# CALIBRATION 6.4.2

Calibrate and check the operation of a pH instrument system at the field site. Two pH buffers are needed to properly calibrate the pH instrument system (pH 7 buffer and either the pH 4 or 10 buffer, depending on the anticipated sample pH). A third buffer can be used to check instrument system performance over a larger range. The pH of the buffer solution is temperature dependent: pH 10 buffers change more per unit change in temperature than do pH 4 buffers. The temperature of buffer solutions must be known, and temperature-correction factors must be applied before calibration adjustments are made. Calibration and operating procedures differ with instrument systems—check the manufacturer's instructions.

**Meters with microprocessors have reliable autocalibration functions and will automatically compensate for buffer temperatures and indicate Nernst slope. For such meters, follow the manufacturer's calibration instructions precisely—do not take shortcuts.**

- Check the records of electrode performance before each calibration and field trip (see 6.4.1). Electrode response is optimum between approximately 98 percent and 99.5 percent. A slope of 94 percent indicates possible electrode deterioration. **At 90 percent slope, the electrode cannot be used.**
- Calibrate or check the temperature sensor at least three times per year, and tag the sensor with the date of District certification. Do not use the automatic temperature compensating function of a pH meter if it has not been District certified within the past 4 months.
- Record calibration in the instrument log book and on field forms at the time of instrument calibration.

***Next, follow the 10 steps listed below:***

1. Temperature equilibration of equipment (this is not needed if using an automatic compensating meter).
   a. Bring the pH buffers, thermometer (if necessary), container, and electrode to the temperature of the sample.
   b. Allow 15 to 30 minutes for the buffers to adjust to the sample temperature. When making temperature corrections, use the correction factors provided by the buffer manufacturer (temperature coefficients can vary with buffer manufacturer).

- To equilibrate to stream temperature, place the buffer bottles in a minnow bucket or mesh bag and suspend them in the stream.
- To equilibrate to ground-water temperature, place the buffer bottles in a mesh bag and suspend them in a bucket or other large container (an ice chest works well) overflowing with water being pumped from the well.

2. Inspect the pH electrode.
   a. Check for damage to the electrode bulb, body, or cables.
   b. Rinse any precipitate off of the electrode with deionized water (the measurement can be affected if precipitate falls into the buffer or sample).
   c. Slide the protective sleeve up or down to uncover the filling hole.
   d. Gently shake or tap the electrode to dislodge and remove air bubbles trapped in the sensing tip of the electrode and to remove excess deionized water. Do not wipe the electrode.

3. Calibration rinse.
   a. Rinse (with pH 7 buffer) the electrode, thermometer or automatic temperature compensating (ATC) sensor, and a container large enough to hold the sensors and buffer. Discard the used pH buffer into a waste container.
   b. Pour fresh pH 7 buffer into the buffer-rinsed container that holds the electrode and thermometer. Allow the instruments to equilibrate for 1 minute (if necessary), then discard the buffer into a waste container.

4. Calibration. Steps c, d, e are not needed for autocompensating meters.
   a. Pour fresh pH 7 buffer into the container that holds the electrode and thermometer or ATC sensor.
      - The bulb of the pH electrode must not touch the bottom or side of the container.
      - Add enough pH buffer to cover the reference junction.
   b. Swirl the sample gently or stir carefully with the electrode. If using a magnetic stirrer, stir slowly enough so that a vortex is not created. Place a thin piece of insulating material (styrofoam or cardboard) between the magnetic stirrer and beaker to prevent transfer of heat to the buffer solution.
   c. Measure the temperature of the buffer solution; remove the thermometer (it is not necessary to remove the ATC sensor).

d. Determine the theoretical pH of the buffer from the temperature-correction tables.

e. Note and record the pH temperature readings. Adjust the meter reading to the pH value using the "standardize" function on the meter (usually a knob or pressure pad). Record the adjusted pH value for the 7.0 buffer and associated millivolt reading.

f. Remove the electrode and ATC sensor (some instruments require that the meter be switched to the standby or off position before removing the electrode from the solution).

- Repeat the calibration steps using fresh portions of reference buffer solution until two successive readings are obtained at the adjusted pH value for pH 7 buffer without further adjustment to the system.
- Discard the used pH 7 buffer into a waste container.

