

CYCLE CHEMISTRY pH MEASUREMENT

David M. Gray and Edward P. Santini
Thornton Associates, Waltham MA

Electric Utility Chemistry Workshop
Champaign, Illinois
May 12-14, 1998

Sponsored by
University of Illinois at Urbana-Champaign
Illinois Department of Natural Resources
Illinois State Water Survey

Cycle Chemistry pH Measurement

David M. Gray and Edward P. Santini
Thornton Associates, Waltham MA

pH measurement in high purity water has met with variable success. The high resistivity of pure water, the vulnerability to contamination, the variability of reference electrodes and additional temperature effects converge to make this a particularly challenging measurement. Overcoming these obstacles requires a thorough understanding of the potential problems and their systematic solution. Provided here is a practical tutorial on instrument and electrode design, installation, calibration and operation which have proven successful.

Why is pH measured in the first place? A good case can be made that in pure water it is unnecessary to monitor pH since a conductivity measurement is simpler and assures high purity. For example, if the conductivity is less than 0.06 $\mu\text{S}/\text{cm}$ then the pH must be between 6.9 and 7.2—the extremes possible with strong acid and base contaminants, respectively. This pH vs. conductivity relationship has been documented in graphic form for strongly ionized acids and bases and for weakly ionized carbon dioxide and ammonia typical of power plant samples.^{1,2,3}

If water treatment systems always produced pure water there would be no need for pH measurement of the product. Conductivity measurement would suffice. However, conductivity is non-specific: it cannot distinguish among acids, bases and salts. Thus when conductivity does increase, the more specific nature of pH provides additional information useful in identifying the source of contamination. pH can be useful in diagnosing deionization system problems.

Despite the term "specific conductivity," it is conductivity's non-specific nature that makes pH measurement necessary. In cycle chemistry control the level of pH-adjusting ammonia or amine requires pH in addition to specific conductivity to give confirmation of the treatment level.

Sampling

One of the first difficulties in making any pure water measurement is preserving the integrity of the sample. Water is properly called the universal solvent. It will dissolve traces of contaminants from sample lines, flow chambers and containers as well as the atmosphere. It is necessary to rinse new or unused sample lines a surprisingly long period of time before representative samples can be obtained.

A constant threat of contamination comes from carbon dioxide in air. Although air contains only 0.03% carbon dioxide, pure water in equilibrium (saturated) with air absorbs enough CO_2 to yield a pH of approximately 5.6 and a conductivity of

approximately 1 $\mu\text{S}/\text{cm}$. Carbon dioxide ionizes in water to form a weak solution of carbonic acid.

Thus a pure water sample cannot be held in a container with air without affecting the measurement. An appreciation for this can be gained by watching the pH of a freshly deionized water sample drop rapidly on exposure to air. If the observer then exhales over the sample, the increased carbon dioxide contamination will lower the pH still further. The rate of contamination and effect on the pH is a function of the surface area exposed, the time elapsed and the buffer capacity of the sample. A sample containing ammonia near 9 pH will be more slowly affected than a pure water sample near 7 pH.

All low ionic strength pH measurements should be made on closed, flowing samples. When laboratory comparisons must be made, the best practice is to take a portable instrument and electrode to the sample source. The sample line should go into a container to the bottom, letting the water overflow the top. The electrode should also be immersed deep in the container so it is surrounded by fresh sample that has not had contact with the air. Process instruments with flow chambers and flexible tubing are recommended.

pH reference electrodes, even of the so-called solid state non-flowing type, invariably diffuse traces of potassium chloride into the sample. These traces of potassium chloride are actually measurable by conductivity and are comparable for all reference electrodes. A pH sample should therefore never be discharged to a conductivity measurement downstream and should not be returned directly to a pure water system. It should go to drain or to a reclaim system.

The flow rate of power plant samples should be high enough that any iron oxide particles or deionizer resin fines are swept through the sample lines and electrode flow chambers. This is especially true of plants where particulate corrosion products are common in samples. If particles accumulate in the flow chamber, the exchange of ionic species with them can slow down response greatly. Low volume flow chambers and small sample line diameters enhance flow velocity and minimize particulate accumulation.

