Module 8

Getting the Highest Accuracy Data, Continued

Overview

Getting the Highest Accuracy
Data: Profiling (continued)

- Field calibrations
  - Pressure
  - Temperature
  - Conductivity
  - Dissolved O_2
- As good as it gets: autonomous profilers

We are going to continue our discussion of methods to ensure the accuracy of profiling equipment, and then we will discuss data from autonomous profilers. We will see that the human influence on conductivity sensors is the greatest obstacle to good conductivity data.

At the end of this module, you should be able to:

- Field calibrate your CTD and Dissolved O_2 sensors.

- Have heightened awareness about the handling of your conductivity sensor.

Field Calibrations

The configuration (*.con* or *.xmlcon*) file has entries for *slope* and *offset* for all standard sensor types except dissolved oxygen. These entries are the means to make adjustments in the sensor calibration by using field observations.

The configuration file does not have *slope* and *offset* entries for dissolved oxygen sensors. For the SBE 43, the calibration coefficients *Soc* and *Voffset* are adjusted through comparison to Winkler titrations of discrete samples. For older oxygen sensors, *Soc* and *Boc* are adjusted.
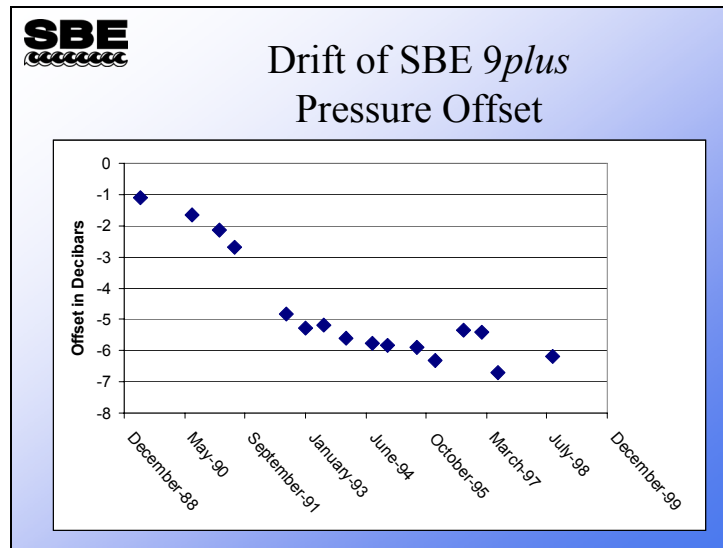
Field Calibrations: Pressure

This discussion is primarily intended as a guide for the SBE 9*plus* with a Digiquartz pressure sensor. However, the technique is sound for all pressure sensor types regardless of sensitivity.

All pressure sensors are sensitive to their orientation, primarily because of gravity's pull on the fluids that fill their capillaries. To correct for this orientation effect, determine the offset with the instrument in the same orientation that it will have when you deploy it.

Pressure sensors exhibit a transient change in their output in response to changes in their environmental temperature. Sea-Bird instruments are constructed to minimize this by thermally decoupling the sensor from the body of the instrument. There is still some residual effect, and the instrument should be allowed to equilibrate in a reasonably constant temperature environment.

Measure the offset required to zero the pressure sensor with a barometer and convert to decibars for the entry in the *.con* or *.xmlcon* file. As the next slide shows, a log of these offsets can provide good confirmation about the drift rate and show when the sensor needs maintenance.

Field Calibrations: Pressure (*continued*)

This sensor shows a typical drift until October 1995, when it begins to change in a more random manner. The random behavior indicates that it is time for a calibration and test by the factory.

Field Calibrations: Pressure (*continued*)
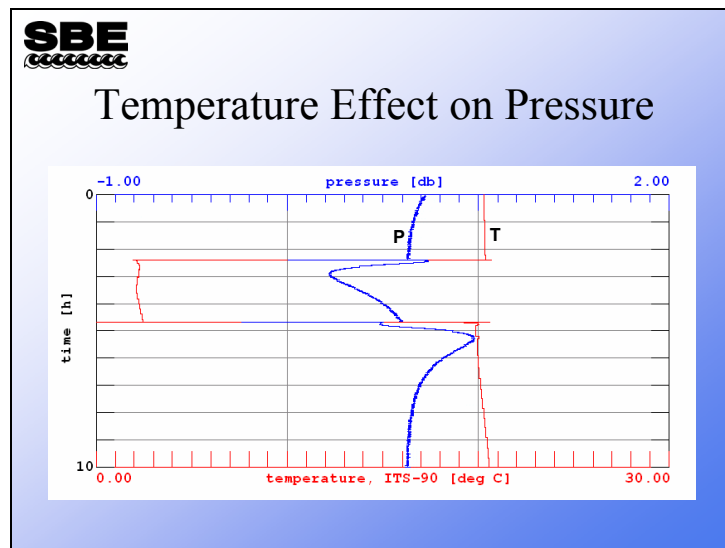
As we mentioned earlier, the SBE 9*plus* pressure sensor exhibits small pressure excursions in response to rapid changes in temperature. If you are attempting to determine an offset for the pressure sensor in the field, you must take care that the instrument is equilibrated in temperature with its environment. As the plot shows, if you pull the instrument up from a very cold depth, it can take 4 to 5 hours for the pressure sensor to completely equilibrate. It is for this reason that Sea-Bird recommends a laboratory determination of offset in relation to a barometer.

