SBE 43 DO Sensor Background Information, Deployment Recommendations, Cleaning and Storage

General Description

The SBE 43 is a polarographic membrane oxygen sensor that has a single output signal of 0 to +5 volts, which is proportional to the temperature-compensated current flow occurring when oxygen is reacted inside the membrane. A Sea-Bird CTD that is equipped with an SBE 43 oxygen sensor records this voltage for later conversion to oxygen concentration using a modified version of the algorithm by Owens and Millard (1985).

The SBE 43 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. 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, resulting in a slow but continuous loss of sensitivity that produces a continual, predictable drift in the sensor calibration with time. This *electro-chemical* drift is accelerated at high oxygen concentrations and falls to zero when no oxygen is being consumed. Accordingly, sensor storage and deployment strategies that produce zero- or near zero-oxygen environments when the sensor is not being sampled can be used to substantially reduce electro-chemical drift, improving long-term data quality.

Membrane fouling also contributes to drift by altering the oxygen diffusion rate through the membrane, thus reducing sensitivity. Non-biological fouling, occurring for example if the SBE 43 was profiled through an oil slick, typically produces an immediate jump toward low oxygen. Biological fouling, particularly on moorings, can be troublesome, because the living organisms either consume or create oxygen. Without protection and/or routine cleaning, a micro-environment around the sensor can produce oxygen levels that are different from the true ambient conditions. By recognizing fouling, both episodic and gradual in nature, and promptly cleaning the sensor using the procedures in this application note, accuracy can be restored.

SBE 43s intended for **moored applications** are plumbed with black Tygon tubing. This minimizes light entering the system, and reduces biological fouling. SBE 43s intended for profiling applications are plumbed with clear tubing.

The concentration of oxygen in the environment can be computed given the flux of oxygen and the geometry of the diffusion path. 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 measurements of **water temperature, salinity, pressure, and oxygen sensor output voltage**. When the oxygen sensor is interfaced with a Sea-Bird CTD, all of these parameters are measured by the CTD system.

The oxygen sensor consumes the oxygen in the water very near the surface of 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. Additionally, if the flow *rate* is not *constant*, the sensor response time will vary, causing dynamic error, particularly when profiling. Maximum accuracy requires that water be pumped (across the membrane) at rates from 20 to 40 ml/second, as provided on Sea-Bird CTDs with SBE 5T or 5P pumps.

Temperature differences between the water and oxygen sensor can lead to errors in the oxygen measurement. The SBE 43 minimizes this difference by using materials that equilibrate rapidly with the environment and incorporating a thermistor placed under the membrane, at the cathode, for accurate temperature compensation. As a result, the SBE 43 is less susceptible to error when profiling through areas of high temperature gradients than previous oxygen sensors.

Use in Moored Applications

As discussed above, the oxygen sensor consumes the oxygen in the water near the sensor membrane. In moored applications, this requires that water be pumped past the oxygen sensor. When used with a SeaCAT (SBE 16, 16*plus*, 16*plus*-IM, 16*plus* V2, 16*plus*-IM V2, or 19*plus* or 19*plus* V2 in moored mode), the SBE 43 flow chamber (plenum) is connected in-line between the pump and conductivity sensor. The pump does not run between samples, trapping water in the plenum. Because the sensor is continuously polarized by an internal battery, oxygen continues to be consumed between samples. The sensor depletes oxygen in the water close to the membrane. If you were to observe the sensor output after the pump stopped, the oxygen concentration inside the plenum would approach a steady state well below ambient oxygen levels. When the pump switches on at the beginning of the next sampling interval, you would observe a curve similar to those shown below for a 0.5-mil membrane. The water flow establishes a normal boundary layer at the membrane, and the sensor equilibrates to the ambient oxygen level. The time required to reach 99% of the final equilibrium value depends on temperature (faster equilibration in warmer water) and on the sensor membrane thickness (faster equilibration with a thinner membrane).

