Measuring pH in Water or CaCl2 Using a pH Meter

Compiled by Darren Murray, June 30, 2011

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OVERVIEW

Measuring soil pH requires preparation of a soil/liquid mixture and stirring it several times before leaving it to settle into a supernatant solution. The liquid is either deionized water or a prepared 0.01M $CaCl_2$ solution that is added to soil in a 1:2 soil to liquid mixture (1:4 for organic soils).

A pH meter provides a reading based on a voltage differential that occurs from immersing an electrode attached to the meter into the prepared supernatant solution. Our lab uses three pH meters: WTW pH 330i, Hanna 8314 and Hanna 9025 which measure pH using the same principle and similar procedures. The WTW pH 330i and the Hanna 8314 are to be used for research only while the Hanna 9025 meter is preferred as a teaching aid or for field use. Readings are derived from a voltage differential in hydrogen ion concentration within the glass of the electrode and outside of the glass in the sample solution that meter reads in pH units. KCl is also present in the electrode to facilitate an electrical connection between the electrode solution and sample solution. Samples are tested by placing the meter's electrode into the sample solution until the reading has stabilized (usually after one minute).

The electrode is a very sensitive and important component and requires careful use and storage which is very straightforward but critical to preserve electrode reliability. **The key to preserving the electrode is to keep it clean, free of any scratches and moist at all times.** Thus rinsing with deionized water after each test and storing the electrode in pH 4.0 buffer solution (in its storage cap) when not in use are very important pH meter procedures. Also avoid electrode contact with anything that could damage the sensitive electrode surface such as tapping on the edge of beakers, touching with fingers or even wiping dry with a towel.

Figure 1: pH electrodes stored in buffer solution held within the electrode storage cap. It is VERY IMPORTANT to store the electrode in pH 4.0 buffer solution when not in use.

PREPARING THE pH METER FOR USE (Calibration and Buffer Solutions)

When is Calibration Required?

Calibration is recommended regularly as the chemistry of the electrode changes over time which will affect pH readings. The suggested time interval between calibrations is one week for the WTW meter and one month for the Hanna meters. Other circumstances where calibration is required is if the battery has been replaced or if a new electrode is being used. If the performance of the pH meter or last calibration date is in doubt, it is advisable to calibrate. Understanding this section is critical to understanding the operation of the pH meters.

Supplies and Preparation

-Buffer solutions (Usually pH 4.0 and pH 7.0 are adequate. If samples are expected to be > pH 7.0, use 10.0 pH buffer solution as well).

-Two or three 30mL beakers for buffer solutions

-One 500mL beaker for rinsing

-A rinse bottle with deionized water

-pH electrode stand

-pH meter with electrode

Use of Buffer Solution

Figure 2: Buffer Solution containers, pH 4.0, 7.0 and 10.0 left to right.

There are several important things to keep in mind with buffer solutions:

- Verify the shelf life and expiration date, remembering that shelf-life overrides expiration date once the container is opened (see Appendix 1)
- Avoid contamination of the buffer solution. Never place the electrode in the buffer solution container or put used buffer solution back into the container.
- Use the appropriate buffer solutions that represent the expected range of most sample values to be tested. Most often soils in our region are slightly acidic and a 4.0-7.0pH two point calibration will be adequate.
- Rinsing the beaker with a small amount of buffer solution will help ensure that any previous chemical residues are removed.
- Between pH measurements thoroughly rinse the electrode with deionized water and lightly shake the electrode to remove water drops to protect against cross contamination.

Further information on buffer solution storage and shelf life are found in Appendix 1.

