Test 2

pH

INTRODUCTION

Water contains both hydrogen ions, H^+, and hydroxide ions, OH^-. The relative concentrations of these two ions determine the pH value.[1] Water with a pH of 7 has equal concentrations of these two ions and is considered to be a *neutral* solution. If a solution is *acidic*, the concentration of H^+ ions exceeds that of the OH^- ions. In a *basic* solution, the concentration of OH^- ions exceeds that of the H^+ ions. On a pH scale of 0 to 14, a value of 0 is the most acidic, and 14 the most basic. A change from pH 7 to pH 8 in a lake or stream represents a ten-fold increase in the OH^- ion concentration.

Rainfall generally has a pH value between 5 and 6.5. It is acidic because of dissolved carbon dioxide and air pollutants, such as sulfur dioxide or nitrogen oxides. If the rainwater flows over soil containing hard-water minerals, its pH usually increases. Bicarbonate ions, HCO_3^-, resulting from limestone deposits react with the water to produce OH^- ions, according to the equation:

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$$

As a result, streams and lakes are often basic, with pH values between 7 and 8, sometimes as high as 8.5.

The measure of the pH of a body of water is very important as an indication of water quality, because of the sensitivity of aquatic organisms to the pH of their environment. Small changes in pH can endanger many kinds of plants and animals; for example, trout and various kinds of nymphs can only survive in waters between pH 7 and pH 9. If the pH of the waters in which they live is outside of that range, they may not survive or reproduce.

Table 1: Effects of pH Levels on Aquatic Life

pH	Effect
3.0 – 3.5	Unlikely that fish can survive for more than a few hours in this range, although some plants and invertebrates can be found at pH levels this low.
3.5 – 4.0	Known to be lethal to salmonids.
4.0 – 4.5	All fish, most frogs, insects absent.
4.5 – 5.0	Mayfly and many other insects absent. Most fish eggs will not hatch.
5.0 – 5.5	Bottom-dwelling bacteria (decomposers) begin to die. Leaf litter and detritus begin to accumulate, locking up essential nutrients and interrupting chemical cycling. Plankton begin to disappear. Snails and clams absent. Mats of fungi begin to replace bacteria in the substrate.
	Metals (aluminum, lead) normally trapped in sediments are released into the acidified water in forms toxic to aquatic life.
6.0 – 6.5	Freshwater shrimp absent. Unlikely to be directly harmful to fish unless free carbon dioxide is high (in excess of 100 mg/L)
6.5 – 8.2	Optimal for most organisms.
8.2 – 9.0	Unlikely to be directly harmful to fish, but indirect effects occur at this level due to chemical changes in the water.
9.0 – 10.5	Likely to be harmful to salmonids and perch if present for long periods.
10.5 – 11.0	Rapidly lethal to salmonids. Prolonged exposure is lethal to carp, perch.
11.0 – 11.5	Rapidly lethal to all species of fish.

[1] The pH value is calculated as the negative log of the hydrogen ion concentration: $pH = -\log [H^+]$.

Factors that Affect pH Levels
Acidic rainfall
Algal blooms
Level of hard-water minerals
Releases from industrial processes
Carbonic acid from respiration or decomposition
Oxidation of sulfides in sediments

Changes in pH can also be caused by algal blooms (more basic), industrial processes resulting in a release of bases or acids (raising or lowering pH), or the oxidation of sulfide-containing sediments (more acidic).

To gain a full understanding of the relationship between pH and water quality, you need to make measurements of the pH of a stream, as described in this test, and also determine the stream's *alkalinity*, as described in Test 11 in this manual. Alkalinity is a measurement of the capacity or ability of the body of water to neutralize acids in the water. Acidic rainfall may have very little effect on the pH of a stream or lake if the region is rich in minerals that result in high alkalinity values. Higher concentrations of carbonate, bicarbonate, and hydroxide ions from limestone can provide a natural buffering capacity, capable of neutralizing many of the H^+ ions from the acid. Other regions may have low concentrations of alkalinity ions to reduce the effects of acids in the rainfall. In the Northeastern United States and Eastern Canada, fish populations in some lakes have been significantly lowered due to the acidity of the water caused by acidic rainfall. If the water is very acidic, heavy metals may be released into the water and can accumulate on the gills of fish or cause deformities that reduce the likelihood of survival. In some cases, older fish will continue to live, but will be unable to reproduce because of the sensitivity of the reproductive portion of the growth cycle.

Expected Levels

The pH value of streams and lakes is usually between pH 7 and 8. Levels between 6.5 and 8.5 pH are acceptable for most drinking water standards. Areas with higher levels of water hardness (high concentrations of Mg^{2+}, Ca^{2+}, and HCO_3^-) often have water with higher pH values (between 7.5 and 8.5).

