Module 8

Getting the Highest Accuracy Data, Continued

Overview



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 O₂ sensors.
- Have heightened awareness about the handling of your conductivity sensor.

Field Calibrations



The *.con* 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 *.con* 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* 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.



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.



As we mentioned earlier, the SBE *9plus* 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: Temperature

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



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)

Field Calibrations: Checking for Leaks Run underwater package down deep to nice, uniform water Close all water bottles Run salinities on each water bottle Compare salinities, fix leakers, and repeat

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



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.



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.



The summation symbol, Sigma (Σ), denotes the addition of a series of values. The script on the bottom of the Σ 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 conductivity of these water samples is determined by a laboratory salinometer and paired with CTD data from the corresponding depths.

CTD Conductivity	Salinometer Conductivity
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

SE	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.

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

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

Step Two:	Conductivity	Correction
• Bottle conducti	vity is calculated a SeacalcW	at CTD corrected
 Note slope show 	wn in CTD – Bott	le conductivity
Note slope sho CTD conductivity	wn in CTD – Bott Bottle	le conductivity CTD – Bottle conductivity
Note slope show CTD conductivity 4.63421	wn in CTD – Bott Bottle conductivity 4.63481	le conductivity CTD – Bottle conductivity -0.00060
Note slope show CTD conductivity 4.63421 3.25349	wn in CTD – Bott Bottle conductivity 4.63481 3.25398	le conductivity CTD – Bottle conductivity -0.00060 -0.00049

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 =

 $\frac{(4.63421 * 4.63481) + (3.25349 * 3.25398) + (3.16777 * 3.16822)}{(4.63421 * 4.63421) + (3.25349 * 3.25349) + (3.16777 * 3.16777)} = 1.000138$

	Step Three:	Conductivity	Correction
•	Slope calculated from	m previous slide is 1.0	00138
•	Place slope in slope Corrected CTD cond	entry of conductivity of ductivity = CTD condu	calibration coefficients; activity * slope
•	Corrected CTD salir conductivity shown	nity is calculated from here, and corrected ter	corrected CTD nperature and pressure
•	Corrected CTD salir conductivity shown from Step 1	nity is calculated from here, and corrected ter	corrected CTD nperature and pressure
•	Corrected CTD salir conductivity shown from Step 1 Corrected CTD conductivity	hity is calculated from here, and corrected ter Corrected CTD salinity	corrected CTD nperature and pressure Bottle Salinity
•	Corrected CTD salir conductivity shown from Step 1 Corrected CTD conductivity 4.63485	hity is calculated from here, and corrected ter Corrected CTD salinity 34.9773	corrected CTD nperature and pressure Bottle Salinity 34.9770
•	Corrected CTD salir conductivity shown from Step 1 Corrected CTD conductivity 4.63485 3.25394	hity is calculated from here, and corrected ter Corrected CTD salinity 34.9773 34.4706	corrected CTD nperature and pressure Bottle Salinity 34.9770 34.4710

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



There are two mechanisms at work in oxygen sensor drift. Since the electrode remains polarized throughout its life, the electrolyte gets used up and there is some diminishing of the sensitivity of the electrode itself. There is also fouling, which can be *an event* like in the conductivity example. Check your oxygen data with bottle samples and make corrections to *Soc* at your discretion.



The basis for calculating dissolved oxygen is work done by Owens and Millard (1985). This equation includes a blank or zero oxygen term, *Boc*, and a term that is proportional to the first derivative of the oxygen sensor output voltage, $\tau * \delta V/\delta t$. The *Boc* term is redundant for the SBE 43, because the sensor output is offset by a *Voffset* term which takes the place of *Boc*.

The term that is proportional to the first derivative of the sensor output was introduced to sharpen the response of the sensor to rapid changes in oxygen concentration. The SBE 43 was designed for profiling applications and does not suffer the poor response times of previous sensors. In consideration of this, the derivative term is left out of the equation used to calculate oxygen concentration from output voltage for the SBE 43.



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.



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*.



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*).



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.



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 SBE43 values using the derived *Soc* and *Voffset*.



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 and learn how to fine tune it with adjustments to *pcor*.



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 *pcor*.





We can make the adjustment to *pcor* empirically. The plots above show the discrepancy between the SBE 43 calculated oxygen and the Winkler titrations with a series of *pcor* values. Clearly, the middle value of 1.5×10^{-4} 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