Processing Argo OXYGEN data at the DAC level
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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.

1 Dissolved oxygen concentration measurements

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 (in particular based on quenched fluorescence).

The official Argo unit for dissolved oxygen concentration is μmol/kg, as in JGOFS and CLIVAR, but none of the existing sensors provides DO data in native units of μmol/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 μmol/kg.

We propose that there should be three columns to describe oxygen in profile data files:

1 - DOXY_RAW would contain the raw values transmitted by the dissolved oxygen sensor, whatever the unit of the sensor output is.

2 - DOXY would contain the dissolved oxygen value in μmol/kg. In DOXY, we would correct for temperature, pressure and salinity effects by using the real-time PRES, TEMP and PSAL fields.

3 - DOXY_ADJUSTED would contain the DOXY values corrected from any drift or offset of the DO, pressure, salinity or temperature sensors. While DOXY is estimated from PRES,

TEMP and PSAL, DOXY_ADJUSTED would be estimated from PRES_ADJUSTED, TEMP_ADJUSTED and PSAL_ADJUSTED.

2 METADATA

2.1 Sensors

When a float provides DO values, SENSOR and SENSOR_MAKER fields are filled:

SENSOR = "DOXY"
= 'TEMP_DOXY" for the Aanderaa Optode when necessary

SENSOR_MAKER = "SeaBird Electronics" or **"Aanderaa"**

Different models can be proposed by the manufacturers. For instance, the Aanderaa optode exists in at least three versions: 3830, 4330 or 4330F. The Seabird model has also some variations: SBE43, SBE43F, or SBE43I. It is very likely that new models will be available in the future. This type of information is contained in SENSOR_MODEL:

SENSOR_MODEL = "3830" or **"4330"** or **"4330F"** for the Aanderaa optode
= "SBE43" or **"SBE43F"** or **"SBE43I"** for the Seabird SBE43

When available, the serial number of the sensor has to be filled. 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.

SENSOR_SERIAL_NUMBER = "XXXXX"

Data delivered and transmitted by the oxygen sensor can have different units. The unit of the sensor output is given in the SENSOR_UNIT field. The raw data transmitted by the sensor are stored in the DOXY_RAW field.

SENSOR_UNIT = 'Hz" or "Volt" for SBE43
= "degree" or "micromole/l" for Aanderaa optode
= "degree Celsius" for the temperature sensor of the Aanderaa optode

The raw data are then converted in µmol/kg, the official Argo unit for dissolved oxygen concentration. When necessary, the dissolved oxygen data are also compensated for pressure and salinity effects. Those data are then stored in the DOXY field. The accuracy and the resolution of the sensors are provided by the manufacturers:

SENSOR_ACCURACY = "2% of saturation " for the SBE43
= "8 µmol/L or 5% " for Aanderaa optode
= "0.1 degree Celsius" (for 4330/4330F) or **"0.05 degree Celsius"** (for 3830) for the temperature sensor of the Aanderaa optode

SENSOR_RESOLUTION = "1 µmol/L " for SBE43 and for Aanderaa optode
= "0.01 degree Celsius " for the temperature sensor of the Aanderaa optode

Note that for the Aanderaa Optode, accuracy and resolution are given in µmol/L.

Sensors and measurement methods		
	Electrochemical method	**Optical method**
SENSOR	**DOXY**	**DOXY** ***TEMP_DOXY****
SENSOR MAKER	Example: **SeaBird Electronics**	Example: **Aanderaa**
SENSOR_MODEL	Example: **SBE43** or **SBE43F** or **"SBE43I"**	Exemple : **3830** or **4330** or **4330F**
SENSOR_SERIAL_NUMBER	To be filled	To be filled
SENSOR_UNITS	**"Hz"** or **"Volt"**	**degree (DPhase) or "micromole/L** ***degree Celsius****
SENSOR_ACCURACY	**2% of saturation (initial accuracy)**	**8 µmol/L or 5%** ***0.1 degree Celsius*** *(for 4330/4330F) or* ***0.05 degree Celsius*** *(for 3830)* *****
SENSOR_RESOLUTION	**1 µmol/L**	**1 µmol/L** ***0.01 degree Celsius****

* when TEMP_DOXY is transmitted

2.2 Data processing, parameters and outputs

2.2.1 Aanderaa Optode

The optode measures a phase shift in degrees. The calibrated phase shift (DPHASE) is then converted in dissolved oxygen concentration. The conversion uses 20 sensor-dependant coefficients (Section 3.1). The dissolved oxygen concentration must also be corrected for salinity and pressure effects (Section 3.2). Dissolved oxygen concentration units from the optode are µmol/L (µM). It must be converted in µ mol/kg by dividing by density (Section 5).

