

Processing Argo OXYGEN data at the DAC level
Version 1.0
August 20, 2010
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Preamble: This document does NOT address the issue of oxygen data quality control (either real-time or delayed mode). As a preliminary step towards that goal, this document seeks to ensure that all countries deploying floats equipped with oxygen sensors document the data and metadata related to these floats properly. We produced this document in response to action item 14 from the AST-10 meeting in Hangzhou (March 22-23, 2009).

Action item 14: Denis Gilbert to work with Taiyo Kobayashi and Virginie Thierry to ensure DACs are processing oxygen data according to recommendations.

If the recommendations contained herein are followed, we will end up with a more uniform set of oxygen data within the Argo data system, allowing users to begin analysing not only their own oxygen data, but also those of others, in the true spirit of Argo data sharing.

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1 Introduction and agreement reached at ADMT10 and AST11

There are two main methods to measure dissolved oxygen (DO) with sensors in the ocean. The first method is an electrochemical method that uses a Clark-type polarographic cell. The second method is an optical method. It is based on the principle of dynamic fluorescence quenching. As of today, SeaBird Electronics provides a DO sensor based on the electrochemical method and Aanderaa provides a DO sensor based on the optical method. The Aanderaa Optode also measures temperature, and in some cases, this temperature is transmitted by Argo floats. One might expect that other manufacturers will soon compete with Aanderaa or SeaBird and provide new sensors based on one of those methods.

The official Argo unit for dissolved oxygen concentration is micromol/kg, as in JGOFS and CLIVAR, but none of the existing sensors provides DO data in native units of micromol/kg. Depending on the sensor, additional conversions must also be done to correct for pressure or salinity effects for example. **As a consequence, whatever the sensor considered, DO sensor output must be transformed to convert the output in dissolved oxygen concentration, to take into account temperature, salinity and pressure effects or to convert the data in micromol/kg.**

The following recommendations have been agreed upon at the ADMT 10 meeting (October 2009, Toulouse, France) and at the AST 11 meeting (March 2010, La Jolla, USA) :

1. Store any data transmitted by the oxygen sensor with meaningful names, whatever the unit of the sensor output is. It is important to store those data if changes occur in the calibration/conversion equations used to convert the sensor output in DOXY. The proposed names are:
 - VOLTAGE_DOXY when SBE43 sensor output is a voltage (Unit = V)
 - FREQUENCY_DOXY when SBE43 sensor output is a frequency (Unit = Hz)
 - COUNTS_DOXY when SBE43 sensor output is counts (no Unit)
 - BPHASE_DOXY when Aanderaa optode output is BPHASE (Unit = degree)
 - DPHASE_DOXY when Aanderaa optode output is DPHASE (Unit = degree)
 - MOLAR_DOXY when Aanderaa optode output is DO concentration at zero pressure and in fresh water or at a reference salinity (Unit = micromole/liter).
 - TEMP_DOXY when the Aanderaa optode transmits its temperature measurement (Unit =degree Celsius)
 - XXX_DOXY for any new variables
2. Store in **DOXY** the dissolved oxygen value in micromol/kg estimated from the telemetered variables and corrected for any pressure, salinity or temperature effects.
3. Fill properly the metadata to document the calibration and conversions equations.
4. Add a second profile in the single cycle netcdf file when the Optode reports in low resolution mode while the CTD reports in high resolution mode (vertical sampling). This second profile contains DOXY and the data reported by the optode as well as CTD data acquired at the optode level measurements (PRES, TEMP and PSAL).

2 Comment on the oxygen related metadata

The accuracy and the resolution of the sensors are provided by the manufacturers and are given in the unit of the DO sensor, and not in the official Argo unit. Accuracy depends on the sensor type but individual calibration of optodes can change the provided accuracy. Data delivered and transmitted by the oxygen sensor have different units. **The unit of the transmitted data that is directly related to the oxygen concentration is given in the SENSOR_UNIT field.**

As for the other sensors, the model number and serial number of the DO sensor must be provided. This can be important if a specific failure concerns all the sensors from the same batch for instance, or if the manufacturing process changes after a certain serial number.

