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SBE 43 Dissolved Oxygen Sensor

General Description

The SBE 43 is a polarographic membrane oxygen sensor having 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.

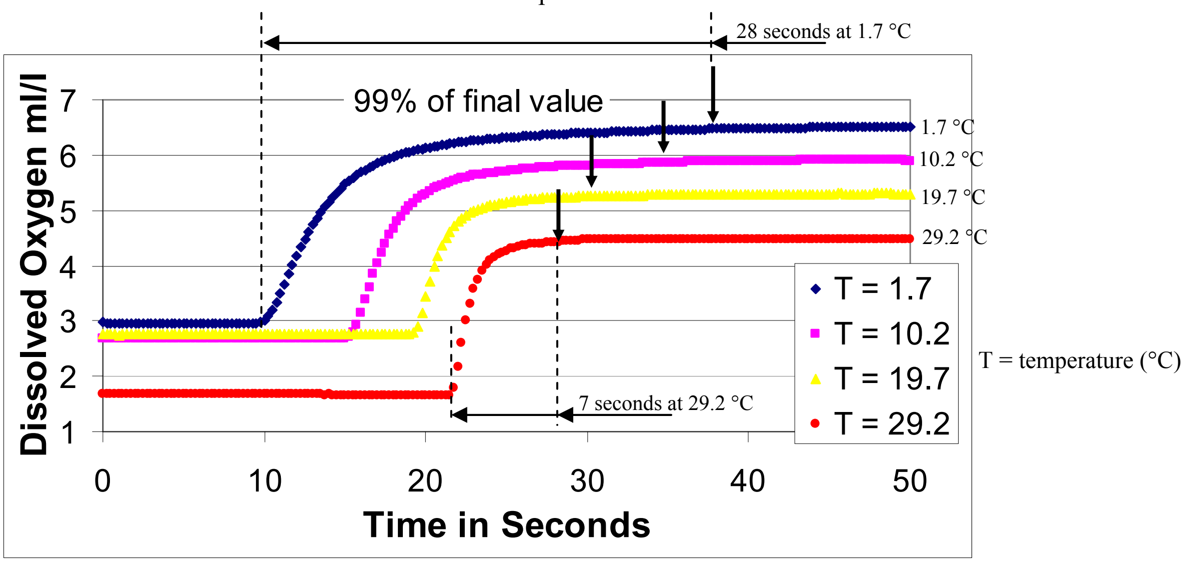
The concentration of oxygen in the environment can be computed given the flux of oxygen and the geometry of the diffusion path. The permeability of the membrane to oxygen is a function of temperature and ambient pressure and is taken into account in the calibration equation. The algorithm to compute 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 pumps.

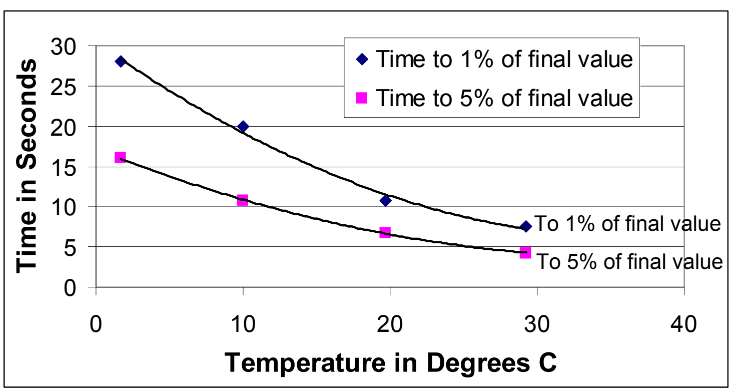
Temperature differences between the water and oxygen sensor can lead to errors in the oxygen measurement. The SBE 43 minimizes this difference by using materials that equilibrate rapidly with the environment and incorporating a thermistor placed under the membrane, at the cathode, for accurate temperature 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 16plus, 16*plus*-IM, or 19*plus* 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. 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, with faster equilibration in warmer water. Vertical arrows on the plot show the point at which the sensor has achieved 99% of the final value at each temperature.



The 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. For simplicity, we generally recommend a minimum pump time of 15 seconds for 15 °C and warmer water, and reference the curves below for colder water.



- *Example:* 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 SEACAT to pump during the entire sample (**MOOREDPUMPMODE=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 SEACAT is in colder than expected water. Note that longer pump times reduce battery endurance.
  ** See the appropriate SEACAT manual for the exact format of these commands; they vary, depending on the product and the telemetry interface.*

Use in Hydrogen Sulfide (H_2S) 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 H_2S 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 field evidence of the effect of mooring Sea-Bird oxygen sensors in H_2S rich environments for periods of days to months.

Oxygen Algorithm

Sea-Bird uses a modified version of the algorithm by Owens and Millard (1985) to convert SBE 43 oxygen sensor data to oxygen concentration. The Sea-Bird algorithm incorporates a term related to the offset voltage produced for zero oxygen signal. In addition, a modification to the Boc term is required, because the SBE 43 output is temperature compensated by $e^{-.03T}$ [i.e., tcor = -0.03].

