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SBE 13, 23, 30 Dissolved Oxygen Sensor Calibration and Deployment

Note: This Application Note does not apply to the SBE 43 Dissolved Oxygen Sensor.

GENERAL DESCRIPTION

The SBE 13, 23, and 30 use either a Beckman sensor element or a modified YSI 5739 oxygen probe. These Sea-Bird oxygen sensors have two, 0 to +5 volt outputs. One of these is proportional to the internal temperature of the sensor and the other is proportional to the oxygen current. SBE 13 sensors produced before February 1992 have a 0 to
+5 volt output (oxygen current) and a -5 to +5 volt output (sensor temperature). Consult the specification sheet that was supplied with your oxygen sensor for additional information. CTD instruments made by Sea-Bird that are equipped with oxygen sensors record these voltages for later conversion to oxygen concentration using the algorithm by Owens and Millard (1985).

Oxygen sensors determine the dissolved oxygen concentration by *counting* the number of oxygen molecules per second (flux) that diffuse through a membrane from the ocean environment to the working electrode. By knowing the flux of oxygen and the geometry of the diffusion path, the concentration of oxygen in the environment can be computed. The permeability of the membrane to oxygen is a function of temperature and ambient pressure and is taken into account in the calibration equation. The algorithm to compute oxygen concentration requires that the following measurements be made: **water temperature, salinity, pressure, oxygen sensor current, and oxygen sensor temperature**. When the oxygen sensor is attached to a Sea-Bird CTD, all of these parameters are measured by the CTD.

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. At the other electrode (anode), silver chloride is formed and silver ions (Ag+) are dissolved into solution. Consequently, the chemistry of the sensor electrolyte changes continuously as oxygen is measured, producing a slow but continuous change of the sensor calibration with time (the slope coefficient, Soc, changes by a factor of two after about 1000 hours of powered-up use in *Beckman* sensors and after a few hundred hours in *YSI*).

Oxygen sensors have operating characteristics that require certain procedures be followed to ensure that accurate and reliable measurements of oxygen concentration are obtained. These characteristics include:

1. When power is applied to the oxygen sensor, it takes up to three minutes for the sensor to polarize and come to a stable reading. This implies that when a CTD is turned on, it must be held at the surface for a least three minutes before a cast is started to ensure accurate oxygen readings.

2. The oxygen sensor consumes the oxygen in the water near the sensor membrane. If there is not an adequate flow of new water past the membrane, the sensor will give a reading that is lower than the true oxygen concentration. This requires that the sensor be moving through the water or that water be pumped past the sensor.

3. Temperature differences between the water and the oxygen sensor can lead to errors in the oxygen measurement. When profiling through areas of high temperature gradients, this error can be substantial. Because of its different construction, the Beckman sensor element is more susceptible to this error source than is the YSI sensor. Aligning the oxygen data in time with ALIGN CTD can minimize this problem and also correct for the water transit time in the plumbing on pumped systems and for the relatively slow response time of oxygen sensors in comparison to other CTD sensors.

OXYGEN ALGORITHM

SEASOFT uses the algorithm by Owens and Millard (1985) to convert SBE 13/23/30 oxygen sensor data to oxygen concentration, but treats the coefficients differently. Only Soc and Boc, the scale and offset coefficients, are allowed to be variable. The other four coefficients (tcor, pcor, tau, and wt) are fixed at reasonable physical values. Sea-Bird provides two programs to compute the values for Soc (sensitivity or scale) and Boc (offset). OXFIT uses the zero oxygen value and air saturated water readings. OXFITW uses the zero oxygen value and an oxygen value measured by Winkler or other methods.