Indications provided in the two following sections and the examples on how to fill metadata are valid as of the date of writing this document. It is very likely that changes in calibrations and conversions equations will occur in the future. Metadata will then have to be filled accordingly with the new procedures.

3 Aanderaa optode

Information provided hereafter is taken from the TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175 (April 2007).

3.1 Measurements and data processing

The optode measures raw phase data that is converted in degrees. The calibrated phase measurement DPHASE is calculated as a 3rd degree polynomial of the uncalibrated phase measurement. The uncalibrated phase measurement (UNCAL_PHASE) is the difference between the phase obtained with blue light excitation (BPHASE) and the phase obtained with red light excitation (RPHASE).

$$\text{UNCAL_PHASE} = \text{BPHASE} - \text{RPHASE}$$

With the 3830 optode model, RPHASE is set to zero because it is not used. As a consequence, BPHASE equals UNCAL_PHASE. But we anticipate that RPHASE could differ from zero with future optode model. DPHASE is calculated from UNCAL_PHASE using Aanderaa's PhaseCoef values (A, B, C, D) as follows.

$$\text{DPHASE} = A + B * \text{UNCAL_PHASE} + C * \text{UNCAL_PHASE}^2 + D * \text{UNCAL_PHASE}^3$$

where the coefficients C and D are usually equal to zero, so that the calibrated phase DPHASE is a linear function of the uncalibrated phase. The coefficients A and B are determined in the laboratory from a two-point calibration (0% and 100% saturation) of individual foils.

DPHASE is then converted to dissolved oxygen concentration in micromol/L (microM) using 20 sensor-dependant coefficients in a 4th degree polynomial:

$$\text{MOLAR_DOXY} = C_0 + C_1 \text{DPHASE} + C_2 \text{DPHASE}^2 + C_3 \text{DPHASE}^3 + C_4 \text{DPHASE}^4$$

where C_0, C_1, \dots, C_4 are temperature dependent coefficients valid for batches of foils and calculated as:

$$C_i = C_{i0} + C_{i1}T + C_{i2}T^2 + C_{i3}T^3$$

with T the temperature in °C.

To improve the optode calibration, some laboratories perform either a quick two points or a more complete calibration generating new calibration coefficients. In that case, the factory calibrations coefficients should be replaced by the new ones and the metadata must be filled accordingly.

The calibration coefficients can be determined either with the optode temperature sensor or with the CTD temperature sensor. To ensure consistency, temperature data from the same sensor must be used to convert DPHASE in MOLAR_DOXY.

The dissolved oxygen concentration must also be corrected for salinity and pressure effects.

The salinity compensation is estimated as:

$$DO_{PSAL} = \text{MOLAR_DOXY} \cdot \exp[(S - S_0)(B_0 + B_1T_s + B_2T_s^2 + B_3T_s^3) + C_0(S^2 - S_0^2)]$$

where S=PSAL and S₀=S_{ref} when MOLAR_DOXY has been internally calculated from S_{ref}, or S₀=0 when DO is estimated on-shore from BPHASE or from DPHASE.

$T_s = \ln[(298.15 - T)/(298.15 + T)]$ where T is the CTD temperature (TEMP) in °C.

B₀=-6.24097e-3; B₁=-6.93498e-3; B₂=-6.90358e-3; B₃=-4.29155e-3; C₀=-3.11680e-7

The pressure compensation is then estimated, following Uchida et al (2008), as:

$$\text{DOXY} = \text{DO}_{PSAL} \cdot [1 + (0.032 \text{ PRES})/1000]$$

This equation supersedes the original equation proposed by Aanderaa in the user manual of model 3830 (in which the 0.032 factor was 0.04).

Dissolved oxygen concentration units from the optode are micromol/L (microM). It must be converted in micromol/kg, the official Argo unit, by dividing by density (Section 4). The density has to be estimated from the CTD temperature and salinity (TEMP, PSAL).

3.2 “SENSOR” metadata

As of today, the Aanderaa optode exists in at least three versions capable of profiling to depths of 2000 m or greater: 3830, 4330 or 4330F. Accuracy and resolution are given in micromol/L. As mentioned Section 2, the SENSOR_UNIT field is filled with the unit of the transmitted data that is directly related to the oxygen concentration.

