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pH

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Calibration - Reagents and Solutions

The following reagents and solutions are required for measuring pH:

- i. pH 4.01 buffer solution
- ii. pH 6.86 (7.0) buffer solution
- iii. electrode storage solution (typically KCl)
- iv. Type I DI water: resistivity >18.0 MΩ.

Calibration

Calibrate as specified in the manual for the pH meter. At a minimum calibrate at two points in the expected pH range. Calibrate before and after measuring each set of precipitation samples.

- 1) Fill the electrode with a filling solution (if required) then rinse the outside of the electrode with deionized water. Check the room temperature and set the temperature of the meter to the current room temperature. If the pH instrument is equipped with a temperature sensor, the temperature correction occurs automatically; no adjustment is needed. It is best if all calibration buffers and samples to be measured are stabilized at room temperature.
- 2) Place the 6.86 buffer solution in a clean polyethylene or borosilicate glass vessel with enough liquid to immerse the measuring bulb of the electrode. If using a glass beaker or vessel, use it only for the 6.86 buffer. Use a separate glass vessel for the 4.01 buffer. Buffers are highly concentrated (some are dyed) and the glass beaker may become “seasoned” with residual salts. If the same beaker were used for both buffers, this residual would carry over and contaminate the other buffer. Check the measured pH of the 6.86 standard. It should be within 0.02 pH units of the certified buffer value. Set the meter to read this calibration value. Thoroughly rinse the electrode with deionized water.
- 3) Place the 4.01 buffer solution in a clean polyethylene or borosilicate glass vessel with enough liquid to cover the glass measuring bulb of the electrode. Check the measured pH of this second standard. It should be within 0.02 pH units of the certified buffer value. Set the meter to read this calibration point. Thoroughly rinse the electrode with DI water.
- 4) Confirm the accuracy of the calibration by measuring the pH 6.86 buffer again, followed by the pH 4.01 buffer. Make sure that the results are within ± 0.02 pH units of the certified values. If not, repeat steps (2) and (3), until the ± 0.02 pH unit criterion is met. Calibration is completed only when this criterion is met.
- 5) Once the calibration is completed, rinse the electrode thoroughly with DI water. Precipitation is not buffered and has much lower ion strength than the buffered calibration standards. Incomplete rinsing will allow the buffers to contaminate precipitation samples and bias the readings.

Quality Control

The following are QCS and other control solutions for pH measurements:

- 1) QCS-1 (4.01 pH unit) solution: Dilute 1.0 g 0.1N H₂SO₄ in 1 L of DI water. QCS-1 is prepared in 10 L amounts and stored in a HDPE container. Stable for up to one year at 4°C.
- 2) QCS-2 (5.05 pH unit) solution: Dilute 100 mL of QCS-1 in 1 L of DI water. Prepare QCS-2 in 10 L amounts and store in a HDPE container. Stable for up to one year at 4°C.
- 3) A check solution comprised of a real precipitation matrix may be prepared by pooling precipitation samples. The pooled sample may be analyzed 20 times over 20 runs to establish a mean and preliminary standard deviation. This solution will not be stable for longer than six months unless sterilized.
- 4) Check the pH of DI water after the meter and electrode have been calibrated with buffers. Water in equilibrium with atmospheric CO₂ has a pH of about 5.65. DI water measurements are slower to stabilize than buffer measurements, because they are very dilute (low ion strength) and typically read between 5.58 and 5.75 pH units.
- 5) The pH value of the QC solutions including DI water should agree within ± 3 standard deviations (in pH units) of the expected value. If larger differences are observed, the system must be calibrated anew. If the QC values are outside acceptable limits, the electrode must be cleaned (see manual) or replaced.
- 6) Analyze a QCS of other control solution every 10 samples to ensure the system remains in control throughout the analytical run.

