



6.4 pH

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pH

pH 6.4

The pH of an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions (Hem, 1985). Water pH is a useful index of the status of equilibrium reactions in which water participates (Hem, 1985). The pH of water directly affects physiological functions of plants and animals, and it is, therefore, an important indicator of the health of a water system.

- ▶ pH is reported on a scale that most commonly ranges from 0 to 14 and that is directly related to the ratio of hydrogen (H^+) and hydroxyl (OH^-) ion activities at a given temperature.
- ▶ A solution is considered acidic if H^+ activity is greater than OH^- activity (pH less than 7 at $25^\circ C$); a solution is considered basic, or alkaline, when OH^- activity is greater than H^+ activity.
- ▶ Carbon dioxide (CO_2)-free water at $25^\circ C$ is considered neutral because activities of H^+ and OH^- are equal.

pH: a measure representing the negative base-ten logarithm of hydrogen-ion activity of a solution, in moles per liter.

6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH must be tested before each field trip, and it must be cleaned soon after use. Because of the variety of pH meters and electrodes available, read thoroughly the instruction manual provided by the manufacturer. Every pH instrument must have a log book in which its manufacturer make and model, serial or property number, and all repairs and calibrations are recorded.

pH can be measured either electrometrically or colorimetrically.

- ▶ **The electrometric measurement method uses a hydrogen ion electrode. This is the only technique which is approved for measuring pH values that are to be reported or entered into the USGS data base.**
- ▶ The colorimetric method uses pH “litmus” indicators that change color with a change in pH. The colorimetric method is suitable only when rough estimates of pH are needed; for example, when assessing the volume of acid or base needed to preserve samples; or, when checking that equipment-cleaning solutions have been adequately neutralized prior to disposal.

pH meters are sophisticated electronic instruments that require care in handling and operation. pH instrument systems and buffers must be protected from dirt and extreme heat or freezing conditions while they are in the field and during storage. Keep instrument systems clean and dry when they are not in use. During field travel, protect pH meters and electrodes from being jostled or from sudden impacts.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer’s instructions.

Table 6.4–1. Equipment and supplies used for measuring pH¹

[Except for the multiparameter instrument, this equipment is required also for ANC or alkalinity determinations (see NFM 6.6); mL, milliliters; °C, degrees Celsius; mV, millivolt; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius]

- ✓ pH meter and pH electrodes
 - Battery powered, solid state, with automatic temperature and slope compensation, or multiparameter instrument (possible alternative to separate pH meter and electrode)
 - Range of at least 2 to 12 pH, preferably 0 to 14 pH
 - Accuracy of at least ± 0.1 units
 - Temperature range of at least 0 to $+45^\circ\text{C}$
 - Millivolt readout with accuracy of ± 1.0 mV or better for instrument resolution of 0.1 mV
 - Bayonet nut connector (BNC) is recommended
- ✓ pH electrodes, gel-filled or liquid-filled, as appropriate for study objectives and site conditions
- ✓ pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
- ✓ Thermometer, calibrated
- ✓ Buffer solutions, 500 mL each of pH 4, 7, and 10; temperature correction chart(s) for buffers
- ✓ Stand for holding pH electrode (or stand for holding multiparameter instrument system)
- ✓ Bottle, delivery (squeeze), for deionized water
- ✓ Deionized water, maximum conductivity of $1 \mu\text{S}/\text{cm}$
- ✓ Beakers or measurement vessels, polyethylene or Teflon™ preferable, assorted, 50 to 150 mL, clean but not acid rinsed
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Flowthrough chamber for ground-water measurements (used with meter and electrode equipment)
- ✓ Minnow bucket with tether or equivalent, used for temperature equilibration of buffer solutions
- ✓ Antistatic spray or polish
- ✓ Waste disposal container
- ✓ Stirrer, magnetic with thin insulating pad; or stirrer, mechanical with Teflon™ coated impeller
- ✓ Stirrer bar, magnetic, Teflon™ coated
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

¹Modify this list to meet the specific needs of the field effort.