Calibration Procedures for Each Meter

WTW pH 330i Calibration Procedures

1. Pour approximately 15mL of each buffer solution into separate 30mL beakers.
2. Connect the pH electrode to the measuring instrument.
3. Press the button with the red “POWER” symbol to turn the meter on.
4. Press the “CAL” button to bring “Ct1” on the display.
5. Remove the storage cap from the electrode.
6. Rinse the electrode with deionized water and shake gently to remove any excess water
7. Place the electrode into the pH 4.0 buffer solution ensuring that the combination electrode is fully immersed into the solution (Figure 2). Use the pH electrode stand to help ensure the electrode is placed vertically.

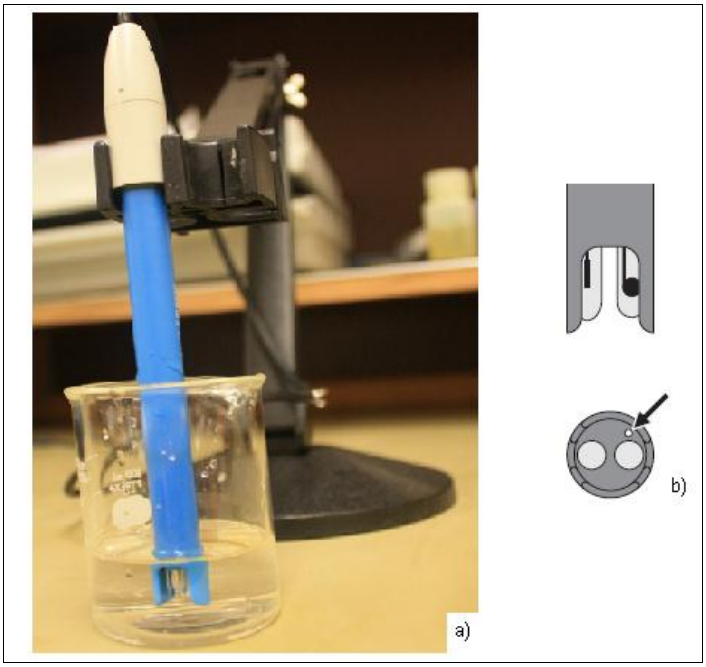

Figure 3: A pH electrode stand (a) is a useful tool for positioning the electrode into the sample and freeing up your hands. When immersing the electrode into the sample ensure that the full depth of the cavity is immersed so that all sensor areas are in contact with the sample particularly, the electrode junction (b), noted by the arrow.

8. Rinse the electrode cap with deionized water to remove any residues and leave to dry.
9. Press the “RUN/ENTER” button on the pH meter.
10. On the bottom of the screen you will see “AutoCal TEC” and to its right “AR” (this stands for AutoRead) flashing repeatedly.
11. “AR” will flash (sometimes for a couple minutes, be patient) until it measures a stable value. Then “Ct2” will appear on the display.
12. Once you see “Ct2” on the display, remove the electrode from the pH 4.0 buffer solutions and rinse with deionized water, then shake the electrode gently to remove excess water.
13. Immerse the electrode in the pH 7.0 buffer solution and press “RUN/ENTER”.
14. On the bottom right of the screen “AR” will begin to flash again until it measures a stable value.

15. Once the reading becomes stable, the results of the calibration will be displayed. The immediate value on the display is the slope represented in mV/pH. To the right of this reading is a picture of an electrode with vertical bars in it (Figure 3). If one or more bars are present the meter is ready for testing and you have successfully completed a two point calibration. However if no bars are present the electrode needs to be cleaned (per the electrode operating manual: http://www.wtw.com/downloads/manuals/ba75740e01_sentix_gel.pdf). Also if you receive an error message such as E3, the calibration is invalid (refer to manual: http://www.wtw.com/downloads/manuals/ba52310e04_pH_330i-340i.pdf , section 6 "What to do if…"). See Appendix 2 for further explanation of calibration results.