The algorithm has the following form:

OX = [Soc * (oc + tau * doc/dt) + Boc] * OXSAT(T,s)*exp(tcor * [T + wt * (To - T)] + pcor * p)

Where:

Description	Abbreviation	Definition
Computed	OX	dissolved oxygen concentration (ml/l)
Measured Parameters	T	water temperature (°C)
	To	oxygen sensor internal temperature (°C)
	s	salinity (PSU)-(ppt)
	p	pressure (dB)
	oc	oxygen current (μA)
	doc/dt	slope of oxygen current (μA/sec)
Calibration Coefficients	Boc	oxygen current bias
	Soc	oxygen current slope
Constants	wt	weighting fraction of oxygen sensor internal temperature
	tcor	temperature correction factor for membrane permeability
	pcor	pressure correction factor for membrane permeability
	tau	oxygen sensor response time
Calculated Value	OXSAT(T,s)	oxygen saturation value after Weiss (1970)

Values for tcor, tau and wt are taken from the Beckman polarographic oxygen sensor technical memorandum. The value for pcor recommended by Sea-Bird deviates from the Beckman memorandum and is based on more recent data analysis (see Application Note 13-3):

tcor = -0.033
pcor = 1.50e-4
tau = 2.0
wt = 0.67 (Beckman type sensors) or 0.85 (YSI type sensors)

OXYGEN SENSOR CALIBRATION

Sea-Bird's calibration method is to measure the oxygen current output in a zero oxygen environment and the oxygen current and oxygen temperature outputs in either air-saturated water (OXFIT) or in water where the oxygen content is independently measured (OXFITW). The voltage outputs are converted to sensor temperature and oxygen current, using the k and c coefficients for temperature and the m and b coefficients for current. The conversion coefficients are found on the original factory calibration sheet for the oxygen sensor. OXFIT and OXFITW calculate the coefficients Soc and Boc that are used in the oxygen algorithm. Enter the computed values for Soc and Boc in the CTD configuration (.con) file.

NOTE: The CTD configuration (.con) file is edited using the Configure menu (in SEASAVE or SBE Data Processing in our SEASOFT-Win32 suite of programs) or SEACON (in SEASOFT-DOS). If using the SBE 16*plus* or 19*plus* with the oxygen sensor, you must use the Windows software to enter the computed values.

The oxygen sensor can be calibrated by itself using a voltmeter, to measure the sensor outputs, and a power supply, to provide power to the sensor. Alternatively, the CTD system can be used to provide power to and acquire data from the oxygen sensor. In this method, SEASOFT can be used to display real-time data from the instrument, including oxygen concentration.

If the oxygen sensor is on a CTD system with a pump, it is recommended that the entire CTD be submerged in the bath, but not powered, for at least one hour prior to the calibration. Supply power to the CTD, oxygen sensor, and pump for 15 minutes prior to the calibration. The oxygen sensor power must not be interrupted for 15 minutes prior to the calibration, so that full polarization and equilibration can be established.

SBE 19 SEACAT Profilers with an optional pump, SBE 19*plus* SEACAT Profilers, and SBE 25 SEALOGGER CTDs have adjustable pump start frequencies which should be set to zero using the SEATERM terminal program, to ensure that the pump will start in fresh water. Use the following command to set the pump start frequency:

- SBE 19 -- **SP** command
- SBE 19*plus* -- **MINCONDFREQ=x** command
- SBE 25 -- **CC** command

The SBE 9 CTD contains circuitry that turns the pump on when the conductivity sensor enters salt water. **To ensure that the pump will turn on in a fresh water bath,** remove the end of the Tygon tubing going between the conductivity cell and the oxygen sensor from the conductivity sensor and place a loop of tubing filled with salt water over both ends of the conductivity cell (or TC duct and conductivity cell). **Note that if salt water is in the conductivity cell and the oxygen sensor is in fresh water, the CTD will compute salinity based on the water in the conductivity cell.** In this case, enter 0 for the salinity value in OXFIT or OXFITW and be aware that the values of OXSAT and Oxygen computed by the software will be incorrect, because the wrong value of salinity will be used for the oxygen computation.

Once the sensor has soaked for the required one-hour period, apply power to the sensor either by turning on the external power supply or the CTD.