CAUTION: Before handling pH buffers or other chemicals, refer to Material Safety Data Sheets (MSDS) for safety precautions. Wear eye guards and protective clothing.

6.4.1.A pH BUFFER SOLUTIONS

pH measurements are only as accurate as the buffers used for calibration. Use buffers that have been certified traceable to the NIST Standard Reference Material; buffers with a pH of 4, 7, and 10 are available from QWSU.

- ▶ Note that the routine buffers obtained for measurement of pH from 4 to 10 have a high ionic strength. For pH measurements of dilute waters, obtain low ionic-strength buffers.
- ▶ Label buffer and reagent containers with the date when they are received.
- ▶ Label every buffer with its expiration date. Copy this date onto any container into which the buffer is transferred.
- ▶ **Discard buffers on their expiration dates.** The pH of the buffers may have changed substantially because of carbon dioxide absorption, mold growth, or evaporation.

Take the following precautions to maximize the accuracy of pH measurement (modified from Busenberg and Plummer, 1987):

1. Always cap buffer bottles to prevent evaporation and contamination from atmospheric carbon dioxide. (In order of greatest to least sensitivity to CO₂ contamination, pH buffer 10 > 7 > 4. Buffers are stable for the short exposure time during electrode calibration.)
2. Never pour used buffer back into stock solution bottles. Never insert an electrode or other material into stock solution bottles containing buffers—always pour the buffer into a separate container.
3. Be very careful not to contaminate the buffer with another buffer or with other fluids (pH 4 buffer is least resistant to contamination).
4. Do not dilute buffer—for example, with water dripping from sensors (more important for pH 7 buffer).
5. Before using buffers, bring them to the temperature of the sample solution, and check with the buffer manufacturer for temperature-correction factors. (In order of greatest to least pH variation with temperature, buffer of pH 10 > 7 > 4.)

pH ELECTRODES: MAINTENANCE, RECONDITIONING, CLEANING, AND STORAGE 6.4.1.B

The slope and the measured potential of a new electrode should be monitored daily for about 1 week before use (Busenberg and Plummer, 1987). The latest instruments have microprocessors that automatically calculate and display the slope. Some older instruments have a percent-slope readout or (and) millivolt readout. For instruments with a millivolt readout, the measured electrode potential is calculated as the difference between millivolts measured at the known pH of two buffers. Because the theoretical Nernst response is known, slope can be calculated from measured potentials as follows:

$$E = E^0 - S(\text{pH})$$

where

S = slope, and

E = electrode pair potential in mV.

Using two buffers of known pH (1, 2),

$$E_1 = E^0 - S(\text{pH}_1)$$

and

$$E_2 = E^0 - S(\text{pH}_2)$$

or

$$S = \frac{E_2 - E_1}{\text{pH}_1 - \text{pH}_2}$$

and

$$E^0 = E_2 + S(\text{pH}_2).$$

The theoretical slope is temperature dependent; the slope in mV can be calculated as follows:

$$S_t = 0.19841(273.15 + t)$$

where

t = temperature in degrees Celsius, and

S_t = slope at a given temperature.

Normally, electrodes drift from day to day and E^0 typically varies by ± 2 mV; the slope remains fairly constant to within ± 0.2 percent Nernst slope after the new electrode has been conditioned. Follow the procedures recommended by the manufacturer. Properly working electrodes commonly drift from about 0.1 to 0.2 mV per hour.

Electrode maintenance

Electrodes with gel-filled references require less maintenance than electrodes with liquid-filled references. Follow manufacturer's instructions.

Deterioration of the electrode is normal, and proper maintenance requires that electrode performance be monitored before every water-quality field trip and again at each site. Electrodes can give years of reliable service if maintained by following steps 1–8:

1. Do not handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with pH measurement. Fingers leave a protein film on the glass that decreases electrode sensitivity.
2. Inspect the electrode and electrode cable for physical damage; for example, check for
 - Scratched or broken bulb.
 - Cut, frayed, or broken cable.
 - Bent or broken connector.
3. **Rinse electrode thoroughly with deionized water before use. Do not wipe electrodes with paper towels or wipes—these scratch the glass bulb. Gently blot** droplets from a wet glass electrode bulb with lens paper or soft tissue by contacting only the droplets to soak up excess solution.

