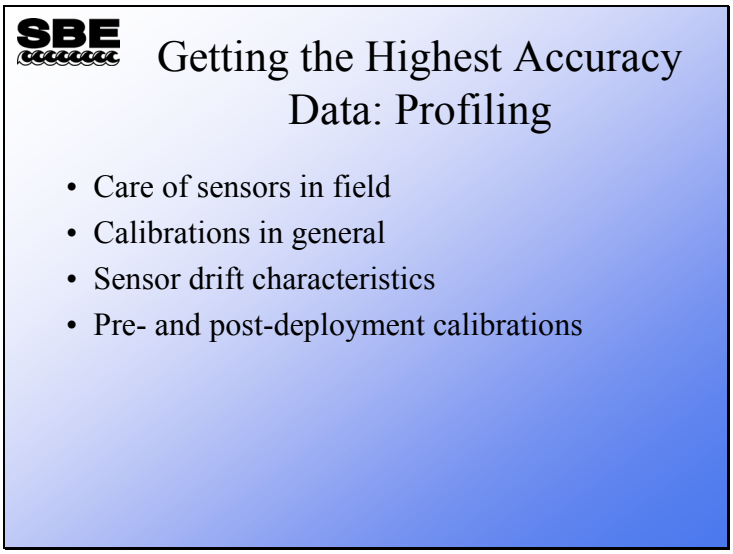
Module 7

Getting the Highest Accuracy Data

Overview

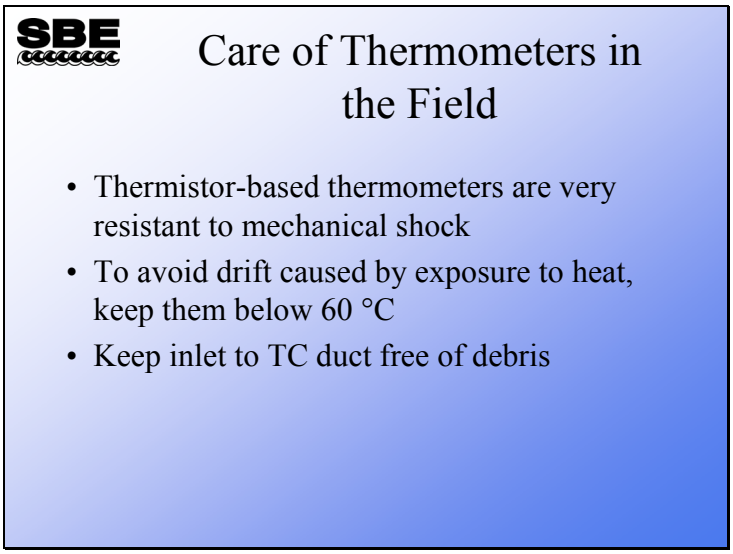


This module covers activities that will improve your data accuracy. Receiving the highest accuracy data from your instrument requires careful handling and attention to calibration. While thermometers are very robust and low maintenance, they still require regular calibration to make sure they are on their historical drift trajectory. A sensor that has a surface that interacts with the seawater, such as conductivity or dissolved oxygen, is another matter. These require careful handling, attention to calibration, and field calibration to assure the highest quality data.

When we finish this module you should be able to:

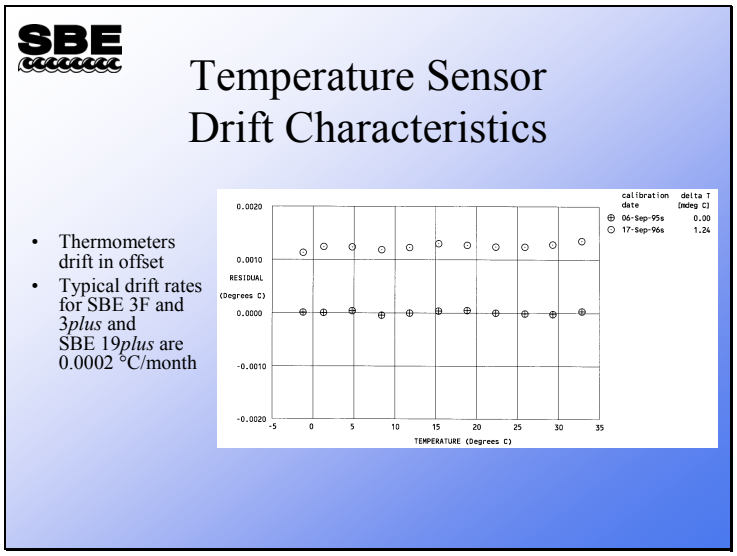
- Minimize handling-induced problems with your sensors.
- Correct your data for calibration drift.

Care of Thermometers in the Field



SBE 3 thermometers are essentially trouble-free. They are mechanically robust and are unaffected by extremes in temperature up to 60 degrees C.

Temperature Sensor Drift Over Time



Temperature sensors tend to drift in offset – that is, the measurements drift in a uniform way over the entire range of measurement. For temperature sensors, the drift direction is dependent on the instrument electronics, and is unique to each temperature sensor. This drift typically continues in the same direction for the entire life of the instrument.

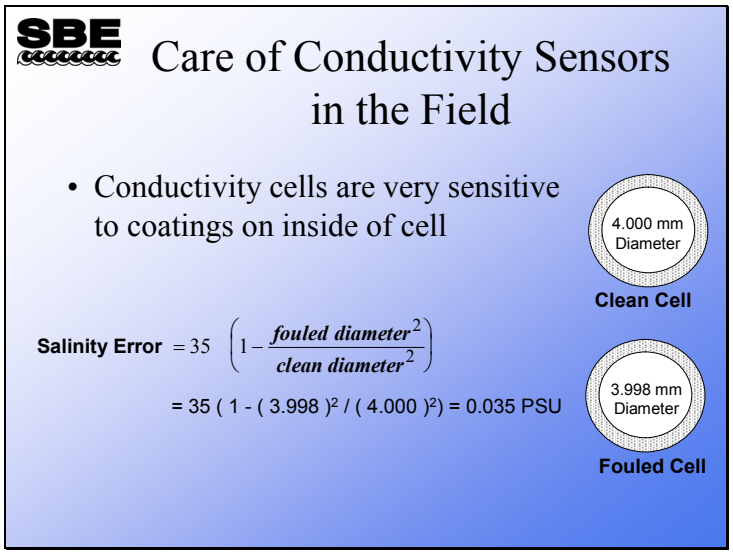
Sea-Bird calculates residual as:

Residual = instrument output – true value

Our calibration certificates always plot the residual on the y axis.

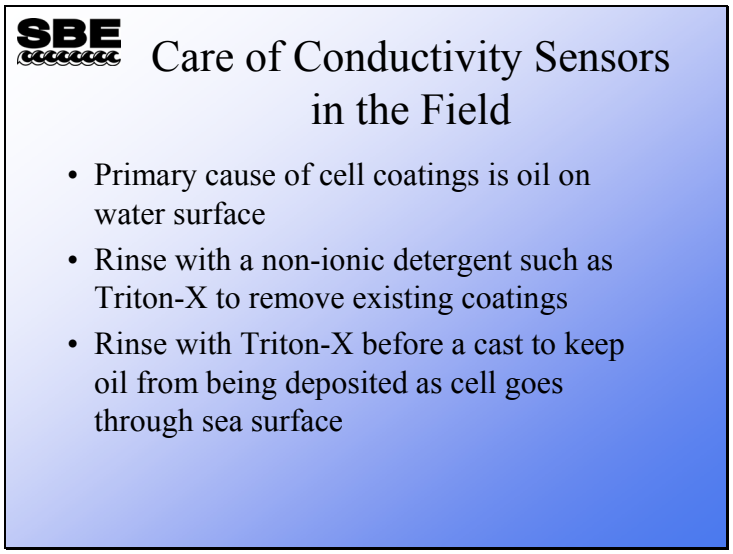
For the plot above, the original calibration in September 1995 shows a residual of 0. A check of the same sensor in September 1996 shows a residual of 1.24 millidegrees. As you can see, the residual is fairly constant across the entire range of the temperature calibration.

