

pH MEASUREMENT IN HIGH PURITY AND LOW IONIC STRENGTH WATER

Measuring the pH of pure water is difficult because of inherently low solution conductivity (between 0.056 and 10.0 microSiemens/cm) or resistivity (between 18.2 and 10 megohm-cm at 25°C). Several problem areas can lead to gross measurement errors in this type of application. Eliminating these potential interferences requires special measurement considerations.

Why Do We Need to Measure Pure Water pH?

The measurement of pure water pH can be one of the quickest indicators of process contamination in the production or distribution of pure water. The presence of gaseous contaminants such as air or carbon dioxide will shift the pH of the pure water, indicating air or gas intrusion into the process line. The exhaustion of resin beds used to prepare or polish pure water can introduce contaminants that will cause a shift in pH. These resin beds are typically cation and/or anion exchange resins in a hydronium ion form (cation exchange) or hydroxide ion form (anion exchange). While conductivity measurements will clearly indicate an ionic leakage, pH measurement changes can be diagnostic as to which resin is exhausted. If the pH increases, the cation resin bed is becoming exhausted; if the pH decreases, the anion resin bed is becoming exhausted.

Boilers require pure water to reduce scaling and carryover of impurities in steam. Corrosion can occur when pH exceeds recommended limits at ranges that are dependent on metallurgies within the steam cycle.

Semiconductors require extremely pure water to maximize product quality. As nanotechnology grows, impurities are like boulders in the path of microcircuits and may cause extraneous short circuits. Measuring pH also can help in the control of corrosion in these products.

International pharmaceutical quality requirements insist on the best water quality for safe and effective medicine. USP 23 standards require a pH range of 5-7 at 25°C.

In summary, the measurement of pure water pH can lead to a confidence that the water being used remains as pure as possible for the application.

Where Are These Measurements Being Made?

The measurement of pure water pH can be made throughout the pure water preparation and distribution system. Measurement of pH at the preparation step insures that the equipment preparing

the pure water is operating as desired and preparing pure water at the desired purity. Measurement of pH throughout the distribution system insures that the distribution system is not introducing contaminants that may be detrimental to the process.

Measurement of pH at the point of use for the pure water insures that the water being used is of the expected purity.

In steam cycle applications, pH can be measured at several locations including after water treatment, condensate pump discharge, after polishers, if used, and boiler water.

At the minimum, semiconductor and pharmaceutical water pH is usually measured after water treatment.

Measurement Considerations

Preventive measures are necessary to ensure the accuracy of pH measurement in pure water. The following factors must be taken into consideration:

ATMOSPHERIC CARBON DIOXIDE (CO₂) INTRUSION

Clean or pure water (typically in the pH 7 range) exposed to the atmosphere will absorb carbon dioxide (CO₂) until equilibrium is reached. CO₂ acidifies the sample, thus lowering the pH. Depending on temperature and pressure, the pH of pure water may drop to as low as 6.2. The best solution to this problem is to pass a sample stream through a low volume, airtight sample chamber containing a pH electrode assembly. An alternative is to heat the water sample to drive off the absorbed CO₂ just before measuring the pH. This method is often used to remove CO₂ from pure water in power plants, by using a reboiler sample system.

Taking grab samples to a lab meter should be avoided because atmospheric CO₂ will contaminate the sample. However, the lab meter can be used at the sample station with an overflowing grab sample. In this method, the sensor is placed in a beaker of sample to be measured. The sample must be introduced through a tube that is immersed to the bottom of the beaker. The sample must purposely be allowed to overflow the beaker to keep out CO₂ intrusion from the surrounding air. Pure water temperature compensation also must be taken into account.

STATIC BUILDUP

Since pure water is a poor electrical conductor, it creates a static charge when flowing past non-conducting materials in the sensor. This can generate "streaming potentials" (stray currents that can mimic pH) in the solution which may cause large errors, or at least, excessive noise in the readings. A low impedance, well shielded and grounded electrode can lower these errors to a minimal value, usually less than ±0.05 pH units.

Because the electrical resistance of a typical measuring cell is so high, the electronics used to measure the cell potential are very susceptible to additional interfering factors - extraneous electrical noise pickup and hand capacitance effects.

JUNCTION POTENTIAL AND PROCESS CONTAMINATION

When two different solutions come into contact with each other, a potential develops at the interface. This potential, called a diffusion gradient, is due to the unequal migration rates of the ions in the solution. Reference electrodes with small liquid junctions enhance this potential by further limiting the surface area in which diffusion may occur. The conventional approach to solving this problem is to use a liquid junction with free-flowing electrolyte.

This provides a stable junction potential and reduces static buildup by raising the conductivity of the process. This method is questionable, however, since altering the makeup of the sample means the measurement will not reflect the true pH of the solution, and greater attention to sensor maintenance is necessary as the electrolyte reservoir needs to be regularly refilled. A more recommended approach is to maximize the surface area of the liquid junction, while minimizing the flow rate of the electrolyte. This lowers the impedance of the reference electrode without contaminating the process.

The Hach 8362sc Measurement Method

Even the best laboratory pH equipment will be in error when used in pure water. Measuring the same sample of pure water with a number of different lab pH meters is likely to produce different readings from each meter. The Hach 8362sc system addresses each of the previously discussed special measurement considerations to provide online pH measurement with enhanced accuracy.

This approach to pH measurement provides a way to measure pH under these difficult conditions. It is different because the housing of the electrode is specially designed against the intrusion of carbon dioxide (CO₂) into the sample by being completely sealed. The housing, including the clear sample chamber, is made of conductive materials, which reduce any streaming potentials. The pH electrode has an open junction and is self-pressurized gel-filled so that the flow rate of the electrolyte is reduced, thus lowering the impedance without contaminating the sample. A stainless steel sheath surrounds the pH electrode for optimum grounding. Quick buffer changes can be made during calibrations due to a removable, thick polymethyl methacrylate cup that is part of the sample cell. Installation is made easy because the probe housing and junction box are pre-mounted on one panel. The only connections are for the sample line and the digital controller.

Measurement and routine maintenance considerations have been fully addressed in a straightforward manner without adding complications to the measurement system.

Operational Considerations

Some precautions are still noteworthy when using the 8362sc system of measurement in pure water applications:

- Preferably, the sample temperature should be in the 20 to 30°C range and remain constant.
- The sample must not be stagnant, since errors will result. Constant flow rates between 50 ml and 150 ml give the best results.
- Air must not be allowed into the sample stream.

In some cases, it may appear that the pH sensor is flow sensitive, however, this may not be the case. By changing the system pressure or flow rate, the degree of dissociation of dissolved gases will change, altering the pH of the solution. Therefore, the process pH, not the pH sensor, is flow sensitive.

Recommended Instrumentation

For best accuracy with this difficult measurement, use the Hach 8362sc pH system with the sc200 or sc1000 controller.

Summary

Conventional pH systems, including laboratory meters, have difficulty providing accurate results in pure water applications. The Hach 8362sc system of measurement is a field proven method, capable of measuring more accurately in pure water applications.



References

- Some Considerations in Making Accurate pH Measurements in High Purity Water, Ultrapure Water, Patko, Coffin and Carter, October, 1986
- pH Measurement in Pure Water, GLI International Technical Bulletin February 2001

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