TECHNICAL NOTE: Wiping glass with paper causes a static charge (polarization) that results in drifting, sluggish, and erratic pH readings. It can take many minutes for the electrode to return to normal operation. Clothing also can produce a static charge that affects electrode response.

Gel-filled electrodes do not require filling, but should not be left in dilute water for long periods of time. (Salt can leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.)

For liquid-filled electrodes:

- a. Remove salt crystal deposits from the electrode, membranes, and junctions. Check that the reference junction is not blocked.
 - Rinse off salt buildup with deionized water.
 - Check that you can observe seepage of the filling solution through the junction.
- b. Always unplug the fill hole before making pH measurements, and replugin it after use. If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the elec-

- trode in air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet it.
- c. Check the filling solution level and replenish it if necessary—it should reach the bottom of the fill hole. Filling solutions differ in molarity and composition—always check that you are using the correct filling solution required by the manufacturer for a particular electrode.
 - d. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (see manufacturer's recommendations).
4. **Monitor electrode response.** Keep a record of electrode operation in the pH meter log book. Record the Nernst slope reading and the millivolt readings at pH 7 and pH 4 after calibration.
- Properly working glass electrodes should give approximately 98.0 to 99.5 percent response of that expected from the theoretical Nernst relation (Busenberg and Plummer, 1987). The theoretical Nernst response is 59.16 mV/pH unit at 25°C.
 - A slope of less than 94 percent signals possible electrode deterioration and the need to monitor closely any further decline in slope percent. If possible, replace or recondition the electrode at this point.
 - **Do not use an electrode with a slope of 90 percent or less.**
5. Keep the electrode bulb moist and capped when not in use. Keep a moist piece of cotton or lint-free tissue in the cap to prevent the bulb from drying out.

Reconditioning liquid-filled electrodes

Before beginning a field trip, if you are unsure of an electrode's condition or have persistent problems during calibration, use the following procedures to recondition the electrode.

1. Remove the old filling solution from the electrode—
 - a. Place the needle of a 1- or 3-mL syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).
 - b. Tilt the pH electrode until the filling solution is near the filling hole and the needle tip is covered with the filling solution.
 - c. Pull back on the syringe plunger until the syringe is full.
 - d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode chamber.

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2. Flush the pH electrode chamber with deionized water—
 - a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with deionized water.
 - b. With a syringe, remove the deionized water from the pH electrode chamber.
 - c. As a result of changes in pressure, temperature, and evaporation, crystals may form in the pH electrode chamber. If they form, repeat steps 2(a) and (b) until all crystals have been dissolved and removed from the pH electrode chamber.
3. Fill the electrode chamber with new filling solution—
 - a. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
 - Partially fill the pH electrode chamber with filling solution.
 - Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
 - Remove and discard the filling solution to a waste container.
 - b. Fill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. Be sure to use the correct molarity filling solution.
 - c. Rinse any excess filling solution from the outside of the electrode with deionized water.

Filling solutions might not be interchangeable for different electrodes—
check manufacturer's instructions.

Electrode cleaning

Electrodes must be kept clean and the liquid junction free flowing in order to produce accurate pH values. Because of the variety of electrodes available, check the manufacturer's cleaning instructions.

- ▶ Rinse the outside of the electrode thoroughly with deionized water after each use. In general, this should be the only routine cleaning needed.
- ▶ Rejuvenation procedures described by the manufacturer should be used if an electrode becomes clogged or extremely dirty.
 - After completing rejuvenation procedures on a liquid-filled electrode, drain, clean and refill the reference electrode chamber with fresh filling solution. Replace the fill-hole plug, and soak the electrode in storage solution overnight. Retest the electrode. If the procedures fail to remedy the problem, discard the electrode. Document electrode reconditioning or replacement in the instrument log book.
 - Gel-filled electrodes can be rejuvenated in some instances by placing the electrode in warm water (approximately 60°C) for about one minute or less. This procedure rejuvenates the junction by liquifying the salt gel.

