

FIELD PROCEDURE: pH

The pH meter needs to be calibrated at the beginning of each day of sampling. The team leader or designee should ideally perform this calibration at home; this can be done several hours prior to leaving for the field. The closer to stream temperature, the better, so you might want to soak or refrigerate the buffer bottles beforehand. A minimum 2-point calibration is necessary, with the two points bracketing the pH values of the sites you'll be sampling. In the vast majority of circumstances on the North Olympic Peninsula, pH will be between 7 & 10, so these two calibration standards are generally used. In the unusual circumstance that you'll be sampling where you suspect pH will be 6.5 or lower, you will need to do a 3-point calibration at pH 4, 7 & 10. We have included instructions for 3-point calibration in brackets; you'll need to get pH 4 buffer from the office, because it won't normally be stocked in the field kit.

EQUIPMENT NEEDED:

Note: Don't leave this equipment out in freezing temperatures unless you're using it. If the air temperature is below 23°F (-5°C), the YSI meter won't operate properly and your teammates probably won't either!

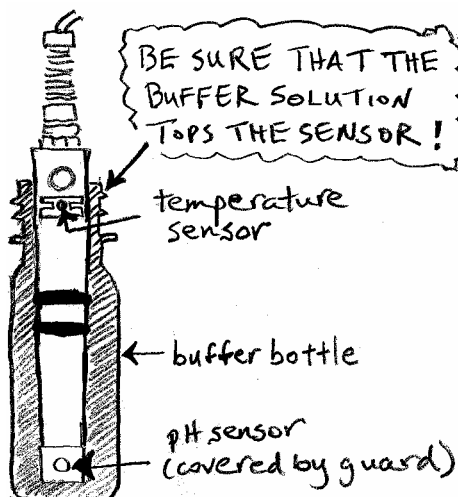
- Tarp
- YSI-60 pH meter
- pH [4,] 7 and 10 buffering solution in high, narrow bottles
- extra buffer solution for top-up
- splash-proof goggles & gloves (not needed, but available; pH 10 buffer is roughly equivalent to Milk of Magnesia)
- foam holder for pH test bottles
- watch with second hand or stopwatch
- bottle of purified water
- lint-free tissues
- 6 extra AA alkaline batteries
- data sheet, clipboard, pencil
- [plastic tub with tight-fitting lid]

CALIBRATION (BEGINNING OF DAY):

1. Turn the instrument on. The instrument will activate all segments of the display for a few seconds, which will be followed by a self test procedure which will last for several more seconds. If "LO BAT" is displayed, you will need to replace the batteries. Also, if the meter locks up, try replacing the batteries. When the meter is first turned on, it should display pH and °C. If not, press "MODE" until you get to the right display on the screen.
2. If the probe is in the long-term storage bottle, remove it and cap the bottle (see last

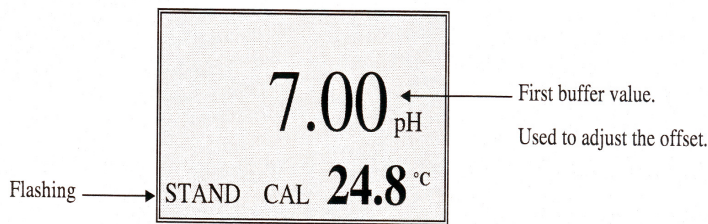
page for details). If the probe is in the transport chamber in the meter, simply remove it from this chamber.

