Application Notes

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APPLICATION NOTE NO. 18-1 **Revised September 2014**

SBE 18, 27, and 30, and AMT pH Sensor Calibration (PHFIT Version 2.1)

This application note applies to the **SBE 18** pH sensor, **SBE 27** pH/ORP (Redox) sensor, **SBE 30** DO/pH/ORP sensor, and **AMT** Analysenmesstechnik GmBh pH sensor.

Sea-Bird software calculates pH as:

$pH = 7 + (Vout - offset) / (1.98416 \times 10^{-4} \times T * slope)$ (see Appendix for derivation of equation)

where
T = temperature (ºK)
Vout = output voltage from pH sensor (0 - 5 volts)
Offset and slope = calibration coefficients, determined by a least-squares fit of voltage and pH in a series of buffer solutions, using the measured temperature of the buffer solutions; coefficients are calculated using PHFIT software

Sea-Bird includes a calibration sheet with the shipment. The calibration sheet provides values for *offset* and *slope*, which have been input by Sea-Bird in the configuration (.con or .xmlcon) file.

Note: If you purchase an AMT sensor as a separate item, not integrated with a Sea-Bird CTD, Sea-Bird provides only the calibration sheet from AMT. This calibration sheet calculates pH as:
$pH = a + bV$
where a and b are calculated by AMT using a least-squares fit of voltage and pH in a series of buffer solutions. If you will be integrating the AMT sensor with a Sea-Bird CTD, use the voltage and pH values from AMT's calibration sheet (and 25 ºC for the temperature) to generate the offset and slope as described below in User Recalibration.

User Recalibration

Sea-Bird provides PHFIT software to use when calibrating pH sensors. PHFIT is installed when you install SBE Data Processing (part of the Seasoft software package). PHFIT can be used on computers running Windows XP service pack 2 or later, Windows Vista, Windows 7, or Windows 8.

- PHFIT installation was added in SBE Data Processing version 7.22.5a, and Seasoft version dated April 26, 2013 (it was previously available as part of our DOS software package, and was incompatible with Windows 7 and 8).
- The latest version of SBE Data Processing and Seasoft are available for download from our website.
- phfit.exe is installed in the same directory as SBE Data Processing (default location C:\Program Files\Sea-bird\SBEDataProcessing-Win32).
- **phfit.exe must be run from a DOS window**.

Note: A recommended source of buffer solutions is https://us.vwr.com/store/catalog/product.jsp?catalog_number=97021-450.

When needed, recalibrate the pH sensor as follows:

1. Prepare a series of buffer solutions (up to 25 solutions); maintain each at approximately the same temperature. Record the temperature.

2. Measure and record the output voltage from the pH sensor for each buffer solution.
Note: For the SBE 18, 27, and 30, an electrical connection between the buffer solution and the anode on the top of the sensor must be made while measuring pH.

3. Run PHFIT from a **DOS window**:
   A. At the prompt, enter the sensor serial number and the temperature (in ºC) of the buffer solutions.
   B. At the prompt, enter the pH and output voltage (Vout) for up to 25 buffer solutions. When you have finished, the program outputs the offset and slope, along with the residuals.

4. Enter the new offset and slope in the CTD's configuration (.con or .xmlcon) file. Instructions are provided below for modifying the configuration file using SBE Data Processing (in Seasoft V2):
   A. Double click on SBEDataProc.exe.
   B. In the Configure menu, select the applicable CTD.
   C. In the dialog box, click Open and select the applicable .con or .xmlcon file for the CTD.
   D. In the sensor list, double click on the pH sensor.
   E. Enter the new offset and slope in the dialog box and click OK.
   F. Click Save or Save As to save the changed configuration (.con or .xmlcon) file.

Appendix - Derivation of Sea-Bird Equation

Vout = offset + [slope * (R * T / F) * ln (10) * (pH - 7)]

Where
R = gas constant = 8.31434
F = Faraday constant = 9.64867 x 10^{-4}
T = temperature (ºK)
Vout = output voltage from pH sensor (0 - 5 volts)

Substituting for R, F, and ln (10):

Vout = offset + [slope * 1.98416 x 10^{-4} * T * (pH - 7)]

Therefore,

pH = 7 + (Vout - offset) / (1.98416 x 10^{-4} x T * slope)

Application Note Revision History

Date	Description
June 1992	Initial release.
July 2001	Add information on AMT pH sensor.
March 2005	Correct typo -- Faraday constant was 9.64867e-04, should be 9.64867e+04.
February 2010	• Change Seasoft-Win32 to Seasoft V2. • Add information on .xmlcon files. • Update address.
April 2013	Update for newer version of PHFIT, which is now installed with Windows software, in same directory as SBE Data Processing.
September 2014	Added URL for a buffer solution supplier.

