

Processing Argo OXYGEN data at the DAC level

Version 1.3

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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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Version/date	Auteurs	Modification
1.0	V. Thierry, D. Gilbert, T. Kobayashi	Initial version
1.1	V. Thierry	COUNTS_DOXY is replaced by COUNT_DOXY
1.2 / February 2011	V. Thierry	Equation for the calculation of Ts corrected
1.3 / January 2013	V. Thierry	<ul style="list-style-type: none"> - Text completed for new Aanderaa optode 4830 and new Seabird Optode SBE63: new variables added (TPHASE_DOXY, C1PHASE_DOXY, C2PHASE_DOXY, PHASE_DOXY, MLPL_DOXY), new calibration equations - The pressure compensation coefficient can be 0.032 and 0.04. - Use of the oxygen saturation instead of the oxygen solubility for some floats equipped with an SBE43 oxygen sensor.

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)
 - COUNT_DOXY when SBE43 sensor output is count (no Unit)
 - PHASE_DOXY when SBE63 sensor output is PHASE (Unit = microsecond)
 - MLPL_DOXY when SBE63 sensor output is oxygen concentration (Unit = ml/l)
 - BPHASE_DOXY when Aanderaa optode 3830 output is BPHASE (Unit = degree)
 - DPHASE_DOXY when Aanderaa optode 3830 output is DPHASE (Unit = degree)
 - TPHASE_DOXY when Aanderaa optode 4330 output is TPhase (Unit = degree)
 - C1PHASE_DOXY and C2PHASE_DOXY when Aanderaa optode 4330 output is C1Phase and C2Phase (Unit = degree)
 - MOLAR_DOXY when Aanderaa optode (3830 or 4330) 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) and from the “TD269 Operating manual oxygen optode 4330, 4835”.

3.1 Measurements and data processing

3.1.1 Optode 3830

The optode 3830 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.

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

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.

3.1.2 Optode 4330

As for the optode 3830, an uncalibrated phase measurement (TPHASE or TPHASE_DOXY in the Argo data stream) is the difference between the phase obtained with blue light excitation (C1PHASE or C1PHASE_DOXY in the Argo data stream) and the phase obtained with red light excitation (C2PHASE or C2PHASE_DOXY in the Argo data stream).

$$\text{TPHASE} = \text{C1PHASE} - \text{C2PHASE}$$

Temperature compensation could be applied to the phase measurements as follow:

$$\text{TPHASE} = A(T) + [\text{C1PHASE} - \text{C2PHASE}] \cdot B(t)$$

but this option is currently not used and $A(t) = 0$ and $B(t) = 1$. See “TD269 Operating manual oxygen optode 4330, 4835” for more details.

TPHASE is then converted to dissolved oxygen concentration in micromol/L (microM). Two methods are possible.

3.1.2.1 First method based on 20 sensor-dependant coefficients

The first method uses 20 sensor-dependant coefficients, a 4th degree polynomial and the air saturation. The equations are described in details in “TD269 Operating manual oxygen optode 4330, 4835”.

The calibrated phase CalPhase is calculated from TPHASE by use of a 3rd order polynomial :

$$\text{CalPhase} = \text{PhaseCoef}_0 + \text{PhaseCoef}_1 \cdot \text{TPHASE} + \text{PhaseCoef}_2 \cdot \text{TPHASE}^2 + \text{PhaseCoef}_3 \cdot \text{TPHASE}^3$$

Similarly, the temperature measured by the optode in °C (TEMP_DOXY in the Argo data stream) is calculated from RawTemp by use of a similar polynomial with coefficients called *TempCoef*.

Based on the calibrated phase (CalPhase) and temperature T (that can be either the CTD temperature TEMP or the optode temperature TEMP_DOXY depending on the temperature used during the calibration) the partial pressure of O2 is calculated by use of a two dimensional polynomial:

$$\Delta p = C_0 \times T^{m_0} \times \text{CalPhase}^{n_0} + C_1 \times T^{m_1} \times \text{CalPhase}^{n_1} + \dots + C_{27} \times T^{m_{27}} \times \text{CalPhase}^{n_{27}}$$

where the polynomial coefficients C_0 to C_{13} are stored in the property FoilCoefA and C_{14} to C_{27} are stored in FoilCoefB. The temperature exponents, $m_{0..27}$, are stored as FoilPolyDegT and phase exponents, $n_{0..27}$, are stored as FoilPolyDegO.

