## APPLICATION NOTE NO. 64-2   Revised August 2005

SBE 43 Dissolved Oxygen Sensor Calibration using Winkler Titrations

This application note describes a method for statistically estimating calibration coefficients for calculating dissolved oxygen in milliliters per liter from SBE 43 output voltage. The technique requires dissolved oxygen concentration in ml/l (determined from Winkler titration of water samples) and SBE 43 oxygen voltage outputs at the times the water samples were collected. Sea-Bird's data processing software, SBE Data Processing, is used to produce a data table suitable for the analysis.
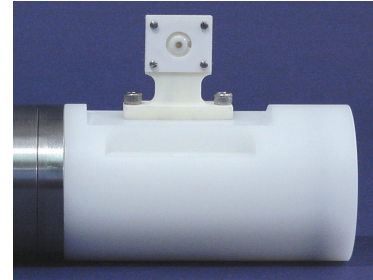
Background

The equation 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):

$$Oxygen\ (ml/l) = \left\{ Soc * \left(V + Voffset + tau * \frac{\partial V}{\partial t} \right) + Boc * e^{(-0.03 * T)} \right\} * Oxsat(T, S) * e^{(tcor * T)} * e^{(pcor * P)} \qquad eqn\ 1$$

Where:
V = SBE 43 output voltage signal (volts)
$\dfrac{\partial V}{\partial t}$ = time derivative of SBE 43 output signal (volts/second)
T = CTD temperature (°C)
S = CTD salinity (psu)
P = CTD pressure (dbars)
$Oxsat(T,S)$ = oxygen saturation (ml/l)
    Note: See *Appendix A* in *Application Note 64: SBE 43 Dissolved Oxygen Sensor* for oxygen saturation values at various temperatures and salinities.
$Soc, Boc, Voffset, tau, tcor,$ and $pcor$ are calibration coefficients

Characterization of the SBE 43 in the laboratory and ocean suggest that the most accurate results are obtained by setting *Boc* and *tau* to zero. Equation 1 then reduces to:

$$Oxygen\ (ml/l) = \left\{ Soc * (V + Voffset) \right\} * Oxsat(T, S) * e^{(tcor * T)} * e^{(pcor * P)} \qquad eqn\ 2$$

The SBE 43 is expected to provide an output voltage that is linear with respect to oxygen concentration. Normal calibration drift manifests itself as a loss of sensitivity and is evident as a change of slope and offset in the linear relationship between oxygen concentration and voltage output. The coefficients *tcor* and *pcor* correct for small secondary responses to temperature and pressure. Because these coefficients change very slowly over time, the values given on the SBE 43 calibration certificate will be used in this analysis.

Setting *Boc* and *tau* to zero, we will rearrange equation 2 into a linear form and perform a linear regression to obtain a new *Soc* and *Voffset*.

Let:

$$\phi = e^{(tcor*T)} * Oxsat(T,S) * e^{(pcor*P)}$$

The oxygen equation then reduces to:

$$oxygen(ml/l) = Soc * (V + Voffset) * \phi$$

This may be expressed in a linear form as shown in equation 3 below. A linear regression is calculated using Winkler oxygen concentration divided by ϕ as the dependent variable and SBE 43 output voltage as the independent variable.
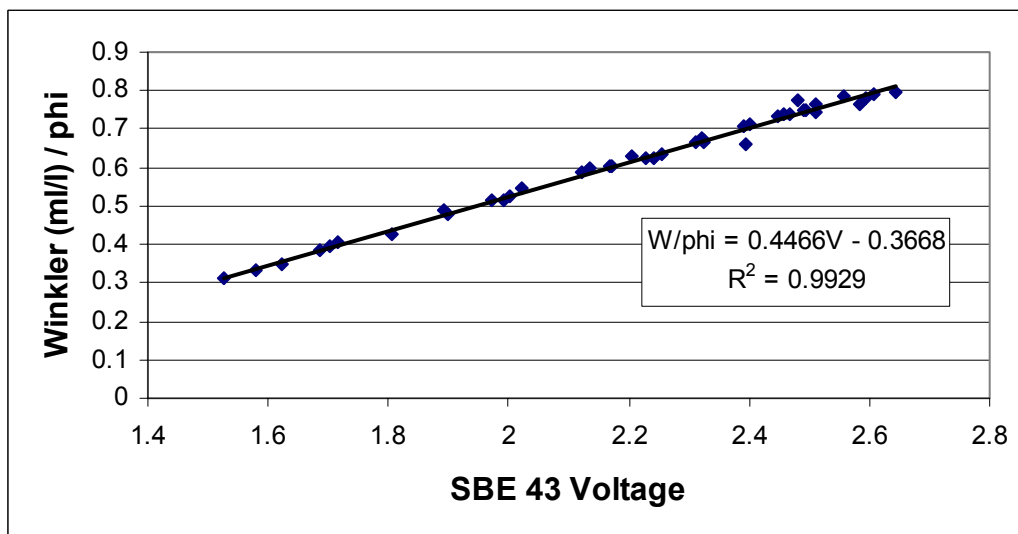
$$\frac{oxygen(ml/l)}{\phi} = Soc * (V + Voffset) = M * V + B \qquad\qquad eqn\ 3$$

Where:
    Soc = M
    Voffset = B / M

The example plot below shows Winkler oxygen divided by ϕ versus SBE 43 output voltage and includes a linear regression line calculated from the data.