Care of Conductivity Sensors in the Field



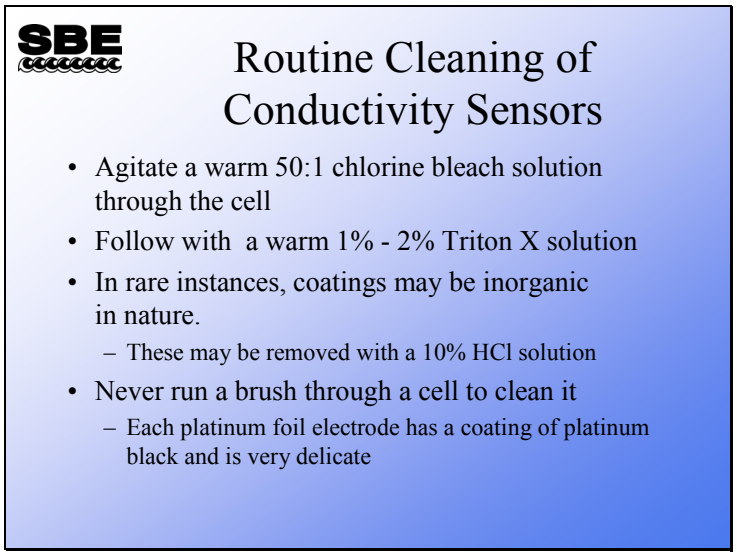
Conductivity sensors have parts that interact with the seawater. There are 3 electrodes that are subject to fouling, and a cell that must maintain constant dimensions. As the slide shows, a 0.001 mm coating will diminish the cell diameter by 0.002 mm, resulting in a salinity error of 0.035 PSU. A film thickness of 0.001 is not uncommon for oils on the sea surface. Another source of fouling is bacterial colonization.

Care of Conductivity Sensors in the Field (*continued*)



Sea-Bird supplies a small amount of Triton-X non-ionic detergent for cleaning conductivity cells. This will remove any oily coating, and an application before deployment will keep films from being deposited as the cell goes through the sea surface. Triton-X is a surfactant. A pre-deployment coating has the added advantage of wetting the electrodes, giving their surface a higher affinity to water.

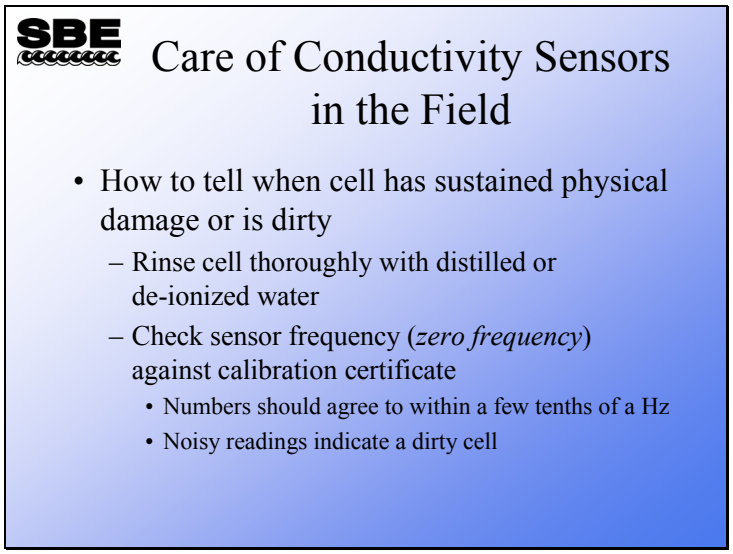
Care of Conductivity Sensors in the Field (*continued*)



The cleaning with dilute bleach and Triton-X may be repeated several times for badly fouled sensors.

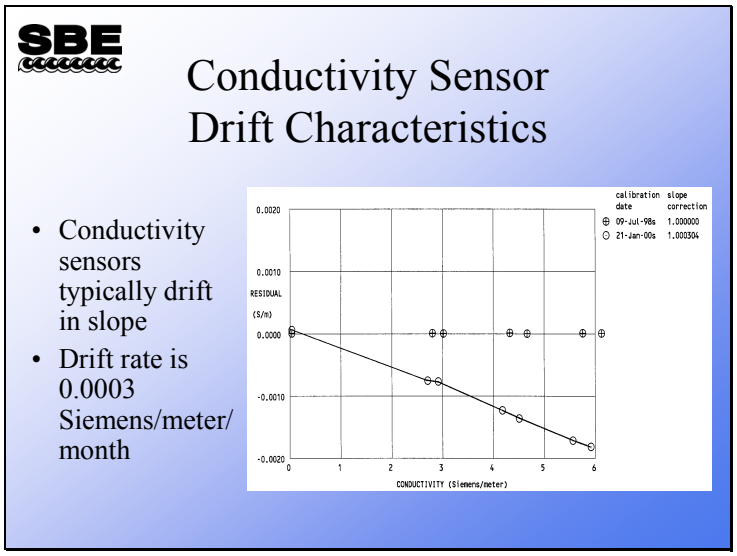
Sea lore has it that in some environments $CaCO_3$ or other inorganic coatings may accrete on the inside of the cell. This is more likely in a moored instrument. A 10% HCl solution will dissolve these. Rather than doing this aggressive cleaning yourself, Sea-Bird recommends that the sensor be returned to the factory for cleaning and inspection.

Care of Conductivity Sensors in the Field (*continued*)



Every conductivity calibration certificate has a frequency output for zero conductivity. This is obtained from a cell thoroughly rinsed in distilled or de-ionized water, with all the water shaken out. This means there are no electrical paths within the cell. A zero frequency that has changed by more that a few 10ths of a Hertz may indicate a cell that is damaged or considerably out of calibration. Noisy readings (± a few 10ths of a Hertz) indicate a dirty cell; we suggest a good rinse with dilute bleach and Triton-X.

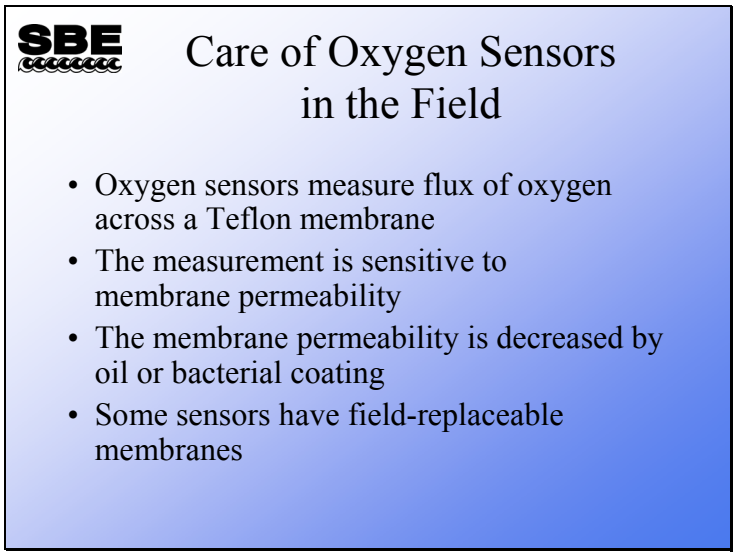
Conductivity Sensor Drift Over Time



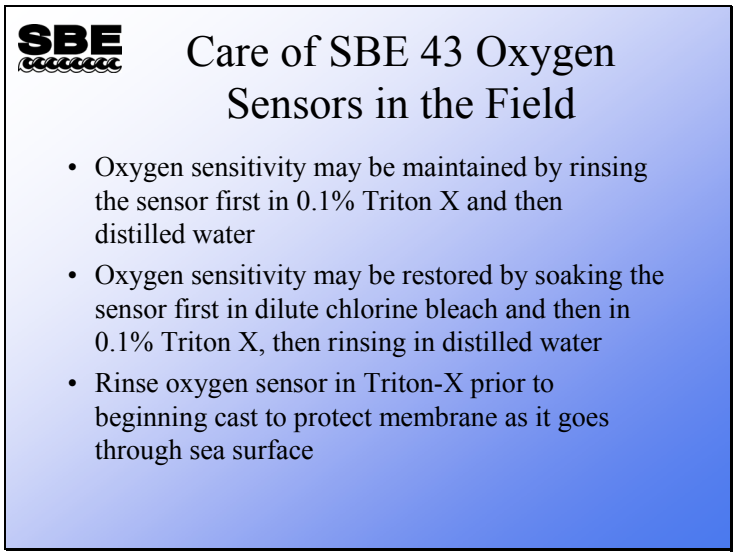
Conductivity sensors usually lose sensitivity as they drift. The drift takes the form of a slope. This is because the conductivity measured by the cell depends on the cell dimensions, which typically change due to fouling.

Note that conductivity cell drift is often episodic rather than linear. This is because fouling events often cause the most significant drift. Perhaps the sensor passes through an oil film when it enters the water, or sits on deck in a warm place full of seawater, growing bacteria on the cell surface.

