight of iodate used and the calibration of the pipette or exchange unit used to dispense it should be noted down on the worksheet.

1. The parameter menu on the Titrino key pad should be set for a 0.3 ml start volume of titrant to reduce the titration time.

2. The conical flasks must be thoroughly washed as for the blank measurements to ensure that they are free of manganese contaminants, then filled with about 90 ml of distilled water. Alternatively the same flask and reagents as used to measure the blank can be used for a standard, this appears to give better precision but as the effect of the blank has already been accounted for it must not then be subtracted from the standard measurement in the final spreadsheet. Seawater must not be substituted for distilled in either the standardisation or blanking as it has its own 'blank'.

3. Add 1 ml sulphuric acid and the stir bar to the distilled water and stir on the mixer before adding 1 ml of sodium iodide-sodium hydroxide then if the solution is colourless add 1 ml of manganous chloride. If the solution is not colourless before the addition of the last reagent discard and wash the flask again. Continue stirring after the addition of each reagent. All reagents must be added using the same pipettes as used for the samples on deck.

4. Add exactly 10.00 ml of potassium iodate standard using a calibrated pipette. Stir and then titrate to a dead stop.

5. Record the results on the worksheet and repeat until the results agree to within 0.5 % for a minimum of three readings. The results should be close to 1 ml of titrant addition. The results are recorded on the paper worksheet then transferred to the Excel worksheet.

7.3 Sample measurement

Sample analysis can be started one hour after sample collection, when the precipitate has settled out. The parameter listing should be set up for a start volume of 0.3 ml of titrant using the PARAMETERS settings on the Titrino keypad. Before each run thoroughly flush the burette out. Run at least three dummy samples until the results are consistent. Check that the aspirator tip is close to the electrode to improve precision, preferably below the electrode tips and that the mix speed remains constant at 3 units.

1. Slowly remove the stopper from the sample to avoid any sample loss and drag the stopper across the neck of the bottle to get as such of the sample off it back into the sample bottles as possible. Add the magnetic stir bar.

2. Start mixing on the stirrer then add 1 ml of sulphuric acid. Insert the electrode and dispensing tube. Start the titration as soon as the precipitate has

disappeared. Titrate to a dead stop. Whilst the automatic titration is being done check the bottle number and record its volume on the logsheet (The Excel worksheet can also be set up to find the bottle volume from a table of numbers and volumes using the "Lookup" function). The next sample can be taken out of the rack ready for titration.

3. Record the titration volume on the paper worksheet.

4. When the titration is complete remove the stir bar using a magnetic stir bar retaining rod, replace the stopper without emptying the contents of the bottle. (Soaking the stopper cleans away any manganous oxide which may contribute to sample contamination.)

5. At the end of the run all of this waste solution must be disposed of in the waste carboy. Place strip of paper between each stopper and bottles and return bottle to rack ready for the next time. At the end of each crossing the bottles must be rised thoroughly with tap water and hard paper used between the stopper and the bottle.

6. During sample collection and processing leave the electrode in the last solution to be titrated. At the end of the crossing rinse off both with distilled water and store in the storage tubes attached to the Titrino.

8.0 CALCULATIONS

8.1 Spreadsheets and oxygen calculation

The oxygen spreadsheet contains information such as: new flask calibrations; iodate weights; pipette calibrations; and any changes in bottle numbers i.e.: bottle volumes used. Blank and standard measurements are typed in as necessary. This information is held as a locked template spreadsheet. The template spreadsheet in Appendix B & C shows the formula and steps used in the calculation of the oxygen results, the equations are explained more fully below.

8.1.1 The blank corrected sample titre

This is the volume of thiosulphate dispensed in the titration of each sample minus the blank reading.

8.1.2 The thiosulphate normality

The thiosulphate normality (Nthio) is calculated from the mean of the thiosulphate standardisation titrations as follows:

$$N_{thio} = (NIO3 * Pcal) / Vs$$

where

NIO3 = iodate normality
Pcal = 10 ml pipette calibration (ml)
Vs = mean standard titration, blank corrected (ml)

The normality of iodate (NIO3) is calculated as follows:

$$NIO3 = 0.01 * (wt / 0.3567) * (1000 / Fcal)$$

where:

wt= weight of potassium iodate (g)
Fcal= calibration of 1L volumetric flask (ml)

This assumes 0.3567g/l potassium iodate is 0.01N which is the case in air, when buoyancy corrected it is 0.0100025N. This will result in changes to the final oxygen calculation of 0.0501%.

8.1.3 The constant:

The absolute amount of oxygen added with 2 ml of reagent was determined by Murray et al. (1968) to be 0.0017 ml of oxygen per litre.

8.1.4 The corrected bottle volume

The corrected bottle volume is calculated using the bottle temperature (the temperature using the formula detailed by Culberson in the WOCE manual (1991).

$$Vcor = Vbot* (1 + (10^-5 * (T-20))) - Vreg$$

where:

Vreg= The volume of sample displaced by the addition of reagents on deck (2 ml).
Vbot= bottle volume as etched onto the glass (ml)
T= fixing temperature on deck (°C)
Vcor= corrected bottle volume (ml)
20= The reference temperature (°C) ie: of the temperature controlled laboratory, used if the bottle temperature is not known.
1.0 *10-5 = expansion factor for borosilicate glass

8.1.5 The WOCE equation

$$O2 (umol/l) = ((((Vx - Vblk,dw) * Nthio)* 10^6) - 1000 * 0.303688) / (Vcor * 4)$$

where:

Vx= thiosulphate titre of the sample (ml)
Vblk,dw= mean thiosulphate titre of pure water blanks (ml)
Nthio= thiosulphate normality
Vcor = corrected bottle volume (ml)
10^6 = conversion to mmol units
1000= conversion to units per L relative to the Ccor given in ml.

8.2 Data processing

Some of the cells in the Excel spreadsheet have been highlighted to show where information is usually to be added, the rest of the spreadsheet involves constants and

formula for calculating the final oxygen concentrations. At each station the sample titration volumes, temperature data, station number and sample number are added to the file manually, following data transcription checking, from the worksheets. The oxygen values are calculated automatically. The duplicate values must also be added and the duplicate differences checked.

9.0 SOURCES OF ERROR

9.1 Sampling

A lack of precision in the data may be due to errors occurring at the sampling stage, some of the most common errors are listed below

1. Stoppers not on tight enough which may result in losses.
2. Samples not shaken long and vigorously enough may not react fully. If the second shaking in the laboratory is not done this can adversely affect the precision.
3. Bubbles going unnoticed in the tubing and in the reagent dispensers may result in higher oxygen in the samples.
4. Wrong bottle volumes due to chips in the glass of the bottle or stopper.