Solution Temperature Compensation

Water ionizes to a greater extent at higher temperature. The widely accepted value of 7 pH for neutral water is valid only at 25°C. Neutral water has a lower pH at higher temperatures as shown in Figure 1 because it has increased hydrogen ion concentration. The water is still neutral because both the hydrogen and hydroxide ions increase equally in concentration. However, pH is a measure of only the hydrogen ion. Pure water only appears to become more acidic at higher temperatures. Figure 1 also shows that a small amount of ammonia not only raises the pH but also increases the temperature influence significantly, shown by the steeper slope.

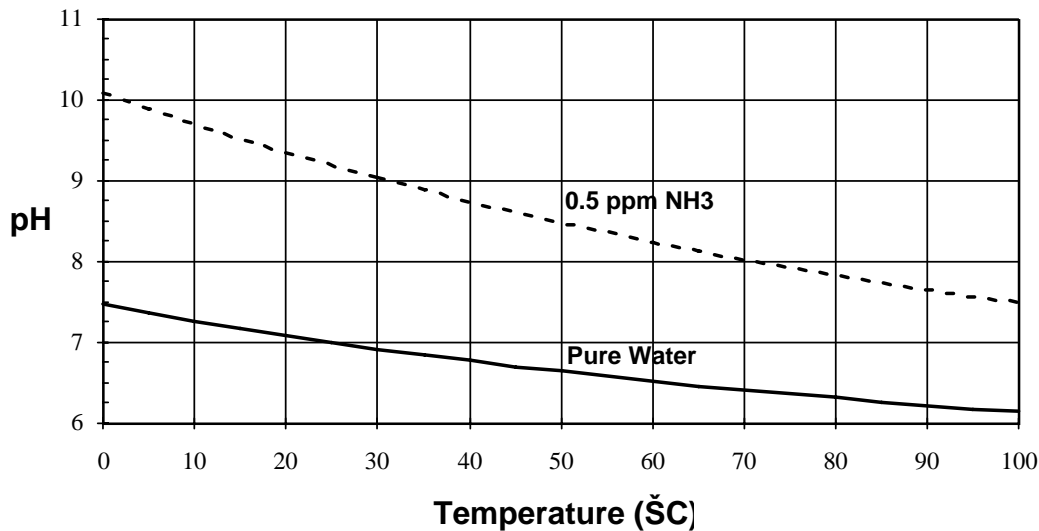


Figure 1 - Solution Temperature Effects on pH

The temperature dependence of pH is ignored in most conventional measurements because it is negligible. The dissolved minerals in natural, potable and waste waters typically have enough buffer capacity to make the pH/temperature curve almost horizontal, at least over the ambient temperature range. Thus there is no need for compensation for this effect in other applications such as cooling towers or plant effluent monitoring. In fact, laboratory pH instrumentation has no provision to compensate for ionization of the sample—another reason to use process instruments for pure water portable measurements. Conventional *electrode* temperature compensation is available on virtually all pH meters but it adjusts only for the varying output of electrodes with temperature, the Nernst effect, which is described later.

The need for solution temperature compensation in high purity water is reflected in the specifications for boilers, steam generators, turbines and pure water systems, which specify pH at 25°C. Instrumentation intended for high purity water measurement should have the capability for solution temperature compensation. It can then measure at other temperatures but provide display, alarm and output signal of pH referenced to 25°C. Modern power plant sampling systems sometimes employ chillers or water baths for sample temperature control to achieve the same goal. Instrumentation with solution temperature compensation can assure continued accurate operation even if the temperature control system should fail. The typical temperature coefficient of ammonia or amine-treated samples of $-0.032 \text{ pH}/^\circ\text{C}$ seems small until it is compared with the narrow pH range requirements of many of the water chemistry guidelines.

During calibration, solution temperature compensation is automatically disabled. Adjustment is made to the true pH (at temperature) of the standard buffer solution which has a different temperature coefficient than that of high purity water. The buffer temperature/pH relationship is usually given in a table of values printed on its container.

pH Electrodes

pH is measured as a millivolt signal developed at the surface of a glass electrode membrane. This signal depends on the glass/solution ionic equilibrium. It is represented by the variable voltage battery symbol at the tip of the measuring electrode membrane in Figure 2. If this could be measured independently, none of the other components shown would be necessary. However, as for any voltage measurement, two connections must be made. For pH measurement, the connections have evolved into complete measuring and reference electrodes. Some electrode systems combine the measuring and reference functions into a single combination probe. Separate electrodes are shown here to facilitate the explanation.