Field Calibrations: Pressure (*continued*)

SBE Pressure Offset in the Lab

- With offset in *.con* or *.xmlcon* file set to 0.0, pressure measured by CTD should equal barometric pressure
- Calculate offset (db) =
  barometer reading – CTD reading
  - Conversion of psia to decibars:
    decibars = (psia - 14.7) * 0.6894759
- Enter calculated offset in *.con* or *.xmlcon* file
- Example:
  - CTD reads -2.5 dbars
  - Barometer reads 14.65 psia.
    Converting to decibars, barometer reads
    (14.65 - 14.7) * 0.6894759 = -0.034 dbars
  - offset (db) = barometer reading – CTD reading
    = -0.034 - (-2.5) = 2.466

Field Calibrations: Pressure (*continued*)

Field Calibrations: Temperature

SBE

Field Calibrations, Temperature

- Mercury deep sea reversing thermometers have an accuracy of ± 0.002 °C
- Electronic deep sea reversing thermometers have an accuracy of ± 0.002 °C, but can be read to ± 0.001 °C
- SBE 3 has an accuracy of ± 0.001 °C
- SBE 35 has an accuracy of > 0.001 °C

Traditional mercury deep-sea reversing thermometers are not capable of resolving temperature accurately enough to field calibrate the SBE 3. Nor do electronic deep-sea reversing thermometers have the accuracy for field calibrations. Sea-Bird markets a deep-sea standards thermometer, the SBE 35, which has the physical configuration to allow calibration in a triple point cell or a gallium melt cell.

However, you have to be very careful making field calibrations of deep-sea thermometers, because the distance between the two thermometers can make a great difference in the water they measure. Additionally, the part of the ocean used for comparison must change temperature very slowly, to avoid artifacts due to location on the sampling package and time constants.

A further difficulty is that the part of the ocean that changes most slowly is the deepest and coldest part. This means that field calibrations may be carried out over a small part of the temperature range of interest. The paper cited below discusses the authors' experiences and the issues discussed above.

It is best to use pre- and post-cruise calibrations for correction of temperature data.

In-situ Temperature Calibration: A Remark on Instruments and Methods, G. Budeus and W. Schneider, Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven, Germany, Int. WOCE Newsletter, #30, March 1998, 16-18.

Field Calibrations: Conductivity and Dissolved Oxygen

SBE Field Calibrations, Conductivity and Dissolved Oxygen

- These require water samples
  - Laboratory determinations of salinity
  - Winkler titrations of dissolved oxygen

Field Calibrations: Discrete Sampling

Most instrument packages are more than a meter tall. If you take your samples for field calibrations in a part of the water column where the salinity or oxygen concentration is changing rapidly, you will not get a good sample for calibrating. Not only is there mixing of the water inside the water sampler, but you will be comparing a large mixed sample with a virtual point sample from the sensors.

Often the surface of the ocean is well mixed and provides good field calibrations for one end of the scale. And the deep ocean offers plenty of water where salinity and oxygen is changing very slowly for the other end of the scale.

Field Calibrations: Discrete Sampling (*continued*)

A water bottle consists of a plastic tube with top and bottom caps. The caps are sealed with o-rings and held in place with a spring or elastic tube. Consider that the instrument package moves through the water column on average at 1 meter per second, and faster when the ship heaves. Leaky o-rings or weak springs can allow an exchange of water between the captured sample and the ocean as the instrument package is brought to the surface. It is good practice to take the instrument package down to a depth where the salinity is changing very slowly, and then close all the sample bottles. Using this method, any leakers will be obvious when the laboratory salinity samples are run. Repair or replace any bottles that leak, or only use bottles that have been shown not to leak in field calibrations.

Field Calibrations: Discrete Sampling (*continued*)
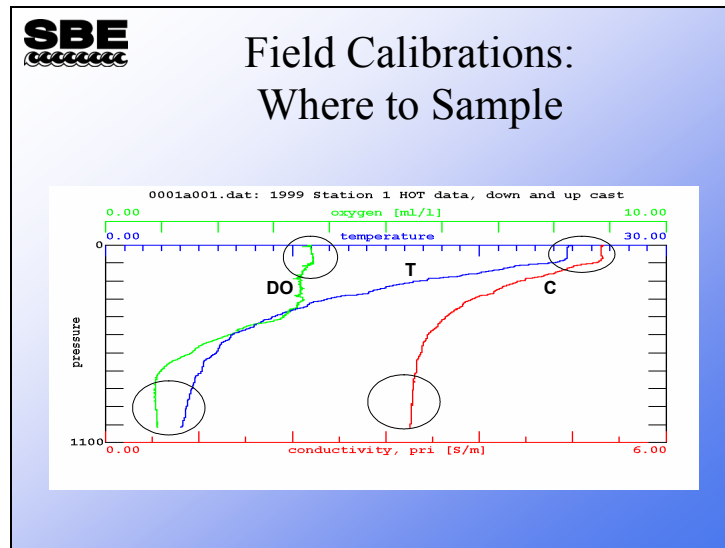
Use samples from depths showing the most uniformity in the parameter you are most interested in.

Field Calibrations: Conductivity
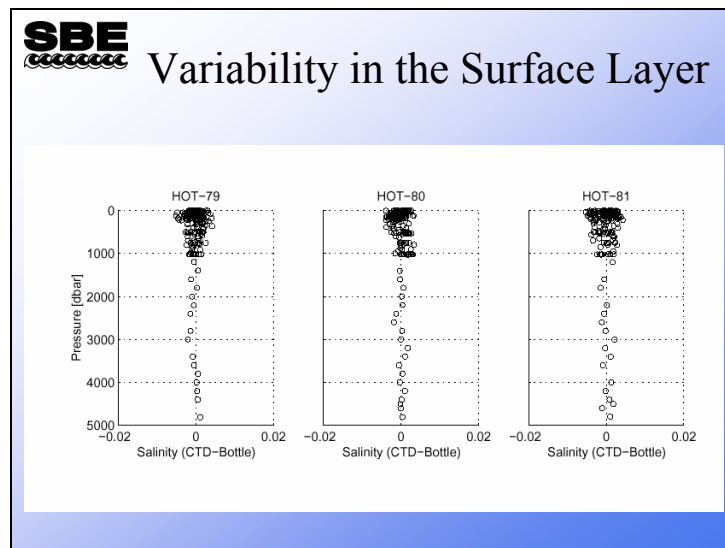
These data are taken from 3 cruises off Hawaii. The problem with using the surface layer to correct CTD conductivity is obvious.