It is important to ensure that the people doing the sampling know the affect of procedures on precision. As many of the errors affecting precision can happen during sample collection it is important to remember to look at the sample closely after the initial shaking on deck for any sign of bubbles. If any bubbles are seen empty the bottle and repeat sampling. Double check that the stoppers are tight and have not 'popped out'.

If precision is poor the following procedures should be checked:

1. That all procedures used by the people taking the oxygen samples are standardised;
2. That the second shaking in the laboratory is done;
3. That poor duplicate precision does not consistently arise from one pair of oxygen bottles, i.e.: change the bottle used for duplicates and check for cracks and chips;
4. That the pipettes are consistently dispensing the correct volume;

9.2 Analysis

Some of the common sources of errors are listed below

1. All titrations should be started as soon as possible after the acid is added, as soon as the precipitate disappears to minimise volatilisation losses.
2. All samples should be analysed within four hours.
3. Bubbles in the burette. These may go unnoticed especially if they are at the top of the piston or in the darker tubing.
4. Sample spillage or loss due to stoppers being put on too tight or from not taking care to drag the last drop of sample from the stopper and into the bottle on removal of the stopper.
5. Contamination due to dirty stoppers.

9.3 Calculations

Care must be taken in ensuring that the right figures have been used in the spreadsheet to calculate the oxygen results. Transcription checking of the titrant volumes should be done. All of the other information, such as blank and standardisation results, can be checked from the worksheets. Errors in the calculation of the thiosulphate for example can result in over 5% changes to the results for a 0.002 change in the normality calculated. If the sample temperature differs by 2°C for example then the change in the calculated oxygen result of the samples will be in the order of 0.003%, likewise changes in the blank measurement of 0.02 units can change the oxygen result by 0.05%.

Table 2 illustrates the relative importance of the variables used in the calculation and details the effect of individual changes to these variables which result in a 0.1% change in the final oxygen result. As the errors are additive then only much smaller changes could be tolerated to achieve the WOCE aim of 0.1% precision in results.

Table 2
Percentage change in individual variables which result in a 0.1% change to the final oxygen calculation.

Variable	% change in variable leading to a 0.1% change to the final result
Normality of thiosulphate	0.1
10ml pipette calibration	0.1
1L flask calibration	0.1
Total on deck reagent volume (2ml)	5.6

Table 3 illustrates the percentage change on the oxygen result when the precision quotes made by the manufacturer are considered. Although the quoted estimates may be allowing for the worst these errors are still additive and the overall effect on data precision may be considerable aside from errors introduced through the technique or the method itself.

Table 3
The % change in the final oxygen calculation resulting from the manufactures quotes of precision made for some of the equipment used in the analysis.

Equipment	Error quoted	Change to final result (%)
Thermometer probe (Jenway)	0.1% accuracy	0.00002
Reagent dispenser (Anachem)	0.1 % precision	0.00075
Repeat pipette (Eppendorf)	0.2 % precision	0.00252
Standard pipette (Finn)	0.3 % CV precision	0.30061
Volumetric flask for std. (BDH)	0.04 % precision (0.4ml tolerance on 1000ml)	0.04007

11. References

Carpenter, J.H., 1965. The Chesapeake Bay Institute Technique For The Winkler Dissolved Oxygen Method. Liminology And Oceanography, 10, 141-143

Culberson, C.H., 1991. Dissolved Oxygen. WOCE Operations Manual, WOCE Rep No 68/91

Grasshoff, K.,Ehrhardt, M. & Kremling, K., 1983. Methods Of Seawater Analysis, 2nd Edition, Verlag Chemie, 419pp.

Murray, C.N., Riley, J.P. & Wilson, T.R.S., 1968. The Solubility Of Oxygen In Winkler Reagents Used For The Determination Of Dissolved Oxygen. Deep-Sea Research, 15, 237 - 238.

Smythe Wright, D., Paylor, R.& Holley, S.E., 1993. Chemical Tracer Studies At IOSDL-4, The Measurement Of Oxygen In Seawater By Photometric And Amperometric Techniques. Institute of Oceanographic Sciences Report No. 303

O2 Method Appendix A:
Worksheet template

OXYGEN WORKSHEET		Date:				
Pride of Bibao		Analysed by:				
Standarisation in PORTSMOUTH and in Bilbao						
Blanks		**1**	**2**	**3**	**PIPETTE**	**ID**
1ml iodate					H_2SO_4 1ml	
2nd addition					Iodate 1ml	
3rd addition					Iodate 10ml	
4th addition						
STANDARDS		1	2	3	4	
10 ml Iodate						
EVENT NO OPERATOR NAME		**TIME OF SAMPLE**	**BOTTLE NO**	**BOTTLE VOL (ML)**	**TEMP (C)**	**TITRATION VOL (ML)**	**NOTES**
1							

O2 Method Appendix B:
Spreadsheet to calculate oxygen concentrations,
Columns for entry of calibration data
(Bottle volume lookup file file also shown

Pride of Bilbao Oxygen

Bottle No	Bottle Vol	Titration Calculations			
201.0000	103.2040	**2007.0000**			
			08-11 May		
202.0000	102.9750	**Crossing dates**	2007		
203.0000	102.9900				
		Numbers in red require			
204.0000	102.4870	**entries to be made**			
211.0000	103.6520				
213.0000	107.1260				
		Preparation of Iodate			
215.0000	106.6470	**Standard**		Date	**37811.0000**
					density at
216.0000	103.0030	**Flask at 20 C**	**998.1900**	density at 20	lab temp
218.0000	102.9380	**lab temp**	**21.4000**	0.9982	0.9979
219.0000	103.4420	**Vol. flask corrected**	**998.2040**		
220.0000	103.2870	**Weight KIO3**	**0.3567**		
221.0000	103.4960	**Normality lab**	0.0100		
222.0000	102.6610	**Normality 20oC**	0.0100		
224.0000	103.9930				
225.0000	102.9570				
227.0000	103.2970				
228.0000	102.7450	**Reagent Blank Correction**			
230.0000	103.3460		First	Second	Third
232.0000	102.7000	**Reagent+1mlKIO3**	**0.0930**	**0.1040**	**0.1105**
234.0000	103.0020	**second**	**0.0975**	**0.0975**	**0.0995**
236.0000	103.2760	**third**	**0.0945**	**0.0970**	**0.0975**
		forth	**0.0975**	**0.0980**	**0.0995**
237.0000	104.2240	**Blank Vol**	-0.0035	0.0065	0.0117
238.0000	103.2680	**Mean Blank Vol**	0.0049		
240.0000	102.8900				
A22	109.4160				
A26	113.7650				