If a pump is being used that is not connected to the CTD, apply power to it. Before power is applied, verify that no air is trapped in the plumbing system. Trapped air will prevent the pump from establishing a good flow.

Most oxygen sensors will come to within 1% of their asymptotic stable reading within five minutes after the application of power. Record this reading (either in units of current or voltage). To obtain oxygen readings that are within +/- 1% of the true reading, the oxygen sensor temperature must be within 0.25 ^{o}C of the bath water, temperature as measured by the CTD or a thermometer.

Zero Oxygen Reading (OXFIT and OXFITW)

It is recommended that the zero oxygen point be taken first. This can be done by two different techniques: flush the sensor with a continuous stream of inert gas (e.g., Nitrogen or Argon), or place the sensor in a 5-10% by weight solution of Na_2SO_3 (sodium sulfite).

Sea-Bird recommends the sodium sulfite method. It is simpler and is not subject to errors (that can occur when using an inert gas) such as poor temperature control and incomplete displacement of oxygen gas diffusing out from inside the oxygen sensor.

On Sea-Bird CTD systems that are equipped with a pump, the oxygen sensor is provided with a *plenum*. The *plenum* can be filled with sodium sulfite solution and closed off with a piece of tubing (or alternatively, inert gas can be flushed through the *plenum*). When using the sodium sulfite solution, ensure that there are no air bubbles trapped on the oxygen sensor membrane. Ensure that power has been applied to the sensor for several minutes before the inert gas or sodium sulfite solution is placed in the sensor. Watch the output of the sensor decrease rapidly towards zero volts. At some point the rapid change will stop, usually within one to two minutes. Record the output after three minutes. This will be the zero value to use in the calibration. Often, depending on the individual sensor, the output will slowly drift towards zero volts. For the purposes of the calibration, the slow drift is not considered.

The original calibration sheet that accompanied the oxygen sensor will contain the zero oxygen current that was obtained during the factory calibration. If the sodium sulfite solution was used, rinse the oxygen sensor thoroughly several times to remove all traces of the solution and carefully clean your hands.

Air Saturated Reading (OXFIT)

The theory is to read the sensor's output in water that is exactly saturated with atmospheric gases. The saturated value of dissolved oxygen at atmospheric pressure and at a given temperature and salinity is computed with the program OXSAT. In practice, this is accomplished by immersing the oxygen sensor in a volume of air-saturated water and drawing water past the sensor with a small submersible pump. If the CTD system is equipped with a pump, this should be used for the calibration along with the plenum that was provided with the oxygen sensor. If another pump is used, it should be a submersible type and configured to pump at a rate of 20 to 30 ml/s.

In this case, purchase a plenum from Sea-Bird to ensure a reliable and repeatable flow of water past the membrane. The water is air saturated by aerating with an aquarium pump and air stone for 24 hours prior to the calibration. Locate the air stone within 10 cm of the surface. The air stone positioned at greater depths will tend to supersaturate the water, because the air is injected at a pressure higher than atmospheric pressure. Stir the water during aeration and before measurements, to ensure that the whole volume contains saturated water. Stirring that is too vigorous can inject air bubbles deep into the bath supersaturating the bath water.

For the highest accuracy work, the temperature of the water used for the calibration should be as close as possible to the temperature of the water where the measurement will be taken. Take care to minimize the ambient temperature changes that the container of water is subjected to. As water is heated, its capacity to hold air is diminished and air will come out of saturation and form bubbles. These bubbles, if present on the oxygen sensor membrane, will interfere with the measurement. As the water heats, it will also tend to supersaturate. If the container is cooled, it will tend to drop below saturation.

Since OXFIT assumes that the water is neither over- nor under-saturated, if the water temperature in the container changes faster than the oxygen can equilibrate, the computed values of Soc and Boc will be incorrect. It may be necessary to wait more than fifteen minutes per liter of water in the container for every degree of temperature change.

Winkler Titration Value (OXFITW)

With this method, the amount of dissolved oxygen in the water is independently measured, so it is not necessary to aerate the water. For accurate results, the oxygen concentration in the bath needs to be stable and constant over the period of the calibration.