In this example, the new *Soc* value is 0.4466. The new *Voffset* value is:

$$Voffset = \frac{-0.3668}{Soc} = \frac{-0.3668}{0.4466} = -0.8213$$

The next plot summarizes the results of the calibration. The diamonds are differences between the SBE 43 dissolved oxygen and Winkler titration dissolved oxygen, using the original calibration. The squares are differences between SBE 43 dissolved oxygen and Winkler titration dissolved oxygen, using *Soc* and *Voffset* derived above.
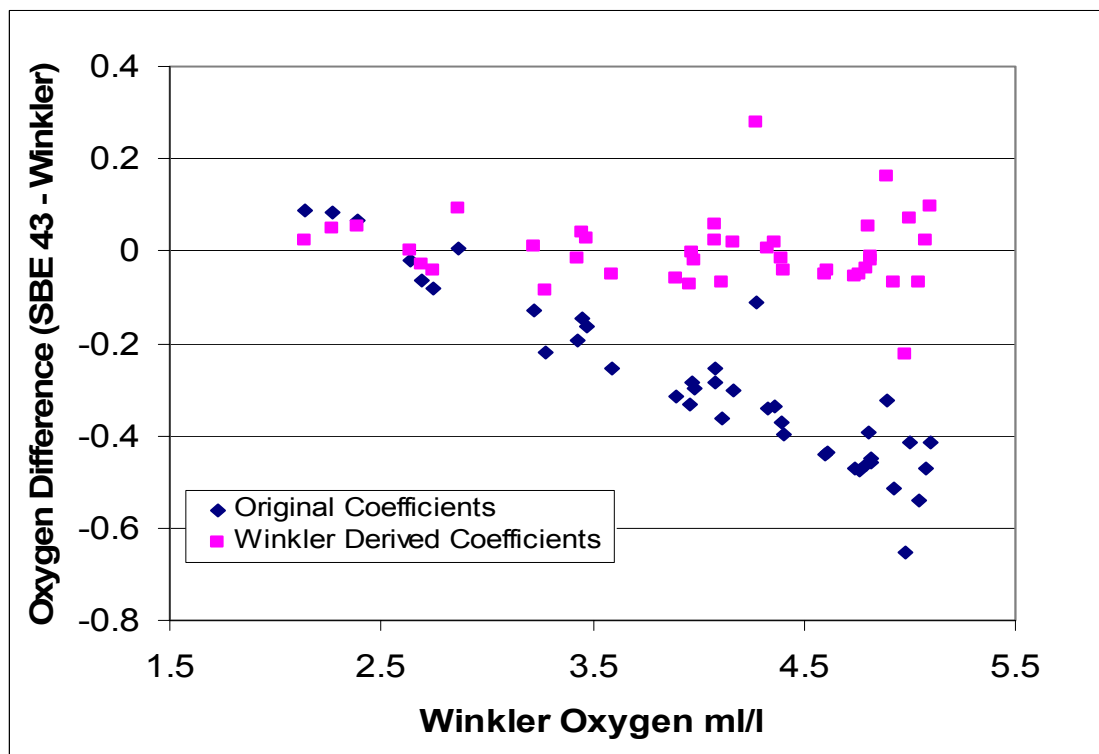
Procedure

The linear regression that yields a new *Soc* and *Voffset* may be accomplished with spreadsheet software, a hand-held calculator with statistical capability, or with perseverance, a calculator, graph paper, and a pencil. As a first step, extract pressure, temperature, salinity, oxygen saturation, and SBE 43 voltage from the parts of your CTD data collected when the water sampler closures occurred.