Electrode storage

Electrodes must be clean before they are stored for any length of time.

Short-term storage. Short-term storage methods are appropriate only for in-service electrodes (those used daily or weekly). Storage solutions for short-term storage of electrodes differ with the type of electrode; follow the manufacturer's recommendations. Storage solutions can have a limited shelf life. Unless otherwise instructed by the manufacturer, avoid storing glass hydrogen-ion electrodes in deionized water or concentrated KCl solutions. In the latter case, absorbed potassium reduces the glass sensitivity to hydrogen ions.

- ▶ Store liquid-filled pH electrodes upright.
- ▶ Keep liquid-filled electrodes wet to maximize their accuracy and response time. Store them so that the bulb is fully immersed in proper electrode storage solution between uses at a field site. Before moving to the next field site, replace the plug on the fill hole, fill the protective cap with storage solution, and cover the electrode bulb with the cap.
- ▶ Gel-filled electrodes must only soak in a solution for short periods during measurements. Follow the manufacturer's instructions for storage of gel-filled electrodes.
- ▶ Clean the connector ends and store them in a plastic bag.

Long-term storage. pH measuring systems must be stored in an area that is clean, dry, and protected from extremely hot or cold temperatures. For long-term storage of liquid-filled electrodes, drain the filling solution from the electrode, rinse the outside of the electrode with deionized water, and store the electrode dry with a protective cap covering the bulb (put either storage or filling solution in the cap before placing the cap on the bulb if the manufacturer recommends that the bulb be kept moist). Clean the electrode connector ends (with alcohol, if necessary), and store them dry in a sealed plastic bag.

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 $\mu\text{S}/\text{cm}$. 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 $\mu\text{S}/\text{cm}$. (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.

6.4.3 MEASUREMENT

The pH of a water sample can change significantly within hours or even minutes after sample collection as a result of degassing (such as loss of carbon dioxide, hydrogen sulfide, and ammonia); mineral precipitation (such as formation of calcium carbonate); temperature change; and other chemical, physical, and biological reactions. The electrometric method of pH measurement described below applies to filtered or unfiltered surface water and ground water, from fresh to saline.

The pH of a water sample must be measured immediately in the field; laboratory-measured pH should not be relied on in place of field-measured pH.

Field conditions, including rain, wind, cold, dust, and direct sunlight can cause measurement problems. To the extent possible, shield the instrument and measurement process from the effects of harsh weather.

- ▶ In dry, windy climates, a static charge can build up on the face of a pH meter and cause erratic readings on the display.
- ▶ Polish the face of the display with a soft, absorbent tissue treated with several drops of antistatic solution (such as plastic polish) to minimize this interference.

TECHNICAL NOTE: Temperature has two effects on pH measurement of a sample: it can affect electrode potential (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect). The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample can be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

SURFACE WATER 6.4.3.A

It is generally preferable to measure pH in situ rather than on a sample taken from a splitter or compositing device. If stream conditions are such that water would pass the in situ pH sensor at a very high rate of flow, however, streaming-potential effects could affect the accuracy of the measurement. For such conditions, it is preferable to withdraw a discrete sample directly from the stream or compositing device and use the subsample measurement procedures described below. The pH instrument system should be set up on board the boat so that pH is measured at the time of sample collection.

Standard pH measurement in flowing surface water represents the cross-sectional mean hydrogen ion activity or median pH at the time of observation.

To compute a mean pH for the stream: (1) Sum the products of each subsection area, using the logarithm of the median pH determined for each subsection; (2) divide the sum by the total area of the cross section; and (3) convert back to pH by taking the antilogarithm of the quotient.