SBE 18, 22, 27, and 30 pH Sensor Storage, Maintenance, and Calibration

(Revised June 2016)

Preparing to Deploy pH Sensor

1. Unscrew the sensor guard.
2. Unscrew the soaker bottle cap, and remove the soaker bottle. An O-ring on the pH electrode retains the cap.
3. Reinstall the sensor guard for deployment.
4. Sea-Bird ships the pH sensor with 2 spare *solid* caps to prevent spillage when the soaker bottle is not installed. Place one of these caps on the soaker bottle and store.

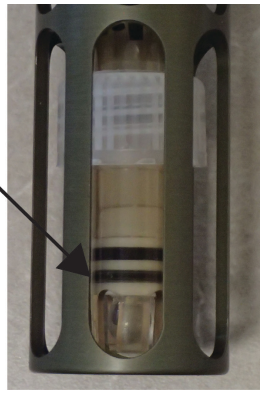
CAUTION: When removing or installing the soaker bottle, do not force the pH electrode sideways. The electrode's outer shell is plastic, but the **inner stem is glass and can break if the electrode is handled roughly.**

Note: All photos are of an SBE 18; details for other sensors are similar.

Storing pH Sensor after Recovery

Optimal performance is obtained when the sensor stays hydrated during storage:

1. Unscrew the sensor guard.
2. Remove the *solid* cap from the soaker bottle.
3. Slide the cap that was retained on the electrode down to the O-ring that is retaining it. Thread the soaker bottle onto the cap.
4. Verify that there is enough fluid in the bottle to cover the end of the probe up to the first O-ring (as shown in the photo).
5. Reinstall the sensor guard.
6. Store the sensor in an upright position (soaker bottle end down).



The *soaker* fluid is 4 Molar Potassium Chloride Saturated with Silver Chloride. Additional solution, if required, may be made using commercially available buffer capsules, KCL crystals, and distilled water. Replace the soaker solution as needed to keep the sensor submerged at least up to the first O-ring.

The sensor will tolerate the periodic absence of the soaker bottle and can be returned to initial performance by soaking for a few hours. However, **exposure of the bare sensor to temperature extremes (e.g., strong direct sunlight on a hot day) can cause a loss of internal electrolyte**. Subsequent cooling will draw air into the sensor, which will lead to pressure-related problems.

Note: The sensor contains a non-organic electrolyte and antibacterial inhibitors designed to optimize its use in marine environments.

Calibrating the pH Sensor

Note: A recommended source of buffer solutions is https://us.vwr.com/store/catalog/product.jsp?catalog_number=97021-450.

Sea-Bird recommends that you recalibrate your pH sensor at the start of every cruise, and then at least once per month, depending on use and storage.

Sea-Bird pH sensors are calibrated with commercial buffer solutions (±0.02 pH). Make periodic corrections by comparison to buffers near the anticipated in situ pH, typically in the 7 - 8 pH range. Best calibration of the sensor is obtained by soaking the sensor in KCl solution (described above in *Storing pH Sensor after Recovery*) for 30 minutes prior to standardization with buffers.

To calibrate:

1. For easier access during calibration, remove the pH sensor from the mount kit holding it to the CTD, but leave the pH sensor cable connected to the CTD end cap.
2. Run Seasave V7, set it up to display the pH voltage (the voltage channel for the pH data is listed on the instrument configuration page in your CTD manual), and start real-time data acquisition.
3. Connect a small-gauge wire to one of the screws at the connector end of the sensor housing and put the other end into the buffer solution bottle.
4. Put the pH probe in the buffer solution and wait 1 minute for complete stabilization. Note the resulting voltage on the computer display.
5. Repeat this process for at least two other values of pH, preferably *bracketing* the range of interest. **Rinse the pH electrode in deionized water between measurements in the different pH buffer solutions.**

See Application Note 18-1 for information about use of the PHFIT program for calculation of pH calibration coefficients. Enter the new coefficients generated by PHFIT in the CTD configuration (.con or .xmlcon) file.