3. Rinse the entire probe with purified water, then carefully dry it with a lint-free tissue, saving the tissue for later. (Or rinse it with some of the extra buffer solution).
4. Place the tall pH 7 buffer bottle in the foam holder, uncap it, insert the probe about 1" into the buffer, shake away any bubbles near the glass sensor, then insert the probe all the way down into this bottle, making sure that the temperature sensor is covered by the solution (see diagram below). If topping up is needed, keep the probe in the buffer and pour against the top part of the probe using the pH 7 refill bottle. Let the probe sit in this solution to stabilize. Meanwhile, on the data sheet for the first site you'll be visiting later that day, record the Meter's kit # or name, time, and pH 7 & pH 10 expiration dates written on the bottles.



pH

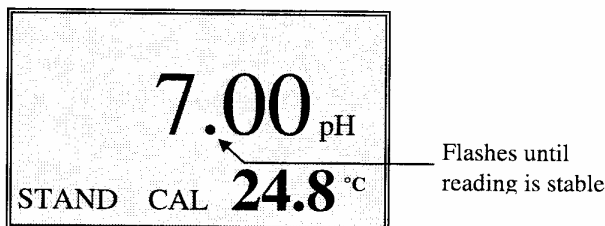
5. Wait for the pH reading to stabilize—not varying by more than 0.01 for 2 min. If the meter still isn't stable after 10 min., see the "Troubleshooting" section below.
6. Record the "Pre-Cal" temperature (to the nearest tenth) and pH reading (to the nearest hundredth) in the "pH7 pre-cal" section of the data sheet.
7. To enter the calibration menu, simultaneously press both the "UP ARROW" and "DOWN ARROW" keys. The display will show "CAL" at the bottom, "STAND" will be flashing and the main display will show 7.00 (the pH of the first buffer you are using).



[Note: The meter automatically accounts for the fact that the true pH of the buffers changes with temperature; therefore, the pH values displayed during calibration won't always display the same values as what's written on the buffer bottles. For a table showing how pH buffer differs with temperature, see the table at the end of this protocol.]

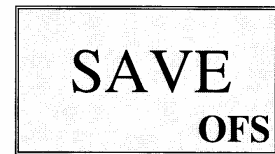
8. Setting the midpoint:

- a. Press the "ENTER" key. The screen will show "CAL" at the bottom, "STAND" will stop flashing and the pH calibration value is shown with the middle decimal point flashing.



- b. When the meter decides the reading is stable, the decimal point will stop flashing. Press and hold the "ENTER" key until "SAVE" along with "OFS" is

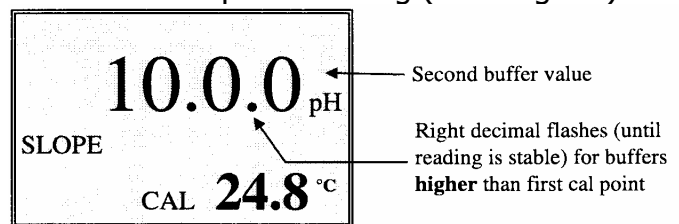
displayed and the display returns to the main screen. "SLOPE" will



now appear on the display and be flashing. This indicates that the slope is ready to be set using the second pH buffer. Take the probe out of the pH 7 buffer solution and cap the bottle.

9. Setting the upper point:

- a. Rinse the entire probe with purified water, then carefully dry the probe. Place the tall pH 10 buffer bottle in the foam holder, uncap it, insert the probe about 1" into the buffer, shake away any bubbles near the glass sensor, then insert the probe all the way down into this bottle, making sure that the temperature sensor is covered by the solution (see prior diagram). If topping up is needed, keep the probe in the buffer and pour against the top part of the probe using the pH 10 refill bottle. Let the probe sit in this solution to stabilize—not varying by more than 0.01 for 2 min.
- b. Press "ENTER." The screen will now show "CAL" at the bottom, "SLOPE" will stop flashing, and the pH value for the pH 10 buffer is shown with the right decimal point flashing (see diagram).



- c. When the reading is stable, the decimal point will stop flashing. Press and hold "ENTER" until "SAVE" flashes on the display along with "SLP" to indicate the second slope value has been saved.



[The next step is for special low-pH situations only—see introduction to this protocol. For normal situations, you'll skip this step and go to the next one, "Completing & testing calibration".]