In situ measurement

Follow the 7 steps listed below for in situ pH measurement:

1. Calibrate a pH system on site (after equilibrating the buffers with the stream temperature, if necessary). Check the electrode performance (see "Electrode Maintenance," in 6.4.1) and the calibration date of the thermometer being used.
2. Record the pH variation from a cross-sectional profile, if possible, to determine if pH is uniform at any given discharge, and select the sampling method (NFM 6.0.2) appropriate for study objectives.
 - **Flowing, shallow stream**—Wade to the location(s) where pH is to be measured.
 - **Stream too deep to wade**—Lower a weighted pH sensor with a calibrated temperature sensor from a bridge, cableway, or boat. Do not attach the weight to sensor or sensor cables.
 - **Still-water conditions**—Measure pH at multiple depths at several points in the cross section.

3. Immerse the pH electrode and temperature sensor in the water to the correct depth and hold them there for at least 60 seconds to equilibrate them to water temperature.
4. Measure the temperature.
 - If the pH instrument system contains an automatic temperature compensator (ATC), use the ATC to measure water temperature.
 - If the instrument system does not contain an ATC, use a separate calibrated thermometer, adjust the meter to the sample temperature (if necessary), and remove the thermometer.
5. Record the pH and temperature values without removing the sensor from the water.
 - Values generally stabilize quickly within ± 0.05 to 0.1 standard pH unit, depending on the instrument system.
 - Record the median of the observed values.
 - If readings do not stabilize after extending the measurement period, note this difficulty on the field forms along with the pH readings, and record the median value of the last five or more readings.
6. EWI or EDI measurements—Proceed to the next station in the cross section. Repeat steps 3 through 5. After all stations in the cross section have been measured, rinse the sensors with deionized water and store them.
7. Record the stream pH on the field forms:
 - **In still water—median** of three or more sequential values.
 - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
 - **EWI—mean or median** of all subsections measured. (Note that pH values must be converted to a logarithm before calculating a mean value.)

Subsample measurement

When streams are fast-flowing or the water contains much sediment or algae, pH measurement of a discretely collected subsample might be preferable to in situ measurement. Representative samples are to be collected and split or composited according to approved USGS methods (Wells and others, 1990). pH measurement in fast-flowing streams should be made at the time of collection from a boat that has been set up for such measurements.

- ▶ Measure pH as soon as possible after compositing the EDI or EWI sample.
- ▶ Filter the sample if the pH continues to drift: measure pH in the field on both unfiltered and filtered subsamples and record both values on the field form.
- ▶ If the filtered sample provides the only stable pH value, report this value as sample pH.

TECHNICAL NOTE: Reported pH values are normally determined on an unfiltered sample. However, large concentrations of suspended sediment or algae can be a source of measurement error; slow settling of clay particles or algal respiration can cause “drift” of an observed pH value.

Throughout collection and processing, avoid excess aeration to prevent losses and gains of dissolved gases (especially CO₂) from solution.

1. Calibrate the pH system on site (after equilibrating buffer temperature with stream temperature, if necessary). Check the electrode performance (see 6.4.1).
2. Select the appropriate sampling method (see NFM 6.0) and collect a representative sample.
3. Withdraw properly homogenized sample(s) from the compositing device.
 - Rinse the collection bottles three times with the sample (use filtrate, if a filtered sample is used).
 - If the samples need to be stored for a short time or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient stream temperature, and measure pH in the field as soon as possible.
4. Rinse thoroughly with deionized water—the pH electrode, thermometer or ATC sensor, stir bar, and a measurement container.
 - For pH, follow the deionized water rinse of equipment with a rinse using sample water.
 - For ANC or alkalinity, rinse with deionized water only; do not rinse with the sample when using this equipment (see NFM 6.6).