L. Tupas, et al., Hawaii Ocean Time-series Data Report 9, 1997. University of Hawaii, School of Ocean and Earth Science and Technology. page 21

Field Calibrations: Conductivity (*continued*)
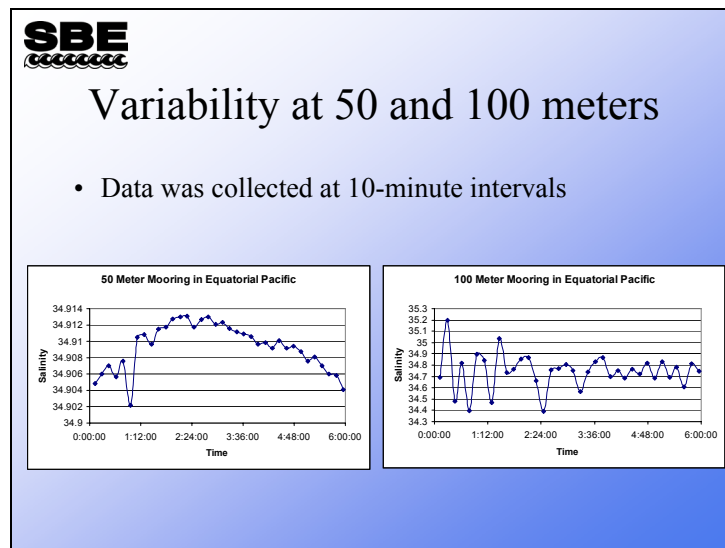
This slide shows data from a mooring near the equator. The 50-meter mooring data shows a change in salinity that might be from tidal influence. The change observed here is of similar magnitude to the correction that might be applied to CTD data based on the difference between discrete samples and the CTD.

The 100-meter mooring data shows changes in salinity that might be caused by internal waves in the thermocline. Changes of this magnitude over this time interval will cause a large and real difference between the upcast and downcast.

Field Calibrations: Conductivity (*continued*)

Because the equation that converts the conductivity sensor output from frequency to conductivity includes pressure and temperature as well as frequency, it is necessary to correct pressure and temperature before correcting conductivity. The usual reason for collecting conductivity data is to calculate salinity. Examining the salinity equation, up to 10% of a possible salinity error could be in the pressure term, 10 – 30% in the temperature term, and the remainder in the conductivity term. It is well worth correcting pressure and temperature in addition to conductivity.

Field Calibrations: Conductivity (*continued*)

The summation symbol, Sigma ($\sum$), denotes the addition of a series of values. The script on the bottom of the $\sum$ is the index of the starting value, the script on the top is the ending value. We wish to use all suitable samples so we will start with one and end with n, the total number of samples.

Example:

Suppose we had 2 salinity samples to go with our CTD cast. The salinity of these water samples is determined by a laboratory salinometer. Using SeacalcW, the salinity is paired with the corresponding corrected temperature and pressure data from the CTD cast, and the conductivity of the salinometer samples is calculated.

CTD Conductivity (α)	Salinometer Conductivity (β)
2.1234	2.1244
4.1234	4.1244

$$slope = \frac{(2.1234 * 2.1244) + (4.1234 * 4.1244)}{(2.1234 * 2.1234) + (4.1234 * 4.1234)}$$

$$slope = 1.00029$$

Field Calibrations: Conductivity (*continued*)

SBE

Example Conductivity Correction

- Raw data is shown below
- Note that CTD temperature shown is ITS-90

CTD pressure	CTD temperature	CTD conductivity	CTD salinity	Bottle salinity
202.7	18.3880	4.63421	34.9705	34.9770
1008.8	3.9831	3.25349	34.4634	34.4710
4064.1	1.4524	3.16777	34.6778	34.6850

This example is a slight variation of the example in **Application Note 31**. You would find the CTD data in your *.ros* file, which is created by the Data Conversion module.

Field Calibrations: Conductivity (*continued*)

SBE

Step One:
Conductivity Correction

- Correct P for +0.5 dbar error
- Correct T for +0.0015 °C error
- Recalculate CTD salinity for comparison to Bottle salinity

Corrected CTD pressure	Corrected CTD temperature	CTD conductivity	CTD salinity (T, P corrected)	Bottle salinity
202.2	18.3865	4.63421	34.9719	34.9770
1008.3	3.9816	3.25349	34.4653	34.4710
4063.6	1.4509	3.16777	34.6795	34.6850

Temperature and pressure are corrected first. CTD salinity is recalculated only for comparison to the bottle salinity. We will be correcting conductivity, not salinity.

Field Calibrations: Conductivity (*continued*)

SBE

Step Two: Conductivity Correction

- Bottle conductivity is calculated at CTD corrected T and P using SeacalcW
- Note slope shown in CTD – Bottle conductivity

CTD conductivity	Bottle conductivity	CTD – Bottle conductivity
4.63421	4.63481	-0.00060
3.25349	3.25398	-0.00049
3.16777	3.16822	-0.00045

The numbers in the column labeled *CTD – Bottle conductivity* are not constant. Rather, they have the slope we have been harping on.

Let's look at calculating the slope:

$$slope = \frac{\sum_{i=1}^{n} \alpha_i \beta_i}{\sum_{i=1}^{n} \alpha_i \alpha_i}$$

Slope =

(4.63421 * 4.63481) + (3.25349 * 3.25398) + (3.16777 * 3.16822)

(4.63421 * 4.63421) + (3.25349 * 3.25349) + (3.16777 * 3.16777)

= 1.000138

Field Calibrations: Conductivity (*continued*)

SBE

Step Three: Conductivity Correction

- Slope calculated from previous slide is 1.000138
- Place slope in slope entry of conductivity calibration coefficients; Corrected CTD conductivity = CTD conductivity * slope
- Corrected CTD salinity is calculated from corrected CTD conductivity shown here, and corrected temperature and pressure from Step 1

Corrected CTD conductivity	Corrected CTD salinity	Bottle Salinity
4.63485	34.9773	34.9770
3.25394	34.4706	34.4710
3.16821	34.6849	34.6850

The correction puts the CTD salinities much closer to the bottle salinities. You may be wondering what to do if you collect bottle salinities with every cast and have many casts in a cruise. It would be a bit onerous to make this calculation for every cast and process each cast with a different offset. Usually, making this calculation and changing the slope value in the conductivity sensor's calibration coefficients each week is sufficient. However as we have discussed, fouling is often *an event*. This being the case, careful scrutiny of your data is warranted to ensure that you catch these events and change the slope correction accordingly.