Care of Oxygen Sensors in the Field



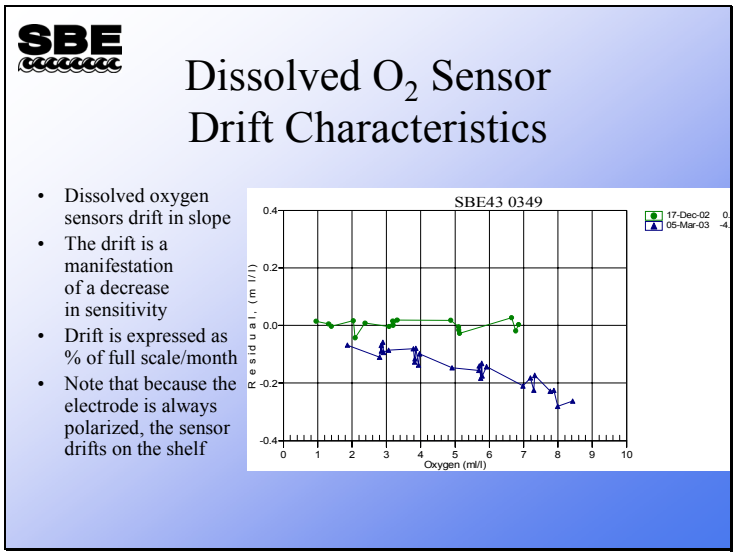
Care of Oxygen Sensors in the Field (*continued*)



In the past, we recommended using Triton X-100 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 is to continue to use Triton X-100 for degreasing (with a short wash), and to use a short wash with a dilute chlorine bleach solution to reduce biological growth.

- Avoid fouling the oxygen membrane with oil or grease as this directly affects (reduces) the sensor output.
- **Preventive Field Maintenance between Profiles**: After each cast, flush with a 0.1% solution of Triton X-100, using a 60 cc syringe, then rinse thoroughly with fresh water. Between casts, ensure that the membrane remains shaded from direct sunlight and stays cool and humidified.
- **Routine (post-cruise) Cleaning (no visible deposits or marine growths on sensor) -** Follow this two-step procedure:
  1. Soak the sensor for 1 minute in a 50:1 solution of bleach (50 parts de-ionized water to 1 part chlorine bleach). After the soak, drain and flush with warm (not hot) fresh water for 5 minutes.
  2. Soak the sensor for 1 minute in a 1% solution of Triton X-100 warmed to 40 ºC. 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.
- **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.**
  - To minimize drift during storage, connect 1 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.

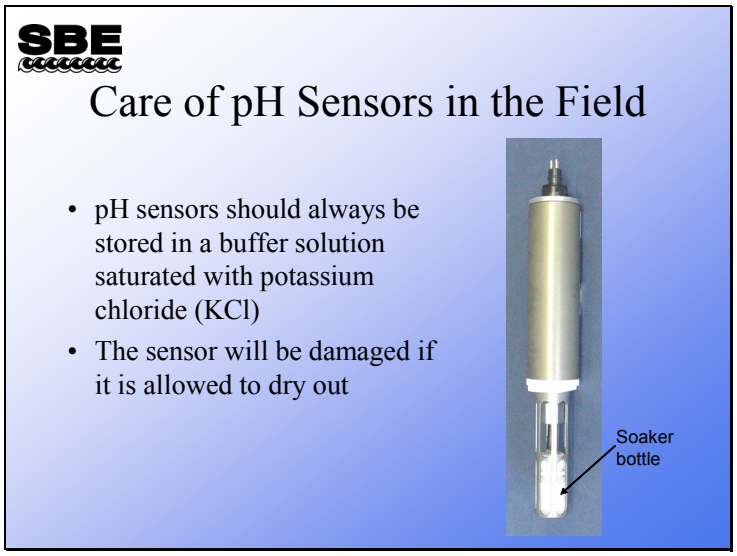
Dissolved Oxygen Sensor Drift Over Time



Dissolved oxygen sensor drift, like conductivity sensor drift, can be episodic in nature. It also has similar causes. The sensor depends on the diffusion of oxygen through a Teflon membrane. Any surface coating that slows the diffusion will affect the sensor sensitivity and its time response.

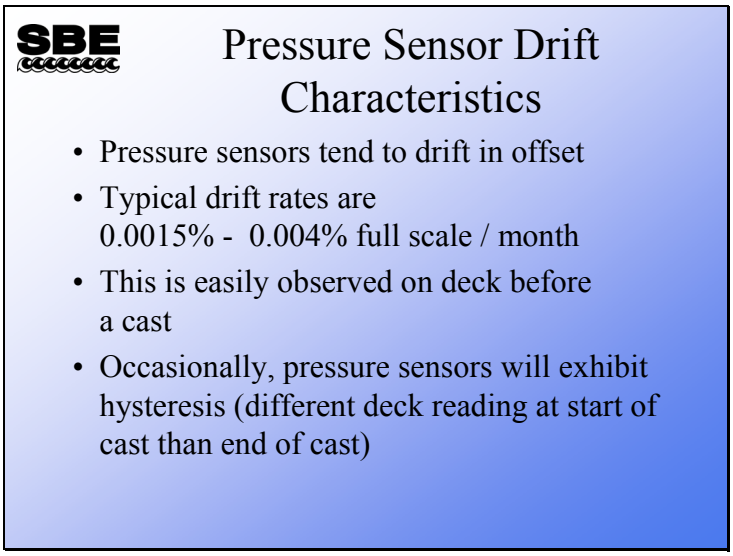
The oxygen sensor drifts in slope. The equation that converts sensor output to dissolved oxygen has a slope term, Soc, which gets larger as the sensitivity of the sensor decreases.

Care of pH Sensors in the Field



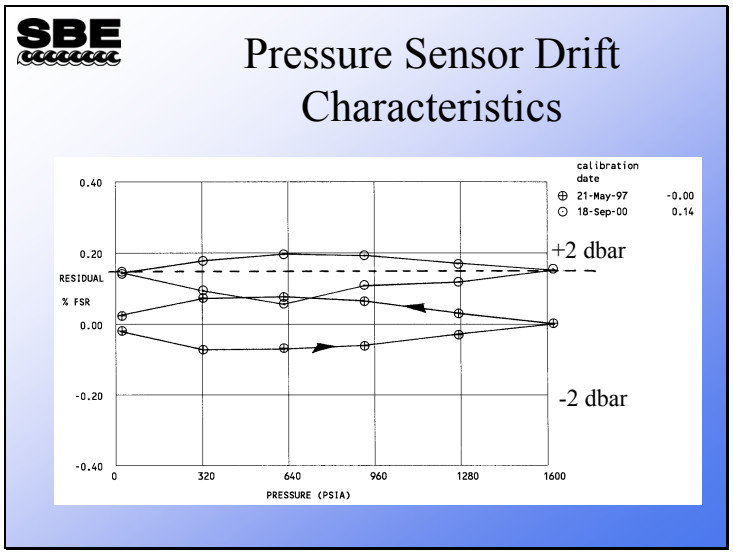
The pH electrode is porous and will dry out if left open to the air. It is always a good practice to keep it in clean, pH 4 buffer solution that has been saturated with potassium chloride (KCl). The electrolyte inside the pH sensor is saturated KCl.

Pressure Sensor Drift Over Time



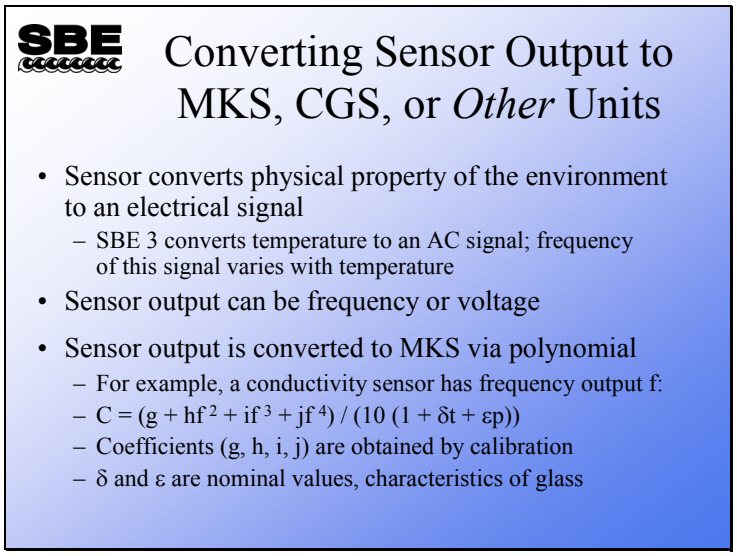
Pressure sensors are usually trouble-free. Drifts are generally in offset. The drift may be read on deck and entered into the coefficient dialog box to make the correction.

Pressure Sensor Drift Characteristics



Here is a plot showing the drift of a 1000 db strain gauge pressure sensor over a 3-year, 4-month period. This sensor meets its drift specification of 0.004% of Full Scale per month (0.00004/month * 1000 db * 40 months = 1.6 db). Also shown is hysteresis; this deviation from a linear behavior is within the sensor's specification for accuracy of 0.1% of Full Scale (0.001 * 1000 db = 1 db).