Summary of Methods

The preferred method is to use a pH Sensor to make on-site measurements of the pH level in a stream or lake.

As an alternative, the water sample is taken from the stream or lake and stored in an ice chest or refrigerator. After returning to the lab, samples are allowed to return to room temperature, and the pH is measured using a pH Sensor.

pH MEASUREMENT

Materials Checklist

___ LabPro or CBL 2 interface
___ TI Graphing Calculator
___ DataMate program
___ Vernier pH Sensor
___ tissues or paper towels
___ 250-mL beaker
___ small plastic or paper cup (optional)
___ pH 7 buffer solution
___ pH 10 buffer solution
___ distilled water

Collection and Storage of Samples

1. This test can be conducted on site or in the lab. A 100-mL water sample is required.

2. It is important to obtain the water sample from below the surface of the water and as far away from shore as is safe. If suitable areas of the stream appear to be unreachable, samplers consisting of a rod and container can be constructed for collection. Refer to page Intro-4 of the Introduction of this book for more details.

3. If the testing cannot be conducted within a few hours, store samples in an ice chest or refrigerator.

Testing Procedure

1. Plug the pH Sensor into Channel 1 of the LabPro or CBL 2 interface. Use the link cable to connect the TI Graphing Calculator to the interface. Firmly press in the cable ends.

2. Turn on the calculator and start the DATAMATE program. Press CLEAR to reset the program.

3. Set up the calculator and interface for the pH Sensor.
   a. Select SETUP from the main screen.
   b. If the calculator displays PH in CH 1, proceed directly to Step 4. If it does not, continue with this step to set up your sensor manually.
   c. Press ENTER to select CH 1.
   d. Select PH from the SELECT SENSOR menu.

4. Set up the calibration for the pH Sensor.

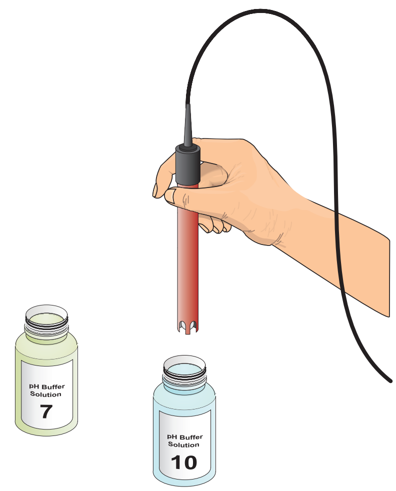
   If your instructor directs you to use the stored calibration, proceed directly to Step 5.

   If your instructor directs you to manually enter the calibration values, select CALIBRATE, then MANUAL ENTRY . Enter the slope and intercept values for the pH calibration, select OK, then proceed to Step 5.

   If your instructor directs you to perform a new calibration for the pH Sensor, follow this procedure.

   First Calibration Point

   a. Select CALIBRATE, then CALIBRATE NOW.



   b. Remove the sensor from the bottle by loosening the lid, then rinse the sensor with distilled water.
   c. Place the sensor tip into pH-7 buffer. Wait for the voltage to stabilize, then press ENTER.
   d. Enter “7” (the pH value of the buffer) on the calculator.

   Second Calibration Point

   e. Rinse the pH Sensor with distilled water and place it in the pH-10 buffer solution.
   f. Wait for the voltage to stabilize, then press ENTER.
   g. Enter “10” (the pH value of the buffer) on the calculator.
   h. Select OK to return to the setup screen.

5. Set up the data-collection mode.
   a. To select MODE, press ▲ once and press ENTER.
   b. Select SINGLE POINT from the SELECT MODE menu.
   c. Select OK to return to the main screen.

6. Collect pH data.
   a. Remove the pH Sensor from the storage bottle. Rinse the tip of the sensor thoroughly with the stream water.
   b. Place the tip of the sensor into the stream at Site 1, or into a cup with sample water from the stream. Submerge the sensor tip in the stream or in a cup to a depth of 3-4 cm.
   c. When the readings stabilize, select START to begin sampling. **Important:** Leave the probe tip submerged while data is being collected for 10 seconds.
   d. After 10 seconds, the pH value will appear on the calculator screen. Record this value on the Data & Calculations sheet.
   e. Press ENTER to return to the main screen.
   f. Select START to repeat the measurement. Record this value on the Data & Calculations sheet (round to the nearest 0.01 pH units).
   g. Press ENTER to return to the main screen.
   h. Rinse the sensor with distilled water and return it to the storage bottle when you have finished collecting your data.