Note: In our Seasoft V2 suite of programs, edit the CTD configuration (.con or .xmlcon) file using the Configure Inputs menu in Seasave V7 (real-time data acquisition software) or the Configure menu in SBE Data Processing (data processing software). Select pH as a voltage sensor when editing the configuration file; the software prompts for slope and offset.

Application Note Revision History

Date	Description
June 1992	Initial release.
July 2001	Add information on AMT pH sensor.
March 2005	Incorporate Seasave V7.
February 2012	• Change Seasoft-Win32 to Seasoft V2. • Add information on .xmlcon file. • Update address
January 2013	Correct description of soaker solution.
January 2014	Add more information on removing/replacing soaker bottle, storing soaker bottle during deployment, and replacing soaker solution when low.
September 2014	• Add URL for a buffer solution supplier. • Add information to store the sensor in an upright position (soaker bottle end down)
June 2016	• Change recommendation for soaking prior to standardization with buffers (soak in KCl instead of deionized water). • Add recommendation on calibration frequency.

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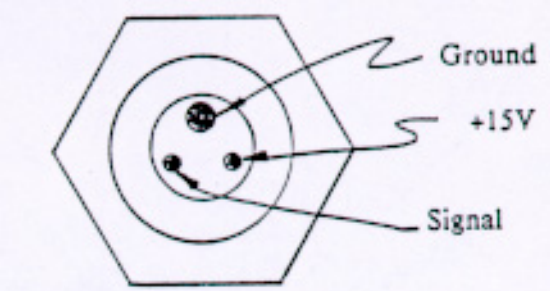
APPLICATION NOTE 18-3 **JULY 2001**

SBE 18 pH Sensor Hookup Instructions

To minimize chances of corrosion, avoid metal-to-metal contact of the aluminum instrument case with the mounting device -- e.g., use insulating tape or heat-shrink tubing over stainless steel hose clamps if they are used to mount the instrument.

The instrument case is filled with dry nitrogen. If it is necessary to open the case at any time, refill the case with nitrogen to prevent possible condensation at low temperatures.

The pin configuration on the instrument case is:



Outside view of Connector

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APPLICATION NOTE NO. 57 **Revised January 2014**

Connector Care and Cable Installation

This Application Note describes the proper care of connectors and installation of cables for Sea-Bird instruments. The Application Note is divided into three sections:

- Connector Cleaning and Inspection, and Cable / Dummy Plug Installation
- Locking Sleeve Installation
- Cold Weather Tips

Note: All photos in this Application Note show standard Impulse XSG/AG connectors. Except as noted, all procedures apply to standard XSG/AG connectors as well as to optional *wet-pluggable* MCBH connectors.

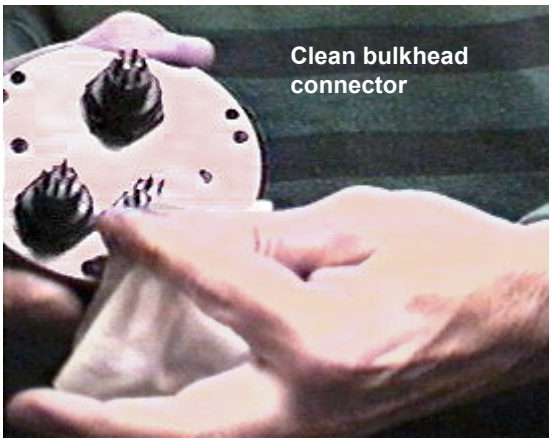
Connector Cleaning and Inspection, and Cable / Dummy Plug Installation