(a) DPHASE is internally converted in DO concentration

In that case, a dissolved oxygen concentration (=DOXY_RAW) is transmitted to the DAC. The concentration is estimated according to a reference salinity (S0), assuming zero pressure and using the temperature measured by the optode itself (TEMP_DOXY). Depending on the sensor model, the quality of the temperature measured by the optode varies. 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 (Section 3.2). DOXY_RAW is then transformed in DOXY by correcting for the pressure and salinity effects and by converting the dissolved oxygen concentration in µmol/kg by dividing by the potential density (see Section 5). The PARAMETER and PREDEPLOYMENT_CALIB fields could be filled as follows:

For DOXY_RAW:

PARAMETER=DOXY_RAW

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 ; O2c=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=35" or "S0=0"

PREDEPLOYMENT_CALIB_COMMENT = "DOXY_RAW is internally calculated 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= O2 exp[(S-S0) (B0+B1Ts+B2Ts^2+B3Ts^3)+C0(S^2-S0^2)]; DO=O2c [1+ 0.032 * PRES/1000]; O2=DOXY_RAW; S=PSAL; Ts=ln[(298.15-t)/(298.15+t)]; t=TEMP (*or TEMP_DOXY);* DOXY[micromole/kg]=DO [micromole/L] / ρ ; ρ= potential density [kg/L] at zero pressure and potential temperature"

PREDEPLOYMENT_CALIB_COEFFICIENT = "S0=35 *(or any other value);* B0= -6.24097e-3; B1=-6.93498e-3; B2=-6.90358e-3; B3=-4.29155e-3 "

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

(b) DPHASE is transmitted to the DAC

When the conversion of the phase shift to DO concentration is done at DAC level, DPHASE is transmitted by the sensor and TEMP_DOXY or TEMP can be used to calculate DOXY, although most users would use TEMP because of the better temperature accuracy of the Argo CTD. The dissolved oxygen concentration is first 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. Finally, the dissolved oxygen concentration is converted in μmol/kg by dividing by the potential density (see Section 5). The PARAMETER and PREDEPLOYMENT_CALIB fields could be filled as follows:

For DOXY_RAW:

PARAMETER="DOXY_RAW"

PREDEPLOYMENT_CALIB_EQUATION = "none"

PREDEPLOYMENT_CALIB_COEFFICIENT = "none"

PREDEPLOYMENT_CALIB_COMMENT = "DOXY_RAW= Calibrated phase measurement (DPHASE); see TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175"

For DOXY:

PARAMETER="DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "O2=C0+C1.P+C2.P^2+C3.P^3+C4.P^4; C_i=Ci0+Ci1.t+Ci2.t^2+Ci3.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/ρ ;with P=DOXY_RAW; t=TEMP, S=PSAL, ρ= potential density"

PREDEPLOYMENT_CALIB_COEFFICIENT = ""Cij for i=0:4 and j=0:3; 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.

(c) If TEMP_DOXY is transmitted (whatever the value of DOXY_RAW is)

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 = "see TD218 operating manual oxygen optode 3830, 3835, 3930, 3975, 4130, 4175"

2.2.2 Sea-Bird Electronics

The SBE DO sensor, SBE 43, determines dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse though 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 43I) converts it to a frequency signal which is proportional to the voltage. The voltage or frequency signal, which is transmitted by floats, is 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 (see Section 4). The dissolved oxygen concentration unit converted from the outputs of the SBE DO sensor is ml/L. It must be converted to μmol/kg.

Note: Some people refer to the SBE 43 as the SBE IDO.

For DOXY_RAW:

PARAMETER="DOXY_RAW"

PREDEPLOYMENT_CALIB_EQUATION = " none"

PREDEPLOYMENT_CALIB_COEFFICIENT = "none"

PREDEPLOYMENT_CALIB_COMMENT = "Sensor output in Hz *(or V)*"

For DOXY:

PARAMETER="DOXY"

PREDEPLOYMENT_CALIB_EQUATION = "O2=Soc*(output+Foffset)*(1.0+A*T+B*T^2+C*T^3)*Oxsat(T,S)*exp{E*P/(T+273.15)} where T=TEMP, P=PRES, S=PSAL, Oxsat(T,S)=oxygen_saturation_function [Weiss (1970) or Garcia and Gordon (1992)]; DOXY[micromole/kg]=44.6596*O2 [ml/L] / ρ ; ρ= potential density [kg/L] at zero pressure and potential temperature"

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

PREDEPLOYMENT_CALIB_COMMENT = "DOXY is calculated on shore from frequency of sensor output and float measurements of TEMP, PSAL, and PRES"

SBE calibrated DO sensors with the oxygen saturation equation of Weiss (1970) until 2008.