Field Calibrations: Dissolved Oxygen

Terms that can be modified by the user to adjust the calibration of the SBE 43:

- *Soc* only (*Soc* can change in time due mostly to fouling)

- *Soc* and *Voffset* together (*Soc* can change in time due mostly to fouling)

- *E* calibration constant

  o The factory value is determined at 0 db and works well for most, but can be adjusted by the user.

  o This is a one-time correction determined using deep pressure sensor and water sample comparison taken at depths > 1000 m.

Field Calibrations: Dissolved Oxygen

**SBE 43 D.O. Sensor –
Fouling**

Fouling:
- Reduces permeability of sensor membrane
- Reduces sensitivity to changes in oxygen
- Causes sensor to read **low** of correct
- Does **not** occur in every deployment
- Can vary depending on location and time out in the field

There are two mechanisms at work when it comes to SBE 43 oxygen sensor drift:

1. The primary cause of sensor calibration drift is **fouling** of the sensor membrane. This can be a slow change over time, as the membrane accumulates oils and other materials during cruises and long deployments. Fouling can also occur in an event, such as after passing through an oil slick or impaling a jelly fish. Following recommended cleaning procedures can take care of most fouling problems (see **Application Note 64**).

2. A lesser concern is electrolyte consumption. The SBE 43 is continuously polarized, so will continue to react with oxygen in its plenum housing when not sampling in the water, unless the oxygen supply is choked off. Though this process is reduced by the semi-enclosed housing of the DO sensor, we do recommend that after cleaning the sensor, that it be stored with a closed loop of Tygon tubing. Enclose with a small piece of damp sponge inside the tubing if there is no risk of freezing. We do not recommend storing the SBE 43 in water, as this can lead to *in situ* fouling.

Field Calibrations: Dissolved Oxygen (*continued*)

SBE SBE 43 –
Winkler Validation in the Field

- Choose depth of CTD and Winkler water sample comparisons where D.O. is not changing much
  - Collect replicate field samples if possible, and use average or "best of"
- If replication not possible, collect samples at multiple locations to get idea of sampling variability and to be sure you do not have a bad sample

Correcting SBE 43 DO Data using Field Validation Requires Care

- Field validations must be carefully executed!

- Things that can contribute to sensor differences from water sample values besides sensor calibration drift or malfunction:
  - Mismatched depths between sensor and bottles
  - Internal waves
  - Non-equilibrated sensor/bottle (not long enough wait time prior to closing bottles)
  - Steep gradients over length of sampling package
  - Poor QA on Winkler titrations (chemicals, blanks, sample draw errors, bubbles in samples, analyst)

Field Calibrations: Dissolved Oxygen (*continued*)

What one needs to consider in the Sea-Bird DO calibration equation:

- The basis for calculating dissolved oxygen is a modified version of the algorithm from Owens and Millard (1985), referred to in our software as the *Sea-Bird* algorithm or *Sea-Bird Calibration Equation*.

- **The calibration slope term *(Soc)*, which changes as the sensor sensitivity is modified, typically by fouling, is the coefficient we are most concerned with.**

- An electronic offset term (*Voffset*) related to the voltage output observed at a zero oxygen signal is unique to each sensor and is constant.

- A third-order polynomial component that compensates for changes in the sensor's sensitivity as a function of temperature remains constant.

- An exponential term that compensates for the instantaneous changes in the sensitivity of the sensor with changes in pressure (*E*) can be modified to fine tune deep-ocean oxygen data (covered in more detail later in this module).

Field Calibrations: Dissolved Oxygen (*continued*)

> **SBE** Field Calibrations:
> Correcting Dissolved O_2
>
> - tau (T,P) * $\delta V/\delta t$ is proportional to the first derivative of the oxygen sensor output voltage.
>   - To remove derivative term, disable *Apply Tau correction* on Miscellaneous tab in Data Conversion; this deletes term from equation.
> - Temperature and pressure time response functions are demonstrably consistent between sensors.
> - The only term you need to be concerned with is the slope term, *Soc*.

What one needs to consider in the Sea-Bird DO calibration equation (*continued*)

- The tau (T,P) * $\delta V/\delta t$ term is proportional to the first derivative of the oxygen sensor output voltage. This term is introduced to sharpen the response of the sensor to rapid changes in oxygen concentration. However, it also amplifies residual noise in the signal (especially in deep water), and in some situations this negative consequence overshadows gains in signal responsiveness. To remove the derivative term, disable *Apply Tau correction* on the Miscellaneous tab in Data Conversion; deleting tau (T,P) * $\delta V/\delta t$ from the equation.

- The SBE 43 has been tested extensively at large ranges of DO, temperatures, and pressures both in the field and the lab to adequately characterize the sensor time responses to changing parameters. The end characterization leads to a highly accurate sensor characterization and data output. Better yet, the temperature and pressure time response functions are demonstrably consistent between sensors, and do not change other than in the final calibration fit provided by the factory.

- *UPSHOT:* The only term to be concerned with is the slope, *Soc*. For advanced or most discerning users, *Voffset* can also be adjusted, but we warn against this in most applications.

- We will show two methods for correcting SBE 43 oxygen data, but will restrict in-class discussion to the *Soc Only* (Case 1) option.

Field Calibrations: Dissolved Oxygen (*continued*)

SBE Field Calibrations:
Correcting Dissolved O_2

- There is a time-dependent hysteresis effect.
  – This is not dealt with in the calibration equation term E.
  – It is corrected separately, as it requires a time- and pressure-dependent algorithm not included in the calibration algorithm.
  – Hysteresis effect is less important for deployments < 1000 meters.

On the separate time-dependent pressure effects we refer to as deep-ocean hysteresis:

- There is a time-dependent hysteresis effect on the sensor membrane that takes effect at all depths, but becomes significant at depths greater than 1000 meters. This is not dealt with in the calibration equation term E.