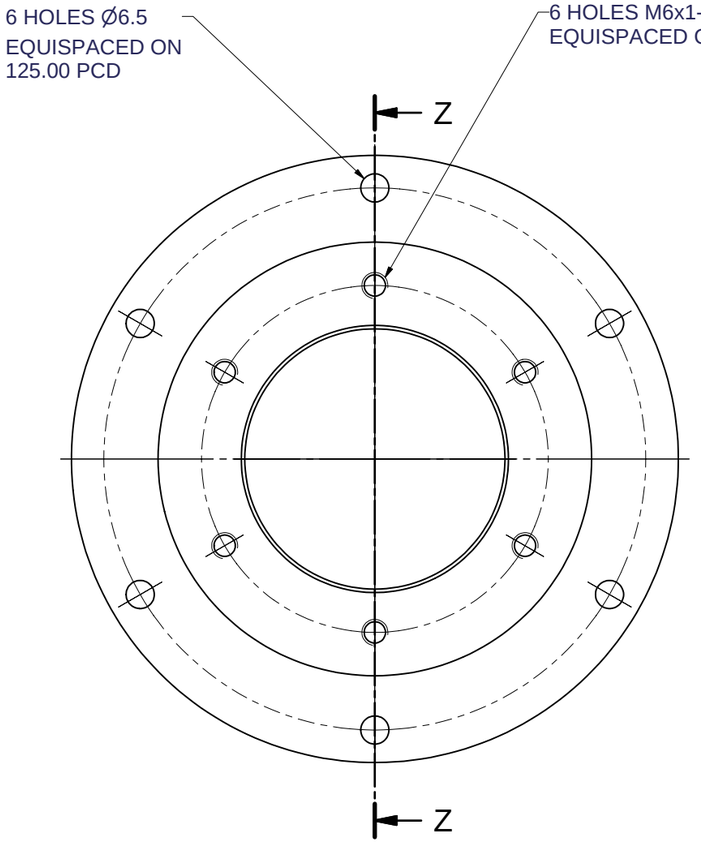
		Standarisation of			
F14	110.7230	**Thiosulphate Titrant**			
F17	108.4040	**Pipette Vol.20 c**	**10.0537**		
K7	114.2500	**Pipette Vol. lab**	10.0538		
L1	115.0450		first	second	third
		Titration Vol.	0.9920	0.9950	0.9935
		mean	0.9946		
		Reag blank correct	0.9897		
		N(thio)	**0.1018**		
		Reagent Dissolved O2 Correction (Murray,Riley and Wilson)			
		Abs DO reg	0.0017	ml	
		Corrtn equi-O2	0.3037		

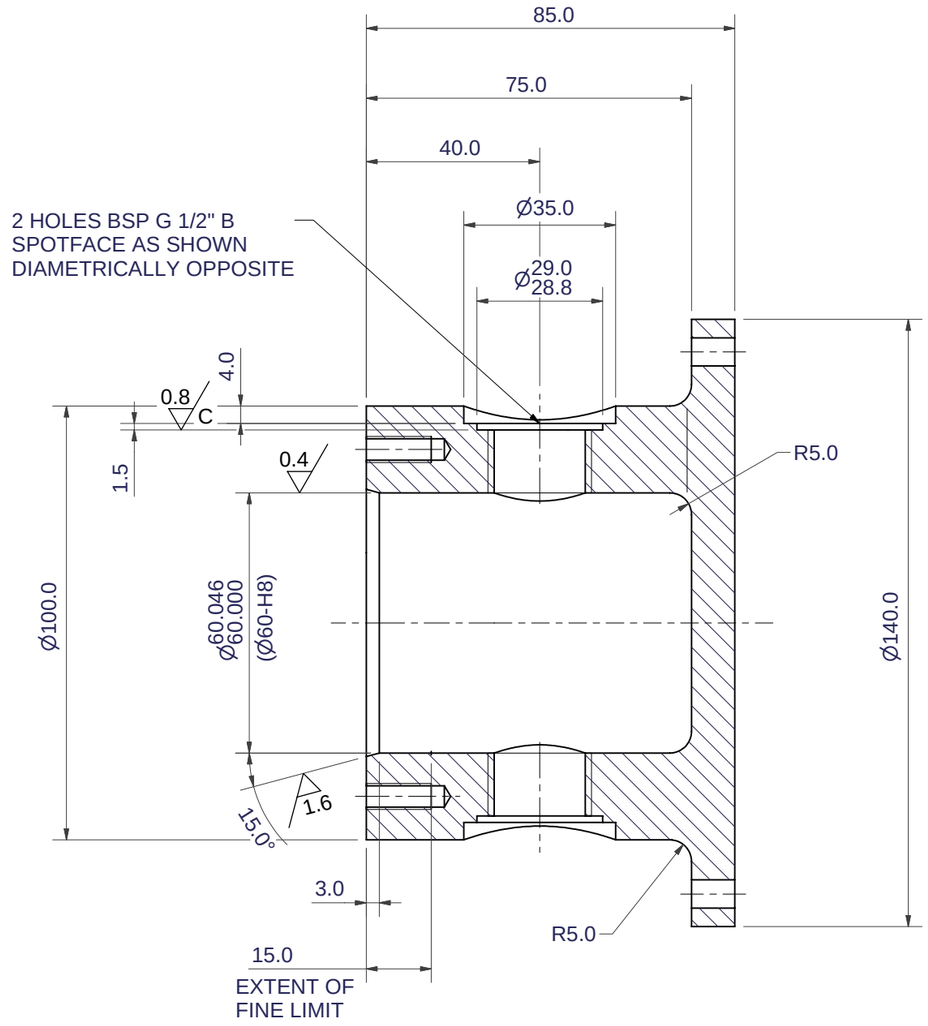
O2 Method Appendix C:
Spreadsheet to calculate oxygen concentrations,
Data entry and calibration part of XLS file

event no	day No	Ox Bot No	titration (ml)	fix T(oC)	Bot Vol	corr bot vol	O2 uM/l	delta_O
2	191	202	1.0170	17.40	102.975	100.972	254.34	
2	191	224	1.0260	17.40	103.003	101.000	256.54	2.20
4	191	237	1.0135	17.00	102.938	100.935	253.55	
4	191	238	0.9930	17.00	103.442	101.439	247.15	-6.40
6	191	216	1.0330	16.10	103.003	100.999	258.31	
6	191	236	1.0350	16.10	103.496	101.492	257.55	-0.75
8	192	204	1.0525	15.36	102.487	100.482	264.57	
8	192	230	1.0560	15.36	103.993	101.988	261.54	-3.03
10	192	201	1.0845	15.21	103.204	101.199	270.75	
10	192	225	1.0750	15.21	102.957	100.952	269.01	-1.73
12	192	227	1.0510	15.03	103.297	101.292	262.08	
12	192	228	1.0410	15.03	102.745	100.740	260.99	-1.09
14	192	216	1.0820	14.99	103.003	100.998	270.66	
14	192	237	1.0925	14.99	103.002	100.997	273.30	2.65
16	192	204	1.0758	15.67	102.487	100.483	270.47	
16	192	225	1.0780	15.67	102.957	100.953	269.77	-0.70
18	192	201	1.0525	15.31	103.204	101.199	262.70	
18	192	227	1.0550	15.31	103.297	101.292	263.09	0.39