Data transmission and processing			
	SBE 43/43F	Aanderaa Optode	
		Transmission of DO in micromole/L	Tranmission of DPHASE
PARAMETER	DOXY_RAW DOXY	DOXY_RAW DOXY *TEMP_DOXY**	DOXY_RAW DOXY *TEMP_DOXY**
PREDEPLOYMENT_CALIB_EQUATION	See text	See text	See text
PREDEPLOYMENT_CALIB_COMMENT	See text	See text	See text
PREDEPLOYMENT_CALIB_COEFFICIENT	See text	See text	See text

* when TEMP_DOXY is transmitted

3 Calibration equations for the Aanderaa optode

3.1 Conversion of DPHASE in dissolved oxygen concentration

Based on the raw data measured by the Aanderaa optode, the internal software of the sensor estimates a calibrated phase measurement (DPHASE). The Oxygen concentration is calculated in µmol/L (µM) from a 4th degree polynomial:

$$O2=C_0+C_1P+C_2P^2+C_3P^3+C_4P^4$$

where P is the calibrated phase measurement (DPHASE) and C_0, C_1, ..C_4 are temperature dependent coefficients calculated as:

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

with t = TEMP or TEMP_DOXY, is the temperature in °C.

3.2 Salinity and pressure compensation

When DPHASE is converted in dissolved oxygen concentration (DO), DO has to be corrected for the pressure and salinity effect.

The salinity compensation is estimated as:

$$DOXY_{PSAL}=DO.\ \exp[\ (S-S_0)\ (B_0+B_1T_S+B_2T_S^2+B_3T_S^3)+C_0(S^2-S_0^2)]$$

where S=PSAL and S_0=Sref when DOXY is internally calculated from Sref, or S_0=0 when DOXY is estimated on-shore from DPHASE.

T_S=ln[(298.15-t)/(298.15+t)] and t=TEMP or TEMP_DOXY

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:

$$DOXY= DOXY_{PSAL}\ .\ [1 + (0.032\ PRES)/1000]$$

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).

4 SBE43

It is known that DO measurements by DO sensor of the SBE 43 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.

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

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

5 Unit conversion of oxygen

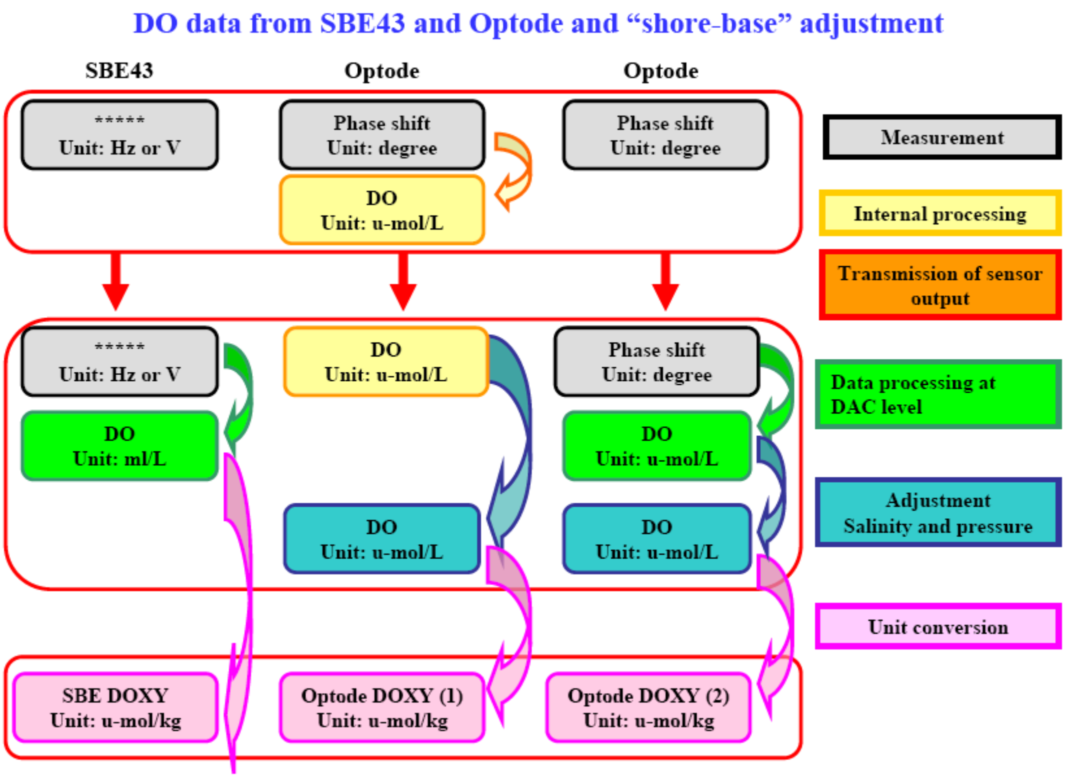
The unit of DOXY is micromole/kg in Argo data and the oxygen measurements are sent from Argo floats in another unit such as micromole/L for the Optode and ml/L for the SBE 43. Thus the unit conversion is carried out by DACs as follows:

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

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

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).

6 Schematic of the oxygen data processing



7 References

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