- Instead, deep-ocean hysteresis is corrected for separately as it requires a series of time-dependent functions not accommodated in the Sea-Bird calibration algorithm.

- To remove the deep-ocean hysteresis prior to data validation and calibration adjustments, run the Data Conversion module with the Hysteresis Correction option enabled (on the Miscellaneous tab) prior to comparing output with bottle data.

Field Calibrations: Dissolved Oxygen (*continued*)

> **SBE**   Field Calibrations:
> Correcting Dissolved O_2
>
> • Recommended calibration approaches based on range of oxygen values you have and quality of your reference samples (Winkler titrations).
>   – *Soc* – only 1 good sample required.
> • Most of the time, the factory setting for *Voffset* is the best to use.
>   – Perform *Voffset* corrections when you have a large number of samples for comparison, **and** the range of DO values is large (for example 2 – 6 ml/L).

When to use Case 1 (*Soc* only corrections):

- We recommend using the Slope only (*Soc*) approach to adjust the SBE 43 calibration in most circumstances, and especially when few sample comparisons are available and/or when the range of oxygen sample comparisons is small (i.e., 3 - 4 ml/L).

- This is a simpler approach for correcting oxygen data and is effective for both profiling and moored data sets.

- The method entails computing the ratio of the Winkler to SBE 43 output from a series of samples. The ratios should yield the same result (*Soc* correction factor is nearly constant for a set of samples).

- This ratio is then multiplied by the original *Soc* term used in the calibration equation to convert and calibrate SBE 43 output voltage, and is therefore used to scale-correct the slope of the sensor calibration.

- Selecting a correction ratio to use to modify the *Soc* term from a series of values can be accomplished by averaging the lot of sample ratios, selecting values from well-mixed regions only, etc.

- Compare the oxygen data from the sensor with oxygen bottle data and make corrections to *Soc* at your discretion.

Field Calibrations: Dissolved Oxygen CASE 1
(Soc Adjustment Only)

SBE SBE 43 – Procedure Overview for Correcting Data for Fouling

Case 1:

- Compare a Winkler value and corresponding SBE 43 value (corrected for deep-ocean hysteresis)
- Compute correction ratio =
                    (Winkler value / SBE 43 Value)
- Multiply factory *Soc* by ratio to get *newSoc*
- Replace factory *Soc* in .con or .xmlcon file with *newSoc*
- Process data from time of correction forward with *newSoc*

Field Calibrations: Dissolved Oxygen CASE 1
(Soc Adjustment Only)

When is a change in *Soc* indicating the sensor needs to be serviced, cleaned, or recalibrated at the factory?

- The correction ratio is typically greater than 1.0 if the sensor is fouling as the loss of sensitivity requires increasing *Soc* to give the correct DO values.

- If the correction factor is greater than 15-20% of the original factory *Soc* (ratio of Winkler/SBE 43 ~ 1.2), and when this cannot be reduced by cleaning, the sensor may need to be returned to the factory for service.

- Other options for data correction are discussed in several papers on our website.

- An exercise in Module 12 is provided to demonstrate this method of DO data correction in a moored application.

- For additional information on SBE 43 data and corrections, see **Application Notes 64, 64-1, and 64-2** on our website.

Field Calibrations: Dissolved Oxygen CASE 2
(Soc and Voffset Adjustments)

SBE

Field Calibrations:
Correcting Dissolved O$_2$

- Case 2: Statistically large sample set through broad range of values (example, 2 – 6 ml/L)
  - *Soc* **and** *Voffset* validations and modifications
  - Compute standard deviation of Winklers to verify QA/QC
  - If Winkler QA/QC inadequate, do not modify *Voffset* from factory value.

When to use Case 2: *Soc* and *Voffset* Corrections:

- Most of the time, the factory setting for *Voffset* is the best to use.

- *Voffset* is a characteristic of the electronics and should not change much over time, if at all. It is an electronic offset most accurately determined at the factory.

- *Voffset* only varies because it is modified to a best fit into the calibration equation, using a large range of highly accurate calibration samples at the factory.

- Only perform *Voffset* corrections when you have a large number of samples for comparison, AND when the range of DO values available to you between your sensor and bottle samples is large (2 - 6 ml/L, for example).

- Only use sensor/bottle comparisons from fairly well-mixed regions, where changes occur over depth intervals larger than your sampling package.

- *Voffset* should not vary much unless the sensor is refurbished. Therefore, we advise its modification only for very high accuracy needs and the availability of high accuracy Winkler results.

- If the *Voffset* value is much different than that from the factory, it might indicate a problem with the data range or with Winkler/sensor QA.

- Compare the oxygen data from the sensor with oxygen bottle data and make corrections to *Soc* and *Voffset* at your discretion.

Field Calibrations: Dissolved Oxygen CASE 2
(Soc and Voffset Adjustments continued)

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SBE   Field Calibrations:
Correcting Dissolved O$_2$

- Disabling time constant correction (uncheck box in Data Conversion):

$$Oxygen\ (ml\,/\,l) = Soc * (V + Voffset) * Oxsol(T,S)$$

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

- SBE 43 produces an output voltage linear with respect to Oxygen concentration.
- *Soc* is the slope term, and changes as the sensor loses sensitivity.
- *A, B, C,* and *E* correct for small secondary responses to temperature and pressure: these change very slowly over time.

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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 (*Soc*) in the linear relationship between oxygen concentration and voltage output.

- The coefficients *A*, *B*, *C*, and *E* 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.

Field Calibrations: Dissolved Oxygen CASE 2
(Soc and Voffset Adjustments continued)

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SBE

Field Calibrations: Correcting Dissolved O_2

- For a field correction we will rearrange the previous equation into a linear form, let:

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

- Oxygen equation reduces to:

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

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Our goal is to rearrange the equation into a linear form that we can use in a linear regression of Winkler titration dissolved oxygen versus SBE 43 voltage output. To simplify this we will collect terms and express oxygen saturation and the corrections for pressure and temperature as *phi*.