Appendix 2

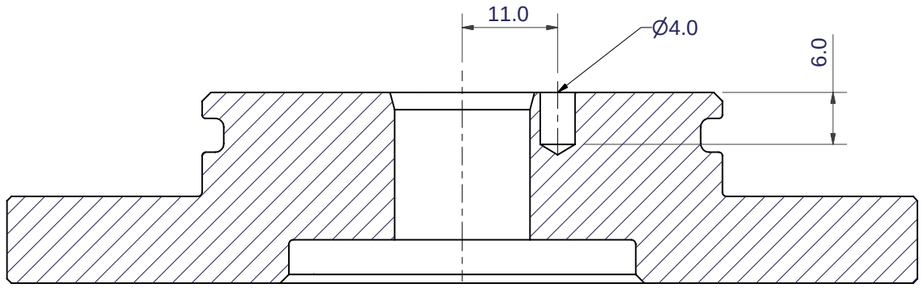
Construction drawings of the Optode flow housing



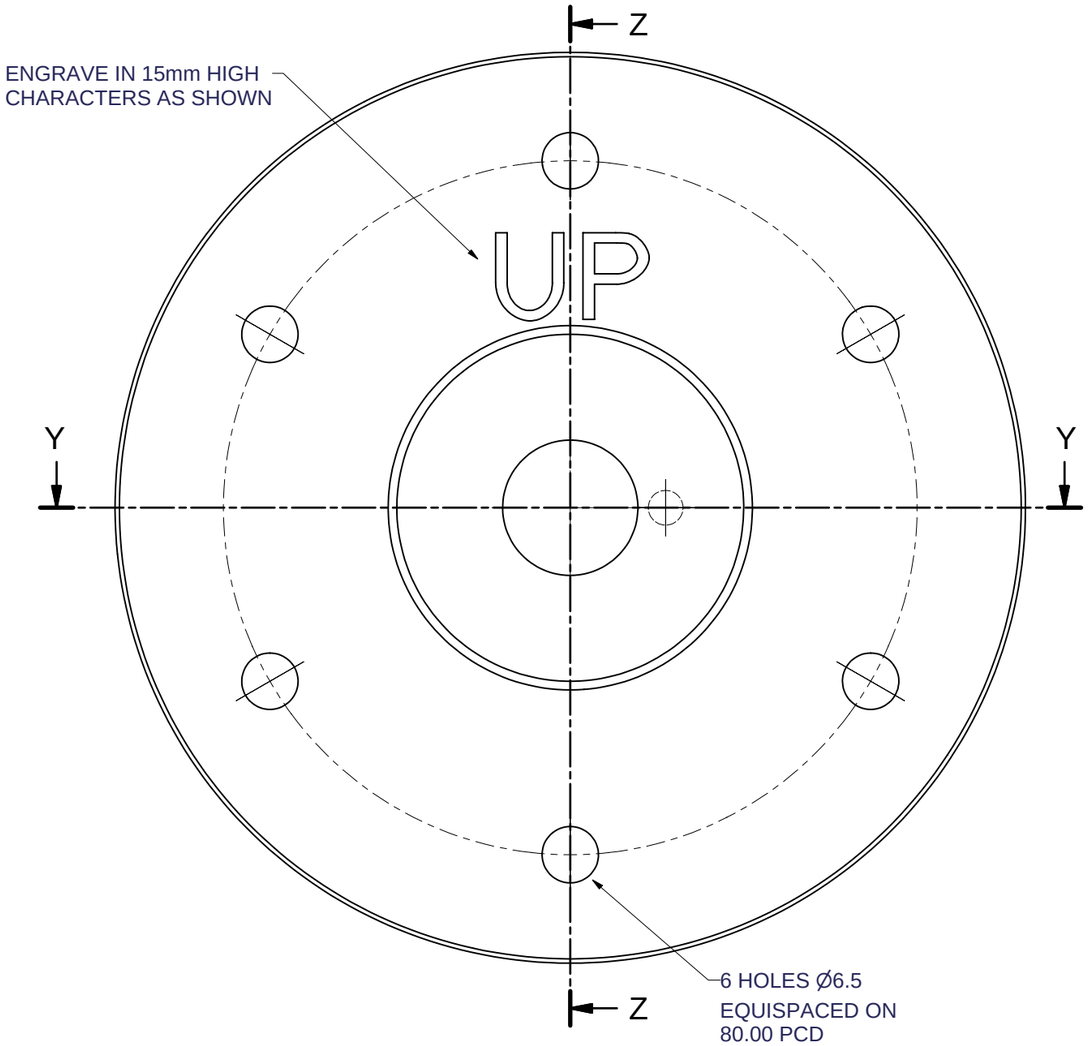


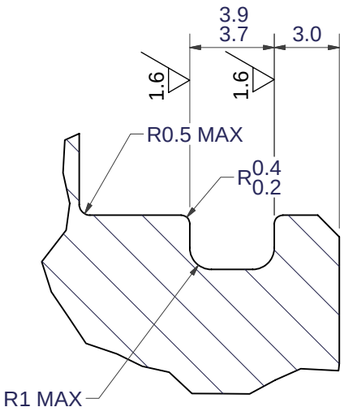
SECTION Z-Z

CHKD	MATERIAL	TOLERANCES	EST. MASS (kg)	THIRD ANGLE PROJECTION	Drawing produced on Inventor
DATE	RIGID PVC	X.=± 0.5 X.X=± 0.25 X.XX=± 0.1 ANG=± 0.25 UNLESS STATED	0.72	REMOVE ALL BURRS AND SHARP EDGES UNLESS STATED	Southampton Oceanography Centre / Ocean Engineering Division / Natural Environment Research Council
DES JBW			SCALE 1:1	DO NOT SCALE	TITLE: FERRYBOX OXYGEN SENSOR HOUSING — A2
DATE 03/11/2004	FINISH	SURFACE TEXTURE			
DRN JBW	NONE	(um) UNLESS STATED	DIMS IN mm	NO OFF PER UNIT 1	DRAWING NUMBER A5750-00-001 — SHT 1 OF 1 — ISS A
DATE 08/11/2004					