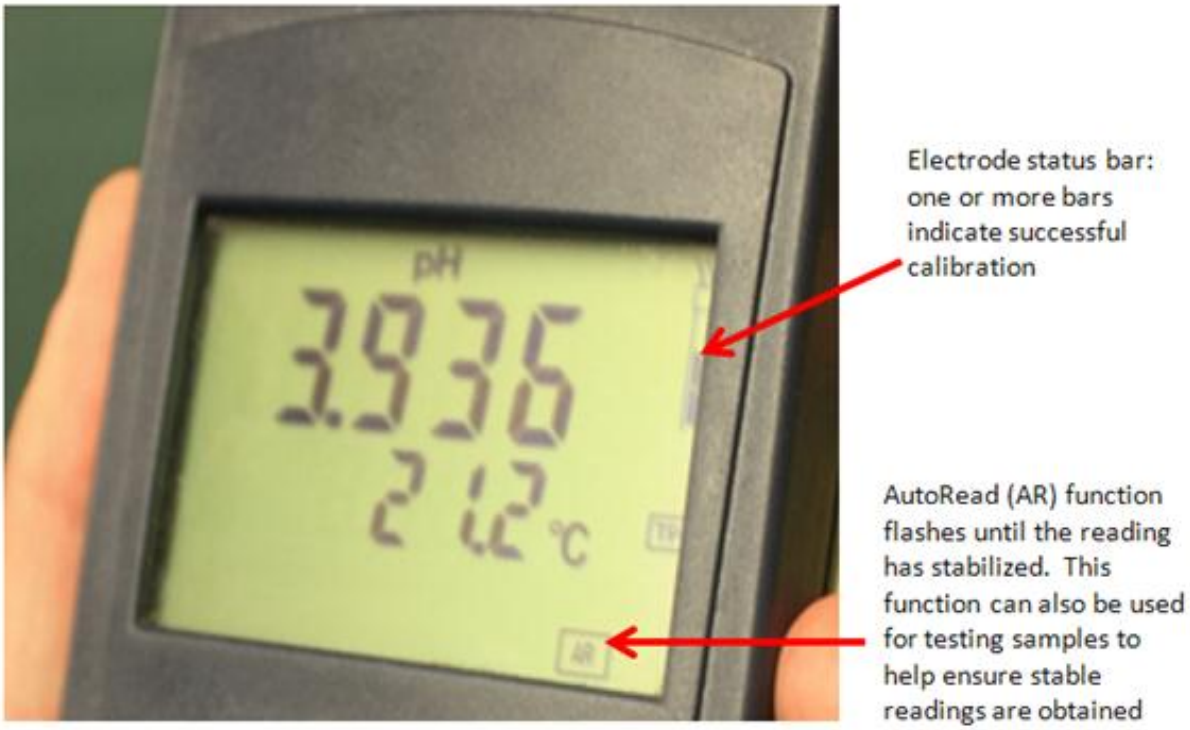

Figure 4: WTW pH meter displaying that a successful calibration has been run recently.

16. If the calibration was successful you can either continue with a three point calibration by following steps 12 and 13 again but with pH 10.0 buffer solution and observing "Ct3" on the display or start testing.

17. Press “M” (measuring mode) button to get into regular testing mode to start measuring samples.

Hanna 8314 Procedures

1. Pour approximately 15mL of each buffer solution into separate 30mL beakers.
2. Connect the pH electrode and temperature probe to the meter and press the “ON/OFF” button.
3. Remove the protective cap from the electrode.
4. Rinse both the electrode and temperature probe with deionized water. Shake gently to remove excess water drops.
5. Immerse the probe and the electrode into the pH 7.0 buffer solution ensuring that the temperature probe is as close as possible to the electrode. The electrode should be submerged at least 1.5 cm into the solution.
6. Rinse the electrode cap with deionized water to remove any residues and leave to air dry.
7. Press the pH and ^{O}C buttons to display respective pH reading and temperature reading options and wait for the pH reading to stabilize (usually within a couple minutes).
8. Adjust the calibration trimmer on the bottom left (STD 1st) with a screw driver supplied in the pH kit so that the pH value is obtained for the corresponding temperature and buffer solution per Table 1 below.