5. Immerse electrode and temperature sensor in sample water for at least 60 seconds to equilibrate to sample temperature.
6. Pour fresh aliquot of the sample water into a container holding the electrode and thermometer. **Do not let the electrode touch the bottom or sides of container during measurement.**
7. Measure and record the initial temperature. Use the ATC, if it is available and calibrated, or use a separate calibrated thermometer and adjust the meter manually to the sample temperature (if necessary).
8. Establish equilibrium between the electrode(s) and sample by stirring **slowly** (no vortex) or by manual swirling.
 - Do not stir if a vortex is formed that affects the electrode performance.
 - Do not use a magnetic stirrer for samples with low conductivity (less than 100 $\mu\text{S}/\text{cm}$).
 - Before recording a pH value, allow the sample to reach quiescence.
9. Record the pH and temperature measurements on the field forms, along with the sampling, processing, and measurement methods used and any observed anomalies.
10. **Quality control**—Repeat steps 6 through 9 with at least two fresh subsamples to check measurement precision. Subsample values should agree within ± 0.1 pH unit (or study-determined criterion). Report the median of the values measured.
11. Rinse the electrode and temperature sensor thoroughly with deionized water. Replace the plug on the fill hole of refillable electrodes and follow the recommended storage procedure.
12. Discard the used sample into a waste container and dispose of it according to regulations.

6.4.3.B GROUND WATER

Measurements reported as ground-water pH must represent aquifer conditions (consult NFM 6.0 for guidance). Measure pH as close to the source as possible, either downhole or within a flowthrough chamber.

- Use equipment that minimizes aeration and operate equipment in a manner to help mitigate losses and gains of dissolved gases in solution (for example, carbon dioxide).

- ▶ Although downhole measurements are likely to be most representative of ground-water pH, proper use of pH instruments with flowthrough chambers can yield comparable values.
- ▶ The downhole system is not practical if samples will be collected after field measurements, because the instrument should not be left in the well during sampling and the pump should not be turned off between purging and sample collection—use a flowthrough-chamber system.
- ▶ Streaming potentials in the flowthrough chamber can result in biased pH values. Make the final (the reported sample pH) measurement in quiescent water.

Bailed or other methods for collecting discrete samples isolated from their source are not recommended for the determination of pH, although such methods are sometimes used owing to site characteristics or study requirements. Record the method used to obtain the sample for pH measurements on the field forms and in the data base.

Downhole and flowthrough-chamber measurements

1. Calibrate the pH instrument system on site.
 - a. If necessary, bring the buffer solutions to the temperature of the water to be measured (discharge the well water into a bucket while suspending the standards in a net bag; allow at least 15 minutes for temperature equilibration; check temperature of the water flowing into the bucket against that of the buffers).
 - Check that the thermometer has been District certified within at least the past 4 months.
 - Check electrode performance (see 6.4.1 and 6.4.2).
 - b. After calibration, rinse the pH electrode thoroughly with deionized water and blot it to remove excess water. Do not wipe the electrode.
2. Install the pH monitoring system for sample measurement (see 6.0.3 in NFM 6.0).
 - **Downhole system**—Lower sensors to the measuring point, followed by the pump, to monitor pH variation during purging.

- **Flowthrough system**—Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged. Check for and eliminate a backpressure condition.
3. During purging (see table 6.0–1 and fig. 6.0–3 in NFM 6.0):
 - Keep the flow constant and laminar.
 - Allow the sensors to equilibrate with the ground water for 5 minutes or more at the flow rate to be used for collecting all of the other samples.
 4. Record pH values at regularly spaced time intervals throughout purging. Compare the variability of the pH values toward the end of purging with the stability criterion:
 - The stability criterion is met when five readings made at regularly spaced intervals of 3 to 5 minutes or more are within 0.1 standard pH unit or less (depending on the equipment). Routine measurement must fall within the ± 0.1 unit criterion. When readings fluctuate rapidly, select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
 - If the criterion is not met, extend the purge period in accordance with study objectives, and continue to record measurements at regularly spaced time intervals. Record any difficulty on the field forms.
 5. Measure and report the pH:
 - If using a flowthrough system, divert the flow from passing into the flowthrough chamber after recording the other field measurements. Measure the sample pH in the chamber as soon as the water is still. Take several readings to be sure that the system has stabilized.
 - If using a downhole method, measure the sample pH after pumping has ceased. This entails installing the downhole sensors in the well after sample collection. If field measurements only are being monitored, stop the pump (after recording the other field-measurement values) and allow the pH to stabilize before recording the pH value.
 - Report the final value measured on a quiescent (no-flow) sample, if the values are stable. If the stability criterion is not met, record the range of values observed for the time interval monitored, and report the median of the final five or more values observed.

