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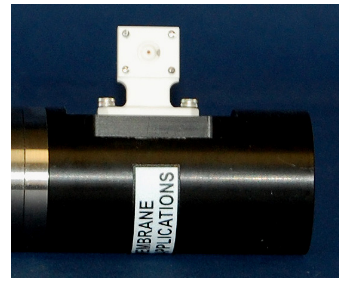
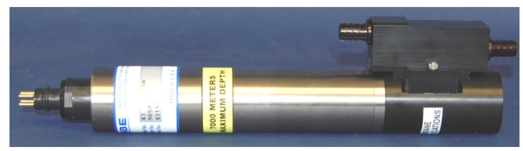
APPLICATION NOTE NO. 64-2 **Revised June 2012**

SBE 43 Dissolved Oxygen Sensor Calibration and Data Corrections

Figure 1. SBE 43





This application note contains a short summary of recommended sensor maintenance and validation procedures, motivated by sensor-implementation experiences of customers as well as Sea-Bird. It describes methodologies for extending factory service intervals for the SBE 43, as well as methods for correcting real-time sensor outputs or post-correcting dissolved oxygen data from both moored and profiling CTD applications.

Routine validations keep sensors operating in the field longer, extending deployment periods, reducing the frequency of site visits, and decreasing overall maintenance costs when fouling is not irreparably impairing sensor performance. Experienced field scientists and instrument technicians are aware that waterborne pollutants and bio-fouling are expected when working in any natural marine and freshwater environment. Therefore, drift thresholds for sensor performance should be established prior to data collection, to determine how often instruments should be serviced, validated, and returned to Sea-Bird for a full service and calibration.

What Causes SBE 43 Sensor Drift?

Changes in sensor electronics and fouling (biological growth on a sensor, or coatings from oil and other materials in the water column) are the main causes of temporal loss of accuracy in aquatic sensors. The SBE 43 DO sensor has very stable electronics; therefore, any loss of accuracy is primarily due to fouling. Often, simply rinsing off the sensor with a soapy non-ionic solution (i.e. diluted Triton-X) restores the sensor's performance.

In moored applications, using the SBE 43 DO sensor as part of a CTD system that is designed to counteract bio-fouling is critical for extending measurements.

Storing the cleaned SBE 43 sensor as directed, in a looped Tygon tubing with a moist sponge for example, will help prevent *in situ* fouling between sampling deployments. Storing in water is not advised.
Note: For cleaning and storage details, see *Application Note 64: Background Information, Deployment Recommendations, and Cleaning and Storage*.

SBE 43 Calibration Equation and the Effect of Fouling

The equation below, used in Sea-Bird's software for calculating dissolved oxygen in ml/L from SBE 43 output voltage, is a form of that given in Owens-Millard (1985):

$$Oxygen\ (ml/l) = \left\{ Soc * \left(V + Voffset + tau(T,P) * \frac{\partial V}{\partial t} \right) \right\} * Oxsol(T,S) * \left(1.0 + A*T + B*T^2 + C*T^3\right) * e^{\left(\frac{E*P}{K}\right)} \qquad eqn\ 1$$

where:

- V = SBE 43 output voltage signal (volts)
- $\partial V/\partial t$ = time derivative of SBE 43 output signal (volts/second), computed over a default window of 2 seconds
- T = CTD temperature (°C)
- S = CTD salinity (psu)
- P = CTD pressure (dbars)
- K = CTD temperature (°K = °C + 273.15)
- *tau(T,P)* = sensor time constant at temperature and pressure
- *Oxsol(T,S)* = oxygen solubility function (ml/L), which converts oxygen partial pressure (sensor measurement) to oxygen concentration (*Garcia and Gordon, 1992*). See Appendix A in *Application Note 64: Background Information, Deployment Recommendations, and Cleaning and Storage* for values at various temperatures and salinities.
- *Soc, Voffset, A, B, C, E*, and *tau20, D1*, *D2* [terms in calculation of *tau (T,P)*] are calibration coefficients

The SBE 43 output is linear with respect to oxygen concentration, and maintains a relatively stable output at zero oxygen (the electronic *Voffset* term in equation 1). Electrochemical drift, a limitation in previous Clark designs, exists somewhere below the calibration uncertainty of 1 µmol/kg for the SBE 43, and has not been observed in several years of factory calibration data nor in long-deployments on Argo floats and moorings. Therefore, any sensor drift with time is primarily attributed to fouling of the membrane, either biological or waterborne contaminants (i.e., oil).