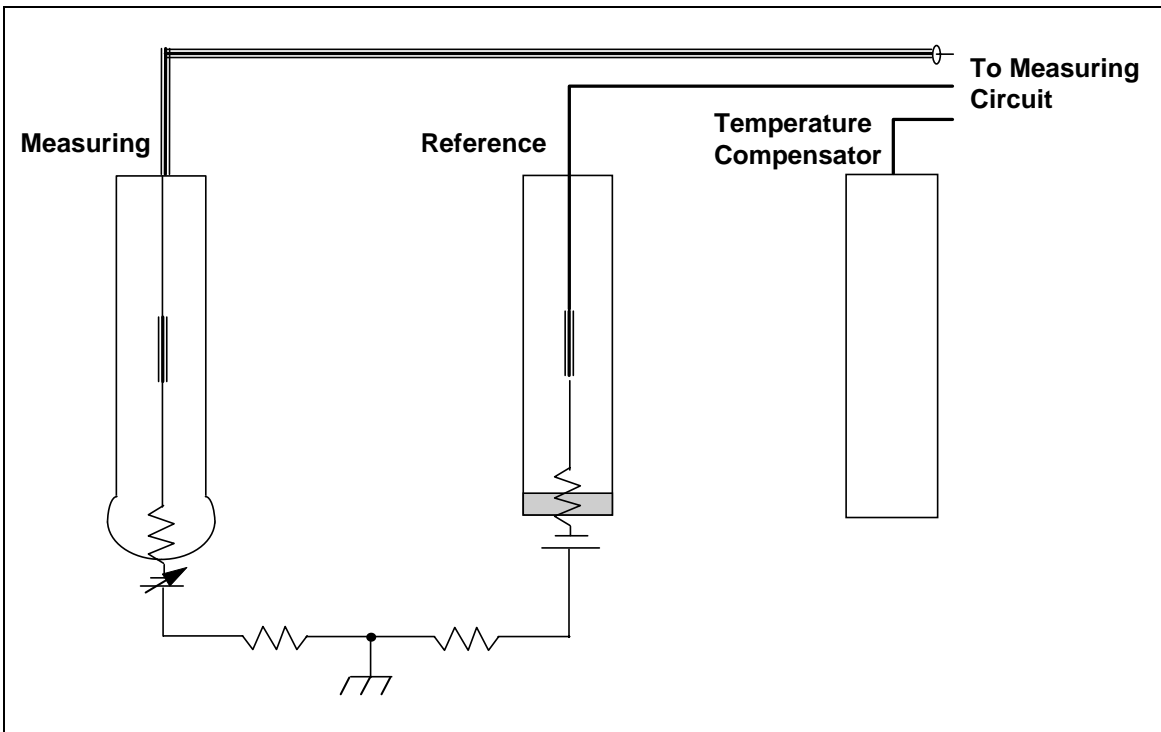


Figure 2 - pH Electrode System Schematic

One connection is through the glass membrane itself which may have a resistance on the order of hundreds of Megohms. The inside of the measuring electrode is filled with a stable pH solution to give a constant potential at the inside surface of the glass. The filling solution also contains potassium chloride which maintains a constant potential in contact with the inner element.

The high impedance signal is vulnerable to loss through any resistance path to ground. Dirty insulation in moist environments can shunt much of the pH electrode signal causing significant errors. The signal is also vulnerable to electrical noise pickup, static electric charges, body capacitance, etc. Coaxial measuring electrode lead wire is used to minimize these problems. Also for these reasons, industrial installations usually employ a preamplifier near the electrodes to minimize the length of high impedance lead wire. Preamplifiers are sealed to exclude moisture.