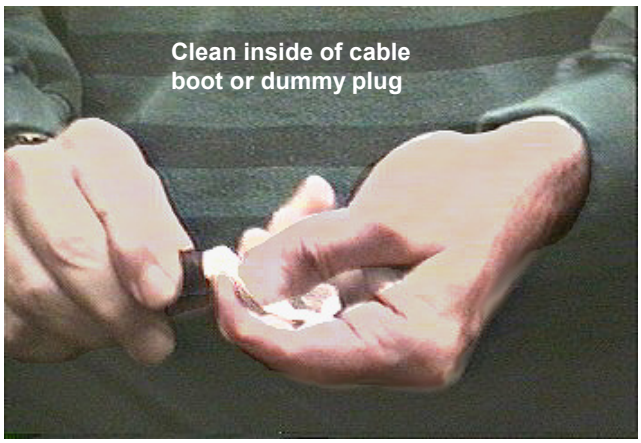
Clean and inspect connectors, cables, and dummy plugs:

- Before every cruise.
- During the cruise – This is a good practice if you have a few days of down time between casts.
- After every cruise – This is the best way to find and remove any corrosion on connector pins before severe corrosion develops.
- As part of your yearly equipment maintenance.

Follow this procedure:

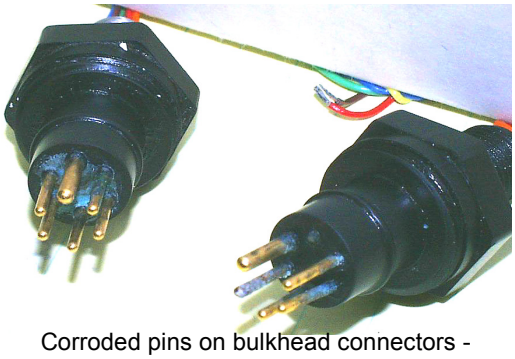
1. Carefully clean the bulkhead connector and the inside of the mating cable's boot or the dummy plug with a Kim wipe. Remove all grease, hair, dirt, and other contamination. **See Cautions in Step 3 regarding lubricants.**





2. Inspect the connector and cable boot or dummy plug:
   A. Inspect the pins on the bulkhead connector for signs of corrosion. The pins should be bright and shiny, with no discoloration. If the pins are discolored or corroded, clean with alcohol and a Q-tip.
   B. Inspect the bulkhead connector for chips, cracks, or other flaws that may compromise the seal.
   C. Inspect the cable boot or dummy plug for cuts, nicks, breaks, or other problems that may compromise the seal.

   Replace severely corroded or otherwise damaged connectors, cables, and dummy plugs - contact Sea-Bird for instructions and a Return Material Authorization (RMA) number.



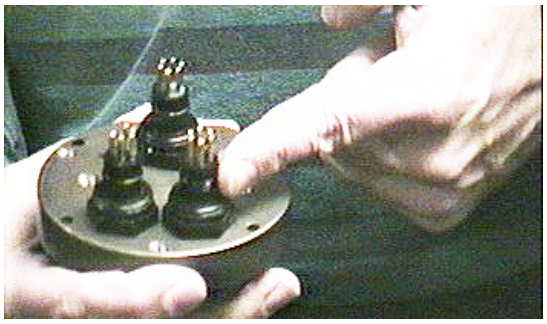
Corroded pins on bulkhead connectors - Connector on right has a missing pin

3. Using a tube of 100% silicone grease (Dow DC-4 or equivalent), grease the bulkhead connector and the cable boot or dummy plug.

CAUTIONS:

- **For all connectors: Do not use WD-40 or other petroleum-based lubricants, as they will damage the connectors.**
- **For optional wet-pluggable MCBH connectors: Silicone lubricants in a spray can may contain ketones, esters, ethers, alcohols, or glycols in their propellant. Do not use these sprays, as they will damage the connectors.** Teledyne Impulse sells a silicone lubricant in a pump spray bottle that may be used with these connectors.

A. Squeeze the silicone grease -- approximately half the size of a pea -- onto the end of your finger. Apply a light, even coating of grease to the molded ridge around the base of the bulkhead connector. The ridge looks like an O-ring molded into the bulkhead connector base and fits into the groove of the mating cable boot or dummy plug.



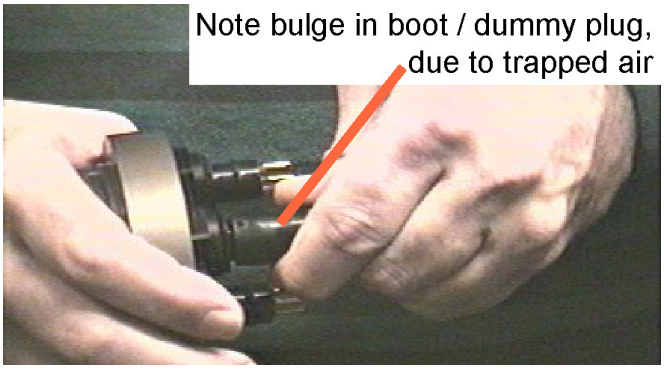
B. Squeeze approximately half the size of a pea of the silicone grease onto the end of your finger. Apply a light, even coating of grease to the inside of the cable boot or dummy plug.