Converting Sensor Output to Scientific Units



As we have discussed, a sensor has an active element that interacts with the environment, and a conditioning circuit that converts the reaction into a signal that is measurable with normal techniques (e.g., Analog/Digital conversion or counting of a frequency). Having acquired a digital representation of temperature or conductivity, we need to convert this into units useful to scientists and engineers.

The simplest sensor might have a linear response to the environmental parameter of interest. For example, a transmissometer has a simple relationship between voltage output and percent transmittance of the water within its path:

$$\%T = (\text{slope} * \text{voltage output}) + \text{offset}$$

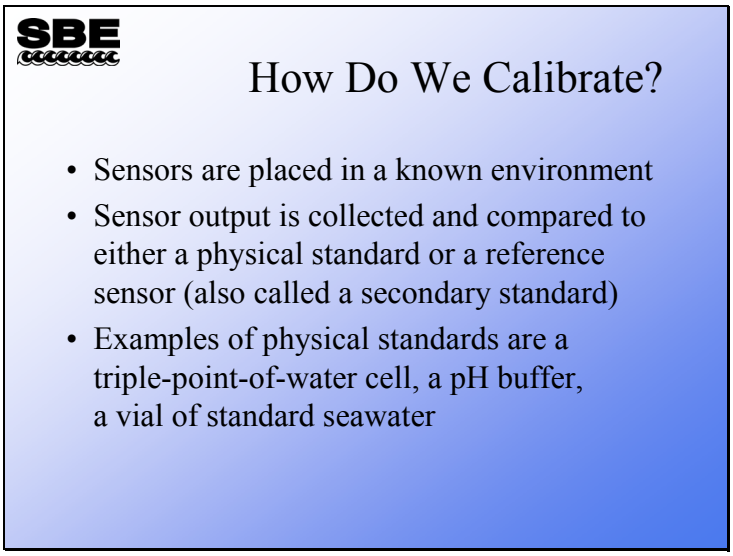
Unfortunately, the output of most sensors in response to environmental parameters is a complex polynomial, often parametric in nature. Consider the equation for conversion from SBE 3 output frequency to temperature. The response is a polynomial because the thermistor responds to changes in temperature in a non-linear fashion:

$$T\,[°C] = [1 / (g + hln(fo/f) + iln^2(fo/f) + jln^3(fo/f))] - 273.15$$

The conductivity sensor's response is a polynomial and parametric, because the sensor has secondary response to temperature and pressure:

$$C = (g + hf^2 + if^3 + jf^4) / (10 (1 + \delta t + \varepsilon p))$$

Converting to Scientific Units: Calibration

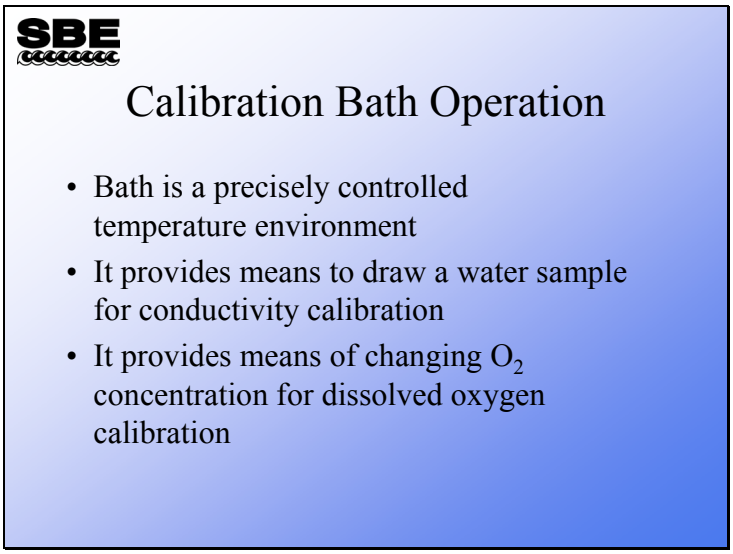


To calibrate a sensor, it is placed in a precisely controlled environment. The output of the sensor is collected at the same time as the environment is measured with a reference sensor. The reference sensor is carefully calibrated and has a well-known history. To gain the careful calibration and history, the reference is calibrated against physical standards such as the triple point of water and the melting point of gallium, or an agreed-upon standard such as IAPSO standard seawater.

Converting to Scientific Units: Calibration (*continued*)

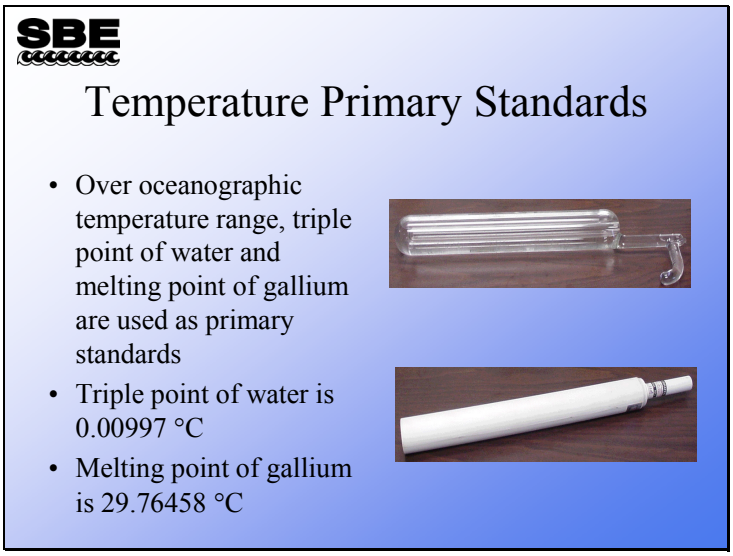
This bath design is common to all of Sea-Bird's calibration activities. The baths are highly insulated and well stirred, and they typically hold temperature to better than 0.0005 °C.

Converting to Scientific Units: Calibration (*continued*)



Baths of this design have been adapted for calibration of all of Sea-Bird's products. The basis is precisely controlled temperature and the ability to draw a water sample for salinity determination. The means to change partial pressures of Oxygen for SBE 43 calibration has been added.

Converting to Scientific Units: Calibration (*continued*)



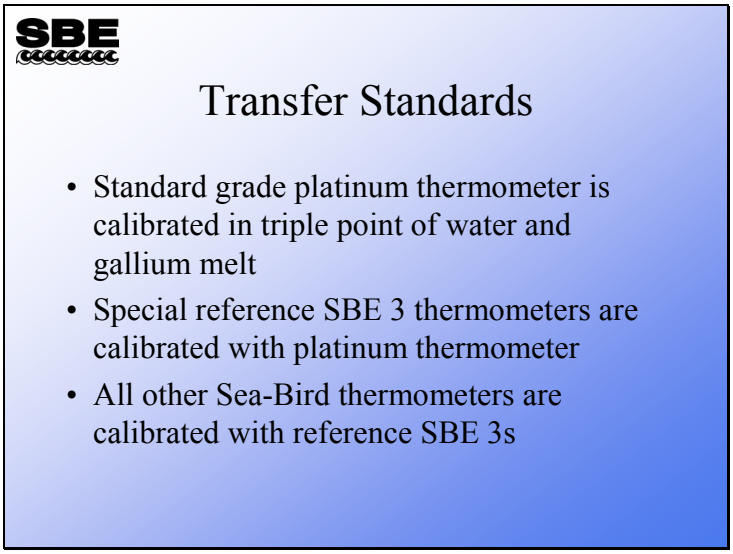
In considering calibration, one runs into the problem of knowing exactly what is the temperature of a particular object. If we only had thermometers to rely on, how do you know which one is right? Instead, we use physical standards. The Celsius temperature scale decrees that water freezes at 0 °C and boils at 100 °C; however, the freezing point and boiling point are subject to uncertainties such as atmospheric pressure. So, instead of the freezing and boiling point, we use two other points:

- The triple point - the temperature at which water exists as a liquid, a vapor, and a solid. The triple point of water is measured in a specially constructed cell that contains no air, only H_20, and occurs at 0.00997 °C.
- The melting point of extremely pure gallium, 29.76458 °C. This pins down the other end of the oceanographic scale.

We calibrate platinum reference thermometers at these points and then calibrate reference SBE 3 sensors with the platinum thermometers. This allows us to trace the temperature measurement used to calibrate all other thermometers back to the physical standards.