5. Slope adjustment rinse.

a. Rinse the electrode and thermometer or ATC sensor thoroughly with deionized water.

b. Rinse a clean container, electrode, and thermometer with a second buffer (usually pH 4 or 10) that brackets the expected pH value of the sample; discard the used buffer into a waste container.

c. Pour the second buffer into a container holding the electrode and thermometer or ATC sensor. Allow the temperature to equilibrate for 1 minute, then discard the used buffer into a waste container.

6. Slope adjustment. This step is automated in modern meters.

a. Pour a fresh portion of the second pH buffer into a container holding the electrode and thermometer or ATC sensor.

b. Stir slowly (no vortex) or swirl manually. Follow the directions in 4b, above.

c. Measure the temperature and pH of the buffer solution and check the pH value of the buffer on temperature coefficient tables. Record the pH and temperature readings.

d. Adjust the slope to the value of the second pH buffer at known temperature. (Some meters have separate slope-adjustment knobs, pressure pads, or other devices, whereas others have to be adjusted by use of a temperature knob.) Record the adjusted pH value and associated millivolt reading.

e. Discard the used buffer into a waste container.

f. Repeat steps 6(a) through 6(e) using successive portions of the buffer solution until two successive readings are obtained without further adjustment.

7. Rinse the electrode and thermometer or ATC sensor thoroughly with deionized water.

8. If using a noncompensating or nonautomated meter, repeat the calibration rinse (step 3) and calibration procedures [steps 4(a) through 4(d)] to ensure that the slope adjustments did not affect the calibration adjustment.

- This step is a check only; no adjustment should be needed, but the result should be recorded. If adjustment is needed, repeat the entire calibration procedure.
- If adjustment is still needed, a systematic problem is likely (see 6.4.4). Inspect the instrument system, clean the electrode or add filling solution, or use a spare electrode or meter.

9. Calibration check rinse.

a. Rinse the electrode and thermometer or ATC sensor with deionized water.

b. Rinse another clean container, electrode, and thermometer with a third buffer (pH 4 or 10) and discard the used buffer into a waste container.

c. Pour the third buffer into a container holding the electrode and thermometer or ATC sensor. Allow the temperature to equilibrate for 1 minute (if necessary), then discard the used buffer into a waste container.

10. Calibration range check.

a. Pour a fresh portion of third pH buffer into a container holding the electrode and thermometer or ATC sensor.

b. Stir without forming a vortex or swirl slowly (see step 4b).

c. Measure the temperature of the buffer solution (remove the liquid-filled thermometer and check the temperature-adjusted pH value), if necessary for the meter being used.

d. The pH instrument system should read the value of the third buffer at a known temperature within ±0.1 pH units.

- Meters reading to three or more places to the right of the decimal may not provide better accuracy than ±0.05 units, and their accuracy must be verified.
- If it checks, the instrument system is calibrated over a range of pH 4 to 10 and is ready for ANC or alkalinity titrations as well as pH measurement.

- If the instrument system does not check over the entire range, recalibrate before measuring the sample pH. Recalibrate before an alkalinity/ANC titration if the sample has a pH greater than 7.0.

e. Discard the used buffer into a waste container.

f. Rinse the electrode and thermometer (or ATC sensor) with deionized water.

**Never reuse buffers or put used buffer solution back into stock container.**

***Calibration for low-conductivity water:***

Proper calibration of pH instrument systems with standard buffers does not guarantee accurate pH measurement in water with conductivity less than 100 µS/cm. The following recommendations for pH measurement in low-conductivity water are taken from Busenberg and Plummer (1987).

1. After calibration with pH 4, 7, and 10 buffers, check electrode performance daily in appropriate sulfuric acid standard solution with conductivity less than 20 µS/cm. (For solution preparation and handling, refer to Busenberg and Plummer, 1987).
   - Before using the sulfuric acid standard solution, check for contamination by measuring conductivity.
2. Check electrode performance with deionized water saturated with an analyzed nitrogen-carbon dioxide gas mixture having a carbon dioxide mole fraction of less than 0.5 percent.
   - Addition of KCl is not recommended because of the potential for contamination and other complications.
3. Rinse the electrode at least three times, preferably with a portion of the sample to be measured.
4. Cap the Lazaran™ reference electrode of retrofitted Hydrolab™ units with saturated KCl solution when not in use.
5. Calibrate and measure pH in quiescent (unstirred) solutions after the sample has been homogenized by stirring.
6. Check the electrode performance (slope) before using the percent Nernst slope and (or) millivolt readings at pH 7 and pH 4. Keep a record of the electrode slope and millivolt readings—they can signal electrode deterioration.