To ensure this, observe the following precautions:

1. Do not use freshly drawn water; it is typically supersaturated in gas and not equilibrated with the atmosphere.
2. Stir the bath vigorously (without mixing in air bubbles) to allow the water opportunity to come in contact with the atmosphere and equilibrate to the atmospheric gas concentrations.
3. The bath temperature must remain stable to better than 0.1 degree C per hour prior to and during the calibration.

If the CTD system is equipped with a pump, this should be used for the calibration along with the plenum that was provided with the oxygen sensor. If another pump is used it should be a submersible type and configured to pump at a rate of 20 to 30 ml/s. In this case, purchase a plenum from Sea-Bird to ensure a reliable and repeatable flow of water past the membrane.

For the highest accuracy work, the temperature of the water used for the calibration should be as close as possible to the temperature of the water where the measurement will be taken. Allow enough time for the oxygen sensor to reach temperature equilibrium and then determine the amount of dissolved oxygen [ml/l] in the water using the Winkler or some other independent measurement method.

OXFIT Prompts

local barometric pressure (millibars)	Pressure read on a barometer (not corrected to sea level)
water temperature (^oC)	Temperature read by the temperature sensor
oxygen current in air saturated water (microamps)	When displaying oxygen current with SEASAVE, make sure the m and b coefficients from the dissolved oxygen sensor calibration sheet are entered. *If oxygen current voltage was recorded, use the **m** and **b** coefficients to convert the voltage to a current*
oxygen current in zero oxygen water (microamps)	Value determined using the inert gas or sodium sulfite solution

OXFIT Calculation

OXFIT calculates Soc and Boc as follows:

Soc = nsa(T,bp) / [exp(tcor * T) * (oc - zoc)]
Boc = -Soc * zoc
oc = air saturated water current (microamps)
zoc = zero air water current (microamps)

See Appendix A for the definition of nsa(T, bp).

OXFITW Prompts

oxygen serial number	Serial number from the original calibration sheet.
m	Value from the original calibration sheet.
b	Value from the original calibration sheet.
k	Value from the original calibration sheet.
c	Value from the original calibration sheet.
salinity [PSU]	Salinity of the water in the container.
water temperature [deg C]	Temperature of the water at the time of the measurement.
winkler value [ml/l]	Measured amount of dissolved oxygen in milliliters per liter. *The Winkler method is described in Carritt, D.E. and J.H. Carpenter. 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater. J. Mar. Res. 24(3), 286-318, and Standard methods for the examination of water and wastewater, editors Clesceri, et al.*
oxygen current voltage for xx [ml/l]	Voltage output by the oxygen current channel after the sensor has equilibrated in the water bath.
oxygen current voltage in air	Voltage from the oxygen current channel when the sensor is in air. *This value is for reference only and is not used to calculate the coefficients.*
oxygen temperature voltage for xx [deg C]	Voltage output by the oxygen temperature channel after the sensor has equilibrated in the water bath.
oxygen current voltage for zero oxygen	Sulfite or an inert gas.

OXFITW Calculation

Soc = measured oxygen / [oxsat(T, S) * exp(tcor * T) * (oc - zoc)]
Boc = -Soc * zoc
oc = air saturated water current (microamps)
zoc = zero air water current (microamps)

See Appendix B for the definition of oxsat(T, S).

A file named SERIALNO.CAL, containing a summary of the calibration data and the computed coefficients, will be written to the current directory.

Verification of SOC and BOC

OXFIT and OXFITW calculate and display the new Soc and Boc coefficients. Compare these to the original factory calibration or the last calibration that was performed. Typically, the Soc value slowly increases with time as the sensor is used. The KCl electrolyte in the oxygen sensor is consumed as part of the reduction reaction. This loss of KCl decreases the sensitivity of the sensor, which is reflected in the slowly increasing Soc value. See Application Note 13-4 for information on the life expectancy of Beckman dissolved oxygen sensors. Application Note 32 contains additional information about the YSI-based oxygen sensors.