4. *Standard XSG/AG connectors only:* Align the *bump* on the cable boot or dummy plug with the large pin on the bulkhead connector, and align the sockets with the pins.

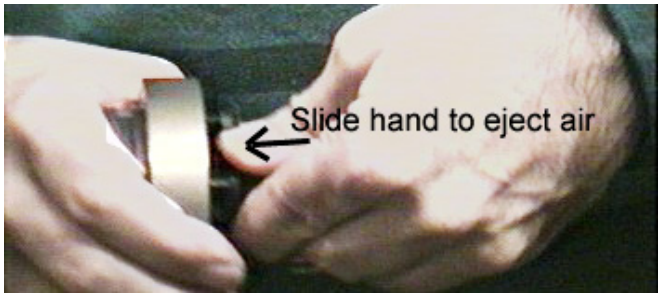
   Optional wet-pluggable MCBH connectors only: Align the non-conducting guide pin and the conducting pins with the mating sockets.

   - Do not twist the cable boot or dummy plug on the bulkhead connector; twisting can lead to bent pins, which will soon break.

5. Push the cable boot or dummy plug all the way onto the bulkhead connector.
   - *Standard XSG/AG connectors only:* You may note a bulge in the boot or dummy plug, which is due to trapped air. There may be an audible pop, which is good. With some newer cables or dummy plugs, or in cold weather, there may not be an initial audible pop.



6. *Standard XSG/AG connectors only:* After the cable or dummy plug is mated, run your fingers along the cable boot or dummy plug toward the bulkhead connector, *milking* any trapped air out of the boot or plug. You should hear the air being ejected.
   CAUTION:
   Failure to eject the trapped air will result in the connector leaking.



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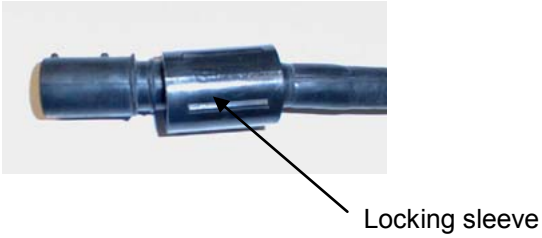
Locking Sleeve Installation

After the cable boot or dummy plug is mated to the bulkhead connector, install the locking sleeve. The locking sleeve secures the cable or dummy plug to the bulkhead connector and prevents them it being inadvertently removed. Important points regarding locking sleeves:

- Tighten the locking sleeve by hand. **Do not** use a wrench or pliers to tighten the locking sleeve. Over-tightening will gall the threads, which can bind the locking sleeve to the bulkhead connector. Attempting to remove a tightly bound locking sleeve may instead result in the bulkhead connector actually unthreading from the end cap. A loose bulkhead connector will lead to a flooded instrument. **Pay particular attention when removing a locking sleeve to ensure the bulkhead connector is not loosened**.
- It is a common misconception that the locking sleeve provides watertight integrity. **It does not, and continued re-tightening of the locking sleeve will not *fix* a leaking connector**.
- As part of routine maintenance at the end of a day's casts, remove the locking sleeve, slide it up the cable, and rinse the connection (still mated) with fresh water. This will prevent premature cable failure.



Cold Weather Tips

In cold weather, the cable or dummy plug may be hard to install and remove.

Removing a *Frozen* Cable Boot or Dummy Plug:

1. Wrap the cable boot or dummy plug with a washrag or other cloth.
2. Pour hot water on the cloth and let it sit for a minute or two. The cable boot or dummy plug should thaw and become flexible enough to be removed.

Installing a Standard XSG/AG Cable or Dummy Plug:

When possible, install cables and dummy plugs in warm environments. If not, warm the cable boot or dummy plug sufficiently so it is flexible. A flexible cable boot or dummy plug will install properly.

