Applications Tip of the Week
pH of Pure Water and Other Low Conductivity Waters
Laboratory and Grab Sample Measurement

Measuring pH in purified water (and other low conductivity waters) can be challenging. This is due to the low ionic strength and un-buffered nature of the sample. These factors may lead to issues such as noisy readings, slow response, drift, and poor precision and accuracy. Challenges and recommendations are discussed here.

Challenges of Testing pH

Low conductivity water is described (by ASTM D5464) as water with a conductivity of < 100 uS/cm. The pH of high purity water is generally in the range of 5.5 to 7.5 pH, depending on the level of carbon dioxide (CO_2) in the water. The challenges of testing pH in pure water and other low conductivity waters are:

1. Low conductivity water is a high resistance sample, which may lead to noisy readings and signal drift.
2. Due to the low concentration of ions in these waters, they are also poorly buffered and so are subject to contamination (e.g. from CO2 or ammonia absorption, and/or cross contamination from other sources, during sampling, transport, storage, handling, and testing).
3. The large difference in ionic strength between the electrode filling solution inside and the sample outside the electrode may lead to significant junction potentials, which can affect accuracy, cause long stabilization times, and lead to poor precision.

Who knew such a "simple" test could be so challenging?

Factors to Optimize Your pH Test Results

There are several different factors which can be optimized to provide high quality pH test results in pure water and other low conductivity waters. These factors include:

- Choice of Electrode/Junction and Filling Solution
  - o Experts do not agree on what type of electrode junction works best, although a low resistance junction is often cited as desirable. See below for our top choices.
    - Avoid a saturated silver electrode filling solution - a precipitate can form on contact with pure water, which may lead to clogging and high resistance in the junction.
  - o Use a well shielded electrode and a high-impedance pH meter to reduce signal noise.
    - In our experience, Orion pH meters used with the following ROSS® electrodes (which use a silver-free filling solution) are the best performers: 8107 triode with capillary junction, 8102 with ceramic junction, and 8172 with Sure-Flow® junction.
  - o Since pH is temperature sensitive, use a triode or an automatic temperature correction (ATC) probe to monitor sample temperature and automatically adjust electrode slope response.
- Sampling Considerations
  - o Handle low conductivity water samples carefully to minimize air absorption and CO_2. Use of glass containers is preferred, since air can diffuse through plastic.
  - o For transportation and storage of samples, containerize samples so that there is no headspace.
  - o Test the samples as soon as possible after collection to minimize temperature changes, sample aeration, and contact time with the sample container.
  - o Make sure that all containers and equipment are triple-rinsed with pure water before use to avoid cross- contamination, which can arise from a variety of sources.

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- Calibration of pH Electrodes
    - Best results are obtained when the calibration standards and samples are within 2 °C of each other. Use an ATC or triode to monitor temperatures.
        - If sample and calibration standards can not be at the same temperature, measure the pH at the temperature as found and use an ATC or triode to measure temperature and adjust the slope accordingly.
        - Report the pH value and the temperature reading together.
    - Rinse well after electrode calibration to avoid cross-contamination of your samples.
        - It takes only a tiny amount of buffer to dramatically shift your pure water pH results.
        - Use the cleanest possible water for rinsing.
- Handling of pH Electrodes
    - Since pure water can leach ions from the pH bulb, store the pH electrode in electrode storage solution to restore the bulb surface composition.
    - If response becomes sluggish, clean the pH electrode to refresh the pH bulb and/or the junction. Try using the Orion pH cleaning solution C (Orion 900023) per instructions.

How to Test pH of Pure Water and Other Low Conductivity Waters
- Option 1 – use best practice rinsing and testing techniques
    - For each sample tested, prepare one test portion and one or more rinse portions. Immerse and gently agitate the pH electrode in the rinse portion(s) before placing into the test portion.
        - The rinsing will: reduce cross contamination; adjust the electrode to the temperature of the sample; rinse and condition the junction to the ionic strength of the sample.
        - The same rinsing technique may be used with the calibration buffer standards.
    - Stir the sample gently to speed the electrode response. Stirring may continue throughout as long as air is not being incorporated into the sample by the stirring action.
    - Use a continuous read option and allow plenty of time for the electrode to respond completely. Best precision and accuracy occur when adequate time is allowed to reach stability.
        - Once a typical response time has been established, consider using a timed reading to promote an adequate wait time that will achieve consistent and precise results.
    - For high precision work, ASTM D1293 recommends testing successive portions of sample until the drift rate is minimal and two successive results agree within the desired criteria. See details in ASTM D1293 at www.astm.org .
- Option 2 – adjust the ionic strength of the sample (e.g., USP Purified Water test protocol)
    - To dramatically improve the precision and response time of the measurement, add an ionic strength adjustor to the water sample. It won't significantly affect the pH[1].
        - By adjusting the ionic strength, the high resistivity of the sample is overcome and the ionic strength differential between the sample and the electrode filling solution is eliminated.
    - Add 0.30 mL of saturated (~3-4M) potassium chloride (KCl) solution to 100 mL of the test sample. Stir briefly and test the pH as usual.
    - Alternately, use the Orion Pure Water pH Test Kit (Orion 700001) which includes diluted buffers in a KCl background and a pHISA ionic strength adjustor solution to match the sample background to the standard background.
        - For details, see Technical Bulletin 501 – pH Measurement in Low Ionic Strength Solutions in our online library at www.thermoscientific.com/waterlibrary .

[1]For example, adding KCl at 0.01M may shift pH by +0.02 pH. (Metcalf, Peck, and Arent, , *Analyst*, July 1990, Vol 115, 899).