Field Calibrations: Dissolved Oxygen CASE 2
*(Soc and Voffset Adjustments continued)*

SBE

Field Calibrations:
Correcting Dissolved O_2

- The previous equation may be expressed in linear form as:

$$\frac{oxygen(ml/l)}{\phi} = Soc * (V + Voffset) = M * V + B$$

- Where:
  - $Soc = M$
  - $Voffset = B / M$

Finally, Winkler titration values divided by *phi* is the independent variable and SBE 43 output voltage is the dependent variable. Note that *Soc* and *Voffset* are constants, so the right side of the equation is expressed as a slope (*Soc*) multiplied by a variable voltage plus a constant offset (*Voffset*).

Field Calibrations: Dissolved Oxygen CASE 2
(Soc and Voffset Adjustments continued)
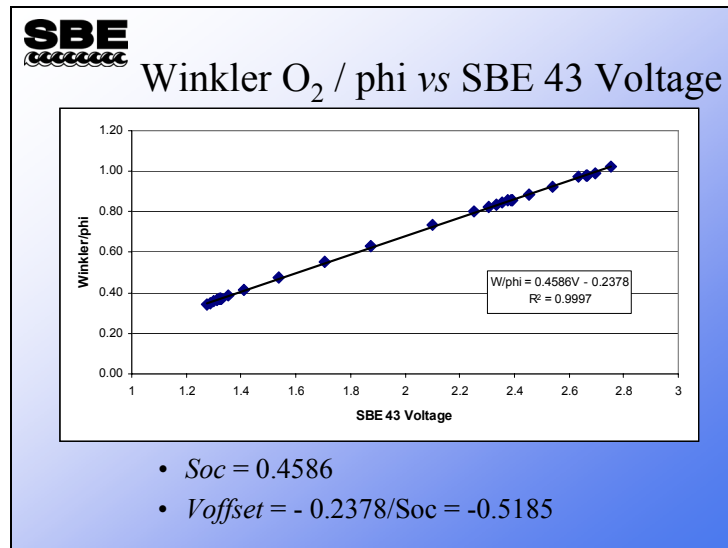
Here is a plot and regression of some data gathered in Puget Sound. Even though Puget Sound is not a well-mixed environment, there is a very strong relationship between Winkler O_2 / *phi* and SBE 43 Voltage.

Field Calibrations: Dissolved Oxygen CASE 2
(Soc and Voffset Adjustments continued)
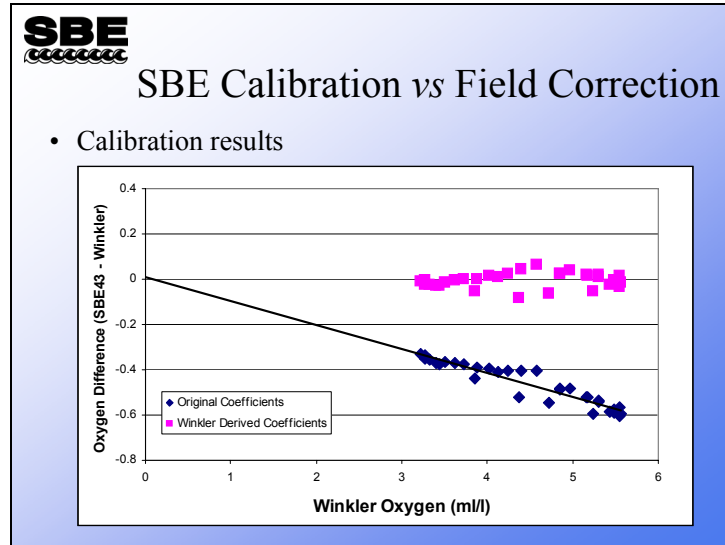
This plot shows the improvement in agreement between the Winkler titrations of dissolved oxygen and the SBE 43 measurement of dissolved oxygen after application of the Winkler-derived *Soc* and *Voffset*. The blue diamonds are the difference between the Winkler values and the SBE 43 values using *Soc* and *Voffset* from the most recent calibration. The pink squares are the difference between the Winkler values and the SBE 43 values using the derived *Soc* and *Voffset*.

Field Calibrations: Dissolved Oxygen Pressure Effects

Adjusting the Pressure Term E in the Calibration Equation


As we mentioned, there are two ways pressure affects the sensor response, and each is handled separately during the initial data processing stages:

1. The time-dependent effect of pressure that affects the membrane permeability by plasticization of the polymer membrane and modification of the ratio of crystalline and amorphous components in the membrane - *remedied in the Hysteresis correction option in the Data Conversion module*.

   a. Most important for profiles conducted deeper than 1000 meters, but is a good option for the highest accuracy data at all depths.

2. The instantaneous effect of pressure on the sensor membrane permeability - *captured in the E term of the calibration equation*.

   a. Necessary for all profile data, regardless of deep or shallow water.

   b. *E* can be adjusted so data are fit to Winkler samples after conducting hysteresis corrections.

   c. Should be a one-time fit; discussed further near the end of this Module.

Field Calibrations: Dissolved Oxygen Pressure Effects
Deep-Ocean Hysteresis
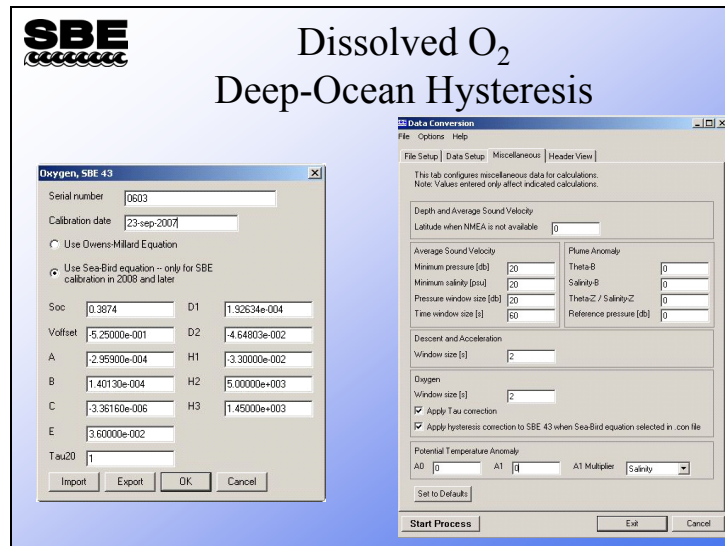
To perform deep-water hysteresis corrections on your SBE 43 oxygen data, select *Apply hysteresis correction to SBE 43 when Sea-Bird equation selected in .con or .xmlcon file* on the Miscellaneous tab in the Data Conversion dialog box. Ranges and default values for the hysteresis correction are:

- H1 - amplitude, range -0.03 to -0.05, **default = -0.033**.