From the partial pressure the air saturation is then calculated as:

$$\text{AirSaturation}(\%) = \Delta p \cdot 100 / [(\text{NomAirPress} - p_{\text{vapour}}(T)) \cdot \text{NomAirMix}]$$

where *NomAirPress* is a property for the nominal air pressure, usually 1013.25 hPa, and *NomAirMix* is the nominal O2 content in air, by default 0.20946.

The $p_{\text{vapour}}(TEMP)$ is the vapour pressure calculated from temperature by the following equation:

$$p_{\text{vapour}}(T) = \exp [52.57 - 6690.9 / (T + 273.15) - 4.681 \cdot \ln (T + 273.15)]$$

The oxygen concentration not compensated for pressure and salinity effect (MOLAR_DOXY), is finally calculated as:

$$\text{MOLAR_DOXY (mumol/L)} = C^* \cdot 44.614 \cdot \text{AirSaturation} / 100$$

where C^* is the oxygen solubility (cm^3/dm^3) calculated from the Garcia and Gordon equation of 1992:

$$\ln (C^*) = A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 + A_4 T_s^4 + A_5 T_s^5 + S (B_0 + B_1 T_s + B_2 T_s^2 + B_3 T_s^3) + C_0 S^2$$

where T_s is the scaled temperature is expressed as a function of the temperature T (in °C) :

$$T_s = \ln [(298.15 - T) / (273.15 + T)]$$

where S is the Salinity given in the optode settings (default set to zero), and where :

$A_0 = 2.00856$	$B_0 = -6.24097e-3$
$A_1 = 3.22400$	$B_1 = -6.93498e-3$
$A_2 = 3.99063$	$B_2 = -6.90358e-3$
$A_3 = 4.80299$	$B_3 = -4.29155e-3$
$A_4 = 9.78188e-1$	$C_0 = -3.11680e-7$
$A_5 = 1.71069$	

3.1.2.2 Second method based on the Stern-Volmer equation

The second method is based on the Stern-Volmer equation proposed by Uchida et al 2008.

$$[MOLAR - DOXY] = \frac{\frac{c4 + c5.T}{c6 + c7.TPhase} - 1}{c1 + c2.T + c3.T^2}$$

with T the temperature measured by the optode or by the CTD, and MOLAR_DOXY the oxygen concentration in $\mu\text{mol/L}$.

3.1.3 Pressure and salinity compensation

The dissolved oxygen concentration must also be corrected for salinity and pressure effects. The salinity compensation is estimated as:

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

where $S=PSAL$ and $S_0=S_{ref}$ when MOLAR_DOXY has been internally calculated from S_{ref} , or $S_0=0$ when DO is estimated on-shore from BPHASE or from DPHASE.

$T_s = \ln[(298.15 - T)/(273.15 + T)]$ where T is the CTD temperature (TEMP) in $^{\circ}\text{C}$.

$B_0 = -6.24097e-3$; $B_1 = -6.93498e-3$; $B_2 = -6.90358e-3$; $B_3 = -4.29155e-3$; $C_0 = -3.11680e-7$

The pressure compensation is then estimated as:

$$DOXY = DO_{PSAL} \cdot [1 + (Pcoef \times PRES)/1000]$$

Following Uchida et al (2008), $Pcoef = 0.032$. This coefficient supersedes the original coefficient proposed by Aanderaa that was set to 0.04. Note that the pressure compensation is calculated with $Pcoef = 0.032$ for most floats but for some floats the pressure compensation is calculated in using $Pcoef = 0.04$.

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 6). 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, DPHASE_DOXY, TPHASE_DOXY, C2PHASE_DOY or C2PHASE_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 6). 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 $C_i=C_{i0}+C_{i1}.T+C_{i2}.T^2+C_{i3}.T^3$; $MOLAR_DOXY=O2 \exp[S$

$(B0+B1.Ts+B2.Ts^2+B3.Ts^3)+C0S^2$]; $Ts=\ln[(298.15-T)/(273.15+T)]$; 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 = “ $O2c= Molar_DOXY \exp[(S-S0) (B0+B1Ts+B2Ts^2+B3Ts^3)+C0(S^2-S0^2)]$; $DO=O2c [1+ Pcoef * PRES/1000]$; $S=PSAL$; $Ts=\ln[(298.15-T)/(273.15+T)]$; $T=TEMP$; $DOXY[\text{micromole/kg}]=DO [\text{micromole/L}] / \rho0$; $\rho0=$ potential density [kg/L] calculated from CTD data”

Pcoef being equal to 0.032 or 0.04.