Enter the new Soc and Boc values into the CTD configuration (.con) file. If the entire CTD was used in the oxygen calibration, you can check the calibration results using SEASAVE to display real-time data (display oxygen concentration in ml/l, water temperature, and salinity). Use OXSAT to calculate the saturation value for the measured temperature and salinity and compare with the real-time reading of oxygen concentration. Alternatively, display the saturated oxygen concentration along with the oxygen sensor reading in SEASAVE. If the oxygen sensor is healthy and the calibration was performed correctly, these values should agree to within 0.1 ml/l. For SBE 9s that have salt water in the cell to turn the pump on, the real-time oxygen readings will be in error because SEASAVE will assume that the water in the bath has the same salinity as the water in the tube.

NOTE: The CTD configuration (.con) file is edited using the Configure menu (in SEASAVE or SBE Data Processing in our SEASOFT-Win32 suite of programs) or SEACON (in SEASOFT-DOS). For the SBE 16*plus* and 19*plus*, you must use the Windows software.

OXYGEN SENSOR CLEANING AND STORAGE

Take care to avoid fouling the oxygen membrane with oil or grease. Rinse the oxygen sensor with a **0.1%** water-solution of Triton X-100 and flush with distilled water after each use. With pumped instruments having a clear plastic plenum, loop tubing from inlet to outlet and partly fill with distilled water between deployments (if there is freezing danger, shake all excess water out of the plenum). With unpumped instruments, put a few drops of water in the DO sensor's protective cap and fasten the cap securely. As an added benefit, the sensor will be kept free of airborne particulates that could otherwise coat the membrane and reduce the sensitivity.

For routine cleaning, soak the sensor in a **1%** solution of Triton X-100 initially warmed to 50 ^{o}C (122 ^{o}F) for 30 minutes. After the soak, drain and flush with warm (not hot) fresh water for 1 minute.

Note: Do not use a Triton solution stronger than recommended above, and do not place Triton **directly** on the sensor membrane. A strong Triton solution can leave a film on the sensor membrane, adversely affecting the results.

OXYGEN SENSOR DEPLOYMENT

1. Connect the pump tubing to the sensor plenum (pumped designs) or remove the protective cap (unpumped designs) before deployment.
   CAUTION: Failure to remove the cap will result in the crushing of the cover at depth and will cause destruction of the oxygen sensor.

2. To allow time for the oxygen sensor to polarize, power the instrument to which it is connected for at least three minutes before beginning the water-column profile. Failure to wait will result in erroneously high oxygen readings.

Notes:

- When taking water samples using a General Oceanics rosette and an Sea-Bird 9/11 CTD which share a single conductor seacable, wait at least two minutes after a bottle has been tripped before resuming the CTD profile. Tripping a bottle momentarily interrupts power to the oxygen sensor, which then must repolarize when power is reapplied. An SBE 911plus CTD which is being used to control the rosette does not lose power when a bottle is tripped.
- **When using an unpumped oxygen sensor, a water flow speed of at least 0.5 meter / second (horizontal motion, current, or vertical profiling rate) must be constantly maintained to avoid local oxygen depletion and erroneously low readings.**

APPENDIX A: CORRECTION FACTOR FOR NON-STANDARD ATMOSPHERE

nsa(T,bp) = (bp/pO) * (1 - (pH_2O/bp)) / (1 - pH_2O/pO)
bp = barometric pressure in kilopascals
pO = 101.325 kilopascals
pH_2O = water vapor pressure in kilopascals
T = water temperature in ^oC
pH_2O = exp[((-216961 * X) - 3840.7) * X + 16.4754]
X = 1/(T+273.15)
For air saturated water at the surface:
oc = air saturated water current (microamps)
zoc = zero air water current (microamps)
{[Soc * (oc - zoc)] / nsa(T,bp)} * exp(tcor * T) = 1
Soc = nsa(T,bp) / [exp(tcor * T) * (oc - zoc)]
Boc = -Soc * zoc