- H2 - non-linear component, does not require tuning between sensors, **default = 5000**.

- H3 - time constant, range 1200 to 2000 sec, **default = 1450 sec**.

   H3 can be adjusted if needed for high accuracy applications, but default values typically produce excellent results.

Hysteresis responses of membranes on individual SBE 43 sensors are very similar; in most cases the default 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) made preferably to > 3000 meters is available. Hysteresis can be eliminated by alternately adjusting H1 and H3 in the .con or .xmlcon file during comparison of the complete profile with corresponding Winkler water sample values. Once established, these parameters should be stable, and can be used without adjustment on other casts collected using the same SBE 43.

Be sure to perform hysteresis corrections to deep profile data being used to modify the *Soc* term.

Field Calibrations: Dissolved Oxygen Pressure Effects
*Adjusting E in the Calibration Equation*

Dissolved Oxygen Measurement in Deep Water

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

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

- The function *Oxsol(T,S)* calculates the maximum partial pressure of oxygen that will not out gas from water of a given salinity and temperature
- *Soc* scales the sensor output to a fraction of oxygen saturation
- Terms containing *A*, *B*, *C*, and *E* correct for secondary effects of temperature and pressure

Recall the dissolved oxygen equation; basically it is a scaling of oxygen saturation based on sensor output with a correction for temperature sensitivity and for pressure sensitivity. In the following discussion we will explore the pressure correction coefficient and learn how to fine tune it with adjustments to *E*.

Field Calibrations: Dissolved Oxygen Pressure Effects
Adjusting *E* in the Calibration Equation (*continued*)
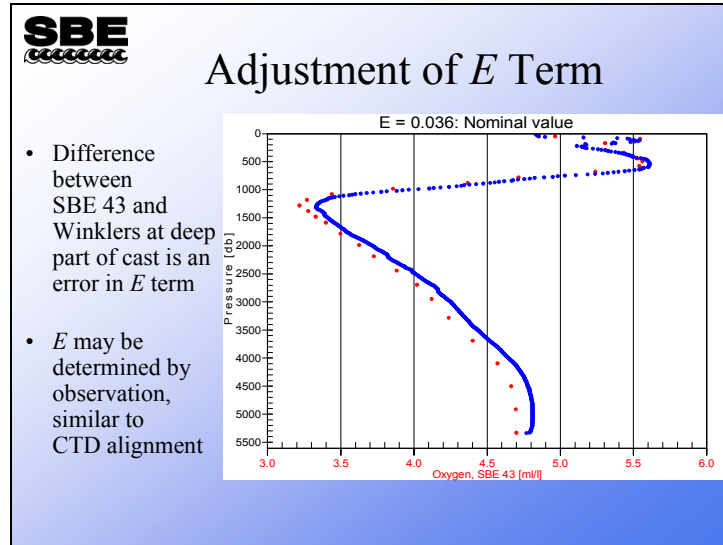
As you might imagine, the term in the equation that corrects for pressure effects has little effect in the upper part of the profile. The slide above illustrates that as the pressure increases, the response of the instrument deviates from the Winkler titrations. We can improve the agreement of the SBE 43 and the Winkler titrations by adjusting *E*.
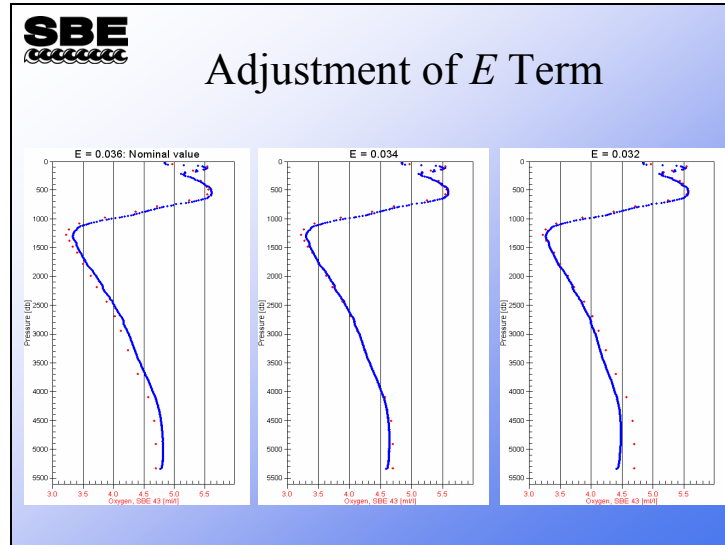
Field Calibrations: Dissolved Oxygen Pressure Effects
Adjusting *E* in the Calibration Equation (*continued*)

Field Calibrations: Dissolved Oxygen Pressure Effects
Adjusting *E* in the Calibration Equation (*continued*)

We can make the adjustment to *E* empirically. The plots above show the discrepancy between the SBE 43 calculated oxygen and the Winkler titrations with a series of *E* values. Clearly, the middle value of E = 0.034 gives the best agreement.

PALACE Float: No Conductivity Drift (almost)

These CTDs have a significant advantage over the usual deployments with regard to conductivity drift. They are deployed from ships with their conductivity cells full of de-ionized water, and have no contact with ships or humans for the remainder of their lives. They are never exposed to the sea surface near a ship with its oil film. Finally, their cells are never allowed to dry, so the electrodes are always stored in biology-resistant water.

The consequence of this is that their conductivity sensors drift negligibly or not at all.