Adverse fouling might take several weeks to months to occur. Fouling of the membrane eventually causes the sensor to read low of correct. When the SBE 43 sensor starts to show drift from fouling, the effect on the sensor calibration is linear, and therefore can be corrected by adjusting the linear slope term of the calibration equation (*Soc* term in equation 1).

If the reference method for making the correction is as accurate (i.e., competent Winklers or another clean/calibrated DO sensor from another instrument), the sensor can continue to report DO concentrations within factory specifications by applying an adjustment to *Soc*. This is particularly useful for long-term deployments, when real-time data accuracy matters.

Soc Adjustment - Real-Time or Post-Recovery

Routine sensor checks can be done in the field while the instrument remains on the mooring, or in the lab before and after deployment / recovery. A qualified reference standard, such as a Winkler water sample or clean, calibrated SBE 43 reference sensor, is needed for in-field validation. This provides a defensible way to adjust the *Soc* term in the calibration equation and the configuration file used to compute oxygen concentration in Sea-Bird software (Seasave real-time data acquisition and SBE Data Processing post-processing software). A similar approach can be used in the lab with a bath and reference sensor or with carefully drawn Winkler water samples. **Note:** The configuration (.con or .xmlcon) file supplies calibration coefficients to Sea-Bird software for converting raw data to engineering units (i.e., for the SBE 43, the calibration coefficients allow the software to convert voltages to ml/L).

Note that the SBE 43 drifts in slope, not offset. This means that applying a simple offset to DO data in a given range of values (e.g., 5-6 ml/L) will give incorrect results in a different range (e.g., 4-5 ml/L).

Follow these simple steps to derive a correction factor to adjust *Soc* (or a series of factors if multiple validation points for a given sensor are available; see Irish et al., 2008):

1. Compute the correction ratio between the Reference value and corresponding SBE 43 sensor value (Reference / SBE 43).
   - The Reference value can be a Winkler concentration, or a value from another DO sensor in a side-by-side validation or controlled bath.
   - Be sure the units for each method are consistent (i.e., ml/L; mg/L; µmol/kg).
2. Multiply the correction ratio by the previous *Soc* in the configuration (.con or .xmlcon) file or on the calibration sheet.
   - New*Soc* = Previous*Soc* * (Reference / SBE 43)
3. Apply the correction to the data:
   - For real-time applications, replace Previous*Soc* with New*Soc* in the configuration (.con or .xmlcon) file going forward.
   - Correct previously recovered raw DO data by assuming a linear drift rate, and using a time rate of change of *Soc* to compute the oxygen concentration.
   - Correct previously recovered and converted data (e.g., ml/L) by multiplying the oxygen concentrations by the slope correction ratio determined for that day or mooring period.

A Few Pointers Regarding Validation Techniques

- When done competently, the *Soc* adjustment updates the sensor calibration equation to report DO concentrations to within factory specification.
- Compared to laboratory reference checks made in a bath, validating *in situ* moored sensors might not allow as accurate an adjustment due to ship drift, internal waves at the mooring site, and errors incurred in water sample collection, including mismatched depths between moored and reference instruments (CTD or water sampler).
- Replicate measurements provide corrections that are statistically more robust, and are recommended for in-field validations.
- Validating sensors with water samples at very low oxygen concentrations is not recommended, as it is very difficult to collect a competent Winkler at oxygen concentrations below 2-3 ml/L. At low concentrations, replicate water samples with separate water bottle samples are recommended, to determine the standard deviation of the sampling method and analysis.
- Routine validations can help determine when the sensor needs factory service or calibration. Routine cleaning often restores a sensor calibration, eliminating the need to return it to the factory. However, when the *Soc* calibration adjustment has changed by a factor of 1.2 from the original factory value (i.e., sensor has drifted 15-20% from the original calibration, and the drift is not corrected by cleaning), the sensor should undergo a factory service inspection and calibration.
  Note: See *Application Note 64: Background Information, Deployment Recommendations, and Cleaning and Storage*.
- Sea-Bird recommends annual to semi-annual factory servicing as a standard protocol for most instruments, as a general maintenance practice (akin to oil changes in a car).