Subsample measurement

pH measurements reported from bailed or other discrete samples need to be identified in the data base by a description of the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

Do not use a subsample method if waters are reducing.

1. Calibrate the pH system on site (after equilibrating the buffers with the ground-water temperature, if necessary). Check the electrode performance (see sections 6.4.1 and 6.4.2).
2. Draw off a subsample through a bottom-emptying device that fits tightly over the bottle opening.
 - **Quality control**—Collect three subsamples to check precision.
 - Rinse the sample bottles three times with sample; use filtrate if filtered sample is used. Cap the bottles until they are ready for use.
 - If the samples need to be stored for a short time or if several subsamples will be measured, collect the sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient ground-water temperature, and measure the pH as soon as possible.
3. Follow the procedures described in steps 4 through 12 for subsample measurement of surface water (6.4.3.A).

TECHNICAL NOTE: An alternative method is to pour the sample into an open container instead of measuring it in a closed system. If this method is used and readings do not stabilize within several minutes, the cause may be out-gassing of carbon dioxide—measure the sample in a closed system. Filter the sample if settling of charged clay particles interferes with the stability of readings.

6.4.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions in table 6.4-2 fail to resolve the problem.

- ▶ If available, use a commercial pH electronic calibrator to check the pH meter function.
- ▶ A large percentage of all problems encountered during pH calibration and measurement can be attributed directly to problems with the pH electrode—refer to 6.4.1.B.
- ▶ New electrodes are susceptible to some of the problems listed in table 6.4-2, and they may need reconditioning before they can be used.
- ▶ Check the voltage of the batteries. Always have good batteries in instruments and carry spares.

Table 6.4-2. Troubleshooting guide for pH measurement

[M, molar; HCl, hydrochloric acid; KCl, potassium chloride; °C, degrees Celsius; ~, about]

Symptom	Possible cause and corrective action
Instrument system will not calibrate full scale	<ul style="list-style-type: none"> • Buffers may be contaminated or old—use fresh buffers. • Faulty electrode—recondition electrode (see discussion in section 6.4.1 on electrode maintenance, cleaning, and storage). • Weak batteries—replace.
Slow response time	<p>For liquid-filled electrodes:</p> <ul style="list-style-type: none"> • Weak filling solution—change filling solution (section 6.4.1). • No filling solution—add fresh solution (section 6.4.1). • Dirty tip—clean with soap solution. Do not scratch electrode tip. • Chemical deposits—place electrode in a 0.1 M HCl solution for about 30 minutes. • Clogged or partially clogged junction—unclog by placing electrode tip in 0.1 M KCl solution at 90°C for about 15 minutes. Do not boil calomel electrodes (section 6.4.1). • Water is cold or of low ionic strength—longer equilibration time is needed (be patient). • Weak batteries—replace with new batteries. <p>For gel-filled electrodes:</p> <ul style="list-style-type: none"> • Dirty bulb—rinse with deionized water. • Clogged junction—liquify gel by placing electrode into warm (~60°C) water for one minute or less.
Erratic readings	<ul style="list-style-type: none"> • Loose or defective connections—tighten, clean, or replace connections. • Broken or defective cable—repair or replace cable. • Static charge—polish face of meter with antistatic solution. • Loose battery connection—tighten. • Air bubbles in the electrode bulb—shake gently. • Too much pressure in flowthrough chamber—reduce pressure. • Weak batteries—replace with new batteries.

REPORTING 6.4.5

Report pH measurements in the data base to the nearest 0.1 standard pH unit.

- ▶ pH values to the nearest 0.05 unit can be published provided the instrument system has been calibrated at the required precision and accuracy.
- ▶ Report the instrument accuracy range with the published values and record the accuracy range in the data base, if possible.
- ▶ Enter the field-determined pH under the correct parameter code on the NWQL analytical services request form and on field forms.