pH VALUES AT VARIOUS TEMPERATURES

TEMP	pH VALUES		
°C	4.01	7.01	10.01
0	4.01	7.13	10.32
5	4.00	7.10	10.24
10	4.00	7.07	10.18
15	4.00	7.04	10.12
20	4.00	7.03	10.06
25	4.01	7.01	10.01
30	4.02	7.00	9.96
35	4.03	6.99	9.92
40	4.04	6.98	9.88
45	4.05	6.98	9.85
50	4.06	6.98	9.82
55	4.07	6.98	9.79
60	4.09	6.98	9.77
65	4.11	6.99	9.76
70	4.12	6.99	9.75

Table 1: Hanna HI 8314, calibrating pH readings to various temperatures.

9. Rinse the electrode and temperature probe and immerse them into pH 4.0 or pH10.0 buffer depending on the expected sample pH range (most likely pH 4.0).
10. Once the pH reading has stabilized use the screwdriver to adjust the other calibration trimmer on the bottom right (SLOPE 2nd) until the pH reading corresponds with the temperature in Table 1.
11. The meter is now ready for sample testing.

Hanna HI 9025 Procedures

1. Pour 15mL of each buffer solution into separate 30mL beakers.
2. Connect the pH electrode and temperature probe to the meter.
3. Remove the protective cap from the electrode and rinse both the electrode and temperature probe and shake gently to remove excess water.
4. Immerse the probe and the electrode into the solution ensuring that the temperature probe is as close as possible to the electrode. The electrode should be submerged at least 1.5 cm into the solution.

5. Rinse the electrode cap with deionized water to remove any residues and leave to air dry.
6. Press the “ON/OFF” button. Note that buttons have a delayed response and holding down lightly for a couple of seconds is required to get a response.
7. If “CAL” does not appear on the left of the screen, press and hold down the “CAL” button and the left side of the screen will flash “NOT READY” until the meter reading stabilizes.
8. Once “CAL” is on the screen you can ensure that the meter is set to calibrate for the appropriate buffer solution by viewing the pH value in the bottom left of the screen (next to “BUF”). If it is not at the appropriate pH for the buffer solution being used, change the value by pressing the up arrow ^{o}C button or the down arrow ^{o}C button