10. Setting the lower point:

- a. Rinse the entire probe with purified water, then carefully dry it. Place the tall pH 4 buffer bottle in the foam holder, uncap it, insert the probe about 1" into the buffer, shake away any bubbles near the glass sensor, then insert the probe all the way down into this bottle, making sure that the temperature sensor is covered by the solution (see prior diagram). If topping up is needed, keep the probe in the buffer and pour against the top part of the probe using the pH 4 refill bottle. Let the probe sit in this solution to stabilize—not varying by more than 0.01 for 2 min.
- b. Press "ENTER." The screen will now show "CAL" at the bottom, "SLOPE" will stop flashing, and the pH 4 buffer value is shown with the left decimal point flashing.
- c. When the reading stabilizes, the decimal point will stop flashing. Press and hold "ENTER" to save the first slope until "SAVE" is displayed along with "SLP," and you return to a normal screen.

11. Completing & testing calibration:

- a. Press the "MODE" button to return to a normal screen and complete the calibration process. The meter is now calibrated at 2 [or 3] points.
- b. Take out the probe and cap the buffer bottle.
- c. Rinse the entire probe with purified water and dry carefully.
- d. Re-immerses the probe into the pH 7 buffer bottle, following instructions above.
- e. Wait for the pH reading to stabilize—not varying by more than 0.01 for 2 min.

- f. On your data sheet, record the "post-cal" temperature (to the nearest tenth) and pH (to the nearest hundredth). Then record the expected reading from the temperature table at end of this protocol, extrapolating as appropriate. Next, record the difference between the actual and expected readings; if this is ≤ 0.10 pH unit, you can check "OK" and you're done. If not, you'll have to try recalibrating; otherwise, all of your pH data from that day may be flagged as "Estimated" or "Rejected".
- g. Rinse the entire probe with purified water and replace it in the meter's storage chamber (no need to dry).
- h. Record your initials on the "pH Calibration" section of your data sheet.
- i. You can now turn off your meter until you get to your first site.

Calibration troubleshooting:

If display reads "undr" or "OVER" while calibrating, try letting it sit for a few minutes to see if the problem goes away. Also make sure that both the pH and temperature sensors are fully immersed, and try jiggling or shaking the probe in the buffer to dislodge any bubbles that might be sticking to it.

If readings do not stabilize after 20-30 minutes, the probe may need cleaning or replacing. Let program managers know about the problem as soon as possible, and if possible, borrow another meter.

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TAKING READINGS AT SITES:

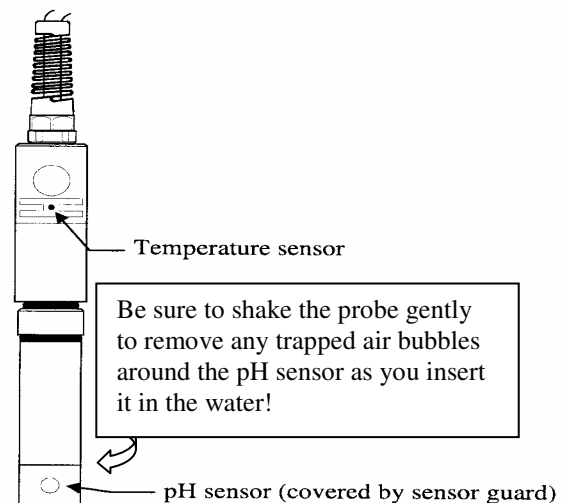
Where to sample: Pick an area where the stream is flowing and appears to be well mixed. ***Do not sample downstream of where your team has disturbed the bottom.***

INITIAL INSTRUMENT PREPARATION:

1. If you haven't already calibrated the meter for the day, do that now (see "Calibration" section at the beginning of this protocol). If you have calibrated already, indicate "Yes" at the top of the data sheet and give the site name of the form on which you recorded the calibration information (this will generally be the first site of the day).
2. If the probe is inside a bottle rather than inside the meter's chamber, see the "Removing the Buffer Bottle" section at the end of this chapter.
3. Turn on the meter. All segments of the display will be activated for a few seconds. Eventually, pH and temperature will be displayed. If "LO BAT" is displayed, you will need to replace the batteries. If pH and temperature are not displayed, press "MODE" until you get to the right display on the screen.
4. Take the probe out of its chamber. (If it won't come straight out, turn it slightly clockwise as you pull.) Check and tighten all connections along the cable, probe, and guard-piece at the end of the probe. Find a safe place in the stream to place it for a warm-up. Put it:
 - downstream of where you will eventually sample (see sampling procedure later in this section);
 - in a place where the water isn't too turbulent;
 - where the bottom isn't silty or muddy (between a couple of rocks would work); and
 - where you can safely place the main part of the meter up on the bank.

pH MEASUREMENT:

1. After the YSI-60 pH meter has warmed up in the water, get a screen that shows pH and temperature. You may need to press "MODE" repeatedly until this screen appears.
2. Place the probe in the water at the spot where you wish to sample, shaking gently to remove any bubbles trapped around the pH sensor. Make sure the pH sensor at the end of the probe and the temperature sensor near the top of the probe are both immersed in a well-mixed part of the stream where the bottom has not been disturbed. You can either:



- Dangle the probe at mid-depth in a well-moving but non-bubbly part of the stream; or
 - Find a well-mixed pool and swing the probe back and forth at mid-depth; or
 - In shallow water, wedge the probe between rocks in the middle of a riffle or the taylor of a pool, where the water is moving well.
3. Read the meter to the nearest hundredth of a pH unit. (But do not record it yet.)
 4. Wait 2 minutes and read the meter again.
 - a) If the reading has not changed by more than 0.01 pH unit, record that reading to the nearest tenth (not hundredth) on your data sheet. (NOTE: Keep in mind Streamkeepers' special rounding convention—see "Quality Assurance.")

- b) If the reading has changed by more than 0.01 unit, wait another two minutes and try again. Repeat as needed until you've met the above criterion.
- 5. If you have to wait more than 10 min. to get a stable reading, note that problem on the field sheet and notify program managers.
- 6. If you are collecting replicates at this site, follow this procedure to take another pH reading; recalibration not needed. Then see the "Water Chemistry—General" protocol to see if your pairs of readings are within the acceptable precision limits, and resample as needed.
- 7. If your reading was 6.5 or lower, AND...
 - You are NOT reporting your data to Clallam County, AND...
 - You did not perform a 3-point calibration at the beginning of the day...

...then record on your data sheet the last 3-point calibration date, written on a sticker on the side of the meter. A later check of the meter will confirm the lower point.

- 8. Shake off the probe, rinse with purified water, and pat it dry with lint-free tissues.
- 9. **Meter calibration check:**

NOTE: It would be adequate to just perform this post-test at the end of each day; however, if the meter fails that test, all data from that day would be invalid. The only way to assure acceptable data is to perform the post-test at each site, and then re-calibrate if the meter fails that test.

- a) Immerse the dried probe all the way into the pH 7 buffer test bottle, using the foam bottle holder to stabilize it. The temperature sensor (see diagram) must be immersed in the buffer—top up as needed from the extra pH 7 bottle. If it's raining, cover the buffer bottles with your body. Also, if possible, have a second person assist you by holding caps and screwing them right back on when finished with them. Keep the lids of

these bottles screwed on tight when not in use.

- b) Wait for the pH reading to stabilize (not varying by more than 0.01 for 2 min.).
- c) On your data sheet, record the "pH 7 post-check" pH (to hundredths) and temperature (to tenths).
- d) Record the expected buffer value from the temperature-corrected chart at the end of the "pH Meter Calibration" protocol (just prior to this one) or from your data sheet. Extrapolate as appropriate from the values in that chart.
- e) Record the difference between the actual and expected readings; if this is ≤ 0.10 pH units, you can check "OK" and you're done. If not, you'll have to try recalibrating, using the "pH Meter Calibration" protocol, and then re-doing the readings; otherwise, the pH data you just took (as well as measurements at all subsequent sites) will be labeled "Estimated" or "Rejected".