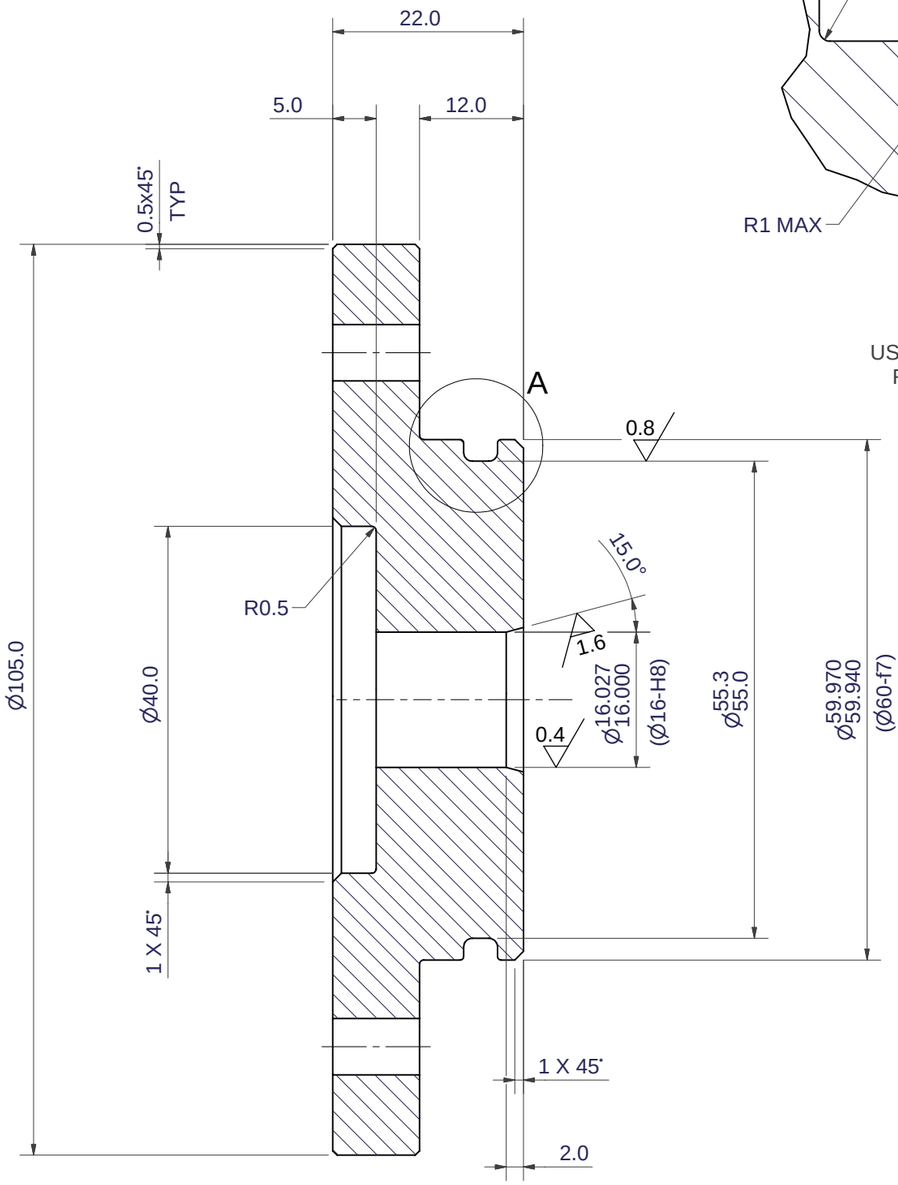


SECTION Y-Y



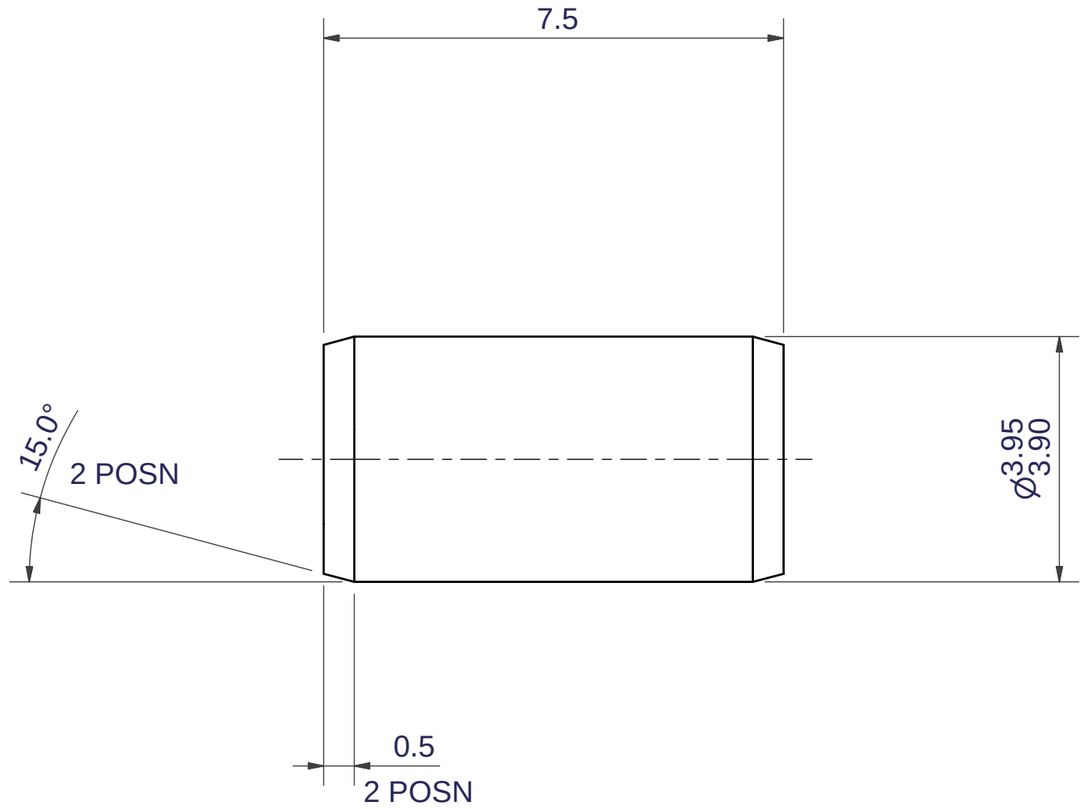


DETAIL A
(5 : 1)
USE 'O' RING BS4518
REF NO. 0545-30



SECTION Z-Z

CHKD	MATERIAL	TOLERANCES	EST. MASS (kg)	THIRD ANGLE PROJECTION	Drawing produced on Inventor
DATE	RIGID PVC	X.=± 0.5 X.X=± 0.25 X.XX=± 0.1 ANG=± 0.25 UNLESS STATED	0.15	REMOVE ALL BURRS AND SHARP EDGES UNLESS STATED	Southampton Oceanography Centre · Ocean Engineering Division · Natural Environment Research Council
DES JBW			SCALE 2:1	DO NOT SCALE	TITLE: FERRYBOX OXYGEN SENSOR END CAP — A2
DATE 05/11/2004	FINISH	SURFACE TEXTURE	DIMS IN mm	NO OFF PER UNIT 1	DRAWING NUMBER A5750-00-002 — SHT 1 OF 1 — ISS A
DRN JBW	NONE	(um) UNLESS STATED			
DATE 08/11/2004					



CHKD	MATERIAL	TOLERANCES	EST. MASS (kg)	THIRD ANGLE PROJECTION	Drawing produced on Inventor	
DATE	STAINLESS STEEL GRADE 316	X.=± 0.5 X.X=± 0.25 X.XX=± 0.1 ANG=± 0.25 UNLESS STATED		REMOVE ALL BURRS AND SHARP EDGES UNLESS STATED	Southampton Oceanography Centre	Ocean Engineering Division / Natural Environment Research Council
DES JBW			SCALE 10:1	DO NOT SCALE	TITLE FERRYBOX OXYGEN SENSOR DOWEL PIN	A3
DATE 05/11/2004	FINISH	SURFACE TEXTURE (um)				
DRN JBW	NONE		DIMS IN mm	NO OFF PER UNIT 1	DRAWING NUMBER A5750-00-003	SHT 1 OF 1 / ISS A
DATE 08/11/2004		UNLESS STATED				

Appendix 3

Aanderaa Oxygen Optode brochure

Oxygen Optodes 3835/4130/4175

OXYGEN OPTODE 3835
OXYGEN OPTODE/TEMPERTURE SENSOR 4130
OXYGEN OPTODE 4175

- *Optical measurement principle*
- *Long time stability*
- *More than one year without recalibration*
- *Low maintenance*
- *User friendly*
- *Optical measurement principle*
- *Use with AADI Current Meters*
- *Use as stand alone sensor*
- *Output format: SR10, RS232, Analog output (refer specifications)*

Since oxygen is involved in most of the biological and chemical processes in aquatic environments, it is the single most important parameter needing to be measured. Oxygen can also be used as a tracer in oceanographic studies.
For environmental reasons it is critical to monitor oxygen in areas where the supply of oxygen is limited compared to demand e.g.:

- In shallow coastal areas with significant algae blooms
- In Fjords or other areas with limited exchange of water
- Around fish farms
- In areas interesting for dumping of mine or dredging waste

The Aanderaa Oxygen Optodes are based on the ability of selected substances to act as dynamic fluorescence quenchers. The fluorescent indicator is a special platinum porphyrin complex embedded in a gas permeable foil that is exposed to the surrounding water. A black optical isolation coating protects the complex from sunlight and fluorescent particles in the water.

This sensing foil is attached to a window providing optical access for the measuring system from inside a watertight titanium housing.

The foil is excited by modulated blue light, and the phase of a returned red light is measured (see illustration overleaf). By linearizing and temperature compensating, with an incorporated temperature sensor, the absolute O_2 concentration can be determined.