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 6). 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)/(273.15+T)]; DO=O2c [1+ Pcoef * PRES/1000];
DOXY=DO/rho0 ;with P=DPHASE; T=TEMP, S=PSAL, rho0= potential density"

Pcoef being equal to 0.032 or 0.04.

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.

3.3.3 Case 3: TPHASE or C1PHASE and C2PHASE are transmitted to the DAC

When the sensor output is either the phase measurement TPHASE or the C1PHASE and C2PHASE, 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 6). 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 TPHASE:

PARAMETER="TPHASE_DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "none"

PREDEPLOYMENT_CALIB_COEFFICIENT = "none"

PREDEPLOYMENT_CALIB_COMMENT ="TPHASE_DOXY = Uncalibrated phase measurement, see TD269 operating manual oxygen optode 4330, 4835"

For C1PHASE:

PARAMETER="C1PHASE_DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "none"

PREDEPLOYMENT_CALIB_COEFFICIENT = "none"

PREDEPLOYMENT_CALIB_COMMENT ="CPHASE_DOXY = Uncalibrated phase measurement from blue light excitation, see TD269 operating manual oxygen optode 4330, 4835"

For C2PHASE:

PARAMETER="C2PHASE_DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "none"

PREDEPLOYMENT_CALIB_COEFFICIENT = "none"

PREDEPLOYMENT_CALIB_COMMENT ="CPHASE_DOXY = Uncalibrated phase measurement from red light excitation, see TD269 operating manual oxygen optode 4330, 4835"

For DOXY (estimated for instance from TPHASE and using the Stern-Volmer equation)

PARAMETER="DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "O2=[(c4+c5*T)/(c6+c7*TPHASE)-1]/[c1+c2*T+c3*T^2]; O2c=O2 exp[S (B0+B1.Ts+B2.Ts^2+B3.Ts^3) + C0.S^2]; Ts=ln[(298.15-T)/(273.15+T)]; DO=O2c [1+ Pcoef * PRES/1000]; DOXY=DO/rho0 ;with T=TEMP, S=PSAL, rho0= potential density"

Pcoef being equal to 0.032 or 0.04.

PREDEPLOYMENT_CALIB_COEFFICIENT = "c1=c1val;c2=c2val; c3=c3val;c4=c4val;c5=c5val; c6=c6val;c7=c7val;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 TPHASE and the Stern-Volmer equation. Pressure and salinity compensation are estimated and DOXY is converted from micromole/L to micromole/kg; see TD269 operating manual oxygen optode 4330, 4835"

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 (SBE43) 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 count, 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. Note that for some floats, the oxygen saturation is used instead of the oxygen solubility.

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 “COUNT_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)*Oxsat(T,S)*exp{E*P/(T+273.15)}; T=TEMP, P=PRES, S=PSAL, Oxsat(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 SBE63 sensor

Information provided hereafter is taken from the SBE63 User's manual.

5.1 Measurements and data processing

The SBE63 optode measures oxygen concentration following the same principle as the one of the Aanderaa optode.

The SBE63 output is either a raw phase (in μsec) or an oxygen concentration in ml/L. The calibration equation is the following :

$$\text{O2 (ml/L)} = [(\mathbf{a0} + \mathbf{a1T} + \mathbf{a2V2}) / (\mathbf{b0} + \mathbf{b1V}) - 1] / \mathbf{Ksv} [\mathbf{SCorr}] [\mathbf{PCorr}]$$

where

- O2 is oxygen concentration (ml/L)
- T is temperature output from SBE 63's thermistor in $^{\circ}\text{C}$
- V is raw measured phase delay in volts : $\mathbf{V} = \phi_r / 39.457071$
- ϕ_r is raw measured phase delay in μsec (PHASE_DOXY in the Argo data stream)
- a0, a1, a2, b0, b1 are calibration coefficients (Uchida et al, 2008)
- Ksv is Stern-Volmer constant (with calibration coefficients c0, c1, c2) (Demas et al, 1999)
- SCorr is salinity correction function (with calibration coefficients SolB0, SolB1, SolB2, SolB3, SolC0)
- PCorr is pressure correction function (with calibration coefficient E)

The Stern-Volmer constant equation is:

$$\mathbf{Ksv} = \mathbf{c0} + \mathbf{c1T} + \mathbf{c2T^2}$$

where

- c0, c1, c2 are calibration coefficients
- T is temperature output from SBE 63's thermistor in $^{\circ}\text{C}$