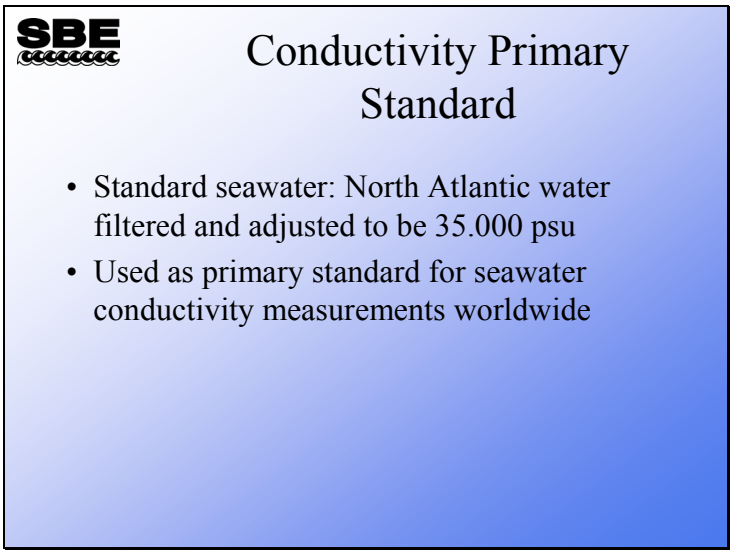
Fixed point cells are called this because when they are in the proper condition their temperature is fixed by the physics of the materials they are constructed of to be a single temperature. The triple point cells are maintained in a water bath very near their natural temperature. This allows them to last a long time. The gallium cells are melted slowly in an oven; the temperature where the gallium changes phase from solid to liquid is used as the calibration temperature.

Converting to Scientific Units: Calibration (*continued*)



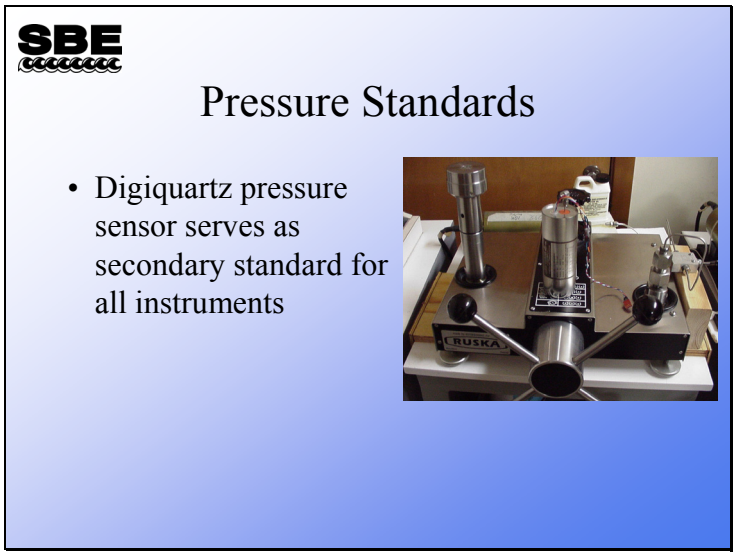
As was previously mentioned, a platinum thermometer is calibrated in the fixed point cells and then used to calibrate the SBE 3 reference thermometers. The platinum thermometer is susceptible to calibration shift due to impact or vibration; because of this it is impractical to use it in routine calibration. The SBE 3s are much more robust. By careful selection of the SBE 3 and the accumulation of a drift history, very accurate calibrations can be accomplished.

Converting to Scientific Units: Calibration (*continued*)



Unlike temperature, a primary standard for the conductivity of seawater is more difficult to come by. In recognition of this, IAPSO commissions the Ocean Scientific International Corporation to provide *standard seawater*. Ocean Scientific sends small ships out into the North Atlantic with large tanks to collect seawater. The seawater is filtered and adjusted in salinity to be 35.000. It is then sealed in vials or bottles and shipped to laboratories worldwide to be used in standardizing laboratory salinometers. Because everyone uses the same water to standardize their salinometers, we are all synchronized with Ocean Scientific. The standard seawater service has been going on for decades under the auspices of various committees of scientists. It was first produced by a laboratory in Copenhagen and was initially dubbed *Copenhagen water*.

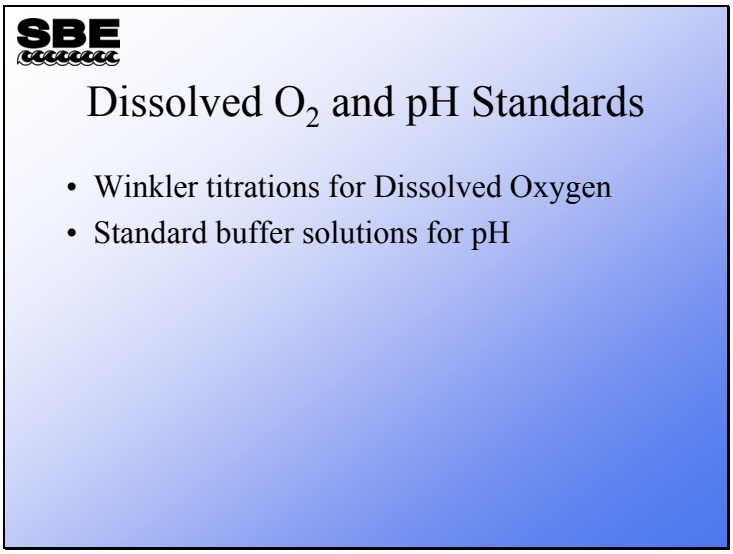
Converting to Scientific Units: Calibration (*continued*)



For instruments that have a strain gauge pressure sensor (Druck, Paine, Ametek, etc.), a complete pressure calibration is performed at Sea-Bird, using our Digiquartz pressure sensor as a secondary standard.

For instruments (SBE 9*plus*, 26*plus*, 53, etc.) that have a Digiquartz pressure sensor, a true calibration of the sensor is performed by the pressure sensor manufacturer. The quality of the Digiquartz is such that an adequate calibration requires a local gravity survey and dead weight tester parts that are certified by the National Institute of Standards and Technology. These requirements, plus the stability of the Digiquartz sensor, make the maintenance of this capability not cost effective for Sea-Bird. However, we do perform a slope and offset check of the pressure sensor in these instruments, using our Digiquartz pressure sensor as a secondary standard.

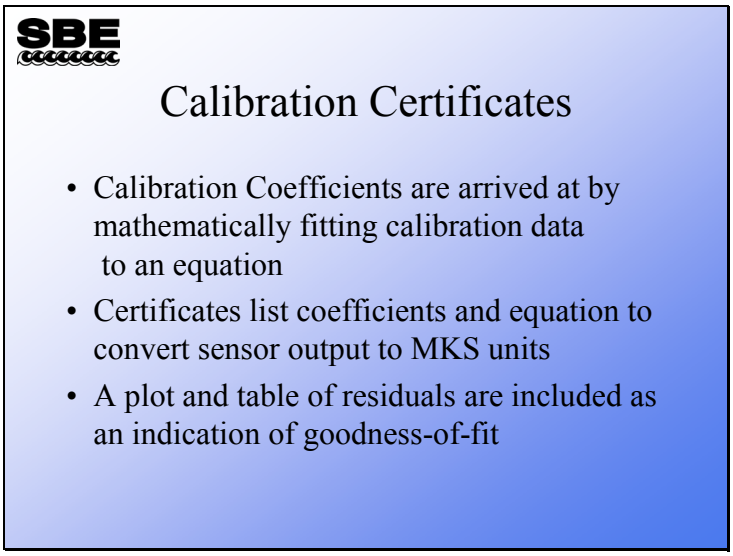
Converting to Scientific Units: Calibration (*continued*)



Dissolved oxygen sensors are calibrated in a bath that is plumbed with oxygen and nitrogen inputs. As gas concentrations are varied during calibration, Winkler samples are collected. These are titrated for dissolved oxygen concentration during the time of the calibration.

pH sensors are calibrated with commercially available buffer solutions.