The lifetime-based luminescence quenching principle offers the following advantages over electro-chemical sensors:
- Not stirring sensitive (it consumes no oxygen)
- Less affected by fouling
- Measures absolute oxygen concentrations without repeated calibrations
- Better long-term stability
- Less affected by pressure
- Pressure behaviour is predictable
- Faster response time.

The sensor is designed to operate down to 300 meters. It fits directly on to the top end-plate of Recording Current Meter RCM 9, and other Aanderaa instruments.

Specifications

PARAMETER	OXYGEN OPTODE 3835		OXYGEN/TEMPERATURE OPTODE 4130		OXYGEN OPTODE 4175	
OXYGEN	*O_2 -Concentration*	*Air Saturation*	*O_2 -Concentration*	*Air Saturation*	*O_2 -Concentration*	*Air Saturation*
Measuring Range:	0 - 500µM[1])	0 - 120%[2])	0 - 500µM[1])	0 - 120%[2])	0 - 500µM[1])	0 - 120%[3])
Resolution:	<1µM	0.4%	<1µM	0.4%	<1µM	0.4%
Accuracy:	<8µM or 5 %[4]) whichever is greater	<5%[4])	<8µM or 5 %[4]) whichever is greater	<5%[4])	<8µM or 5 %[4]) whichever is greater	<5%[4])
Settling Time (63%):	<25s		<25s		<25s	
TEMPERATURE						
Range:	-0°C to +36°C		-7.5°C to +41°C		-0°C to +36°C	
Resolution:	0.01°C		0.05°C		0.01°C (0 - 5V)	0.02°C (4 - 20mA)
Accuracy:	±0.05°C		±0.1°C		±0.1°C (0 - 5V)	±0.15°C (4-20mA)
Settling Time (63%):	<10s		30s		<10s	
Operating Temperature	0 - 40°C (32 - 104°F)		0 - 40°C (32 - 104°F)		0 - 40°C (32 - 104°F)	
Operating Depth:	0 - 300m (984.3ft)		0 - 300m (984.3ft)		0 - 300m (984.3ft)	
Sampling Rate:	SR10: controlled by the datalogger. RS-232: From 1s to 255 minutes		Controlled by the datalogger		From 1s to 255 minutes	
Output Formats:	Aanderaa SR10[5])(Only Oxygen) RS-232[6])		Aanderaa SR10[5]) (Oxygen) and VR22[5]) (Temperature)		0 - 5V outputs: ±0.1% of FS[7]) 4-20mA output: ±0.2% of FS[7]) RS-232[6])	
Current Consumption:	SR10: 10mA/T where T is recording interval in minutes RS-232: 80mA/S +0.3mA where S is recording interval in seconds		10mA/T where T is recording interval in minutes		80mA/S +0.3mA +Ia where S is recording interval in seconds and Ia is quiescent: 5 - 45mA when analog adaptor enabled	
Supply Voltage:	SR10: -6 to – 14Vdc RS-232: +5 to +14Vdc		SR10: -6 to –14Vdc		Analogue: +7 to +14Vdc RS-232: +5 to +14Vdc	
Dimensions:	Ø36 x 86mm (Ø1.42 x 3.386in)		Ø40 x 168mm (OD1.575 x 6.61in)		Ø40 x 175.5mm (Ø1.42 x 6.9in)	
Weight:	120g (4.23oz)		385g (13.58oz)		370g (13.05oz)	
Materials:	Titanium, Hostaform (POM)		Titanium, Hostaform (POM)		Titanium, Hostaform (POM)	
Accessories included:	Sensor Cable 3854					
Accessories not included:	Sensor Cable 3855 to PC[8]) Foil Service Kit 3853 PSt[5])		Sensor Cable 3855 to PC[8]) Foil Service Kit 3853 PSt[5])		Sensor Cable 3855 to PC[8]) Foil Service Kit 3853 PSt[5]) Cable 3485 with free end	
Warranty:	Two years against faulty material and workmanship (4130, 3835, 4175)					