The salinity correction equation is:

$$\mathbf{SCorr} = \exp [\mathbf{S} * (\mathbf{SolB0} + \mathbf{SolB1} * \mathbf{Ts} + \mathbf{SolB2} * \mathbf{Ts}^2 + \mathbf{SolB3} * \mathbf{Ts}^3) + \mathbf{SolC0} * \mathbf{S}^2]$$

where

- Salinity correction coefficients are constants (Benson and Krause, 1984) -

$$\text{Sol}_{B0} = -6.24523\text{e-}3$$

$$\text{Sol}_{B1} = -7.37614\text{e-}3$$

$$\text{Sol}_{B2} = -1.03410\text{e-}2$$

$$\text{Sol}_{B3} = -8.17083\text{e-}3$$

$$\text{Sol}_{C0} = -4.88682\text{e-}7$$

- $\mathbf{Ts} = \ln [(298.15 - \mathbf{T}) / (273.15 + \mathbf{T})]$ where T is temperature output from SBE 63's thermistor in $^{\circ}\text{C}$

- S = salinity. Note that for oxygen in ml/l output directly from SBE 63, SetRefSal= is used as the salinity value in the salinity correction equation. When the SBE 63 is integrated with a CTD, salinity calculated from the CTD should be used to calculate converted oxygen (ml/L, mg/L, etc.).

The pressure correction equation is:

$$P_{\text{corr}} = \exp(E * P / K)$$

where

- Pressure correction coefficient is constant $E = 0.011$
- K = temperature in Kelvin = $T + 273.15$ where T is temperature output from SBE 63's thermistor in $^{\circ}\text{C}$
- P = pressure (dbar) from CTD data. Note that for oxygen in ml/l output directly from the SBE 63, SetRefP= is used as the pressure value in the pressure correction equation. When the SBE 63 is integrated with a CTD, pressure calculated from the CTD data should be used to calculate converted oxygen (ml/L, mg/L, etc.).

Sea-Bird provides two calibration sheets with each SBE 63 :

- One relates the SBE 63 oxygen sensor output to oxygen concentration in ml/L – with coefficients $a_0, a_1, a_2, b_0, b_1, c_0, c_1, c_2$, and E .
- One relates the SBE 63 thermistor output to temperature ($^{\circ}\text{C}$) – with coefficients ta_0, ta_1, ta_2, ta_3

5.2 “SENSOR” metadata

SBE63 sensor	
SENSOR	DOXY
SENSOR MAKER	SeaBird Electronics
SENSOR_MODEL	SBE63
SENSOR_SERIAL_NUMBER	To be filled
SENSOR_UNITS	“microsecond” for PHASE_DOXY or “ml/l” for MLPL_DOXY
SENSOR_ACCURACY	+/- 3 μmol/kg
SENSOR_RESOLUTION	0.2 μmol/kg

5.3 Parameters

For the transmitted data:

PARAMETER=”PHASE_DOXY” or “MLPL_DOXY”

PREDEPLOYMENT_CALIB_EQUATION = “none”

PREDEPLOYMENT_CALIB_COEFFICIENT = “none”

PREDEPLOYMENT_CALIB_COMMENT = “SBE63 sensor output in microsecond (or ml/l)”

For DOXY (when estimated from PHASE_DOXY):

PARAMETER=”DOXY”

PREDEPLOYMENT_CALIB_EQUATION = to be done

PREDEPLOYMENT_CALIB_COEFFICIENT = to be done

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

6 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:

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

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

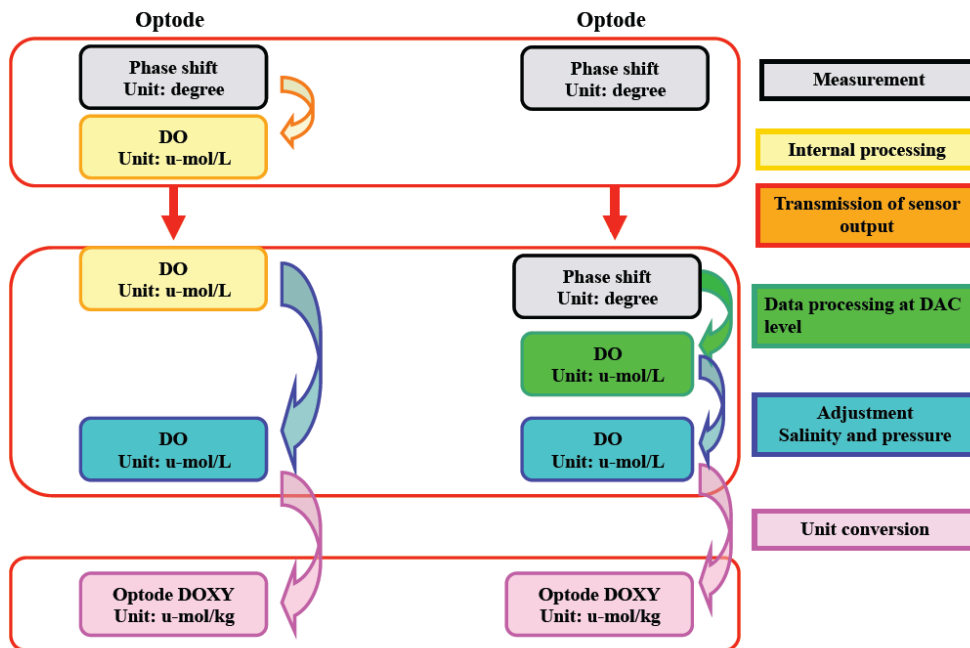
Here, ρ is the potential density of water [kg/L] at zero pressure and at the potential temperature (e.g., 1.0269 kg/L; e.g., UNESCO, 1983). The value of 44.6596 is derived from

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).

7 Schematic of the oxygen data processing

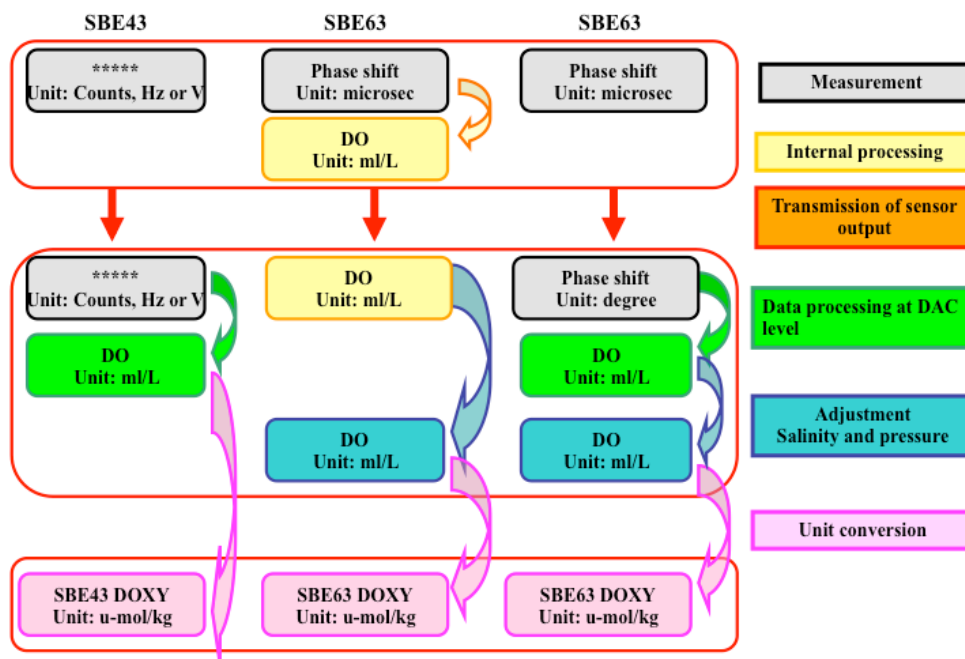
7.1 Aanderaa optodes

DO data from Aanderaa Optode 3830 and 4330 and “shore-base” adjustment



7.2 Seabird sensors

DO data from SBE43 and SB63 sensors and “shore-base” adjustment



8 References

- García, H.E. and L.I. Gordon (1992): Oxygen solubility in sea water: better fitting equations. *Limnol. Oceanogr.*, **37(6)**, 1307-1312.
- Uchida, H. T. Kawano, I. Kaneko, and M. Fukasawa (2008): In situ calibration of Optode-based oxygen sensors. *J. Atmos. Oceanic Tech.*, **25**, 2271-2281.
- UNESCO (1983): Algorithms for computation of fundamental properties of seawater. *Unesco technical papers in marine science*, **44**, 53pp.
- Weiss, R. F. (1970): The solubility of nitrogen, oxygen, and argon in water and seawater. *Deep Sea Res.*, **17**, 721-735.