Note about Wet-Pluggable (MCBH) Connectors:

As an option, Sea-Bird offers *wet-pluggable* (MCBH) connectors in place of the standard Impulse XSG/AG connectors. Wet-pluggable connectors have a non-conducting guide pin to assist pin alignment and require less force to mate, making them **easier to mate reliably under dark or cold conditions**, compared to our standard connectors. Wet-pluggable connectors may be mated in wet conditions; their pins do not need to be dried before mating. By design, water on the connector pins is forced out as the connector is mated. However, they must not be mated or un-mated while submerged. Like standard connectors, wet-pluggables need proper lubrication and require care during use to avoid trapping water in sockets.

If desired, Sea-Bird can retrofit your existing instruments with wet-pluggable connectors; contact Sea-Bird for pricing information.

Application Note Revision History

Date	Description
September 1999	Initial release
May 2003	Add caution to not use WD-40 or other petroleum-based lubricants.
August 2007	• Revise recommendations on how frequently to unmate and check connectors. • Add recommendation to lube inside of cable boot. • Make more general – cover all cables and/or dummy plugs. • Add description of wet-pluggable connectors in section dealing with cold weather installation.
February 2010	• Update to include more information about MCBH connectors. • Update address.
January 2014	Update to include caution about using silicone spray that contains propellants incompatible with MCBH connectors.

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APPLICATION NOTE NO. 76 **revised March 2008**

pH or pH/ORP Sensors and Moored Applications

Sea-Bird's pH and pH/ORP sensors (SBE 18 and SBE 27) were originally developed for use on profiling CTDs. Users familiar with laboratory sensors for these *electrochemical* parameters are generally aware of their inherent weaknesses and limitations (e.g., limited depth capability, drift and attendant need for frequent re-calibration, pressure hysteresis, fragility, limited life expectancy, etc). Carefully handled, they are nevertheless useful for water column profiling in many survey and research applications.

Results on moorings have been less satisfactory because frequent calibration is often impractical, and constant immersion hastens the diffusion of seawater into the reference (all pH and ORP sensors use some kind of porous interface between outside seawater and the inside electrolyte), which causes drift and eventual failure. Drift (uncertainty) is further compounded by bio-fouling, and we are unaware of a method to protect the pH electrode from fouling. We have also recently become aware of additional uncertainties associated with the intermittent sampling inherent in moored applications - where the host instrument (for example, a SEACAT) wakes up, powers the pH or pH/ORP sensor, and then goes back to sleep. Because electrochemical sensors such as these exhibit fairly long and somewhat indeterminate stabilization times, successive samples may be significantly different. These sample-to-sample differences appear as noise in the time series record, but the mean value may also be in error because the signal never fully equilibrates. As a result of the many uncertainties and problems associated with these sensors, **we no longer recommend their use in moored applications**.

In general, bio-fouling is not an issue when profiling, nor are stabilization times on the order of 30 to 90 seconds. Profiling does not entail continuous immersion, which means that the sensor is readily accessible for frequent re-calibration, and diffusion resulting from lengthy seawater exposure is much reduced.

Those who choose to continue using pH and pH/ORP sensors in moored applications should increase the time interval between applying power to and logging a reading from the sensor. A relatively long interval of at least 60 seconds is necessary to reach stabilization.

- ***plus* production SEACATs (SBE 16*plus*, 16*plus*-IM, 16*plus* V2, and 16*plus*-IM V2; SBE 19*plus* and 19*plus* V2 in moored mode) -**
  Set the delay before sampling to at least 60 seconds, using the appropriate command.
  - SBE 16*plus* (RS-232), 16*plus* V2 (RS-232), 19*plus*, and 19*plus* V2: set **DelayBeforeSampling=60**.
  - SBE 16*plus* (RS-485), 16*plus*-IM, 16*plus* V2 (RS-485), and 16*plus*-IM V2: set **#iiDelayBeforeSampling=60**.

- **Older SEACATs (SBE 16 and SBE 19 in moored mode) -**
  Set the voltage delay to at least 60 seconds. Note that the format of the command (whether the delay is entered in seconds or in milliseconds) and the SEACAT default that is added to the user-input delay varies, depending on your instrument type and the firmware version. Consult the manual that came with your SEACAT for the voltage delay command for your instrument.