

The sometimes maddening science of pH measurement

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Anyone familiar with pH measurement knows that electrochemistry (when everything is working properly) is the most accurate means of determining pH. It can also be the most problematic due to a variety of error sources. Errors can range from residual reference-junction potentials and bad buffers to inaccurate temperature measurement and imprecise calibration software. Other potential sources for undetected error include high electrode impedance, induced voltages from radiofrequency (rf) interference, improperly designed signal stabilization criteria, sample contamination, stirring effect, and sodium error.

The problem of contamination and residual reference-junction potential

The reference junction acts as an electrically conductive bridge between the reference electrolyte and the sample to be measured. This junction must be designed to allow free movement of electrons. It must also isolate the reference electrolyte from the sample, ideally allowing only a small amount of diffusion of the reference electrolyte into the sample and no flow of sample into the reference electrolyte.

Reference junctions made of porous materials can produce significant error by absorbing the sample and eventually clogging. Even more frustrating is the fact that the junction potential changes according to sample characteristics, contributing uncertainty to calibration procedures and sample readings. “Free-flowing” sleeves of annular-ring configuration (either an epoxy cone or glass-on-glass seam) typically allow a higher rate of electrolyte diffusion into the sample than porous materials and tend to dump electrolyte in an uncontrolled manner when manually refreshed.

The sensION™ platinum pH probe (*Figure 1*) (Hach Co., Loveland, CO), featuring a 0.04-in.-diam capillary tube and a medium-viscosity gel electrolyte, maintains good electrical conductivity while restricting the flow of electrolyte into the sample. The probe allows virtually no diffusion of sample into the reference cell and eliminates contamination of the reference electrolyte itself. The sensION junction is renewable at the click of a but-



Figure 1 sensION 2 portable pH/mV/ISE meter and Platinum Series pH electrode.

ton, dispensing a precise, 6- μ L amount of electrolyte into the sample.

How inaccurate buffers can produce inaccurate results

Buffers are not always the stable entities they are reputed to be. Their pH value changes as a function of temperature. Basic buffers soak up CO₂ from the atmosphere and become more acidic over time. Additionally, volume loss through evaporation also affects pH.

Buffers formulated to NIST standards are well characterized, which means that the pH temperature profile has been well documented. There are other pH buffer standards available, but their pH dependence on temperature is not nearly as well characterized as the NIST buffers. sensION meter software “knows” what a NIST standard buffer pH

value is over a wide temperature range. The meters are designed to recognize NIST buffers, and the solutions and premeasured buffer powders (**Hach**), which can be easily and freshly prepared for each calibration, strictly follow NIST formulations.

Not all buffers follow NIST formularies. A buffer listed as “NIST traceable” merely means that its pH, at the temperature tested (usually 25 °C), is the same as that of a NIST buffer at the same temperature. It does not necessarily mean that the buffer has the same formulary or well-known pH values over a wide temperature range.

The challenge of time and temperature

It is not feasible to wait all day for everything to reach the same temperature. When buffers are a different temperature than the sample, it is expected that the meter will adjust the calibration slope accordingly. In addition to the nonlinear relationship of buffer pH values with temperature (a four-constant third-order polynomial describes the relationship very well), there exists a linear relationship between electrode slope and temperature, from the Nernst equation:

$$E_H = - \left(\frac{RT}{nF} \right) \ln [a_H]$$

sensION meters make adjustments for both the linear and nonlinear temperature effects during calibration. During the sample measurement, the electrode slope is adjusted to the temperature of the solution so that the proper slope is calculated, producing an accurate reading regardless of calibration standard or sample temperature.

What if the temperature sensor is slow to respond or in error? In Platinum Series electrodes (**Hach**), the temperature sensor has been designed to respond quickly to changes in temperature. Also, the reference element is in close proximity to the sample so that all the elements of the probe—the reference element, pH bulb, and sample—come into thermal equilibrium quickly.

Impact of electrical noise on high-impedance bulbs

Glass is a material with high electrical resistance. pH bulbs have resistances measured in megohms. As the resistance of the glass increases, electrical noise present in the environment becomes more of a problem, as the electrode cable acts like a radio antenna and the pH meter picks up these stray electrical fields in much the same way as an FM radio picks up radio waves and static. **Hach Co.** subjects its electrochemical testing products to thorough compliance testing so that the consumer can be confident

that the published specifications are met, even when using these high-impedance pH electrodes.