Comparing Sensor Measured Percent Saturation to Theoretical Oxygen Saturation as Validation

Comparing theoretical saturation values based on the 100% oxygen saturation capacity of the water at a given temperature and salinity to the actual measured percent saturation from the SBE 43 sensor is another way to examine sensor performance and water quality trends in time. These comparisons are best made near the surface, where oxygen saturation in the water column is typically near 100%.

Note that the measured oxygen concentration can be lower or higher than theoretical saturation due to natural causes:

- Near the sea-bed, direct exchange with the air-sea interface is restricted to overturning of the water column; therefore, measured saturation can be lower than theoretical saturation values.
- Saturation can be low or high near the thermocline, due to biological respiration and decay of material at the density interface.
- Surface sensors may measure supersaturated oxygen concentrations that are caused by algal blooms or wind mixing/bubble injection from waves, whereas theoretical oxygen saturation never exceeds 100%.

Trends may differ between the measured and theoretical percent saturation, largely due to non-conservative behavior of dissolved oxygen in natural waters from biological photosynthesis and respiration and also organic matter chemistry. If the saturation measured by the sensor does not match the theoretical saturation based on temperature and salinity alone, this does not mean the sensor is reporting incorrectly.

Recipe for Making Corrections to Slope Term (*Soc*) and Oxygen Data

The main term of interest for correcting fouling drift is the *Soc* term in the SBE 43 sensor calibration equation:

$$Oxygen(ml/l) = Soc * (V + Voffset) * \phi \qquad \text{eqn 2}$$

where:

- ***Soc* is the linear slope scaling coefficient**
- *V* is the SBE 43 output voltage signal (volts)
- *Voffset* is a fixed sensor voltage at zero oxygen (volts)
- φ includes terms that correct for the effects of temperature and pressure, and also includes oxygen solubility dependence on temperature and salinity. Because these terms remain essentially constant with fouling and sensor age, we will ignore φ for these corrections.

Note: Earlier versions of this application note described a method for deriving a slope (*Soc*) **and** *Voffset* correction. However, most data collection efforts are not accurate enough and do not collect enough water samples over a full scale range of values to make *Voffset* corrections that are accurate enough for the reporting specification of the sensor. Therefore, we no longer recommend that older approach.

The loss of sensitivity attributed to sensor membrane fouling is observed as a linear change in sensor output when compared to a set of reference samples (Figure 2 and Table 1). The ratio of the reference sample values to SBE 43 measured DO concentrations remains constant over the sensor range (for multiple values of DO as shown in Table 1). This allows for adjustment in the slope term *Soc* using just one quality reference sample, because any of the reference values provide the same correction in an otherwise healthy sensor.

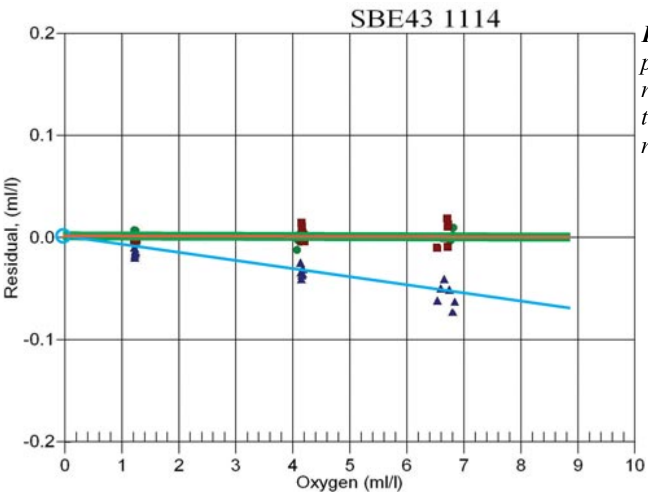


***Figure 2.** SBE 43 sensor SN 1114 original factory calibration (green dots); post-recovery calibration prior to sensor cleaning (blue triangles); re-calibration after sensor cleaning (red squares). Note the loss of sensitivity in the post-recovery calibration (blue triangles) is strictly linear, and that cleaning restored the SBE 43 to its pre-deployment calibration accuracy (red squares).*

