Instruction Sheet

Technical Bulletin 501 – pH Measurements in Low Ionic Strength Solutions

Background Information

pH measurements are typically made in solutions that contain relatively large amounts of acid or base or contain substantial amounts of dissolved salts. Under these conditions, conventional pH electrodes can make measurements quickly and precisely. There has been a growing interest in making pH measurements in pure water. Pure water is water in which the total amount of acid or base is very small and in which there is a low level of dissolved salts. The terms pure water and low ionic strength can be used interchangeably. Sample that may fall into this category include:

- Distilled waters
- Some surface waters
- Some process waters
- Well waters
- Deionized waters
- Treated effluent water
- Boiler feed water

Measurement in these pure water samples are more difficult. Although electrodes respond quickly in buffers, in pure water the electrode response is often unsatisfactory - slow, drifting, noisy, non-reproducible and inaccurate.

The Problem

These commonly observed problems can be attributed to the low conductivity of the sample, differences between low ionic strength solutions and normal ionic strength buffers, changes in the liquid junction potential, and absorption of carbon dioxide.

Since pure water solutions are poor conductors, the solution will tend to act as an antenna and the electrode response can be noisy. Standardization of an electrode in a high ionic strength buffer 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 be of similar ionic strength. When any two solutions come in contact, diffusion occurs until equilibrium is reached. Since ions have different mobility and diffuse at different rates, a charge imbalance occurs at the point of contact. A junction potential occurs when the reference electrode filling solution meets the sample. This charge imbalance will be large if there is a large difference in composition between the filling solution and the sample. It is important that the junction potential be constant during measurement. If the two solutions are quite different, normal fluctuations in the boundary layer will produce noise. Constant, reproducible junction potentials are achieved by measuring in samples and standards with ionic strengths similar to the filling solution.

Since pure waters contain little dissolved material, their buffering capacity is small. Absorption of carbon dioxide from the atmosphere will cause a slow change in pH, observed as a drifting pH reading and a different pH from the original sample. Samples that are not previously saturated with carbon dioxide must be handled with care.

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Conventional Approaches

The most widely accepted solutions to these problems involved the use of low resistance glass pH electrodes or the use of a reference electrode with a fast, continuous leak rate. When placed in a pure water sample, these electrodes show improved time response and stability, due to dissolution of the low resistance glass into the low ionic strength solutions and the non-quantitative addition of a salt solution from the reference into the sample, respectively. Both techniques raise the conductivity, but, at the same time, may change the sample pH at the electrode surface. Response is improved, but an error is added to the measurement, which depends upon the amount of dissolved material. Increased sample conductivity is desirable, whereas variable alteration of pH is not.

The Pure Water™ Solution

We have developed an easy-to-use method that minimizes the problems encountered when measuring pH in pure waters. The method uses a high quality glass pH electrode and a kit consisting of a pure water ionic strength adjustor (pure water pHisa) and a special set of pure water L.I.S. buffers that contain the same background of the pure water pHisa. For the best results, a ROSS Ultra electrode, Cat. No. 8102BNUWP, is recommended.

Adding pure water pHisa to samples increases the ionic strength, thus reducing noise and improving response time. The shift in pH caused by the addition of pHisa is minimal, between 0.005 and 0.01 pH units. Since the same amount of pHisa is added to the buffers and samples, any effect on the pH is negligible.

Why the Pure Water Solution is Better

Calibration is performed using pure water L.I.S. buffers with pHisa already added. Measuring with samples and buffers of the same ionic strength improves accuracy, precision and electrode stability. Contamination due to carryover from higher ionic strength buffers is also minimized.

Errors in pH measurement due to liquid junction potential variations are minimized by using buffers and samples at similar ionic strengths. Addition of pHisa to both the buffers and samples achieves this condition.

Junction potentials will vary depending on the style of junction and choice of electrode filling solution. A high quality pH electrode will provide better response when compared to the universal standard, the hydrogen electrode. To optimize the measurement, we recommend using the glass ROSS Ultra pH electrode, Cat. No. 8102BNUWP.

Our pure water method uses:

- Pure water L.I.S. calibration buffers
- Pure water pHisa ionic strength adjustor
- A ROSS Ultra pH electrode

These special dilute buffers and adjustor are provided in the pure water pH Test Kit, Cat. No. 700001, or they may be purchased separately. The ROSS Ultra pH electrode must be ordered as a separate item. Refer to the **Ordering Information** section for more details.

Measuring Hints

- Before measuring samples, perform a two buffer calibration. Standardize with one buffer periodically during the day.
- Measure the temperature of all samples and buffers. If the temperatures are different, temperature compensation is recommended. Refer to the meter user guide for calibration procedures using temperature compensation.
- Use fresh buffers for each calibration.
- Add pure water pHisa to each sample. Add 1 mL of pHisa to every 100 mL of sample. Other sample volumes may be used, as long as the ratio of pHisa to sample remains 1:100.
- Stir all buffers and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stirrer and the beaker to prevent drift due to heat transfer.
- Before placing the electrodes into any solution, rinse them with an additional aliquot of the solution. Do not rinse into the solution being measured. Do not wipe the electrode, since contamination or polarization may occur.

Procedure

1. Condition the electrode as described in the electrode user guide. Refer to the meter user guide for meter calibration details.
2. Choose two of the pure water L.I.S. pH buffers that bracket the expected sample pH.
3. Pour 100 mL of the first L.I.S. pH buffer into a 150 mL beaker.
4. Rinse the electrode with distilled water and then the buffer used in step 3. Place the electrode into the beaker with the first buffer.
5. When a stable reading is obtained, calibrate the meter to display the pH value of the buffer at the measured temperature. A table of pH values at various temperatures is supplied on the buffer bottle.
6. Pour 100 mL of the next L.I.S. pH buffer into another 150 mL beaker.
7. Rinse the electrode with distilled water and then the buffer used in step 6. Place the electrode into the beaker with the second buffer.
8. When a stable reading is obtained, set the meter to display the pH value of the second buffer at the measured temperature.
9. Pour 100 mL of sample into a 150 mL beaker. With the syringe provided, add 1 mL of pHisa to this sample solution.
10. Rinse the electrode with distilled water and then the sample. Place the electrode into the sample beaker. Wait for a stable reading and record the sample pH and temperature.

Ordering Information

Cat. No.	Description
700001	Pure water pH test kit, includes pure water L.I.S. pH 6.97 buffer A (4 x 475 mL bottles), pure water L.I.S. pH 4.10 buffer B (4 x 475 mL bottles), pure water pHisa ionic strength adjustor (2 x 60 mL bottles), syringe and instructions
700702	Pure water L.I.S. pH 6.97 buffer A, 4 x 475 mL bottles
700402	Pure water L.I.S. pH 4.10 buffer B, 4 x 475 mL bottles
700902	Pure water L.I.S. pH 9.15 buffer C, 4 x 475 mL bottles
700003	Pure water pHisa ionic strength adjustor, 5 x 60 mL bottles
8102BNUWP	ROSS Ultra combination pH electrode with glass body and waterproof BNC connector
8102BN	ROSS combination pH electrode with glass body and BNC connector
810200	ROSS combination pH electrode with glass body and U.S. standard connector
8102SC	ROSS combination pH electrode with glass body and screw cap connector, requires separate cable
810007	ROSS pH electrode filling solution, 5 x 60 mL bottles

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