Converting to Scientific Units: Calibration (*continued*)

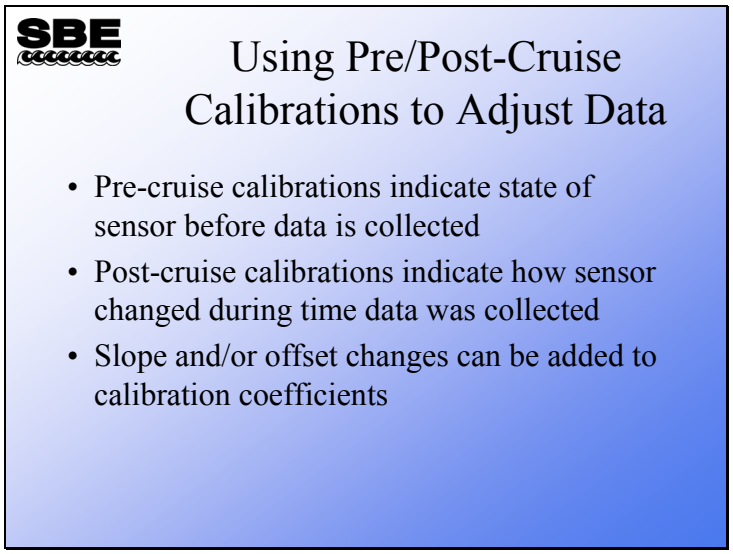


The calibration certificate is a listing of all the information required to convert sensor output to scientific units. There is also a table of calibration data and a plot of residuals that indicates a goodness-of-fit. Residuals are expressed as the difference between the instrument parameter and the bath parameter (the *true* value):

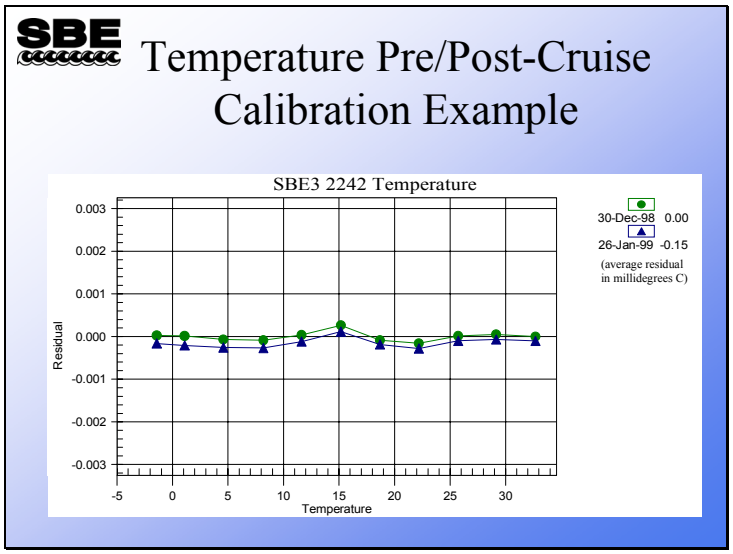
residual = instrument – bath

If the residual is positive, the sensor is reading high of reality; if negative, the sensor is reading low.

Using Calibrations to Improve your Data

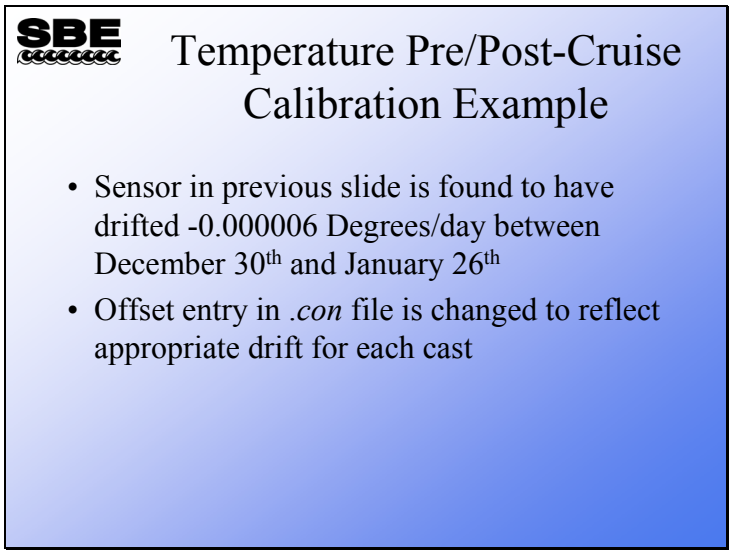


Temperature: Using Calibrations to Improve your Data



Temperature drift is shown to the right of the plot and is expressed as the average residual. The residual is the instrument temperature – the true temperature.

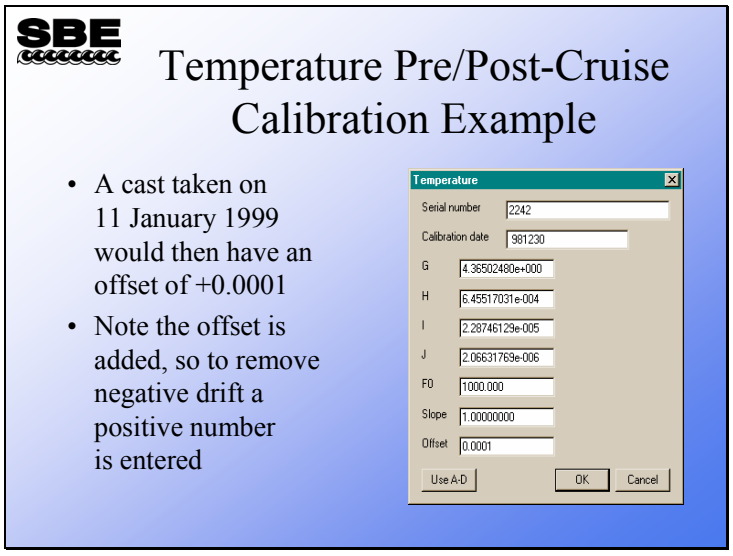
Temperature: Using Calibrations to Improve your Data (*continued*)



The SBE 3 in the previous slide drifted -0.00015 degrees over 27 days, this is -0.000006 degrees per day.

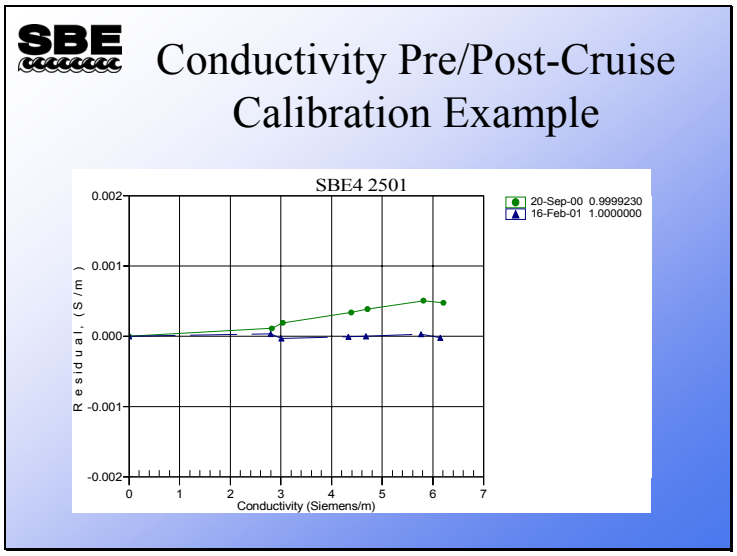
Application Note 31 has a detailed discussion of correcting thermometers with pre-cruise and post-cruise calibrations. Briefly, calibration coefficients are calculated with the post-cruise calibration. Using the post-cruise calibration coefficients and the pre-cruise calibration data, a mean residual over the calibration temperature range is calculated. The residual is the (instrument temperature - bath temperature). The mean residual is divided by the number of days since the pre-cruise calibration. This number is the offset per day. The offset per day is multiplied by the number of days between the pre-cruise calibration and the day the data was collected to get the offset that should be entered into the configuration file.

Temperature: Using Calibrations to Improve your Data (*continued*)



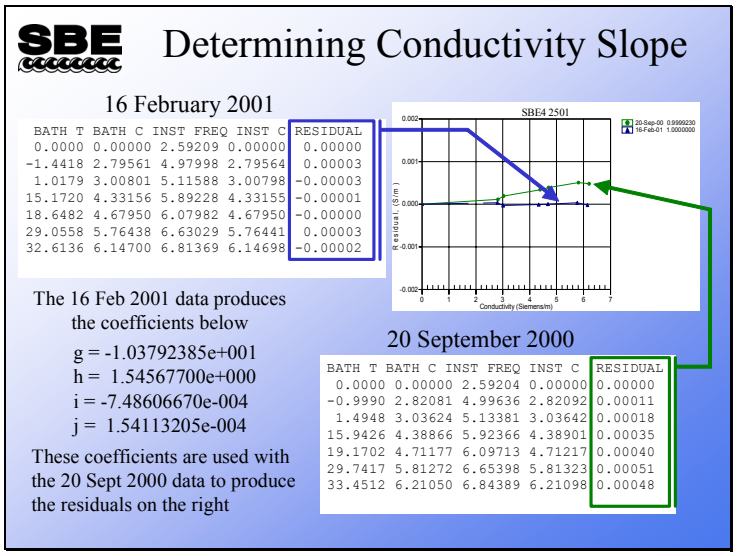
As we noted in the previous slide, the SBE 3 drifted -0.00015 degrees over 27 days, this is -0.000006 degrees per day. Because we are *adding* an offset in the .con file, we need to reverse the sign of the residual before entering it in the .con file (i.e., we need to add an offset of +0.000006 degrees per day). The first day of the cruise is January 11th. Therefore, the offset will be +0.000072 (0.000006 degrees/day x 12 days since the calibration) and will increase +0.000006 every day of the cruise. In the slide above we have rounded the offset to +0.0001.