Vertical arrows on the plot show the point at which the sensor has achieved 99% of the final value at each temperature.
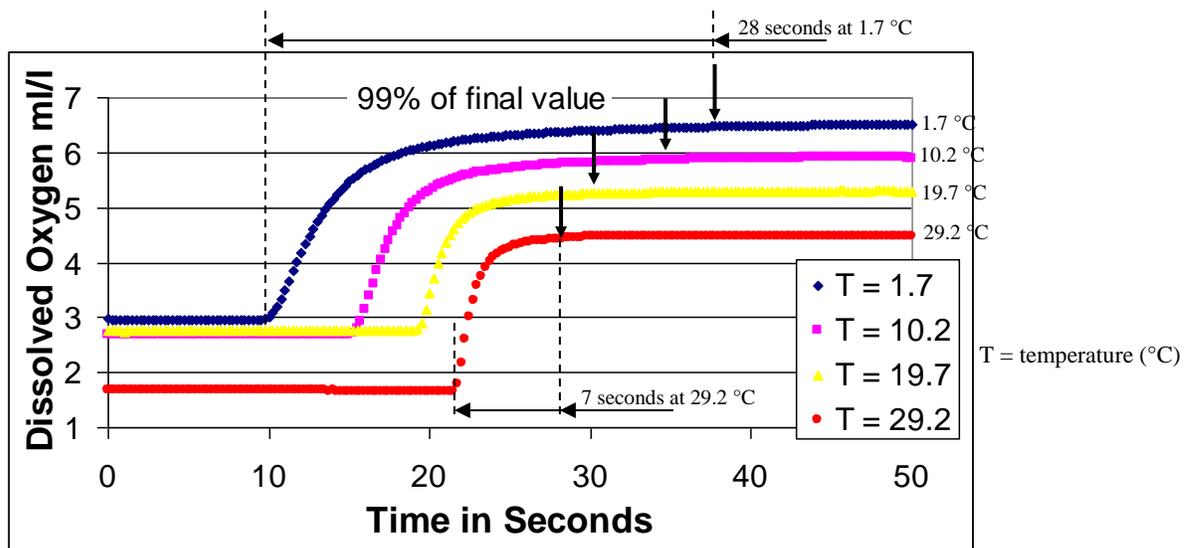

Response Time at Several Temperatures for *0.5-mil* Membrane

Sea-Bird offers two membrane thicknesses – 0.5 mil (faster response, typically for profiling applications) and 1.0 mil (slower response but more durable, typically for moored applications).

Summary of Response Times for Moored Applications

The first plot below is derived from the preceding plot and may be used to determine the time required from power-up and pump turn-on to the availability of an acceptable dissolved oxygen sample with a **0.5-mil** membrane. For simplicity, we generally recommend a minimum pump time of 15 seconds for 15 °C and warmer water, and reference the 1% curve below for colder water.

**Summary of Response Times for *0.5-mil* Membrane**
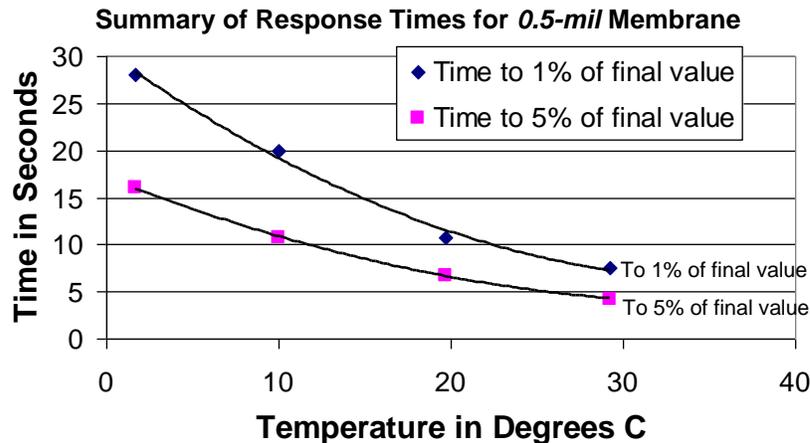
Example – SBE 16plus with SBE 43 with 0.5-mil membrane:

If working in 20 °C water and wanting oxygen data to within 1% of actual oxygen concentrations, pump time of at least 11 seconds is required. Set the SBE 16*plus* to pump during the entire sample (**PumpMode=2**)*, and set the delay before sampling to 15 seconds (**DelayBeforeSampling=15**)*. We have allowed an extra 4 seconds of pump time; this ensures that the sample will still be good if the SBE 16*plus* is in colder than expected water. Note that longer pump times reduce battery endurance.

> * *Refer to the appropriate CTD manual for the exact format of these commands; they vary, depending on the product and the telemetry interface.*

The next plot was derived in a similar fashion, and may be used to determine the time required from power-up and pump turn-on to the availability of an acceptable dissolved oxygen sample with a **1.0-mil** membrane. For simplicity, we generally recommend a minimum pump time of 25 seconds for 15 °C and warmer water, and reference the 1% curve below for colder water.

Summary of Response Times for *1.0-mil* Membrane
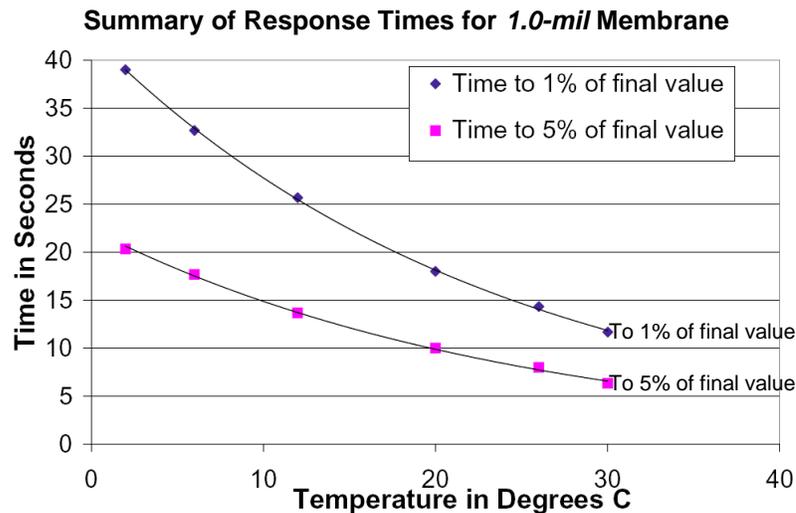
Use in Hydrogen Sulfide (H₂S) Environments

SBE 43 oxygen sensors can be used for hours in hydrogen sulfide rich environments with no ill effects to sensor elements or signal calibration.

Poisoning of oxygen sensors in hydrogen sulfide environments was a phenomenon common to early sensor designs that used silver as the cathode element. The SBE 43 uses a noble metal (gold) as the cathode and silver as the anode, and shows no degradation of signal or calibration when used for profiling in hydrogen sulfide environments. In particular, a month of intensive hydrographic profiles in the Black Sea using Sea-Bird oxygen sensors has demonstrated that these sensors can operate repeatedly in the H₂S rich depths for durations of hours without any degradation of signal or calibration over that experienced in equivalent profiling work in the open, oxygenated ocean.

We have no laboratory or field evidence of the effect of mooring Sea-Bird oxygen sensors in H₂S rich environments for periods of days to months.

Oxygen Algorithm

Sea-Bird uses an algorithm based on that of Owens and Millard (1985) to convert SBE 43 oxygen sensor data to oxygen concentration. The algorithm incorporates a term related to the offset voltage produced for zero oxygen signal. In addition, there is a third-order polynomial that compensates for changes in sensitivity with temperature and an exponential term that compensates for changes in sensitivity with pressure.