Run SBE Data Processing, and select Data Conversion in the Run menu. Select the appropriate configuration (.*con*) and data (.*dat* or .*hex*) files on the *File Setup* tab. Click the *Data Setup* tab and set *Convert data from* to *Upcast and downcast* and *Create file types* to *Create bottle (.ros) file only*.
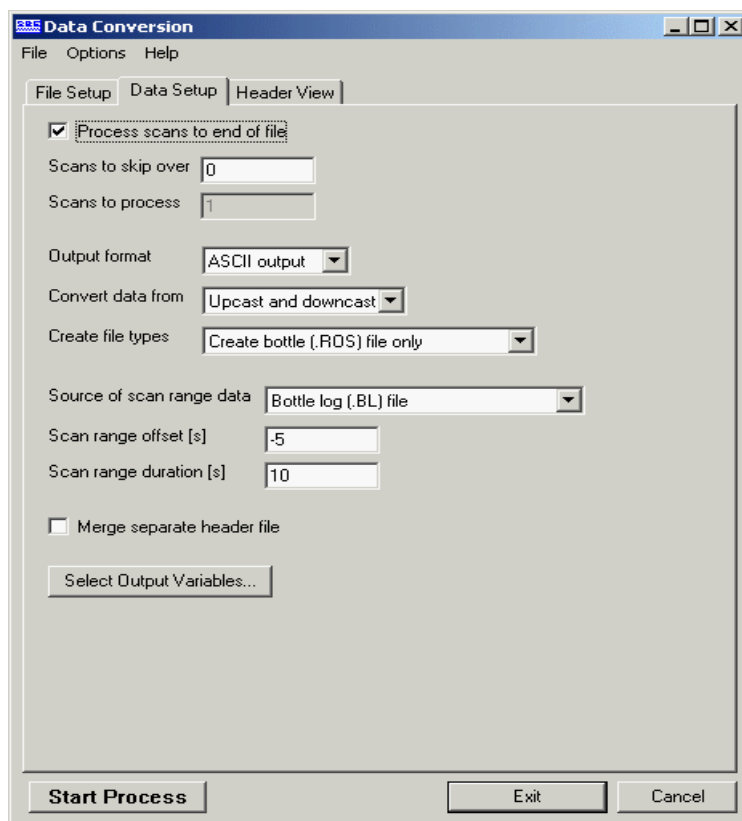

To extract CTD data concurrent to the water sampler closures, Data Conversion must know when the closures occurred. Select an appropriate *Source of scan range data*, depending on your instrument type and how the sampler was commanded to close bottles:

- SBE 9*plus* with SBE 11*plus* or 17*plus* - The data stream is marked with a *bottle confirm* bit each time a closure occurred.
- Using SEASAVE to operate the water sampler - A .*bl* file, with scan ranges corresponding to closures, is created during the cast.
- SBE 19, 19*plus*, or 25 with Auto Fire Module (AFM) - The .*afm* file contains scan ranges.

Like all sensors, the SBE 43 has a finite response time to a change in dissolved oxygen concentration. This response time is usually on the order of 6 seconds. For this reason, good sampling procedure dictates that the instrument package should be stopped in the water column long enough for the SBE 43 and all other sensors to completely equilibrate before closing the water sampler. An equilibration time of 5 to 6 response times, or 30 to 36 seconds, is adequate.

In the example above, Data Conversion will begin extracting data 5 seconds before each water sampler closure (*Scan range offset = -5 s*) and will extract a total of 10 seconds of data (*Scan range duration = 10 s*). Note that 10 seconds is longer than the SBE 43 response time. Because we are extracting data for 5 seconds after the water sampler closure, the instrument package must remain stopped for at least this long.

To estimate *Soc* and *Voffset*, you need pressure, temperature, salinity, oxygen saturation (ml/l), and SBE 43 Oxygen Voltage to go with each Winkler titration data value. Click *Select Output Variables* and add each of the required parameters; the dialog box is shown below.
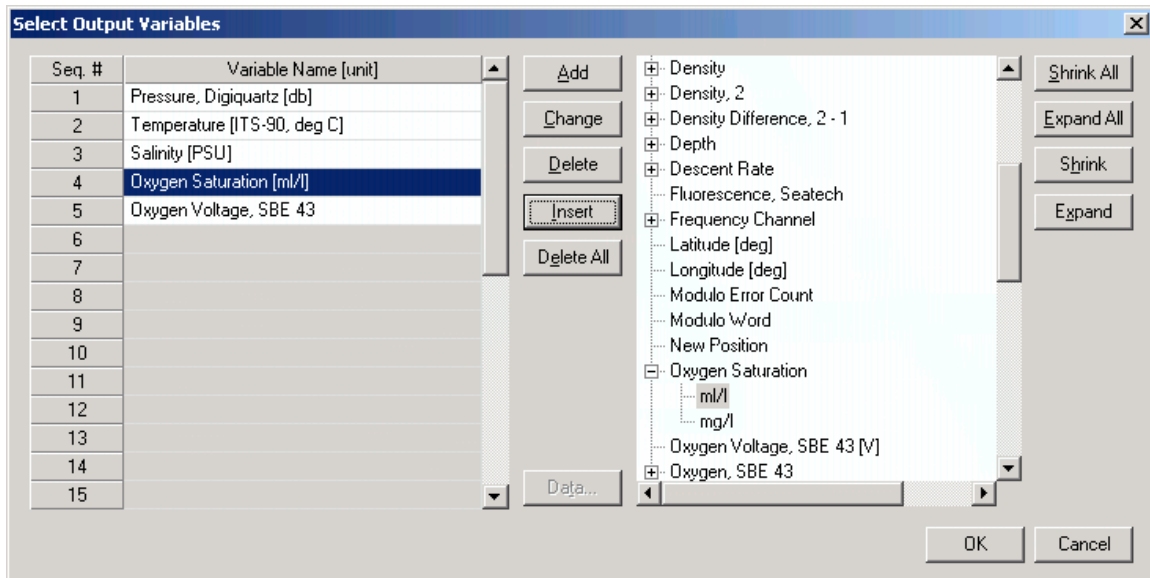
After selecting all the variables, click *OK* to return to the Data Conversion Data Setup tab. Then click *Start Process* to create the *.ros* file.