Conductivity: Using Calibrations to Improve your Data



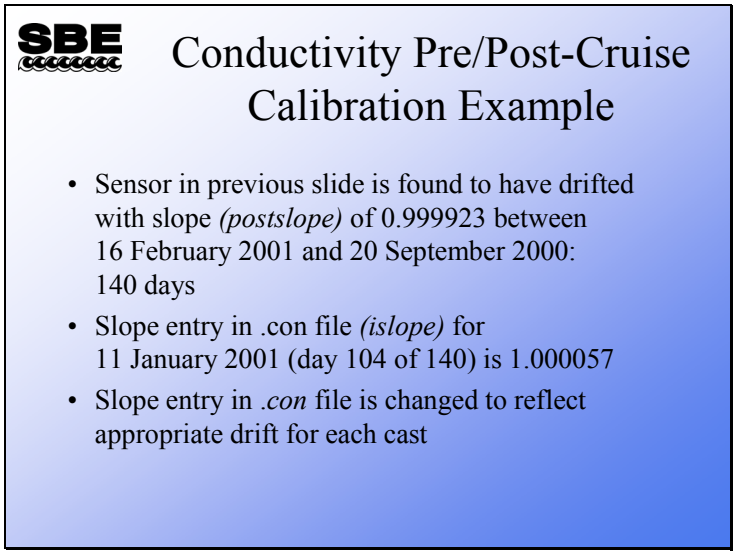
Conductivity sensors usually lose sensitivity as they drift. The drift takes the form of a slope. This is because the conductivity measured by the cell depends on the cell dimensions, which typically change due to fouling.

Conductivity: Using Calibrations to Improve your Data (*continued*)



Conductivity slope is determined by calculating calibration coefficients using data from one calibration date and applying the coefficients to data from another calibration date. Note that the residuals (instrument conductivity – true conductivity) are very small for the 16 February 2001 data. Using the calibrations coefficients calculated from the 16 February 2001 calibration data to calculate instrument conductivities results in the larger residuals seen in the 20 September 2000 data. The results of this show the error that would be incurred from calibration drift.

Conductivity: Using Calibrations to Improve your Data (*continued*)



Refer to Application Note 31 for a detailed discussion of how to apply pre- / post-cruise calibrations to SBE 4 conductivity sensors. Briefly, a calibration is done before and after the cruise. Let alpha be the conductivity that the instrument measured in the pre-cruise calibration, calculated using post-cruise coefficients. Let beta be the true conductivity of the pre-cruise calibrations. Then:

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

Where:
i = 1..n calibration points

The interpolated slope, which is entered in the coefficient dialog box, is:

$$islope = 1 + \left(\frac{b}{n}\right)\left(\frac{1}{postslope} - 1\right)$$

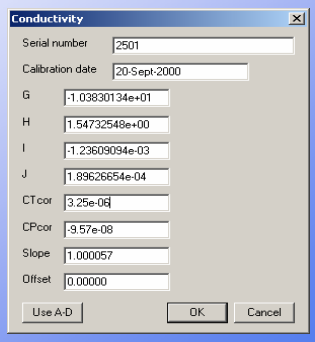
Where:
n = the number of days between pre- and post-cruise calibrations
b = the number of days between pre-cruise calibration and the cast to be corrected
islope = the interpolated slope, which is entered as the slope in the coefficient dialog box
postslope is calculated above

Example: Calculate *islope* for day 104 (11 January 2001) using calibration data from previous slide -
postslope = 0.999923 (at top right of calibration sheet in previous slide)
islope = 1 + (104 / 140) [(1 / 0.999923) – 1] = 1.000057

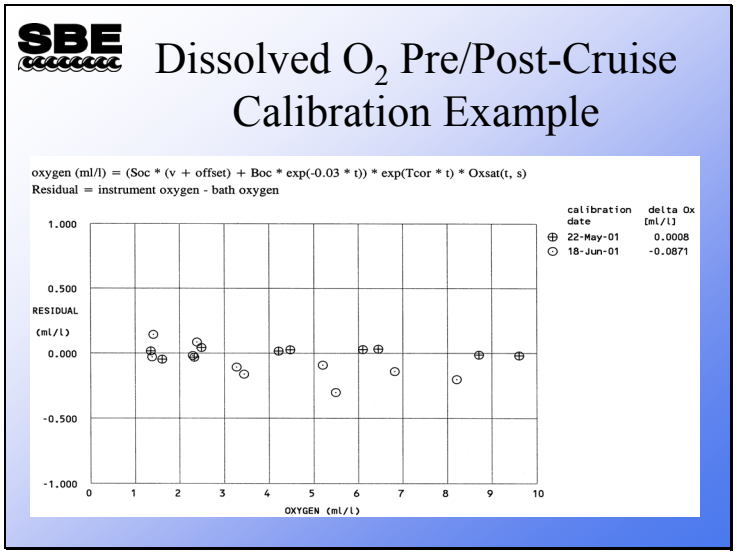
Conductivity: Using Calibrations to Improve your Data (*continued*)

Conductivity Pre/Post-Cruise Calibration Example

- A cast taken on 11 January 2001 would then have slope of 1.000057
- Typical slope corrections may be calculated on weekly interval

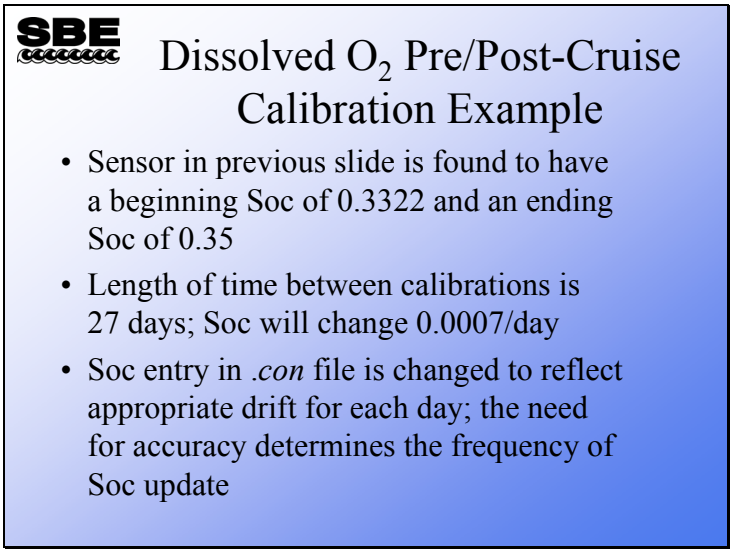


Oxygen: Using Calibrations to Improve your Data



Dissolved oxygen sensors are expected to drift in a similar manner to conductivity. For chemical reasons, they lose sensitivity over time. The equation for calculating oxygen concentration from sensor output has a slope term, Soc, and an offset term, Boc. It is expected that Soc will slowly increase with time, indicating a decrease in sensitivity.

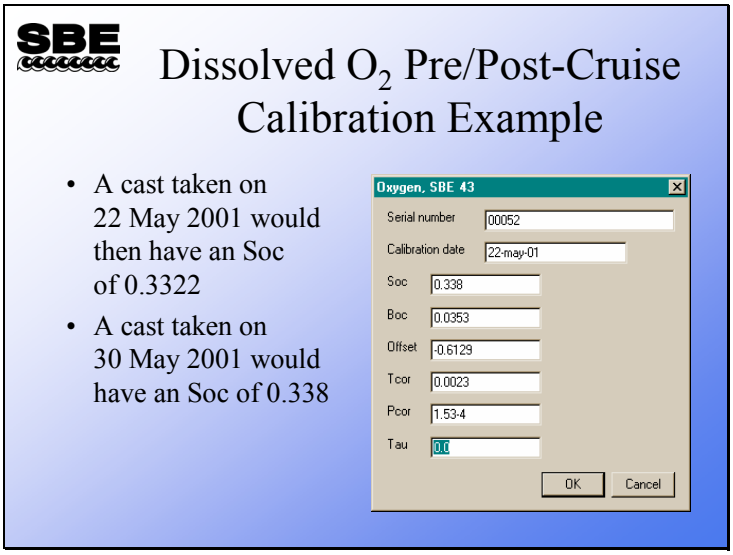
Oxygen: Using Calibrations to Improve your Data (*continued*)



The oxygen sensor calibration sheet provides the value for Soc (that portion of the calibration sheet is not shown in the previous slide).

Note that this strategy of drift correction assumes a uniform, linear change over the time between calibrations. A sensor that is handled carefully, both in deployment and on deck, will exhibit this behavior. However, fouling of the membrane by either oils or bacteria will result in a drift of a more episodic nature.