The electrodes themselves are best shielded by a conductive (stainless steel) flow chamber that has been earth grounded. This not only protects from external electrical noise but also from internally generated streaming potentials. Streaming potential is a phenomenon occurring in high purity water as it flows past insulating surfaces. It can develop a static charge along an in-line plastic electrode flow chamber, yielding an unstable, flow-sensitive pH signal. Low flowrates and a conductive flow chamber material prevent this charge build-up. A completely sealed flow chamber also prevents carbon dioxide contamination of the sample. An especially small internal volume produces faster flow velocity which carries particles all the way through the flow chamber, as mentioned previously.

Reference Electrodes

The pH circuit is completed through the process sample and reference electrode. The most critical part of the circuit is the reference junction where the potassium chloride electrolyte inside the electrode has restricted contact with the process sample. The junction can be made of porous ceramic or plastic, a narrow passage, or fibers. The purpose is to provide reliable electrical continuity without introducing a voltage contribution of its own.

The typical sealed reference electrodes which require no refilling with electrolyte are usually satisfactory for normal pH measurements in cooling, service, waste or other waters of relatively high conductivity. However, when they are used on high purity samples their junctions are rinsed out by the flowing high purity water and can develop a high resistance and related offset potential. This typically produces a drift of 0.2 to 0.4 pH unit within a short time after buffer calibration.

With a flowing junction reference electrode (which requires a continuous supply of electrolyte solution, usually from a reservoir), the junction is continuously maintained at low resistance and constant potential by the electrolyte bleeding through it. Junction conditions are maintained nearly constant whether in buffer solution or in high purity sample.

In Figure 2, a flowing junction reference electrode would have a source of electrolyte solution to replenish that which bled through the junction. Figure 3 illustrates this on a system using a combination measuring and reference electrode. The gravity head of the electrolyte reservoir assures a continuous bleed through the junction of a few milliliters per day. At installation, a vent tube allows release of any air trapped inside the reference electrode.

It should be noted that the sample must discharge to an open drain with no back pressure to assure consistent electrolyte bleed. The result is stable junction potential and accurate transfer of calibration in buffer solution to measurement in high purity samples.

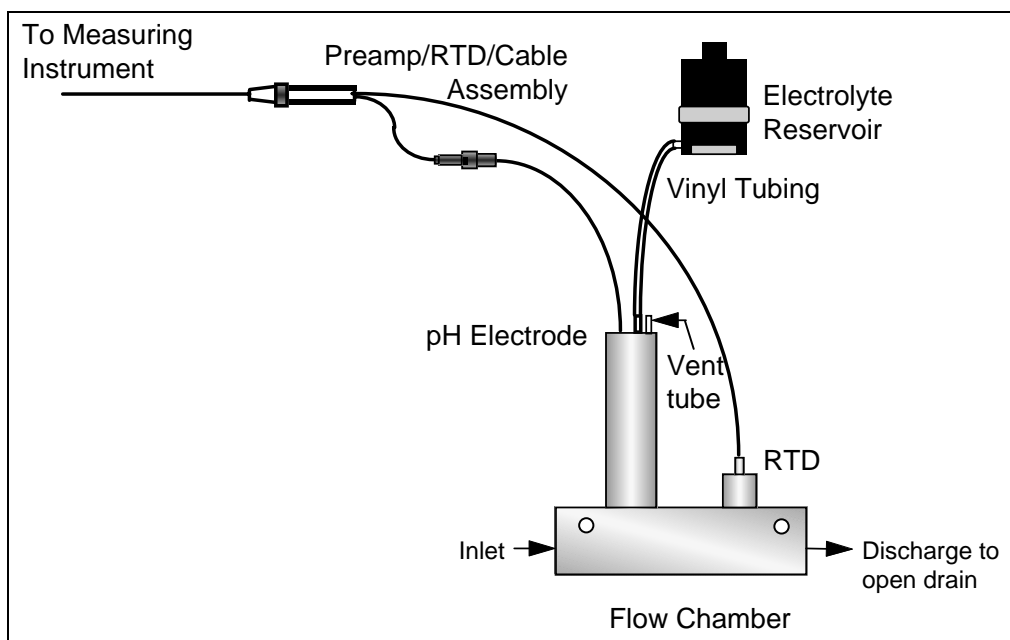


Figure 3 - High Purity pH System

Electrode Temperature Compensation

The voltage produced at the pH membrane surface is proportional to absolute temperature as well as pH. All pH measurements require *electrode* temperature compensation for this output change with temperature—the so-called Nernst effect. This compensation translates the millivolt electrode signal into pH *at the process temperature*, as shown in Figure 4. Cycle chemistry guidelines for pH, however, are referenced to 25°C. This requires the additional step of *solution* temperature compensation described previously.