Sea-Bird's algorithm has the following form:

$$Oxygen \ (ml/l) = \left\{ Soc * \left(V + Voffset + tau(T,P) * \frac{\partial V}{\partial t} \right) \right\} * Oxsol(T,S)$$

$$* \left(1.0 + A*T + B*T^2 + C*T^3 \right) * e^{(\frac{E*P}{K})}$$

where.....

Description	Symbol	Definition
Computed	Oxygen	Dissolved oxygen concentration (ml/l)
Measured Parameters	T	CTD Temperature (ITS-90, ºC)
	P	CTD Pressure (decibars)
	S	CTD Salinity (psu)
	V	SBE 43 temperature-compensated output oxygen signal (volts)
Calibration Coefficients	Soc	Oxygen signal slope
	Voffset	Voltage at zero oxygen signal
	A, B, C	Residual temperature correction factors
	E	Pressure correction factor
	tau20	Sensor time constant tau (T,P) at 20 ºC, 1 atmosphere, 0 PSU; slope term in calculation of tau (T,P)
	D1, D2	Temperature and pressure correction factors in calculation of tau (T,P)
	H1, H2, H3	Hysteresis correction factors
Calculated Value	Oxsol(T,S)	Oxygen saturation value after Garcia and Gordon (1992); see *Appendix A*
	δV/δt	Time derivative of SBE 43 output oxygen signal (volts/second)
	tau(T,P)	Sensor time constant at temperature and pressure = tau20 * exp (D1 * P + D2 * [T − 20])
	K	Absolute temperature

The software requires you to enter Soc, Voffset, A, B, C, E, tau20, D1, D2, H1, H2, and H3 in the configuration (.con or .xmlcon) file; values are taken from the Calibration Sheet provided with the sensor.

Note: H1, H2, and H3 values are available on calibration sheets for SBE 43s calibrated after October 2008. Refer to *Application Note 64-3: SBE 43 Dissolved Oxygen Sensor Hysteresis Corrections* for the appropriate values to use if your calibration sheet does not show these coefficients.

Tau Correction

The derivative term [tau(T,P) * δV/δt] function is to improve the response of the measured signal in regions of large oxygen gradients. However, this term also amplifies residual noise in the signal (especially in deep water), and in some situations this negative consequence overshadows the gains in signal responsiveness. In Seasave V7 and SBE Data Processing, this *Tau correction* can be disabled if desired, deleting the entire derivative term from the equation for **calculated oxygen**.

Hysteresis Correction

Under extreme pressure, changes can occur in gas permeable Teflon membranes that affect their permeability characteristics. Some of these changes (plasticization and amorphous/crystalinity ratios) have long time constants and depend on the sensor's time-pressure history. These slow processes result in *hysteresis* in long, deep casts. The hysteresis correction algorithm (using H1, H2, and H3 values entered for the SBE 43 in the configuration [.con or .xmlcon] file) operates through the entire data profile and corrects the **oxygen voltage values** for changes in membrane permeability as pressure varies. At each measurement, the correction to the membrane permeability is calculated based on the current pressure and how long the sensor was at previous pressures.

Hysteresis responses of membranes on individual SBE 43 sensors are very similar, and in most cases the default hysteresis parameters provide the accuracy specification of within 2% of true value. For users requiring higher accuracy (±1 µmol/kg), the parameters can be fine-tuned, if a complete profile (descent and ascent, preferably to greater than 3000 meters) is available. H1, the effect's amplitude, has a default of -0.033, but can range from -0.02 to -0.05. H2, the effect's non-linear component, has a default of 5000, and is a second-order parameter that does not require tuning between sensors. H3, the effect's time constant, has a default of 1450 seconds, but can range from 1200 to 2000. Hysteresis can be eliminated by alternately adjusting H1 and H3 in the configuration file during analysis of the complete profile. Once established, these parameters should be stable, and can be used without adjustment on other casts with the same SBE 43.