APPENDIX B: COMPUTATION OF OXSAT

OXSAT(T,s) = exp(A1 + A2*(100/T) + A3*ln(T/100) + A4*(T/100)+ s*(B1 + B2(T/100) + B3*(T/100)*(T/100)))

The units are ml/l, the oxygen saturation value is the volume of the gas (STP) absorbed from water saturated air at a total pressure of one atmosphere, per unit volume of the liquid at the temperature of measurement where:
s = salinity in parts per 1000
T = ^oC + 273.15 (absolute temperature)
A1 = -173.4292
A2 = 249.6339
A3 = 143.3483
A4 = -21.8492
B1 = -0.033096
B2 = 0.014259
B3 = -0.00170

APPENDIX C: COMPILATION OF OXYGEN SATURATION VALUES

The following table contains oxygen saturation values at atmospheric pressure, calculated using the OXSAT equation in Appendix B. Units of oxygen are ml/l. To compute units of mg/l, multiply the values in the table by 1.42903.

	Salinity (PSU)								
Temp °C	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**32**	**35**
-2	10.82	10.46	10.10	9.76	9.42	9.10	8.79	8.67	8.49
0	10.22	9.88	9.54	9.22	8.91	8.61	8.33	8.21	8.05
2	9.67	9.35	9.04	8.74	8.45	8.17	7.90	7.79	7.64
4	9.16	8.86	8.57	8.30	8.02	7.76	7.51	7.41	7.26
6	8.70	8.42	8.15	7.89	7.64	7.39	7.15	7.06	6.92
8	8.28	8.02	7.76	7.52	7.28	7.05	6.82	6.74	6.61
10	7.89	7.64	7.41	7.17	6.95	6.73	6.52	6.44	6.32
12	7.53	7.30	7.08	6.86	6.65	6.44	6.24	6.17	6.05
14	7.20	6.99	6.77	6.57	6.37	6.17	5.99	5.91	5.80
16	6.90	6.69	6.49	6.30	6.11	5.93	5.75	5.68	5.58
18	6.62	6.42	6.23	6.05	5.87	5.70	5.53	5.46	5.36
20	6.35	6.17	5.99	5.81	5.64	5.48	5.32	5.26	5.17
22	6.11	5.93	5.76	5.60	5.44	5.28	5.13	5.07	4.98
24	5.88	5.71	5.55	5.39	5.24	5.09	4.95	4.89	4.81
26	5.66	5.51	5.35	5.20	5.06	4.92	4.78	4.73	4.65
28	5.46	5.31	5.17	5.03	4.89	4.75	4.62	4.57	4.50
30	5.28	5.13	4.99	4.86	4.73	4.60	4.47	4.43	4.35
32	5.10	4.96	4.83	4.70	4.58	4.45	4.34	4.29	4.22

REFERENCES

Carritt, D.E. and J.H. Carpenter. 1966: Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater. J. Mar. Res. 24(3), 286-318.

Clesceri, L.S. A.E. Greenberg, and R.R. Trussell ed. 1989, Standard methods for the examination of water and wastewater, 17th edition, American Public Health Assoc. Washington D.C. ISBN 0-87553-161-X.

Gnaigner, E., and H. Forstner, Ed., 1983: Polarographic Oxygen Sensors: Aquatic and Physiological Applications. Springer-Verlag, 370 pp.

Millard, R, C., Jr., 1982: CTD calibration and data processing techniques at WHOI using the 1978 practical salinity scale. Proc. Int. STD Conference and Workshop, La Jolla, Mar. Tech. Soc., 19 pp.

Owens, W.B., and R.C. Millard Jr., 1985: A new algorithm for CTD oxygen calibration. J. Physical Oceanography., 15, 621-631.

Weiss, R.F., 1970: The solubility of nitrogen, oxygen and argon in water and seawater. Deep-Sea Res., 17., 721-735.