A block diagram of pH instrument functions is shown in Figure 5, illustrating both types of compensation. Both are required for high purity measurements and are available on process instruments designed for this application. The first block represents the main computation of pH based on the millivolt signal from the electrodes and the temperature value from the compensator. It also takes into account the Adder (standardize or asymmetry) and Multiplier (slope) values determined by the instrument during its last calibration. The first block produces the pH at the process temperature. If a solution temperature coefficient, e.g. $-0.032\text{pH}/^\circ\text{C}$, has been entered into the instrument, then it is used to compute the pH at 25°C for the sample.

It should be noted that laboratory instruments do not include solution temperature compensation and therefore require a manual correction. Laboratory instrumentation is designed for higher conductivity samples.

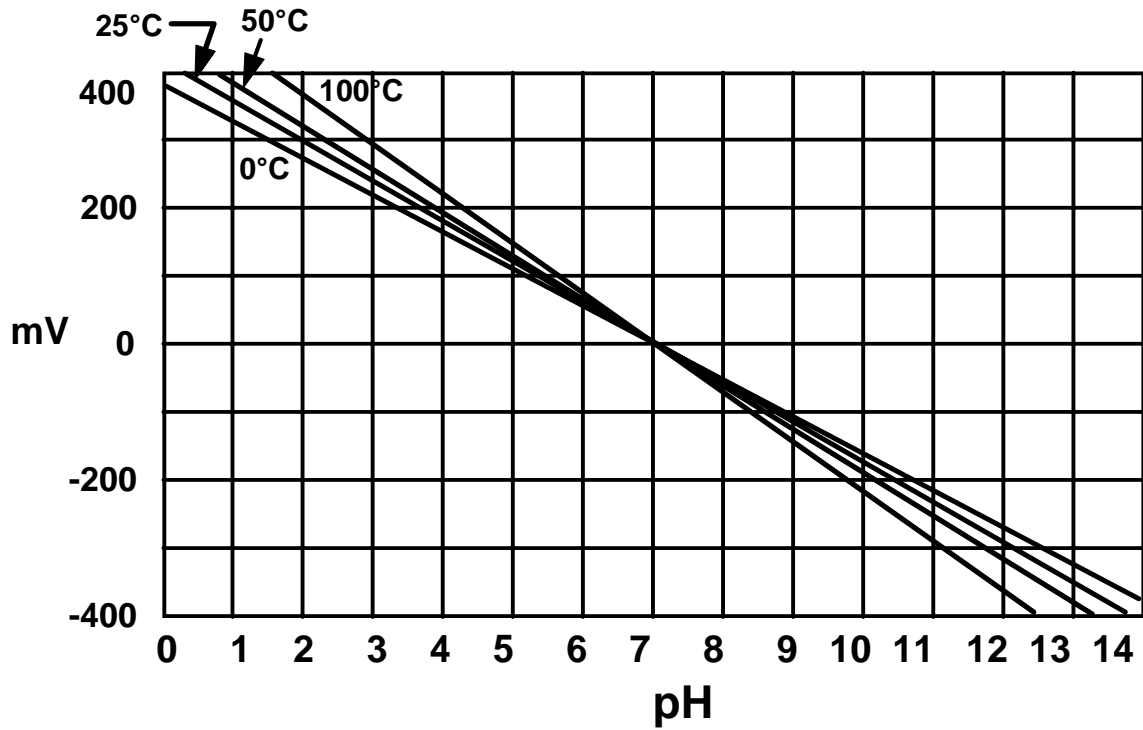


Figure 4 - pH Electrode Output vs. Temperature (Nernst Response)