Software

Sea-Bird software allows you to select the SBE 43 oxygen sensor (labeled *Oxygen, SBE*) and use the Sea-Bird equation documented in this application note when setting up the configuration (.con or .xmlcon) file for the CTD:

- **SBE Data Processing**
  Enable / disable the Tau correction on the Miscellaneous tab in Data Conversion, if you are outputting calculated oxygen at this step. Enable / disable the hysteresis correction on the Miscellaneous tab in Data Conversion, if you are outputting oxygen voltage and/or calculated oxygen at this step.
  You can also enable / disable the Tau correction on the Miscellaneous tab in Derive.

- **Seasave V7**
  Enable / disable the Tau correction and/or the hysteresis correction on the Miscellaneous tab in Configure Inputs. Note that these corrections are applied to data displayed in the software and to **calculated** values output by the software; however, *raw* oxygen voltage output by Seasave V7 to the CTD data file is not corrected.

- **Seasave-Win32**
  The Sea-Bird equation is called the *Murphy-Larson* equation in this software, but performs the same *basic* calculation as in Seasave V7 and SBE Data Processing. However, the hysteresis correction is not available. Additionally, to disable the Tau correction, the user must set tau20=0 in the configuration (.con) file; this deletes the term [tau(T,P) * δV/δt] from the calibration equation.

The latest version of the software is available for download from our website (www.seabird.com).

Notes:
1. There are several types of oxygen data that can be calculated, as desired, in all of these software versions:
   - **Oxygen, SBE** (units of ml/l, mg/l, or micromoles/kg, as selected) – measured SBE 43 oxygen, based on the equation shown above in *Oxygen Algorithm*.
   - **Oxygen saturation** (units of ml/l or mg/l, as selected) – theoretical saturation limit of the water at the local temperature and salinity value, but with local pressure reset to zero (1 atmosphere). This calculation represents what the local parcel of water could have absorbed from the atmosphere when it was last at the surface (p=0) but at the same (T,S) value. See *Appendix A* for computation of oxygen saturation.
   - **Oxygen, SBE, percent saturation** – ratio of measured SBE 43 oxygen to oxygen saturation, in percent.
2. When entering calibration coefficients for the SBE 43 in the configuration file for the CTD, you can select the older *Owens-Millard* equation or the recommended *Sea-Bird* equation (documented in this application note).

Data Conversions

Sea-Bird uses the following equations to convert oxygen to various engineering units:

[mg/L] = [ml/L] * 1.42903

[µmole/Kg] = [ml/L] * 44660 / (sigma_theta(P=0,Theta,S) + 1000)

where

Sigma_theta (potential density) is the density a parcel of water would have if it were raised adiabatically to the surface without change in salinity. Sigma_theta is calculated with:

- pressure = 0;
- Theta (potential temperature; temperature a parcel of water would have if it were raised adiabatically to the surface); and
- S (salinity)

(Sigma_theta Discussion: As a water parcel moves within the ocean below the mixed layer, its salt and heat content can change only by mixing with other water. Measurements of temperature and salinity are used to trace the path of the water. The most effective method for doing this is to remove the effect of compressibility. Potential temperature Theta is defined as the temperature a parcel of water would be at the sea surface after it has been raised adiabatically from some depth in the ocean (i.e., without exchanging heat with its surroundings as it is raised).

Because changes in pressure primarily influence the temperature of the water, the influence of pressure on density can be removed, to a first approximation, by using the potential density.

Potential density Sigma_theta is the density a parcel of water would have if it were raised adiabatically to the surface without change in salinity, e.g., calculated using potential temperature.)

For the µmole/Kg conversion, there is disagreement in the scientific community about the 44660 conversion constant:
- The value 44660 is exact for oxygen gas.
- The value 44615 is the average value for atmospheric gas (N2,O2,Ar,H2O,CO2,...). It is not exact for any individual gas, but has been used historically by oceanographers.

The argument distills to exact versus historic, with oceanographers split; Sea-Bird uses 44660 in all calculations.