The shielded coaxial cable used by the company prevents interference from most electrical fields. Even so, at certain frequencies (such as high-gain signals of three volts per meter in specific regions in the MHz range, far outside the bands reserved for cell phones, FM radio, and television) the meter may pick up these electrical fields, causing a shift of 0.04 pH units at most. (Use of the ferrite bead on the **Hach** electrode cable completely eliminates this extremely rare problem.) In other meters tested by the company during compliance review, such induced currents completely swamped out the normal functions of the meters.

The challenge of time and stabilization

Many analysts grow impatient during the time it takes for pH readings to stabilize, but what if one could toggle from pH to mV mode at the push of a key and monitor drift and noise oneself? Even better, what if one could set a meter to stabilize at the exact moment it achieves 0.0 pH resolution, which happens more quickly than 0.00 or 0.000 pH resolution?

sensION meters not only allow one to toggle to mV and observe the electrode output more directly, but also to set the stabilization criteria to match the pH resolution required. To achieve a higher resolution, such as 0.01 pH, the stabilization criteria can be adjusted to that higher level of certainty. It takes more time to stabilize, but when it does settle in, one can be certain of the reading. For those who have time and require the utmost accuracy, a 0.001-resolution can be selected as well.

The problem of sample contamination and carryover

Even when analysts practice special care in washing, rinsing, and drying storage containers and storing samples, strict protocols are not always practicable. Samples can be compromised by carryover from previous samples, even when laboratory glassware is dedicated to various standards and types of sample and containers are rinsed well with deionized (DI) water and aliquots of sample before critical measurements are made.

When sample carryover takes place within the junction of porous-junction electrodes, there is little that can be done about it. This can bedevil a day's work, especially if the instrument has already been calibrated and the water being tested has very low conductivity and thus little buffer capacity. In this case, carryover in the junction can have a significant effect. Platinum pH electrodes, with patented reference junctions, totally eliminate this problem.

With just a few clicks of the electrolyte dispensing button and an electrode rinse, there is no risk of carryover or a change in junction potentials interfering with careful work.

How stirring can speed response (and compromise quality)

While stirring the sample may initially speed up response, it can be a source of trouble in pH measurement. For one thing, stirring can adversely affect any junction potential that may exist. In tests conducted by **Hach Co.**, this effect was frequently noted in porous junctions and was often present in annular-ring sleeve type junctions as well. The patented reference junction presented the smallest stirring noise and was an order of magnitude smaller than comparable electrodes.

In addition to the problem of potential shifts and noise, stirring may also cause any volatile components present to evaporate from the sample. An agitated surface also causes the sample to more readily take up CO₂ from the atmosphere. All of these factors lead to false readings.

The sodium ion dilemma

The presence of the sodium ion is the greatest source of error in basic solutions typically above pH 12 or 13, although sometimes observable as low as pH 10. Because the pH bulb does not easily discriminate between the sodium ion and the hydrogen ion at these elevated pH values, the meter can indicate a reading that is lower than the actual pH in the presence of sodium ions (falsely more acidic). It is important that electrode manufacturers accurately characterize this sodium—or alkaline—error in their pH glass so that reliable readings can be cal-

culated for users who routinely measure highly caustic solutions with a known sodium content.

The only reliable way this can be done is by comparing the bulb response with the response of a standard hydrogen electrode. (Anyone who has used a standard hydrogen electrode can easily appreciate how wonderful it is that pH glass bulbs were invented to measure pH.) **Hach Co.** carefully characterized the sodium error and working ranges of its electrodes, providing differing types of glass formularies to suit unique applications—from fast response in cold, near neutral solutions with low ionic strength to caustic solutions in which very low sodium error is guaranteed. The company's published graphs and carefully worded procedures help the analyst correct for sodium error.

Conclusion

Despite the many difficulties that can plague electrochemical measurement, from inaccurate temperature measurement to sample contamination, it pays to understand the underlying causes, employ the best possible laboratory technique, and select instrumentation and procedures that have been specially developed to minimize, if not eliminate, such problems.

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