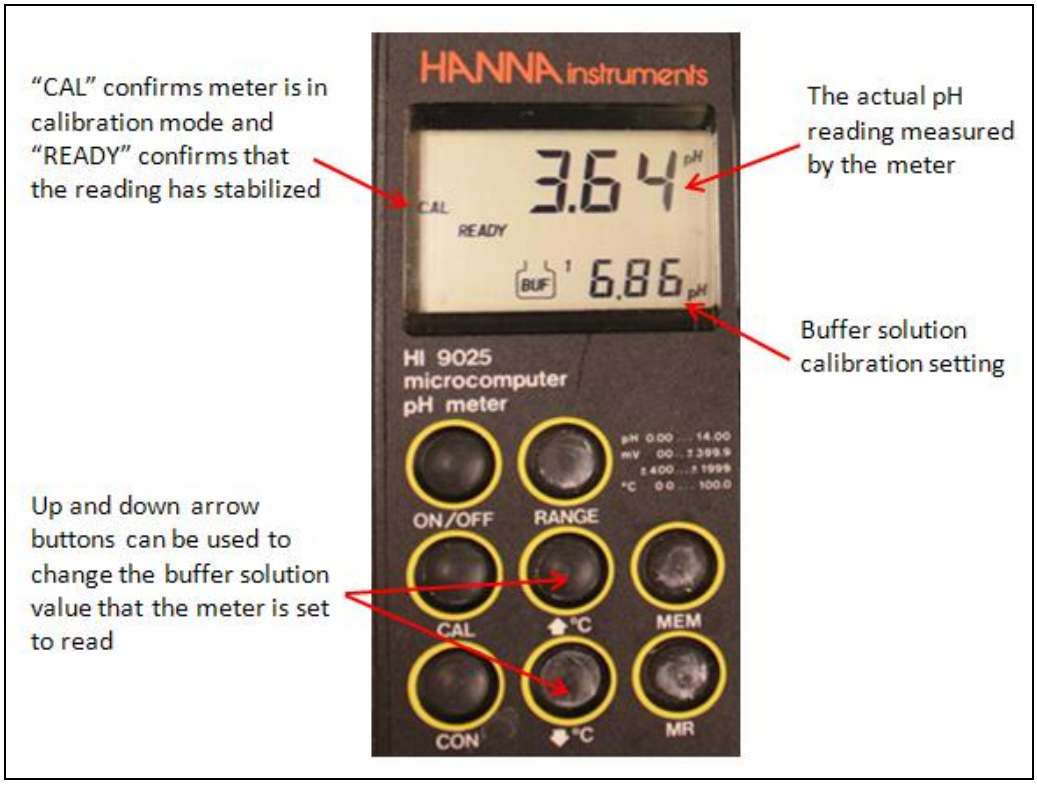

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Figure 5: Hanna 9025 pH meter displaying several functions. The meter is currently reading pH 3.64 and is stabilized because it is measuring solution in the electrode cap. Once the cap is removed and the electrode is inserted in buffer solution, “NOT READY” will start to flash until the reading restabilizes. Adjust the buffer solution calibration setting from 6.86 pH to 4.01pH or 7.01pH by pressing the down or up arrow buttons respectively.

9. Once the reading is stable it will change to “READY” and “CON” will flash.
10. Press the “CON” button to confirm the calibration. If the reading was not close to the selected buffer “WRONG” will flash on the display. If the reading is close to the selected buffer, the meter stores the reading and the buffer value is displayed.
11. If “WRONG” is flashing ensure that the meter is set to calibrate to the pH value of the buffer solution. For example, 4.01pH should be on the bottom left of the display if using the 4.0 buffer solution. If the meter is set correctly, rinse the electrode ensuring it is free of residues. Turn the pH meter off and restart at step #3.
12. If the reading was close to the selected buffer solution “BUF 2” should appear at the bottom of the screen. Remove the electrode and temperature probe and rinse them with deionized water.
13. Immerse the temperature probe and the electrode into the next buffer solution.
14. Ensure the pH value for “BUF 2” matches the buffer solution being used. For example, 7.01 for 7.0 buffer solution. Change with up or down arrow buttons if required.
15. Once the reading is stable it will change to “READY” and “CON” will flash.
16. Press the “CON” button to confirm the calibration. If the reading was not close to the selected buffer, “WRONG” will flash on the display. If the reading is close to the selected buffer, the meter stores the reading and the buffer reading is displayed.
17. Upon successful calibration with the second buffer solution, the values will be stored and the meter will now be in operating mode. A pH value and a temperature reading will be on the screen and no other words or images should be present.

TESTING SAMPLES

Supplies and Setup

-1L Volumetric Flask

-0.01M $CaCl_2$ solution: Dissolve 1.47g $CaCl_2*2H_2O$ in 1 L of water in a volumetric flask. Verify that the pH of this solution is between 5.0 and 6.5. If required adjust the pH with $Ca(OH)_2$ or HCl. This should provide enough solution for testing at least 60 samples.
-plastic vials (70mL capacity) for samples

The remaining materials would have been used for calibrating the meters as well:

-Buffer solutions: usually 4.0 and 7.0 are adequate. If samples are expected to be > pH 7.0, use 10.0 pH buffer solution as well.