Sensors and measurement methods		
SENSOR	DOXY	TEMP_DOXY*
SENSOR MAKER	Aanderaa	Aanderaa
SENSOR_MODEL	3830 or 4330 or 4330F	3830 or 4330 or 4330F
SENSOR_SERIAL_NUMBER	To be filled	To be filled
SENSOR_UNITS	degree (for BPHASE_DOXY or DPHASE_DOXY) or “micromole/L (for MOLAR_DOXY)	degree Celsius*
SENSOR_ACCURACY	8 micromol/L or 5%	0.1 degree Celsius (for 4330/4330F) or 0.05 degree Celsius (for 3830) *
SENSOR_RESOLUTION	1 micromol/L	0.01 degree Celsius*

3.3 Oxygen related parameters

In the following, sensor dependant coefficients are provided as example.

3.3.1 Case 1: Transmission of MOLAR_DOXY to the DAC

When the sensor output is a dissolved oxygen concentration (called MOLAR_DOXY in the previous section), the calibrated phase DPHASE is calculated from UNCAL_PHASE and gets converted to a dissolved oxygen concentration by the optode itself. The concentration is estimated using the reference salinity (S0), assuming zero pressure and using the optode temperature (TEMP_DOXY). Typically, S0 is set to 0 or 35 prior to float deployment. The value of S0 must be known to precisely correct for the salinity effect on shore. MOLAR_DOXY is then transformed in DOXY by correcting for the pressure and salinity effects and by converting the dissolved oxygen concentration in micromol/kg by dividing by the potential density (see Section 4). For those calculations, the temperature from the CTD has to be used (TEMP). Examples on how to fill the PARAMETER and PREDEPLOYMENT_CALIB fields are given hereafter.

For MOLAR_DOXY_:

PARAMETER= “MOLAR_DOXY”

PREDEPLOYMENT_CALIB_EQUATION = “O2=C0+C1.P+C2.P^2+C3.P^3+C4.P^4 with Ci=Ci0+Ci1.T+Ci2.T^2+Ci3.T^3 ; MOLAR_DOXY=O2 exp[S (B0+B1.Ts+B2.Ts^2+B3.Ts^3)+C0S^2]; Ts=ln[(298.15-T)/(298.15+T)]; with P=DPHASE, T=TEMP_DOXY, S=S0”

PREDEPLOYMENT_CALIB_COEFFICIENT = “S0=0” or “S0=35”

PREDEPLOYMENT_CALIB_COMMENT = “MOLAR_DOXY is calculated by the optode from DPHASE, TEMP_DOXY, PRES=0 and S0; see TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175”

For DOXY:

PARAMETER=”DOXY”

PREDEPLOYMENT_CALIB_EQUATION = “O2c= MOLAR_DOXY exp[(S-S0) (B0+B1Ts+B2Ts^2+B3Ts^3)+C0(S^2-S0^2)]; DO=O2c [1+ 0.032 * PRES/1000]; S=PSAL; Ts=ln[(298.15-T)/(298.15+T)]; T=TEMP; DOXY[micromole/kg]=DO [micromole/L] / rho0 ; rho0= potential density [kg/L] calculated from CTD data”

PREDEPLOYMENT_CALIB_COEFFICIENT = “S0=35; B0= -6.24097e-3; B1=-6.93498e-3; B2=-6.90358e-3; B3=-4.29155e-3; C0= -3.11680e-7 ”

PREDEPLOYMENT_CALIB_COMMENT = “Pressure and salinity compensation are estimated to convert MOLAR_DOXY to DOXY. DOXY is converted from micromole/L to micromole/kg; see TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175”

3.3.2 Case 2: DPHASE or BPHASE are transmitted to the DAC

When the sensor output is either the calibrated phase measurement DPHASE or the uncalibrated phase measurement BPHASE, the conversion of the phase shift to DO concentration is done at the DAC level. Note that the temperature data used for the conversion of the phase shift to a dissolved oxygen concentration must be provided by the same sensor as the one used for the calibration of the optode. At this stage the dissolved oxygen concentration is estimated assuming zero pressure and that the probe is immersed in freshwater (S=0).