Winkler DO of Bath, ml/L	SBE 43 Output, ml/L	Residual (SBE 43 – Winkler)	Correction factor (Winkler/SBE 43)
6.80	6.75	-0.05	6.80 / 6.75=1.007
4.20	4.17	-0.03	4.20 / 4.17=1.007
1.20	1.19	-0.01	1.20 / 1.19=1.007

***Table 1.** Reference Winkler water samples and sensor readings at 3 DO concentrations during post-recovery calibration of SBE 43 sensor SN 1114 (Figure 2). The ratio of the Winkler values to the corresponding SBE 43 outputs can be used to calculate the Soc correction factor. Note the correction factor remains constant at each validation point over the range of values shown, illustrating that any single validation point alone could be used to correct the slope. Also illustrated is that the difference between the SBE 43 and reference Winkler is not constant.*

Simply multiplying the pre-deployment *Soc* value by the correction factor, given by the ratio (Winkler DO Value / SBE 43 DO Value) provides a correction to the linear slope term (*Soc*) in the calibration equation and offers a powerful and scientifically defensible way to make residual corrections to data from unattended, long-term deployments.

Example of In Situ Data Correction for Continuous Real-Time Mooring Data Applications

In this example, we use data collected with an SBE 43 DO sensor deployed in an urban marina for 4 months during the biologically active spring and summer seasons. The integrated SBE 43 and CTD (conductivity, temperature, and depth sensor) was moored at 2 meters water depth and sampled every 10 minutes following a 30-second flush cycle. Replicate Winkler samples were collected bi-weekly from a 1.2-liter Niskin bottle adjacent to the moored SBE 43 sensor, at the time of a sample. The SBE 43 measured dissolved oxygen within 5% of Winkler reference values for over 107 days (~3 months) during high biological fouling conditions (Figure 3).