Oxygen Sensor Cleaning and Storage

Prolonged exposure of the sensor membrane to detergent is harmful and causes the sensor's calibration to drift. Our recommendation, detailed below, is to use a non-ionic surfactant (detergent) for degreasing (with a short wash), then use a short wash with a dilute bleach solution to reduce biological growth, and store the sensor in an anoxic (or near zero oxygen) condition. See *Materials* below for a discussion of detergent, bleach, and water.

Avoid fouling the oxygen membrane with oil or grease, as this causes a calibration shift toward erroneously low readings. An oil-fouled membrane can be cleaned using the following procedures.

CAUTION: During service and storage, maintain temperature at or below 30 ºC (86 ºF). If temperatures are raised above 40 ºC (104 ºF), sensors exhibit a temporary increase in sensitivity of a few percent. This relaxes back to historical sensitivity after a few days when temperatures return below 30 ºC (86 ºF).

- **Preventive Field Maintenance Between Profiles**: After each cast, flush with a **0.1%** solution of **detergent**, using a 60 cc syringe (see *Application Note 34*). Then rinse thoroughly with fresh water. Between casts, ensure that the sensor remains shaded from direct sunlight and stays cool and humidified. Plugging the inlet and exhaust of the plumbing after rinsing will trap sufficient humidity.
- **Routine (post-cruise) Cleaning (no visible deposits or marine growths on sensor)** - Follow this two-step procedure:
  A. **Flush** the sensor for **1 minute** with a **1%** solution of **detergent** warmed to 30 ºC (86 ºF). **Drain and flush** with warm (not hot) fresh water for **5 minutes**.
  B. **Soak** the sensor for **1 minute** in a **500 – 1000 ppm** solution of **Bleach**. After the soak, **drain and flush** with lukewarm (not hot) fresh water for **5 minutes**.
- **Cleaning Severely Fouled Sensors (visible deposits or marine growths on sensor)**: Soak the sensor in de-ionized water overnight to loosen deposits. Repeat the *Routine Cleaning* procedure up to 5 times. Do **not** attempt to clean the membrane with high pressure flow or by wiping or touching the membrane.
- **Long-Term Storage (after field use)**: **Do not fill the tubing with water, detergent solution, or Bleach solution.**
  ➢ If there is no danger of freezing, loop tubing from inlet to outlet. Place a small piece of clean sponge, *slightly dampened* with fresh, clean water, in the center of the tubing (not near the membrane).
  ➢ **If there is danger of freezing,** shake all excess water out of the plenum and loop tubing from inlet to outlet, leaving the sensor membrane dry.
  ➢ Because the sensor is continuously polarized by an internal battery, oxygen in the plenum and tubing will

continue to be consumed, depleting the electrolyte and causing drift. Storing the sensor in a zero-oxygen environment will stop calibration drift between uses. To minimize drift during storage, if possible, connect one end of the tubing loop to the plenum, displace the air in the plenum and tubing with Nitrogen gas, and connect the other end of the tubing to the plenum. If tubing is not available, displace the air in the plenum with Nitrogen gas and close off the plenum with a cap on each end (tape can be used if nothing else is available); do not insert a cap or plug inside the plenum.

Materials

- **Non-ionic surfactant (detergent): 100%** detergent is included with every CTD shipment and can be ordered from Sea-Bird; dilute as directed above. Use only scientific grades that have no colors, perfumes, glycerins, lotions, etc.
- **Bleach:** Bleach is a common household product used to whiten and disinfect laundry. Commercially available bleach is typically 4% - 7% (40,000 ppm – 70,000 ppm) **sodium hypochlorite** (Na-O-Cl) solution that includes stabilizers. Some common commercial product names are Clorox (U.S.) and eau de Javel (French). Clean the SBE 43 with a 500 – 1000 ppm solution of water and sodium hypochlorite. **Dilute** the concentrated household bleach 50 to 1 (50 parts water to 1 part bleach) to produce the proper concentration to clean the oxygen sensor.
- **Water:** We recommend de-ionized (DI) water because it is reliably pure, but commercially distilled water or fresh clean tap water is also sufficient for all uses above. *On ships, fresh water can occasionally contain traces of oil and should not be used for rinsing, cleaning, or storing sensors, unless there is no alternative*.

