Application Note 005

Measuring pH of Pure Water and Other Low Conductivity Waters

Water Analysis Instruments, Thermo Fisher Scientific

Key Words
pH, pure water, low conductivity water, low ionic strength, electrodes, solutions.

Goal

The following application note describes the challenges and recommendations when measuring pH in purified water and other low conductivity waters.

Introduction

Measuring pH in pure water may seem simple in theory. For example, pure water should be neutral-pH 7.0 and there should be no interferences.

Measuring the pH of pure water is challenging because the pH electrode response tends to drift and may be slow, non-reproducible and inaccurate. Measurements in these samples are more difficult because of the low conductivity of the sample, differences between the low ionic strength solutions and normal ionic strength buffers, changes in the liquid junction potential and the absorption of carbon dioxide into the sample. Since pure water solutions have a low conductivity, the solution will tend to act as an "antenna" and the electrode response can be noisy.

By understanding the challenges associated with measuring pH in pure water and other low conductivity liquids, you can overcome them and ensure that your pH measurements are reliable and repeatable.

Quick Facts: Pure Water

Low conductivity water is described by ASTM D5464 as water with a conductivity of < 100 µS/cm.

The pH of high purity water is generally in the range of 5.5 to 7.5, depending on the level of carbon dioxide (CO_2) in the water.

Purified water that has very few ionic species is said to be low in alkalinity, ionic strength, or have low conductivity/high resistivity.

Pure water samples include distilled water, deionized water, some process waters, well water, some surface waters, some treated effluents, boiler feed water and rain water.

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The three most common challenges when testing pH in pure water and other low conductivity waters are:

1. **Electrode Drift**
   Low conductivity water is a high resistance sample. This may lead to noisy readings and signal drift.

2. **Contamination of Sample**
   Due to the low concentration of ions in these waters, they are also poorly buffered and so are subject to contamination (e.g. from CO_2 or ammonia absorption, and/or cross contamination from other sources, during sampling, transport, storage, handling, and testing).

3. **Inaccurate Measurement**
   The large difference in ionic strength between the electrode filling solution inside and the sample outside the electrode may lead to significant junction potentials. This can affect accuracy, cause long stabilization times, and lead to poor precision.

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:

- Choosing the right pH electrode
- Sampling considerations
- Calibrating your pH electrode
- Handling your pH electrode

Choosing a pH Electrode

There are many different types of electrodes available for pH measurement. When selecting your electrode, it is important to consider the electrode features and its compatibility with the sample being measured. A low resistance junction works best when measuring pure water samples. 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.

Use a well-shielded electrode and a high-impedance pH meter to reduce signal noise. Thermo Scientific™ Orion™ pH meters used with Thermo Scientific™ Orion™ ROSS™ pH electrodes are the best performers. The Orion ROSS 8107 triode with capillary junction, the Orion ROSS 8102 with ceramic junction, and the Orion ROSS 8172 with Thermo Scientific™ Orion™ Sure-Flow™ junction all use silver-free filling solution.

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.

Take the guesswork out of your pH electrode selection. Use our interactive selection guide to match the exact pH electrode model to your application needs. Visit orionelectrodes.thermoscientific.com

Sampling Considerations

1. Handle low conductivity water samples carefully to minimize air and CO_2 absorption. Using glass containers is recommended, since air can diffuse through plastic.

2. For transportation and storage of samples, containerize samples so that there is no headspace.

3. Test the samples as soon as possible after collection to minimize temperature changes, sample aeration, and contact time with the sample container.

4. 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.

Calibrating your pH electrode

Calibration of a pH electrode in high ionic strength buffers will increase the time required for stabilization when measuring a low ionic strength sample. In addition, the possibility of sample contamination will be increased. For most precise measurements, buffers and samples should have a similar ionic strength. 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 cannot 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. When documenting the results, 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 your pH electrode

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

1. 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.

   Rinsing will reduce cross contamination, adjust the electrode to the temperature of the sample, and rinse and condition the junction to the ionic strength of the sample. The same rinsing technique may be used with the calibration buffer standards.

2. 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.

3. 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.

4. 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)

1. 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^.

   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.

2. 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 Thermo Scientific™ Orion™ Pure Water™ pH test kit (Cat. No. 700001) which includes diluted buffers in a KCl background and the Thermo Scientific™ Orion™ pHISA™ ionic strength adjustor solution to match the sample background to the standard background.

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

The Orion Pure Water pH test kit has been developed to minimize the problems encountered when measuring pH in pure waters.

This test kit uses a pure water pH additive called pHISA adjustor and low ionic strength buffers that contain the same background as the pHISA adjustor. For the most accurate results, a Thermo Scientific™ Orion™ ROSS Ultra™ or ROSS pH electrode is recommended.

Adding pHISA adjustor to samples increases the ionic strength, reducing the noise and improving the response time. The shift in pH caused by the addition of pHISA adjustor is minimal – between 0.005 and 0.01 pH units. Since the same amount of pHISA adjustor is added to the buffers and samples, the net effect on the pH is negligible. Calibration is performed using the low ionic strength buffers with pHISA adjustor already added.

Measuring with samples and buffers with the same ionic strength increases accuracy, precision and time response. Contamination due to carryover from higher ionic strength buffers is also minimized.

Summary

It can be quite difficult and often frustrating to obtain reproducible pH values in samples with low-ionic strength. By employing some best practices and following the recommendations outlined in this application note, you can increase measurement accuracy, reduce electrode drift and prevent sample contamination with your pH measurements.

To purchase an Orion ROSS pH electrode or an Orion Pure Water pH Test Kit, please contact your local equipment distributor and reference the part numbers listed below.

Product	Description	Part Number
ROSS pH Elecrodes	Thermo Scientific Orion ROSS Ultra pH/ATC Triode with epoxy body, low maintenance gel	8107BNUMD/8107UWMMD
	Thermo Scientific Orion ROSS Ultra combination pH electrode with extended life	8102BNUWP/8102BN/8102SC
	Thermo Scientific Orion ROSS Sure-Flow combination pH electrode with epoxy body	8172BNWP
Solutions and Accessories	Orion Pure Water low ionic strength pH test kit	700001
	Orion pH Electrode Cleaning Solution C, for general cleaning	900023

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