Analytical Procedures

The procedure for measuring pH is as follows:

- 1) Maintain all solutions to be measured at the same temperature. Allow samples and control solutions to come to room temperature.
- 2) Calibrate the pH meter and electrode according to the procedure outlined in the previous section.
- 3) Rinse the electrode with DI water. If sample volume allows, rinse the electrode with an aliquot of the sample by placing the sample solution in a clean polyethylene or borosilicate glass vessel with enough liquid to cover the glass measuring bulb (Figure 4.21) of the electrode.
- 4) Immerse the electrode in the sample vessel and swirl the sample gently for a few seconds to condition the electrode with the sample. Do not stir the sample with a rod or magnetic stirrer. Discard this sample aliquot. Do not rinse off the electrode.
- 5) Place a fresh aliquot of the same sample in a clean polyethylene or borosilicate glass vessel again with enough liquid to cover the glass measuring bulb of the electrode. Immerse the electrode in the sample vessel and swirl the sample gently for a few seconds. Do not stir the sample with a rod or magnetic stirrer.
- 6) Allow the electrode to equilibrate until a stable pH value is obtained. Samples with pH in the range of 6 to 7 are slower to stabilize. Observe the reading on the meter. The reading may appear to still be increasing even though the meter signals a stable reading. Press *Read* again until the value stops climbing. Record the pH value (to 0.01 unit).

- 7) Enter data into the data set. See section 4.3.14 for manual data verification if the pH meter does not have a data export function. Report values to the required decimal places. Account for missing samples and samples too contaminated to be analyzed. Add comments or codes as needed to account for all samples.

Troubleshooting

Problem 1: Measuring pH in precipitation is difficult due to the low ionic strength of the samples.

Solution 1: Some pH systems allow for a 1 μL injection of KCL to add ionic strength to the sample without changing the pH. It is not an ideal solution and the laboratory should conduct a study to see if pH results with KCl injections are the same as those without. Purchase an electrode specifically designed for low ion strength or pure water samples.

Problem 2: pH is affected by temperature.

Solution 2: Samples refrigerated at 4°C must be brought to room temperature for analysis. Enter the room temperature into the pH meter to ensure an internal default temperature is not applied to the result or use a system equipped with a temperature sensor. Ensure buffers, QCS and samples are all at the same temperature during analysis.

Problem 3: Two main problems with pH measurements is aging of the electrode and using the electrode for samples other than precipitation. Electrodes tend to become less sensitive with age and may give incorrect measurements for precipitation samples, while giving correct readings for the calibration buffers. Probes used to analyze other water samples, such as stream water or drinking water, can also become insensitive and unresponsive to the low ion strength of precipitation samples.

Solution 3: Confirm electrode calibration and function by using real precipitation samples to make QC checks. Real precipitation has the advantage of being a low ion-strength solution. Use pH electrodes **only** for analyzing precipitation samples.

Problem 4: Bubbles in the glass measuring bulb cause unstable readings.

Solution 4: Electrode care and maintenance is important. Replace the electrode fill solution per manufacturer's specifications. Inspect the bulb for bubbles and if present swing the electrode down in an effort to get the bubbles to rise out of the bulb.

Problem 5: Static electricity builds up on the glass bulb and causes erroneous measurements. Using a magnetic stirrer may produce the same effect.

Solution 5: Never dry the outside of the electrode by rubbing or wiping it with a Kimwipe®. Instead, rinse the electrode with sample solution but don't dry it. Do not allow the fill solution or the glass measuring bulb to dry out. When not in use, store the electrode in deionized water or electrode storage solution. Don't use stirring systems that continuously agitate the sample.

Problem 6: Poor calibration and control results. Recalibration does not solve the problem and response is slow.

Solution 6: A periodic cleaning procedure is recommended to remove built up organic material and to rejuvenate the electrode. Empty the electrode fill solution and soak the probe in a pH 4.0 solution for a minimum of 24 hours, then soak it in DI water for 24 hours. Refill the electrode with fill solution and performance test the electrode. If this does not solve the problem, replace the electrode. Cleaning procedures vary with the type of electrode but usually involve soaking the electrode in a weak basic solution followed by a weak acidic solution. The acidic solution rejuvenates the glass membrane.

Tips to Improve Performance

1. Document maintenance procedures in a log book.
2. Mark QC charts to document when maintenance is performed and to see the potential impact of maintenance on measurements.
3. Clean electrodes on a weekly basis or every 150 samples.
4. Use an electrode specifically configured for low ionic strength or pure water samples.

5. Set aside samples containing contaminants and measure them separately **after** measuring the clean and clear samples. Clean the electrode after analyzing contaminated samples.
6. Use a sample aliquot to rinse and condition the electrode prior to taking the reading.
7. Do not rush the analysis.
8. Do not measure hard water (lake, river, or tap water) samples using the same electrode that is used for measuring precipitation samples.
9. Routinely check internal fluid levels and refill as necessary.