Notes:
- Do not use stronger solutions or longer wash times than recommended above.
- Do not place concentrated detergent or bleach **directly** on the sensor membrane. A strong detergent solution can leave a film on the membrane, adversely affecting results.

Appendix A - Computation of Oxygen Solubility (Oxsol; Garcia & Gordon)

Oxsol(T,S) = exp {A0 + A1(Ts) + A2(Ts) ^{2} + A3(Ts) ^{3} + A4(Ts) ^{4} + A5(Ts) ^{5} +
$\qquad$ S * [B0 + B1(Ts) + B2(Ts) ^{2} + B3(Ts) ^{3}] + C0(S) ^{2}}

Where

- Oxsol(T,S) = oxygen saturation value = volume of oxygen gas at standard temperature and pressure conditions (STP) absorbed from humidity-saturated air at a total pressure of one atmosphere, per unit volume of the liquid at the temperature of measurement (ml/l)
- S = salinity (psu)
- T = water temperature (ITS-90, ºC)
- Ts = ln [(298.15 – T) / (273.15 + T)]
- A0 = 2.00907   A1 = 3.22014   A2 = 4.0501   A3 = 4.94457   A4 = -0.256847   A5 = 3.88767
- B0 = -0.00624523   B1 = -0.00737614   B2 = -0.010341   B3 = -0.00817083
- C0 = -0.000000488682

The table below contains oxygen saturation values at atmospheric pressure calculated using the Oxsol equation. Units are ml/l. To compute mg/l, multiply the values in the table by 1.42903.

Oxsol: Oxygen Saturation Concentrations in Fresh and Ocean Water (ml/l)									
Temperature (°C)	Salinity (PSU)								
	0	5	10	15	20	25	30	32	35
-2	10.84	10.46	10.10	9.74	9.40	9.07	8.75	8.63	8.45
0	10.23	9.88	9.54	9.21	8.90	8.59	8.30	8.18	8.01
2	9.68	9.35	9.04	8.73	8.44	8.15	7.88	7.77	7.61
4	9.17	8.87	8.58	8.29	8.02	7.75	7.49	7.39	7.24
6	8.71	8.43	8.15	7.89	7.63	7.38	7.14	7.05	6.91
8	8.29	8.02	7.77	7.52	7.28	7.04	6.82	6.73	6.60
10	7.90	7.65	7.41	7.18	6.95	6.73	6.52	6.44	6.31
12	7.54	7.31	7.08	6.86	6.65	6.45	6.25	6.17	6.05
14	7.21	6.99	6.78	6.57	6.37	6.18	5.99	5.92	5.81
16	6.91	6.70	6.50	6.31	6.12	5.93	5.75	5.68	5.58
18	6.62	6.43	6.24	6.06	5.88	5.70	5.53	5.47	5.37
20	6.36	6.18	6.00	5.82	5.65	5.49	5.33	5.27	5.17
22	6.12	5.94	5.77	5.61	5.45	5.29	5.14	5.08	4.99
24	5.89	5.72	5.56	5.41	5.25	5.10	4.96	4.90	4.82
26	5.68	5.52	5.37	5.22	5.07	4.93	4.79	4.74	4.66
28	5.48	5.33	5.18	5.04	4.90	4.77	4.63	4.58	4.51
30	5.29	5.15	5.01	4.87	4.74	4.61	4.49	4.44	4.36
32	5.11	4.98	4.84	4.71	4.59	4.46	4.34	4.30	4.23

Note: As implemented in Sea-Bird software, the Oxsol equation is valid for -5 < T < 50 and 0 < S < 60. Outside of those ranges, the software returns a value of -99 for Oxsol.

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.

Garcia and Gordon (1992) "Oxygen solubility in seawater: Better fitting equations", Limnology & Oceanography, vol 37(6), p1307-1312.