[1]) O_2 Concentration in mM = mmol/l. To obtain mg/l, divide by 31.25

[2]) The saturation range covered by SR10 is 0-150%, the temperature range covered by SR10 is -5C to 40C

[3]) The saturation range covered by analogue 0-5V and 4-20mA is 0-150%, the temperature range covered is -5C to 40C

[4]) Aanderaa SR10a/VR22 are signal protocols that are used with Aanderaa equipment only

[5]) Valid for salinity 33 - 37ppt

[6]) 9600 Baud, 8 data bits, 1 stop bit, No Parity, Xon/Xoff Handshake

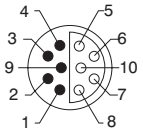
[7]) The accuracy of the Analogue Adaptor in 0 - 5V output mode is specified to 0.1% of FS. Note however that at the end of the scale (<0.0 - 0.07> and <4.93 -5.0>) the error may be larger

[8]) In order to change settings or calibrating the Optode the Sensor has to be connected to a PC. To gain access to the Optode 4130's RS-232 signals its cylindrical body must be removed, see Operating Manual TD 218

PIN CONFIGURATION:

Receptacle, exterior view;

pin = ●, bushing = ○



[A]) Ground for SR10

[B]) Supply for RS-232

[C]) Ground for RS-232

[D]) Supply for SR10

3835	4130	4175	When used with Cable 3485	
			Plug	Colour
1: Positive Supply[A], [B]	1: System Ground	1: Positive Supply	8	Green
2: Ground[C]	2: Not Connected	2: Ground	7	Black
3: -9V[D]	3: -9V	3: Analogue Output 1	6	White
4: Reserved, Do Not Connect	4: Not Connected	4: Return Ground 1	5	Blue
5: Bridge Voltage (BV)	5: Bridge Voltage (BV)	5: Analogue Output 2	4	Violet
6: Reserved, Do Not Connect	6: SR10 (Oxygen)	6: Return Ground 2	3	Yellow
7: RXD (RS-232)	7: Not Connected	7: RXD (RS232)	2	Brown
8: TXD (RS-232)	8: Bridge Ground	8: TXD (RS232)	1	Grey
9: Control Voltage	9: Control Voltage	9: Not Connected	10	Red
10: SR10 (Oxygen)	10: VR22 (Temperature)	10: Not Connected	9	Orange

Applications

Optode Model	3835	4130	4175
Description	Integrally/Direct Mounted	Immersion Body for cable or sensor string	Immersion Body with Analog and Serial Outputs
Output	Dual Channel: RS-232 data string (Oxygen,Temp.) or Single SR10 (Oxygen) channel to RCMs or RDCPs	Dual Channel: SR10 (Oxygen) and VR22 (Temp.)	Dual Channel: 0 - 5V (Oxygen, Temp.) or 4 - 20mA (Oxygen, Temp.) and/or RS-232 (Oxygen, Temp)
Application	Add sensor(s) to Top End-plate of our RCM 9, RDCP 600 or for OEM/Third party use	For use with Aanderaa DL series dataloggers; added sensors to Weather Stations AWS 2700, Data Buoys DB 4280 or our self-contained recording instruments	General Purpose use with third party dataloggers, e.g. CTDs, ARGO floats, ROVs; PLCs, process industry controllers, recorders, data acquisition and control systems.
Sample Rate	Set by host. RCM: continuously* – 120 minute RDCP: 1minute – 8 hours. Internal interval setting for input to third party RS-232 interface.	Set by host. DL 3960: continuously* - 180 minutes DL 7: 1 minute – 180 minutes DB 4280: continuously* - 180 minutes AWS 2700: continuously* - 180 minutes	
Multi-sensor Configuration	RCM 9: Yes, 2nd 3830/3835 via Cable 3296 and Receptacle 3622R. RDCP 600: 300m version: as for RCM 9	DL 3960: Max 15 sensors, depending on the configuration DL 7: Max 5 sensors DB 4280: Max 15 sensors, depending on the configuration Sensor attachment: single points on cable use 3913; In-line 5-Sensor Disk 3829 RCM/RDCP: contact factory.	
Stand-alone Sensor (0–300m)	Use Cable 3485. Output: RS-232 (Oxygen,Temp.). Sampling Rate: 1 Hz to 255 minutes		User furnished datalogger or controller, Cable 3485 Output: 0 - 5Vdc; 4 - 20mA, dc; or RS-232 (Oxygen, Temperature) Sampling Rate: 1 Hz to 255 min.

***)** Note that when the Optode is connected to an instrument like the RCM, CMB, AWS or a datalogger, the sampling rate in a continuous recording mode depends on the number of channels for storage etc.

Oxyview© Program

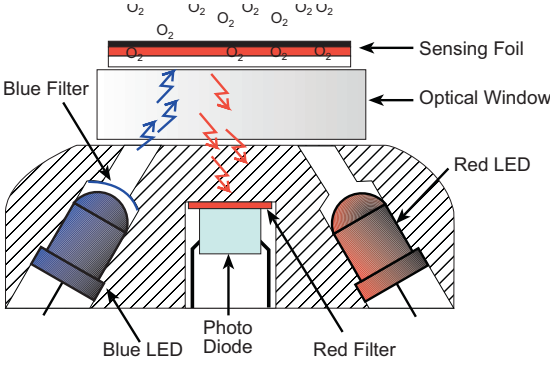
Oxyview©, has been designed for use with Oxygen Optode/ Temperature Sensor 3830/3835. The program allows display of Oxygen Concentration, Oxygen Saturation and Temperature both in tables and graphical forms.