-Two or three 100mL beakers for buffer solutions

-One 500mL beaker for rinsing

-A rinse bottle with deionized water

-pH electrode stand

-pH meter with electrode

Once calibration has been completed, samples can be tested. As mentioned earlier soil samples can be made up of a suspension of either deionized water or 0.01M $CaCl_2$. Sometimes samples are distributed between two sets of vials, where $CaCl_2$ is applied to one set and water is applied to the other set. Testing with both methods is time consuming so before testing it is advisable to understand the requirements of the data you are collecting to see if one or both methods is required. Forestry Canada highlights several advantages of measuring soil pH in 0.01 M $CaCl_2$ solution (Appendix 3). Generally the pH measured in the $CaCl_2$ solution samples is 0.5pH lower than that measured in water.

Testing Procedure

1. Label vials, (if testing both $CaCl_2$ and water you will need to label two sets of vials clearly noting which set will have deionized water or $CaCl_2$ applied). Also note Appendix 4 for quality control measures for reference samples and duplicate samples.
2. Weigh 5.00g of soil +/-0.02g, preferably field moist or refrigerated for a short time after field collection (or air-dried and sieved samples) into each vial.
3. For measuring pH in water: add 10mL of water to each mineral soil sample and 20mL of water to organic soil samples.
4. For measuring pH in $CaCl_2$: add 10mL of 0.01M $CaCl_2$ solution to each mineral soil sample and 20mL of 0.01M $CaCl_2$ solution to organic soil samples.
5. Allow soil to absorb water and or $CaCl_2$ solution without stirring.
6. Place plastic stir sticks in each vial and stir each sample for 10 seconds.
7. Over the next 30 minutes stir all samples 4-5 times each.
8. Allow samples to settle for 30 minutes.
9. Prepare pH meter for use by verifying calibration.
10. Prepare a worksheet to record sample numbers and results, ensuring that quality control tests are recorded as well.
11. Place electrode in the supernatant solution (if there is a separate temperature probe insert as close as possible to the electrode). Use the pH stand to ensure electrode is placed at an appropriate depth to immerse the shaft (Figure 2).
12. Record the pH value after the reading has stabilized, which normally takes approximately one minute. On the WTW meter stabilization can be observed on the meter by pressing “AR” and then “RUN/ENTER”. “AR” will flash in the bottom right of the display until the meter has taken a stable reading (within 0.02) for > 30 seconds.
13. IMPORTANT: After testing is complete be sure to rinse electrode thoroughly, ensuring it is clean. Fill the electrode storage cap half full with pH 4.0 solution and place the electrode in electrode storage cap. Disconnect electrode and temperature probe (if necessary) and carefully place each pH meter component

in its proper storage section of the pH kit storage case. See Appendix 6 for addressing electrodes that have excessive residues or corrosion issues.

A**PPENDIX 1: Buffer Solutions**

Shelf-life: The typical shelf-life for technical buffers is 2 years unopened and 3-6 months open. However, this is not valid for alkaline buffers (pH buffer 10 or higher). Alkaline solutions will change their pH noticeably when they come into contact with carbon dioxide in the air. The typical shelf-life for alkaline buffers is 1 month open.

Make sure you check the expiration date for your pH buffer solution. Look at the label of the package or at the related certificate of analysis. Do not use a buffer if the expiration date has passed. Also note that the expiration date is for an unopened container.

Storage: Store the buffers at room temperature, 15 to 30 °C (60 to 90 °F), or refrigerated, 2 to 8 °C (35 to 45 °F). Also it is very important to keep your pH buffers in tightly closed containers.

Buffer Solution Pricing: in June 2011

BDH5052-500ML pH 7 - poly bottle (500ml) - $6.24 (each)
BDH5024-500ML pH 4 - poly bottle (500ml) - $4.83 (each)
BDH5078-500ML pH 10 - poly bottle (500ml) - $5.81 (each)

APPENDIX 2: WTW pH Meter Calibration Analysis (Taken from WTW manual)

Calibration evaluation

After the calibration, the measuring instrument automatically evaluates the current status of the electrode. The asymmetry and slope are evaluated separately. The worst evaluation appears on the display.