Then the dissolved oxygen value is corrected for the pressure and salinity effects. For those calculations, the temperature from the CTD has to be used (TEMP). Finally, the dissolved oxygen concentration is converted in micromol/kg by dividing by the potential density (see Section 4). Again, the temperature from the CTD has to be used (TEMP). Examples on how to fill the PARAMETER and PREDEPLOYMENT_CALIB fields are given hereafter:

For BPHASE:

PARAMETER="BPHASE_DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "none"

PREDEPLOYMENT_CALIB_COEFFICIENT = "none"

PREDEPLOYMENT_CALIB_COMMENT = "BPHASE_DOXY = Uncalibrated phase measurement, see TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175"

For DPHASE:

PARAMETER="DPHASE_DOXY"

**PREDEPLOYMENT_CALIB_EQUATION = "UNCAL_PHASE = BPHASE-RPHASE;
DPHASE_DOXY = A + B*UNCAL_PHASE + C*UNCAL_PHASE^2 +
D*UNCAL_PHASE^3"**

PREDEPLOYMENT_CALIB_COEFFICIENT = "A = 1.40628; B = 9.74106e-1; C = 0; D = 0;"

PREDEPLOYMENT_CALIB_COMMENT = "DPHASE_DOXY = Calibrated phase measurement, see TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175".

For DOXY (estimated for instance from DPHASE with calibration coefficients provided by Aanderaa)

PARAMETER="DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "O2=C0+C1.P+C2.P^2+C3.P^3+C4.P^4;
C_i=C_{i0}+C_{i1}.T+C_{i2}.T^2+C_{i3}.T^3 ; O2c=O2 exp[S (B0+B1.Ts+B2.Ts^2+B3.Ts^3) +
C0.S^2]; Ts=ln[(298.15-T)/(298.15+T)]; DO=O2c [1+ 0.032 * PRES/1000];
DOXY=DO/rho0 ;with P=DPHASE; T=TEMP, S=PSAL, rho0= potential density"

PREDEPLOYMENT_CALIB_COEFFICIENT = "C_{ij} coefficients available at
dedicated_web_page_name; B0= -6.24097e-3; B1=-6.93498e-3; B2=-6.90358e-3; B3=-
4.29155e-3"

PREDEPLOYMENT_CALIB_COMMENT = "DOXY is calculated at DAC level from
DPHASE. Pressure and salinity compensation are estimated and DOXY is converted from
micromole/L to micromole/kg; see TD218 operating manual oxygen optode 3830, 3835,
3930, 3975, 4130, 4175"

Note: Expressions were simplified because they were too long to fit in the 256 characters
allowed.

3.4 Transmission of TEMP_DOXY

PARAMETER="TEMP_DOXY"

PREDEPLOYMENT_CALIB_EQUATION =
"TEMP_DOXY=T0+T1*output+T2*output^2+T3*output^3"

PREDEPLOYMENT_CALIB_COEFFICIENT = "T0=2.128787e+01, T1=-3.094217e-02,
T2=2.932877e-06, T3=-4.214184e-09"

PREDEPLOYMENT_CALIB_COMMENT = "Optode temperature; see TD218 operating
manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175"

3.5 CTD and oxygen data reported with different vertical sampling schemes

Some floats with SBE41CP CTD operating in continuous mode are paired with Aanderaa
optodes. In these cases, the CTD T and S data in continuous mode are reported at high vertical
resolution (e.g. 2-dbar bin average), while the optode oxygen and optode temperature are
reported at low vertical resolution.

As CTD and oxygen data are reported with different vertical sampling schemes, a second
profile is added in the single cycle netcdf file.

CTD data acquired at high vertical resolution are stored in the first profile.

The second profile contains DOXY and DOXY related fields, the intermediate variables
reported by the optode as well as the instantaneous CTD data acquired at the optode level
measurements.

A description of this single cycle netcdf file with two profiles is provided in the Argo Data
Management User's Manual available on the ADMT webpage (<http://www.argodatamgt.org>).