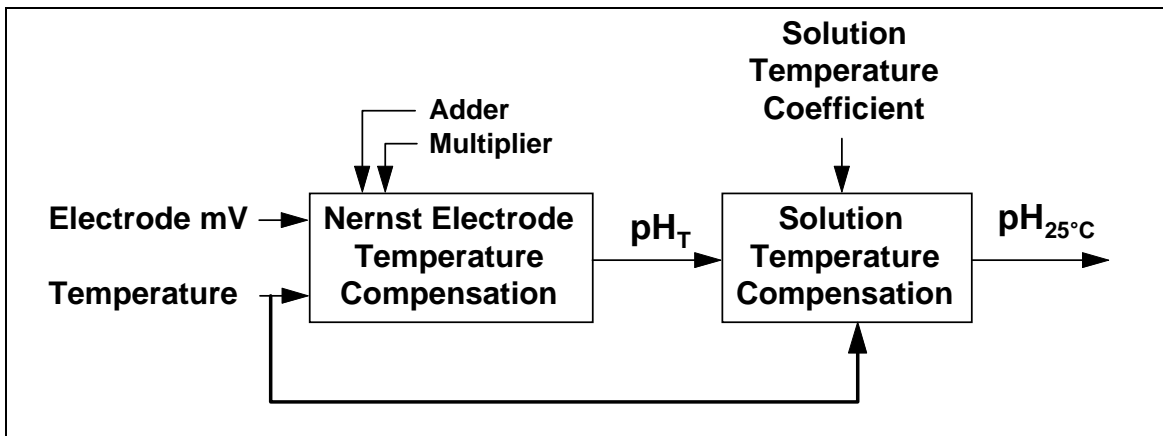


Figure 5 - pH Temperature Compensation

Calibration

The ultimate pH standards are the Standard Reference Materials from NIST.⁴ Any commercial buffer solution should be traceable to these, with a known tolerance and table of pH values versus temperature.

During calibration, solution temperature compensation is disabled so that the actual pH of the buffer at its temperature is used. Buffer solutions have much different temperature coefficients from that of high purity samples. Disabling solution temperature compensation is accomplished on many instruments by activating a "hold" function which also holds relays and analog outputs to prevent false alarms or control action when removing electrodes from the sample.

The most reliable transfer from a pH standard to high purity water is done with direct buffer calibration using an electrode system with a flowing junction reference electrode. It maintains the most consistent junction conditions in both high ionic (buffer) and low ionic (high purity) samples. This is the recommended system and calibration to use.

The second choice, if a sealed (general purpose) reference electrode is used for on-line high purity measurements, requires an indirect means of calibration. It must refer to another (portable) electrode system that *is* using a flowing junction reference in a procedure such as the following:

1. Disable solution temperature compensation on both instruments for all calibration steps.
2. Perform a two-point calibration of both on-line and portable instruments and electrodes in quality buffer solutions. (For on-line electrodes, this step is necessary only at installation and at infrequent intervals thereafter, to correct for any gradual changes in slope response.)
3. Place the on-line and portable electrodes back in their flow chambers in identical parallel flowing samples. Allow rinsing until electrode temperatures reach equilibrium and readings are stable. (This could take an hour or more if a buffer calibration of the on-line system was performed immediately beforehand.)
4. Perform a one point calibration of the on-line instrument to make its readout agree with the portable instrument with flowing junction reference.
5. Re-activate solution temperature compensation

Conclusion

Factors that contribute to the most reliable high purity pH measurements include a sealed, low volume stainless steel flow chamber, a low, constant sample flowrate, a flowing junction reference electrode, a quality high impedance measuring circuit and solution temperature compensation as well as electrode temperature compensation.

Portions of this paper are based on a presentation at the Electric Utility Chemistry Workshop, March 1994.

References

1. Hunt, R. C., "Conductivity and pH Measurement in High Purity Water," *Ultrapure Water*, Vol 3, No 2, March/April 1986, pp 39-45.
2. Lane, R. W. et al., "Continuous Conductivity Monitoring of Anions in High Purity Water," *Power Plant Instrumentation for Measurement of High-Purity Water*, Special Technical Publication 742, American Society for Testing and Materials, 1981, pp 185-195.
3. Standard Test Method for On-Line pH Measurement of Water of Low Conductivity, D5128, American Society for Testing and Materials, Conshohocken, PA, 1995.
4. Certificates for Standard Reference Materials 185-192, National Institute of Standards and Technology, Gaithersburg, MD.