A Calibration Wizard is included in the program. This Wizard helps calibrate the Optode.

Oxyview© can also be used to configuring the Oxygen Optode.

The Optical System

The principle of measurement is based on the effect of dynamic luminescence quenching (lifetime based) by molecular oxygen.



Appendix 4

Chelsea Technologies Group MiniPack manual specification data pages

Fact Sheet No: 29/11

MINI*pack* CTD-F

Compact, Smart™ based multi-parameter monitoring system for oceanography and limnology

MINI*pack* is a low cost, compact, robust and fully integrated CTD-F sensor suite designed to meet the demands of open ocean, estuarine and fresh water environmental monitoring, incorporating a 24 channel data logger.

MINI*pack* is designed to be a multi-parameter sensor data logger than can be deployed individually or at the core of a larger multi-parameter system. As such, it may be used as discrete profiling instrument, installed on a data buoy, moored in the ocean or to form the core of a towed undulating vehicle system.

OVERVIEW

MINI*pack* is the latest evolution of the highly successful AQUA*pack*. MINI*pack* is one-third the size of the AQUA*pack*, with greater versatility and increased memory capacity. It is a low cost, compact, robust and fully integrated conductivity, temperature, depth and fluorimeter measuring system. It is designed to meet the demands of open ocean, estuarine and fresh water environmental monitoring. It incorporates a high performance 24-channel data logging and transmission system, monitoring the integral CTDF sensors and any auxiliary instruments. MINI*pack* is highly versatile and there are a number of different determinants (see optical specification table). Each application uses an LED light source but requires a unique set of light filters in both the excitation and detection paths. The configuration is factory set by the selection of optical filters and spacers.

MINI*pack* is designed to be mounted on a towed vehicle such as the Chelsea AQUA*shuttle*, Nν-Shuttle or SeaSoar - deployed on buoys, on a mooring, or as the core of a profiling system. It can be operated to depths of 600 metres from dedicated oceanographic research vessels or ships of opportunity.

MINI*pack* has been designed specifically for easy installation into Chelsea's range of towed vehicles.

MINI*pack* may be used in a pre programmed stand-alone mode, powered from its internal battery with data stored in onboard memory. For real time applications, the MINI*pack* is provided with a transmission system with the capability of providing power to and acquiring data from up to 16 external sensors (14 differential channels & 2 single ended channels). These may typically include dissolved oxygen, pH, PAR, up and downwelling sensors, fluorimeters and transmissometers.

The highly versatile SmartMedia™ is used for pre-programming and storing of measured data. This data is easily extracted by a PC and presents data in ASCII files in engineering units that are easily processed by propriety software packages. Data may be stored on the internal SmartMedia™ Card (for standalone mode) or transmitted in real-time up the cable using RS422 (RS232 option) format. An interface unit is available to convert RS422 (or RS232) for onward transmission to a PC when long cables are required. A user-friendly Windows based GUI enables error free programming of the internal logger and data extraction.

SPECIFICATION

Size	114 mm dia. x 200mm (sensors to end caps)
Weight	3.25 kg (in air); 1.8 kg (in water)
Depth Rating	600m
Housing Material	Titanium / Acetyl
External Input	
via interface unit	18-72 VDC
via external battery pack	10-15 VDC
Logger Capacity	16Mbyte
Number of readings	100K across all channels
Number of channels	24
Interface Type	RS422 (RS232 option)
Data rate	9600 baud
Scanning rate	1Hz to 1 sample/day

Sensors	Type	Range	Accuracy	Resolution
Temperature	Pt resistance	-2 to +35^{O}C	0.003^{O}C	0.0005^{O}C
Conductivity	Induction Cell	0-70mmho/cm	0.005mmho/cm	0.001mmho/cm
Pressure	Strain Gauge with temp. compensation	0-600 dbar	0.2 dbar	0.01 dbar

Optical

	Chlorophyll a	Chlorophyll a	Rhodamine	Amido Rhodamine	Fluorescein
Excitation wavelengths	430/30 nm	470/30 nm	470/30 nm	425/30 nm	480/80 nm
Emission wavelength	685/30 nm	685/30 nm	590/45 nm	550/30 nm	530/30 nm
Concentration range	0.03-100 µg/l	0.03-100 µg/l	0.03-100 µg/l	0.04-200 µg/l	0.03-100 µg/l
Resolution	0.01 µg/l	0.01 µg/l	0.01 µg/l	0.025 µg/l	0.01 µg/l
Calibration standard:	Chlorophyll-a in acetone	Chlorophyll-a in acetone			

	Nephelometer	Phycoerythrin	Phycocyanin
Excitation wavelengths	*470/30 nm	530/30 nm	590/35 nm
Emission wavelength	*470/30 nm	580/30 nm	645/35 nm
Concentration range	*0.04-100 FTU	0.03-100 µg/l	0.03-100 µg/l
Resolution	*0.01 FTU	0.01 µg/l	0.01 µg/l

*the wavelengths for the turbidity filters are a customer option but must be in the range 400 to 700 nm. Also, the same wavelength is used in both the excitation path and the emission path.

TECHNICAL DESCRIPTION

There are two basic configurations of the MINI*pack*, Real-time and Standalone. The difference lies in the associated end caps. The MINI*pack* can be powered from its internal battery pack or an external battery pack, Chelsea Technologies Group's Portable Interface Unit or from the mains powered Standard Interface Unit. Battery life is dependent on acquisition time and the external sensor load connected.

Real-time Configuration

The end can be provided with the following connectors:

Connector	Use
MCBH16F Micro 16 Female connectors (1 off standard, 1 off optional)	Differential Channels for external sensors. (7 standard, 14 with option)
MCBH8M Micro 8 Male connector	Power & RS422 (RS232 option) Comm's
MCBH4F Micro 6 Female connector – **Option**	Switched Power & 2 single ended channels

Standalone Configuration

The End Cap Assembly for the Standalone configuration is configured to take the internal battery pack, comprised of two 3.6V Lithium 'D' cells. It has no external connectors. In Standalone mode the instrument is configured by a start-up file stored on the internal Smart Media Card.

This novel use of SmartMedia card technology enables the user to pre-programme the card, and extract data files directly with a PC. This gives 16Mbytes of easily removable onboard storage.