4 SBE-IDO sensor

4.1 Measurements and data processing

The SBE DO sensor, SBE-IDO, determines dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through the membrane from the ocean environment to the working electrode. At the working electrode (cathode), oxygen gas molecules are converted to hydroxyl ions (OH⁻) in a series of reaction steps where the electrode supplies four electrons per molecule to complete the reaction. The sensor counts oxygen molecules by measuring the electrons per second (amperes) delivered to the reaction. (from Application note No. 64, revised in April 2008; prepared by Sea-Bird Electronics, Inc.) The measurable electrical current is converted to a voltage by the sensor electronics. The voltage signal varies linearly with partial pressure of oxygen. Among SBE DO sensors, the SBE 43 outputs the voltage itself whereas the SBE 43F (SBE-IDO) converts it to a frequency signal which is proportional to the voltage. Some SBE DO sensors transmit counts. Counts, voltage or frequency signals, which are transmitted by floats, are then converted in dissolved oxygen concentration on shore. The conversion uses a set of sensor-dependant coefficients with temperature, salinity, and pressure measured by the floats. The dissolved oxygen concentration unit converted from the outputs of the SBE DO sensor is ml/L. It must be converted to $\mu\text{mol/kg}$.

SBE calibrated DO sensors with the oxygen saturation equation of Weiss (1970) up until 2008. They now use the Garcia and Gordon' (1992) equations.

It is known that dissolved oxygen (DO) measurements by DO sensors of the SBE-IDO series are influenced by changes of sensor membrane characteristics due to temperature and pressure. The sensor has a circuit for compensation of the temperature effect on membrane permeability; however a residual temperature effect remains after the compensation. Changes occur in gas-permeable Teflon membranes that affect their permeability characteristics under higher pressures than e.g., 1000 dbar. These changes have long time constants, depend on the sensor's time-pressure history, and result in hysteresis at depths greater than 1000 meters.¹

These effects are considered to be predictable and also correctable; however, until now there is no effective method for the adjustments of the pressure effects for the DO sensor at profiling floats under operation. Thus, scientific calibration of the DO measurements by the SBE-IDO sensor remains an important issue for the future.

¹ In « Application Note 64-2 », see the equation for tau(T,P). Some of the floats may actually be using this equation

4.2 “SENSOR” metadata

SBE-IDO sensor (Electrochemical method)	
SENSOR	DOXY
SENSOR MAKER	SeaBird Electronics
SENSOR_MODEL	SBE-IDO or SBE43F or “SBE43I”
SENSOR_SERIAL_NUMBER	To be filled
SENSOR_UNITS	“Hz” or “Volt” or “(no unit)”
SENSOR_ACCURACY	2% of saturation (initial accuracy)
SENSOR_RESOLUTION	1 μmol/L

4.3 Parameters

For the transmitted data:

PARAMETER=”VOLTAGE_DOXY” or “FREQUENCY_DOXY” or “COUNTS_DOXY”

PREDEPLOYMENT_CALIB_EQUATION = “none”

PREDEPLOYMENT_CALIB_COEFFICIENT = “none”

PREDEPLOYMENT_CALIB_COMMENT = “SBE DO sensor output in V (or Hz or no unit)”

For DOXY (estimated from VOLTAGE DOXY for instance):

PARAMETER=”DOXY”

PREDEPLOYMENT_CALIB_EQUATION =
 “O₂=Soc*(VOLTAGE_DOXY+Voffset)*(1.0+A*T+B*T²+C*T³)*Ox_{sat}(T,S)*exp{E*P/(T+273.15)}; T=TEMP, P=PRES, S=PSAL, Ox_{sat}(T,S)=oxygen_saturation_function [Garcia and Gordon (1992)]; DOXY[micromole/kg]=44.6596*O₂ [ml/L]/rho0; rho0=potential density [kg/L]”

PREDEPLOYMENT_CALIB_COEFFICIENT = “Soc=2.8046e-004, Voffset=-792.6461, A=-3.8289e-003, B=2.3342e-004, C=-4.4573e-006, E=0.036” Those values are provided as example since they are sensor dependent.