Display	Asymmetry [mV]	Slope [mV/pH]
	-15 ... +15	-60.5 ... -58
	-20 ... +20	-58 ... -57
	-25 ... +25	-61 ... -60.5 or -57 ... -56
 Clean the electrode according to the electrode operating manual	-30 ... +30	-62 ... -61 or -56 ... -50
E3 Eliminate the error according to chapter 6 WHAT TO DO IF...	< -30 or > 30	... -62 or ... -50

APPENDIX 3: Advantages of measuring soil pH in 0.01 M $CaCl_2$ solution (Forestry Canada):

a) The pH is almost independent of dilution over a wide range of soil.
b) It provides a good approximation of the pH of the soil solution under field conditions.
c) Results are more reproducible than pH measured in H2O.
d) The values obtained are less dependent on the positioning of the electrode.
e) 0.01 M $CaCl_2$ solution is similar in electrolyte composition to soil solutions found in optimum moisture conditions for plant growth in nonsaline soils.
f) The $CaCl_2$ solution masks the variability in salt content of soils, and soil is maintained in a flocculated condition, eliminating suspension effects.

APPENDIX 4: pH Testing Quality Control Measures (Forestry Canada)

a) A minimum of one reference sample should be analyzed per batch of 40 samples or less to verify if the pH meter is reading accurately. Buffer solution can be used as the reference sample as it has a known value. Note Appendix 5 for an explanation of why to avoid using deionized water as a reference sample.
b) A duplicate sample should be prepared for 5% of samples to verify the pH meter is reading precisely. Therefore a batch of up to 40 samples should contain two duplicates. The precision should be less than or equal to 5% and can be calculated as follows:
Two samples with pH results of 5.85 and 6.00 is a 0.15 difference:
(0.15/5.85)*100 = 2.56% which is acceptable precision.

APPENDIX 5: Mission Impossible: Measuring the pH of Pure Water!

You wouldn't think it would be so darn difficult!

By Frank Paparone, Technical Support Leader, OAKTON Instruments

What could possibly be so difficult about reading the pH of pure water? It should be neutral—pH 7.0—without any ion interference, right? In fact, it can be quite difficult and often frustrating to obtain reproducible pH values in samples with low-ionic strength.

Water that has very few ionic species is said to be low in alkalinity, ionic strength, or to have low conductivity/high resistivity, such as with distilled or deionized (DI) water. And due to the varying junction potentials that develop across the reference junction, when attempting to measure DI water it is common to attain different pH values even with new, sealed electrodes that calibrate perfectly in pH buffers.

Please see:
http://www.coleparmer.ca/techinfo/techinfo.asp?htmlfile=pHPureWater.htm&ID=556 for the remainder of this article.

APPENDIX 6: Electrode Cleaning and Restoration

Some samples such as clay will stubbornly remain on the electrode even after thorough rinsing. To remove stubborn residues soak the electrode in pH 4 buffer solution at 50°C for 2-4 hours.

Often pH kits can go unused for long periods of time and there can be issues with the electrode. One thing to periodically check is for corrosion within the interior wire of the electrode. If corrosion is visible, the electrode will need to be replaced. Also if an electrode has been left to dry it can be restored by soaking it in tap water for a couple hours and then filling the electrode cap half full with pH 4.0 buffer solution and storing the electrode in the cap with solution over night before testing.

REFERENCES

(All websites accessed June 2011)

Cole-Parmer Technical Library
http://www.coleparmer.ca/techinfo/techinfo.asp?htmlfile=pHPureWater.htm&ID=556

Hanna 8314 pH meter manual: http://www.hannainst.com/manuals/manHI_8314.pdf

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http://www.mbhes.com/Adobe%20files%20for%20hyperlinks/HI%209025c.pdf

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WTW pH electrode manual:
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Photographs taken by Qingcen Cai