Sea-Bird's algorithm has the following form:

$$Oxygen\ (ml/l) = \left\{ Soc * \left(V + Voffset + tau * \frac{\partial V}{\partial t} \right) + Boc * e^{(-0.03*T)} \right\} * Oxsat(T,S) * e^{(tcor*T)} * e^{(pcor*P)}$$

where.....

Description	Symbol	Definition
Computed	Oxygen	Dissolved oxygen concentration (ml/l)
Measured Parameters	T	CTD Temperature (ºC)
	P	CTD Pressure (decibars)
	S	CTD Salinity (psu)
	V	SBE 43 temperature-compensated output oxygen signal (volts)
	δV/δt	Time derivative of SBE 43 output oxygen signal (volts/second)
Calibration Coefficients	Soc	Oxygen signal slope
	Boc	Oxygen signal bias
	tcor	Residual temperature correction factor
	Voffset	Voltage at zero oxygen signal
	pcor	Pressure correction factor
	tau	Oxygen sensor response time
Calculated Value	Oxsat(T,S)	Oxygen saturation value after Weiss (1970); see *Appendix A*

Our software requires you to enter Soc, Boc, Voffset, tcor, pcor, and tau in the configuration (.con) file. Values for Soc, Boc, Voffset, tcor, and pcor are taken from the Calibration Sheet provided with the sensor. We recommend that you set tau = 0, deleting the correction term (tau * δV/δt) from the calibration equation. The correction term's function is to improve the sluggish 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 we believe that this negative consequence overshadows the marginal gains in signal responsiveness. Therefore, we recommend using tau=0.

Software

The following versions of Sea-Bird software allow you to select the SBE 43 oxygen sensor (labeled *Oxygen, SBE*) when setting up the configuration (.con) file for the CTD:

- SEASOFT-DOS version 4.248 or later
- SEASOFT-Win32: SEASAVE version 1.20 or later, and SBE Data Processing version Beta 1.3 or later

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

Note:
There are several types of oxygen data that can be calculated, as desired, in Sea-Bird software:

- **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.

Oxygen Sensor Cleaning and Storage

Sea-Bird has altered our recommendations with regard to cleaning and storage of the SBE 43. In the past, we recommended using Triton X-100 detergent for the combined purpose of degreasing and discouraging biological growth. We recently discovered that prolonged exposure of Triton X-100 to the sensor membrane is harmful and causes the sensor's calibration to drift. Our present recommendation, detailed below, is to continue to use Triton X-100 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 Triton X-100 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.

- **Preventive Field Maintenance Between Profiles**: After each cast, flush with a **0.1%** solution of **Triton X-100**, 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. **Soak** the sensor for **1 minute** in a **500 – 1000 ppm** solution of **Bleach**. After the soak, **drain and flush** with warm (not hot) fresh water for **5 minutes**.
  B. **Soak** the sensor for **1 minute** in a **1%** solution of **Triton X-100** warmed to 40 ºC (104 ºF). After the soak, **drain and flush** with warm (not hot) fresh water for **5 minutes**.

- **Cleaning Severely Fouled Sensors (visible deposits or marine growths on sensor)**: 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, Triton 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.

Materials:

- **Triton X-100 - 100%** Triton X-100 is included with every CTD shipment and may be ordered from Sea-Bird; dilute as directed above. Triton X-100 is Octyl Phenol Ethoxylate, a mild, non-ionic surfactant (detergent), and is manufactured by J. T. Baker (see *www.jtbaker.com/distrib/distrib.asp?seg=lab* for local distributors).
  Other liquid detergents can probably be used, but scientific grades having no colors, perfumes, glycerins, lotions, etc. are required.

- **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 Triton or bleach **directly** on the SBE 43 sensor membrane. A strong Triton solution can leave a film on the membrane, adversely affecting results.

Appendix A - Computation of Oxygen Saturation (Oxsat)

$Oxsat(T,S) = \exp\{A(T_a) + S * B(T_a)\}$
$= \exp\{[A1 + A2 * (100/T_a) + A3 * \ln(T_a/100) + A4 * (T_a/100)] + S * [B1 + B2 * (T_a/100) + B3 * (T_a/100)^2]\}$

Where

- Oxsat(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 (^oC)
- T_a = absolute temperature (^oC + 273.15)
- A1 = -173.4292 A2 = 249.6339 A3 = 143.3483 A4 = -21.8492
- B1 = -0.033096 B2 = 0.014259 B3 = -0.00170

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

Oxsat: Oxygen Saturation Concentrations in Fresh and Ocean Water (ml/l)

Temperature (°C)	Salinity (PSU)								
	0	**5**	**10**	**15**	**20**	**25**	**30**	**32**	**35**
-2	10.82	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

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