PREDEPLOYMENT_CALIB_COMMENT = “DOXY is calculated on shore from VOLTAGE_DOXY and float measurements of TEMP, PSAL, and PRES”

5 Unit conversion of oxygen

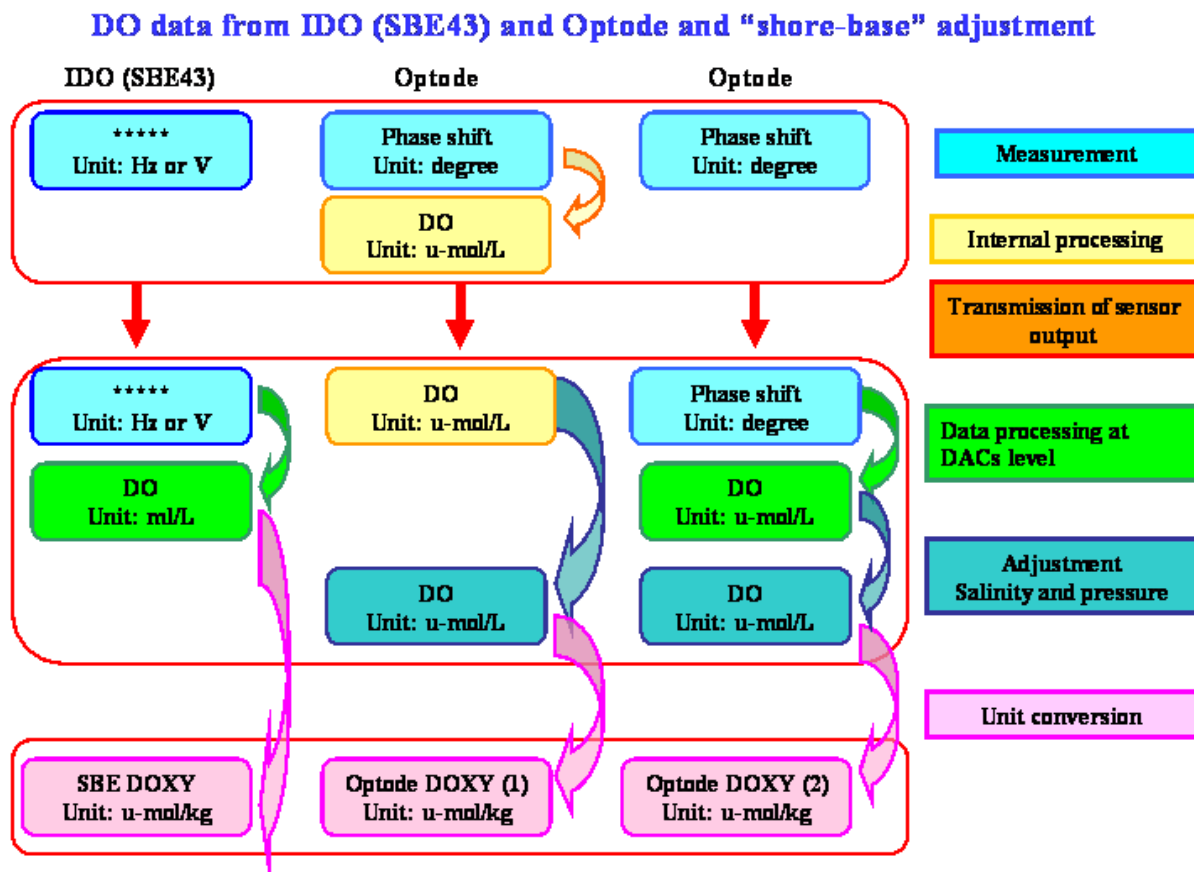
The unit of DOXY is micromole/kg in Argo data and the oxygen measurements are sent from Argo floats in another unit such as micromole/L for the Optode and ml/L for the SBE-IDO. Thus the unit conversion is carried out by DACs as follows:

$$O_2 [\text{micromole/L}] = 44.6596 \times O_2 [\text{ml/L}]$$

$$O_2 [\text{micromole/kg}] = O_2 [\text{micromole/L}] / \rho$$

Here, ρ is the potential density of water [kg/L] at zero pressure and at the potential temperature (e.g., 1.0269 kg/L; e.g., UNESCO, 1983). The value of 44.6596 is derived from the molar volume of the oxygen gas, 22.3916 L/mole, at standard temperature and pressure (0°C, 1 atmosphere; e.g., García and Gordon, 1992). The CTD temperature (TEMP) has to be used to estimate the potential temperature (and not the optode temperature TEMP_DOXY).

6 Schematic of the oxygen data processing



7 References

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