DATA & CALCULATIONS

pH Measurement

Stream or lake: ______________________ Time of day: ______________________

Site name: ______________________ Student name: ______________________

Site number: ______________________ Student name: ______________________

Date: ______________________ Student name: ______________________

Column	A
Reading	pH (pH units)
1	
2	
Average	

Column Procedure:

A. Record the pH value from the calculator.

Field Observations (e.g., weather, geography, vegetation along stream) ______________________

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Test Completed: ______________ Date: ______

ADDITIONAL INFORMATION

Tips for Instructors

1. Step 4 of the student procedure provides three alternatives for loading or performing a pH calibration:

   The easiest option is to use the pH calibration stored in the DataMate program. This is done automatically when the pH Sensor is chosen from the setup screen. Using this stored calibration will generally yield accuracy to within ±0.2 pH units.

   A second option is to perform a two-point calibration in the lab, using the PERFORM NOW option in the CALIBRATION menu (described in Step 4 of the student procedure, using buffers of pH 7 and pH 10). After this calibration is completed, record the calibration *slope* and *intercept* values that are displayed on the calculator screen. We recommend that you record these two values on a piece of label tape attached to the pH Sensor. When students get to the field at a later time, they can use the MANUAL ENTRY option of the CALIBRATION menu to manually enter the slope and intercept values for their pH Sensor. Since there is very little change in pH Sensor performance over short periods of time, we think this is a good way for students to handle pH calibrations. With careful calibration, this method can provide accuracy within ±0.05 pH unit.

   The third option has students perform a two-point calibration *in the field*, using the PERFORM NOW option in the CALIBRATION menu (using buffers of pH 7 and pH 10). Carrying buffer solutions to the field and performing a two-point calibration in uncertain conditions may not gain enough accuracy over the second option to justify the extra effort.

2. If you choose to calibrate the pH Sensor, it is important to have adequate supplies of pH buffer solutions available. Vernier sells a pH buffer package for preparing buffer solutions with pH values of 4, 6, 7, and 10. You simply add the capsule contents to 100 mL of distilled water. The order code is PHB, and the price is $10.00.

   You can also prepare pH buffers using the following recipes:

   pH 4.00: Add 2.0 mL of 0.1 M HCl to 1000 mL of 0.1 M potassium hydrogen phthalate.

   pH 7.00: Add 582 mL of 0.1 M NaOH to 1000 mL of 0.1 M potassium dihydrogen phosphate.

   pH 10.00: Add 214 mL of 0.1 M NaOH to 1000 mL of 0.05 M sodium bicarbonate.

3. The pH Sensor can be stored short term (up to 24 hours) in pH-4 or pH-7 buffer solution. For long-term storage (more than 24 hours) the pH Sensor should be stored in a buffer pH-4/KCl storage solution in the storage bottle. The pH Sensor is shipped in this solution. You can prepare additional storage solution by adding 10 g of solid potassium chloride, KCl, to 100 mL of buffer pH-4 solution.

4. Your Vernier pH Sensor is not temperature compensated. Commercial pH electrodes are not usually temperature compensated, because most measurements or calibration will be done at room temperature—any errors related to temperature variation are most likely negligible. If you are taking pH measurements in a stream that is significantly warmer or cooler than room temperature, the error may still be very small or negligible. This is because the pH Sensor has an *isopotential* value of pH 7.0. The isopotential point is that pH value where the response of the electrode does not vary with temperature. If you are making pH measurements in water with a value near pH 7, then almost no pH error results with changing temperature. Even if you were measuring a sample with a pH of 8.0 at a temperature that is 15°C lower than the temperature at which your calibration was

performed, the error that results from neglecting the temperature factor is only 0.05 pH units. Another option, of course, would be to take the sample back to the lab, and let it return to room temperature just before taking its pH reading. Since the sample is at the same temperature at which the calibration is performed, no error results.

5. The SINGLE POINT data-collection mode was designed to make measurements easier and more accurate. When SINGLE POINT mode is used, the interface takes readings for 10 seconds. These readings are averaged and this average value is displayed on the calculator. This method has several advantages over other data-collection modes: (1) It eliminates the need for students to choose one value over another if that value is fluctuating; (2) If the readings are fluctuating a little, an average of the values is desirable; (3) It requires the students to hold the sensor in the water longer that they might tend to otherwise.

How the pH Sensor Works

The Vernier pH Sensor is a general-purpose pH measurement system. The electrode has a gel-filled half cell that is sealed—it never needs to be refilled. The glass bulb at the tip of the electrode measures the H^+ concentration. The voltage produced varies linearly with the log of the H^+ concentration; therefore, because pH = $-\log[H^+]$, the voltage varies linearly with pH.