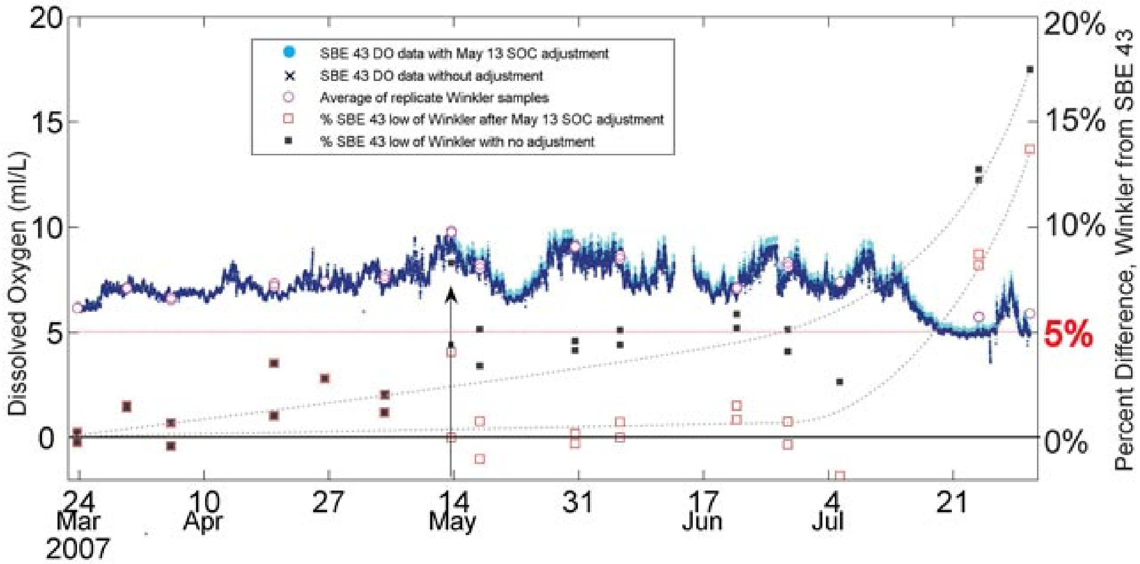


Figure 3. *SBE 43 dissolved oxygen time series in dark blue, March 23 – July 31, 2007. Data with a slope adjustment made after May 13 are co-plotted in cyan. Average Winkler values are open pink circles, and the percent difference between the SBE 43 and Winkler averages are co-plotted along the right y-axis as black solid squares (before the May 13 validation and slope adjustment), and as red open squares (from May 13 forward following the adjustment). The dashed curved lines illustrate how correcting the in situ data can prolong deployment while maintaining accuracy in real-time (or post-processed) data. Mean standard deviation of the Winkler replicates is 0.03 ml/L.*

A single validation point made on May 13 is used to demonstrate the correction of *in situ* sensor data without servicing or recovering the instrument (see arrow in Figure 3). The average of the replicate Winkler values on May 13 is 9.737 ml/L; the SBE 43 reported 9.308 ml/L. To adjust the calibration for data after May 13, a new *Soc* is obtained by multiplying the pre-May 13 *Soc* (1.3256e-04) by the ratio of the reference value to the sensor value. Verify the units of each are compatible (ml/L, mg/L, µmol/kg, or % saturation).

[(Winkler value ml/L) / (SBE 43 value ml/L)] => (9.737/9.308 = 1.046):
New*Soc* = previous*Soc* * ([Winkler] / [SBE 43])
1.3866e-04 = 1.3256e-04 *1.046

The result of using New*Soc* on data collected after May 13 (cyan blue line ml/L and open squares % difference) demonstrates how sensor accuracy is maintained near initial calibration accuracy by using a single quality reference sample. See the next example for a description of how to apply a correction to data preceding the May 13 reference sample (time rate of change in drift correction).

Example of Post-Processing Data Correction and Computing Time Rate of Change in Soc

Sometimes, in-field validation is not possible. This restricts correction of possibly fouled data to post-processing, and requires a reference validation sample be taken at the end of the deployment or soon after the instrument is recovered. The reference validation sample could be a water sample taken in the field prior to recovery or a factory post-calibration.

A simple method for data correction in post-processing is to assume a linear fouling adjustment per day (or week, or month) for the entire period or between field validation data collection periods. The resultant rate of change in the sensor measurement can then be programmed into a simple algorithm to calculate corrected DO data with time.

Post-Processing Correction Example 1:

The fouling drift in sensor data shown in Figure 3 is linear with time. To apply a correction, simply compute the rate of change per day in the *Soc* value from the beginning of the deployment to May 13, when an *in situ* reference sample was made (50 days).

Soc rate = (New*Soc* – previous*Soc*) / # of days → 0.0012e-04 per day = (1.3866e-04 – 1.3256e-04) / 50

Post-Processing Correction Example 2:

For this example, pre- and post-calibration data from sensor 1114 are used (Table 1). Sensor 1114 was deployed in a high-fouling coastal lagoon for 2 months with no interim servicing. After recovery, the sensor was returned to the factory for calibration and shown to have fouled ~1% (Table 1). The post-calibration *Soc* value prior to cleaning, and the rate of change in *Soc*, are computed as follows:

New*Soc* = previous*Soc* * ([Winkler] / [SBE 43]) → 0.3837 = 0.3810 * 1.007
Soc rate = (New*Soc* – previous*Soc*) / # of days → 4.445e-05 per day = (0.3837 – 0.3810) / 60

During the 2-month deployment period, the sensor experienced an *Soc* change rate of about 0.000045/day. In reality, a sensor may not exhibit fouling for several weeks to months (as shown here, fouling was minimal), so the user needs to decide how best to determine the time span and data correction criteria of fouled data. Interim water samples or reference checks (using a CTD) between service intervals can provide valuable information on fouling. Variations on the methods used for post-correcting data are also possible.

Data corrections are only as good as the reference samples used to correct the data. We therefore recommend replicate water sample collection, or validation methods that employ a sensor that is as accurate as the moored sensor being tested.

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