Oxygen: Using Calibrations to Improve your Data (*continued*)



A word about Tau:

Tau, a coefficient that is part of the Owens and Millard equation, relates oxygen sensor electrode current to dissolved oxygen concentration. Its purpose is to sharpen the oxygen sensor response to time by the inclusion of a derivative term in the equation.

Owens and Millard:

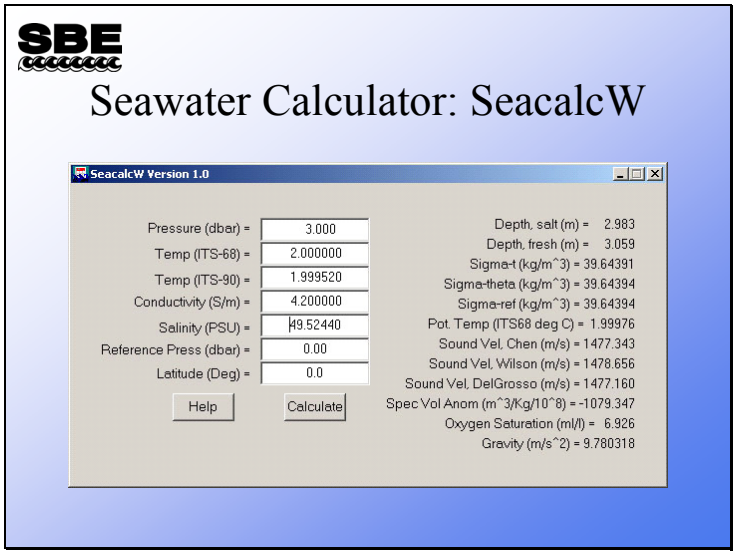
OX = [Soc * (oc + **tau** * doc/dt) + Boc] * OXSAT(T,s)*exp(tcor * [T + wt * (To - T)] + pcor * p)

Where the parts of this equation pertinent to this discussion are:

OX = oxygen concentration
Soc = Slope coefficient
oc = oxygen electrode current
tau = the coefficient we are discussing
doc/dt = the change in electrode current with time

Thus, Tau sharpens the response by adding a term dependent on the change of electrode current with time. This is an imperfect representation of the behavior of the sensor. Because of this, Sea-Bird recommends that Tau be set to zero. It is an entry in the calibration coefficients because it is still present in the equation. If you feel that your sensor could benefit from sharpening, feel free to experiment with Tau.

Calculating Parameters with SeacalcW



SeacalcW is a seawater calculator in SBE Data Processing that computes a number of derived variables from one user-input scan of pressure, temperature, and either conductivity or salinity.

- You can enter temperature in ITS-68 or ITS-90; SeacalcW automatically computes the other value.
- SeacalcW *remembers* whether you last changed conductivity or salinity, and calculates other parameters based on this. For example, if you change conductivity, salinity is recalculated; if you then change temperature, salinity is recalculated again (based on input conductivity and temperature). Conversely, if you change salinity, conductivity is recalculated; if you then change temperature, conductivity is recalculated again (based on input salinity and temperature.
- Reference pressure is used only to compute Sigma-ref.
- Latitude is used only to compute gravity and salt water depth.

Activity: Correct T & C via Pre / Post-Cruise Calibrations

Pressure db	CTD Temperature	CTD Conductivity	Uncorrected CTD Salinity	Corrected CTD Temp	Corrected CTD Cond	Corrected CTD Salinity	Water Bottle Salinity	Corrected CTD Salinity- Water Bottle Salinity
4.9	24.0798	5.236377	35.1885				35.2055	
519	6.6922	3.439905	34.0769				34.0848	
850.6	4.4142	3.276592	34.3667				34.3738	
1000.8	4.003	3.254754	34.4616				34.472	
1202.3	3.5221	3.224822	34.5083				34.5148	
1401	3.039	3.193778	34.5452				34.5503	
1599.6	2.6724	3.171902	34.5692				34.5769	
1800.5	2.3456	3.153669	34.5947				34.601	
1999.1	2.1309	3.1445	34.6131				34.6194	
2200.8	1.9531	3.138118	34.6259				34.6351	
2400.2	1.7884	3.132729	34.6392				34.6463	
2601.2	1.6718	3.131169	34.6486				34.6562	
2798.9	1.5911	3.132338	34.6563				34.6645	
3000	1.5372	3.135717	34.6623					
3200.1	1.4927	3.1397	34.6674				34.676	
3399.7	1.4739	3.145626	34.6708				34.6789	
3600.3	1.4587	3.151747	34.6737				34.6829	
3800.4	1.4465	3.157985	34.6763				34.6846	
4001.5	1.4537	3.165678	34.6772				34.6853	
4201.2	1.4608	3.173241	34.6785				34.689	
4401.9	1.4766	3.181421	34.6790				34.6871	
4500.7	1.4868	3.185577	34.6788				34.6883	
4600.8	1.4969	3.189761	34.6789				34.6883	
4809.4	1.5119	3.19792	34.6795				34.6884	

Note: Cruise date is 15 December 1999, Julian day 348.

(dates from calibration sheets)	**Temperature**	**Conductivity**
Pre-cruise calibration	23 November 1999, Julian day 326	17 June 1999, Julian day 167
Post-cruise calibration	28 December 1999, Julian day 361	30 December 1999, Julian day 363

Use the calibration data from the C and T calibration sheets on the following pages to answer these questions and fill in a few rows of the table:

1. Calculate a temperature offset for the cruise; apply the offset to the temperature data.
2. Calculate a conductivity slope for the cruise; apply the slope to the conductivity data.
3. Calculate corrected CTD salinity with SeacalcW. Compare the corrected CTD salinity to the salinity measured from the water bottle samples.

Corrected T and C using Pre- / Post-Cruise Calibrations

Pressure db	CTD Temperature	CTD Conductivity	Uncorrected CTD Salinity	Corrected CTD Temp	Corrected CTD Cond	Corrected CTD Salinity	Water Bottle Salinity	Corrected CTD Salinity- Water Bottle Salinity
4.9	24.0798	5.236377	35.1885	24.0798	5.237190	35.1947	35.2055	-0.0108
519	6.6922	3.439905	34.0769	6.6922	3.440439	34.0828	34.0848	-0.0020
850.6	4.4142	3.276592	34.3667	4.4142	3.277101	34.3726	34.3738	-0.0012
1000.8	4.003	3.254754	34.4616	4.003	3.255259	34.4676	34.472	-0.0044
1202.3	3.5221	3.224822	34.5083	3.5221	3.225323	34.5143	34.5148	-0.0005
1401	3.039	3.193778	34.5452	3.039	3.194274	34.5511	34.5503	0.0008
1599.6	2.6724	3.171902	34.5692	2.6724	3.172395	34.5753	34.5769	-0.0016
1800.5	2.3456	3.153669	34.5947	2.3456	3.154159	34.6006	34.601	-0.0004
1999.1	2.1309	3.1445	34.6131	2.1309	3.144988	34.6191	34.6194	-0.0003
2200.8	1.9531	3.138118	34.6259	1.9531	3.138605	34.6319	34.6351	-0.0032
2400.2	1.7884	3.132729	34.6392	1.7884	3.133216	34.6452	34.6463	-0.0011
2601.2	1.6718	3.131169	34.6486	1.6718	3.131655	34.6547	34.6562	-0.0015
2798.9	1.5911	3.132338	34.6563	1.5911	3.132824	34.6623	34.6645	-0.0022
3000	1.5372	3.135717	34.6623	1.5372	3.136204	34.6682		
3200.1	1.4927	3.1397	34.6674	1.4927	3.140188	34.6735	34.676	-0.0025
3399.7	1.4739	3.145626	34.6708	1.4739	3.146115	34.6768	34.6789	-0.0021
3600.3	1.4587	3.151747	34.6737	1.4587	3.152236	34.6796	34.6829	-0.0033
3800.4	1.4465	3.157985	34.6763	1.4465	3.158475	34.6823	34.6846	-0.0023
4001.5	1.4537	3.165678	34.6772	1.4537	3.166170	34.6832	34.6853	-0.0021
4201.2	1.4608	3.173241	34.6785	1.4608	3.173734	34.6845	34.689	-0.0045
4401.9	1.4766	3.181421	34.6790	1.4766	3.181915	34.6851	34.6871	-0.0020
4500.7	1.4868	3.185577	34.6788	1.4868	3.186072	34.6849	34.6883	-0.0034
4600.8	1.4969	3.189761	34.6789	1.4969	3.190256	34.6849	34.6883	-0.0034
4809.4	1.5119	3.19792	34.6795	1.5119	3.198417	34.6856	34.6884	-0.0028