For this example, the *.ros* file contains 10 seconds of data centered on the moment the bottle closure occurred for every bottle closure. To make a useful table, select Rosette Summary from SBE Data Processing's Run menu. Rosette Summary calculates averages and standard deviations for the variables selected in Data Conversion. Select the appropriate *.con* and *.ros* files on the *File Setup* tab. Click the *Data Setup* tab and then click the *Select Averaged Variables* button; the dialog box is shown below.
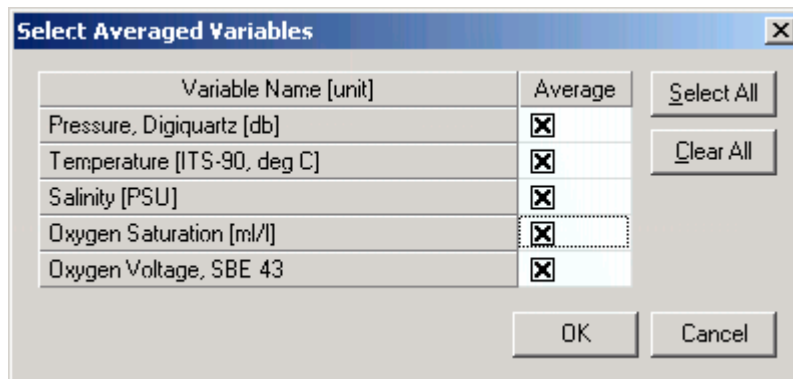
After selecting all the variables, click *OK* to return to the Rosette Summary Data Setup tab. Then click *Start Process* to create a data table file with the *.btl* extension.

Create a table with average pressure, temperature, salinity, oxygen saturation, and SBE 43 output voltage for each water sampler closure depth, by importing the .btl file into a spreadsheet. Then, enter by hand the Winkler titration dissolved oxygen values from your titration log, matching water sampler closures to pressures. Calculate $\phi = Oxygen\,Saturation * e^{(T\,*\,tcor\,+\,P\,*\,pcor)}$, using tcor and pcor from the SBE 43 calibration sheet. Then, calculate $Winkler\,O_2\,/\,\phi$. An example table is shown below (using tcor = -0.0011 and pcor = 0.000135), with ϕ (phi) in column 7 and $Winkler\,O_2\,/\,\phi$ (Winkler/phi) in column 8.

Pressure db	Temperature Deg C	Salinity	Oxygen Saturation ml/l	SBE 43 Output Voltage	Winkler Oxygen ml/l	phi	Winkler / phi
75.51	8.358	32.239	6.672	1.893	3.281	6.67868	0.49126
52.51	8.552	32.061	6.650	1.973	3.431	6.63460	0.51714
32.22	8.686	31.940	6.635	2.021	3.589	6.60056	0.54374
22.34	9.342	31.201	6.568	2.242	4.078	6.52049	0.62541
12.09	9.881	30.579	6.516	2.447	4.743	6.45609	0.73466
7.39	9.922	30.439	6.515	2.489	4.818	6.45071	0.74689
1.76	9.944	30.414	6.513	2.510	4.928	6.44368	0.76478

Perform a linear regression, with:
- $Winkler\,O_2\,/\,\phi$ (shown as Winkler/phi in the table) as the *Y* data
- SBE 43 output voltages as the *X* data

If a spreadsheet or statistical calculator is not available, the regression equations are:

$$M = \frac{n * \sum\left(V * \frac{Winkler\,O_2}{\phi}\right) - \sum V * \sum\left(\frac{Winkler\,O_2}{\phi}\right)}{n * \sum V^2 - \left(\sum V\right)^2}$$

$$B = \frac{\sum\left(\frac{Winkler\,O_2}{\phi}\right) - M * \sum V}{n}$$

Where:
　　n = number of data pairs
　　M = Slope
　　B = Offset

And:
　　$Soc = M$
　　$Voffset = B/M$

Reference

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