PALACE Float: Compared to Historical Data
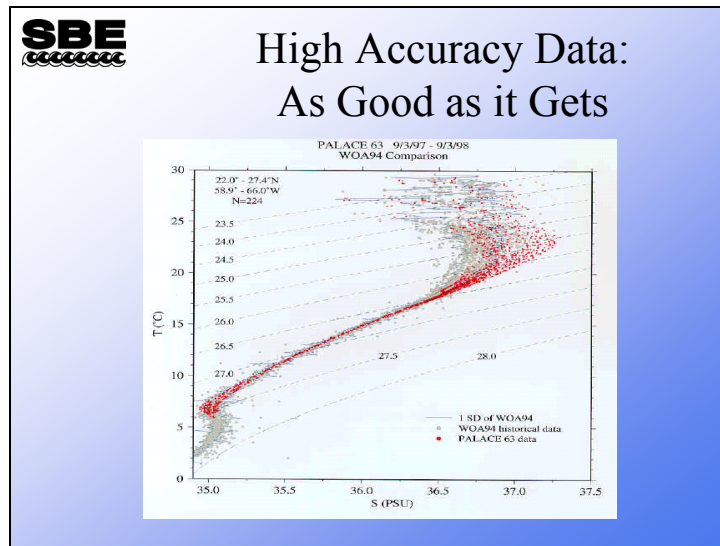
Note the low scatter in the mid-region compared to historical CTD data. Also, note the shift in surface values, PALACE being saltier than historical data.

Activity: Correct CTD Conductivity with Water Samples

Pressure db	CTD Temp	CTD Cond	Uncorrected CTD Salinity	Water Bottle Salinity	Water Bottle Cond	Corrected CTD Temp	Corrected CTD Cond	Corrected CTD Salinity	Corrected CTD Salinity-Water Bottle Salinity
4.9	24.0798	5.23638	35.1885	35.2055		24.0798			
519	6.6922	3.43991	34.0769	34.0848		6.6922			
850.6	4.4142	3.27659	34.3667	34.3738		4.4142			
1000.8	4.003	3.25475	34.4616	34.472		4.003			
1202.3	3.5221	3.22482	34.5083	34.5148		3.5221			
1401	3.039	3.19378	34.5452	34.5503		3.039			
1599.6	2.6724	3.1719	34.5692	34.5769		2.6724			
1999.1	2.1309	3.1445	34.6131	34.6194		2.1309			
2400.2	1.7884	3.13273	34.6392	34.6463		1.7884			
2798.9	1.5911	3.13234	34.6563	34.6645		1.5911			
3200.1	1.4927	3.1397	34.6674	34.676		1.4927			
3600.3	1.4587	3.15175	34.6737	34.6829		1.4587			
4001.5	1.4537	3.16568	34.6772	34.6853		1.4537			
4401.9	1.4766	3.18142	34.6790	34.6871		1.4766			
4500.7	1.4868	3.18558	34.6788	34.6883		1.4868			
4600.8	1.4969	3.18976	34.6789	34.6883		1.4969			
4809.4	1.5119	3.19792	34.6795	34.6884		1.5119			

1. What temperature scale is CTD temperature reported in? What temperature scale is used to calculate conductivity?

2. Use SeaCalcW to calculate "Water Bottle Conductivity" using "Corrected CTD Temp" and "Water Bottle Salinity".

3. Calculate a conductivity correction slope based on the shaded portion of the table. We are using 3 data rows in class as a quick exercise. Normally, how much of the table would you use? Recall pages 17 and 20.

CTD Conductivity Corrected With Water Samples

Pressure db	CTD Temp	CTD Cond	Uncorrected CTD Salinity	Water Bottle Salinity	Water Bottle Cond	Corrected CTD Temp	Corrected CTD Cond	Corrected CTD Salinity	Corrected CTD Salinity-Water Bottle Salinity
4.9	24.0798	5.23638	35.1885	35.2055	5.23862	24.0798	5.23763	35.1980	-0.0075
519	6.6922	3.43991	34.0769	34.0848	3.44062	6.6922	3.44073	34.0861	0.0013
850.6	4.4142	3.27659	34.3667	34.3738	3.27720	4.4142	3.27737	34.3758	0.0020
1000.8	4.003	3.25475	34.4616	34.472	3.25563	4.003	3.25553	34.4708	-0.0012
1202.3	3.5221	3.22482	34.5083	34.5148	3.22537	3.5221	3.22559	34.5175	0.0027
1401	3.039	3.19378	34.5452	34.5503	3.19420	3.039	3.19454	34.5544	0.0041
1599.6	2.6724	3.1719	34.5692	34.5769	3.17253	2.6724	3.17266	34.5785	0.0016
1999.1	2.1309	3.1445	34.6131	34.6194	3.14502	2.1309	3.14525	34.6223	0.0029
2400.2	1.7884	3.13273	34.6392	34.6463	3.13331	1.7884	3.13348	34.6484	0.0021
2798.9	1.5911	3.13234	34.6563	34.6645	3.13301	1.5911	3.13309	34.6655	0.0010
3200.1	1.4927	3.1397	34.6674	34.676	3.14039	1.4927	3.14045	34.6767	0.0007
3600.3	1.4587	3.15175	34.6737	34.6829	3.15250	1.4587	3.15250	34.6829	0.0000
4001.5	1.4537	3.16568	34.6772	34.6853	3.16634	1.4537	3.16644	34.6864	0.0011
4401.9	1.4766	3.18142	34.6790	34.6871	3.18208	1.4766	3.18218	34.6883	0.0012
4500.7	1.4868	3.18558	34.6788	34.6883	3.18636	1.4868	3.18634	34.6881	-0.0002
4600.8	1.4969	3.18976	34.6789	34.6883	3.19054	1.4969	3.19052	34.6881	-0.0002
4809.4	1.5119	3.19792	34.6795	34.6884	3.19865	1.5119	3.19868	34.6888	0.0004

Note: For Shaded section of table:
        Sum of CTD conductivity * Water Sample conductivity = 30.55649
        Sum of CTD conductivity * CTD conductivity = 30.54918
        Ratio used to correct CTD conductivity = 1.000239