10. Record sampler's initials.

11. Rinse with purified water, reinsert into the chamber, and turn off the meter.

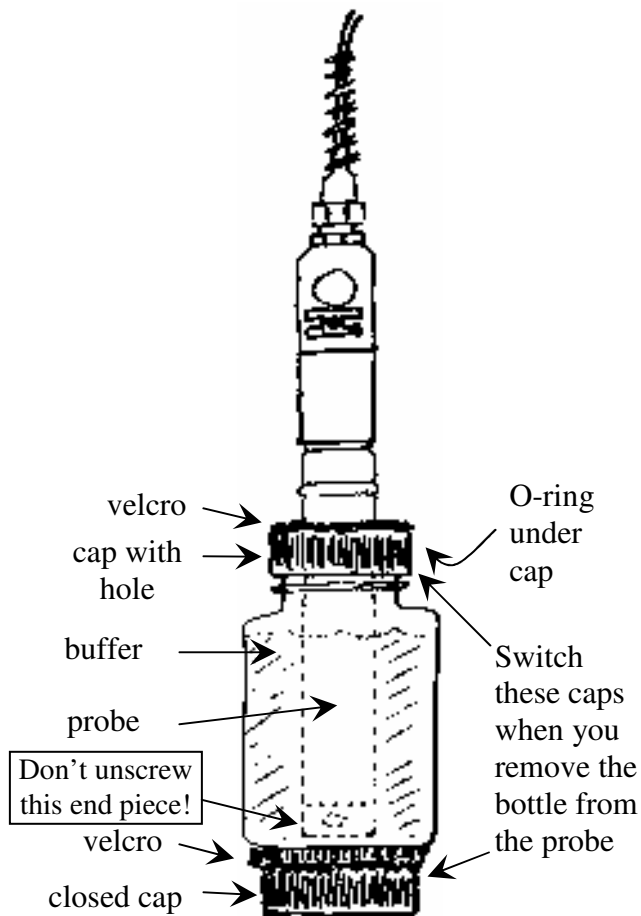
ALTERNATIVE WATER-CHEMISTRY PROCEDURES FOR POOR CONDITIONS: See "Water Chemistry—General Guidelines" protocol.

Generalized pH Buffer Values at Various Temperatures (from BDH buffers 2009)

Temperature	pH 4	pH 7	pH 10
0°C	4.00	7.12	10.31
5°C	4.00	7.09	10.23
10°C	4.00	7.06	10.17
15°C	4.00	7.04	10.11
20°C	4.00	7.02	10.05
25°C	4.00	7.00	10.00
30°C	4.01	6.99	9.95
35°C	4.02	6.98	9.91

(Actual values will vary from product to product, but these should be close enough to check instrument calibration.)

Removing the buffer bottle from the pH probe (YSI-60):



We store the pH probe in pH4 buffer solution to keep it in good shape if it's not going to be used for a while. Sometimes we may neglect to take the probe out of this bottle before we send out the kit. If this happens:

1. Remove the "closed cap" from the Velcro at the bottom of the bottle.
2. Holding the bottle upright, unscrew it from the cap with the hole ("open cap") and screw the closed cap onto it.
3. Rinse the probe and open cap with purified water.
4. Slide the open cap toward the cord to expose the O-ring beneath the cap. Roll off the O-ring, then slide the open cap off the end of the probe.
5. Sandwich the O-ring between the Velcro on the bottom and the Velcro on the open cap,

so that it doesn't fall out. Thus, the bottle, both caps, and O-ring are all stored together in a single "package" (see drawing below).

6. Remove the tape that's covering the probe chamber on the side of the meter, being careful not to lose the little sponge that's inside.
7. Add a few drops of purified water to the little sponge inside the chamber.
8. If possible, soak the probe in creek water for 30 minutes before taking your first reading.
9. Wrap the buffer-bottle "package" in a small ziplock bag and store in the treasure box.
10. If you know that the meter won't be used for a few days, store the probe back in this buffer-solution bottle (see first diagram) after finishing your monitoring.

