

Improved pH Measurement

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The pH meter, electrode, and calibration buffers are standard equipment in most analytical laboratories. The familiar process of generating an accurate pH measurement has benefited over the years from a host of innovations. These include electrode improvements such as the combination electrode, more versatile pH glass, high-performance electrode junctions, and application-specific electrodes. pH meters have provided similar innovations such as automatic buffer recognition, automatic temperature compensation, and Good Laboratory Practice (GLP) features. Although the pH measurement process has been streamlined and simplified, there is still much to consider for the system to perform reliably.

Even a well-maintained system will, over time, provide results that do not meet expectations. This is often due to problems with the electrode, which is the most delicate part of the system. Common sources of error include a clogged junction; exhausted, dirty, or dry membrane; exhausted or contaminated electrolyte; and physical damage.

Moreover, the electrode will eventually reach the end of its useful life and require replacement. This situation is difficult to anticipate, since a pH electrode normally lasts from six months to a year, depending on proper maintenance and the harshness of the measurement environment. However, the electrode lifespan can be significantly reduced if, for example, the electrode is exposed to extreme temperatures or to highly aggressive or acidic samples. As the electrode becomes exhausted, response time deteriorates and readings become subject to loss of repeatability and linearity. This applications note illustrates the importance of a properly cleaned electrode and how the reliability of pH measurements can be improved.

Electrode basics

The pH electrode is a very high-impedance galvanic cell in which the potential developed between the pH half-cell and the reference half-cell is the sum of various potentials. Figure 1 shows a typical glass combination pH electrode in which the pH half-cell and the reference half-cell are combined into a single design.

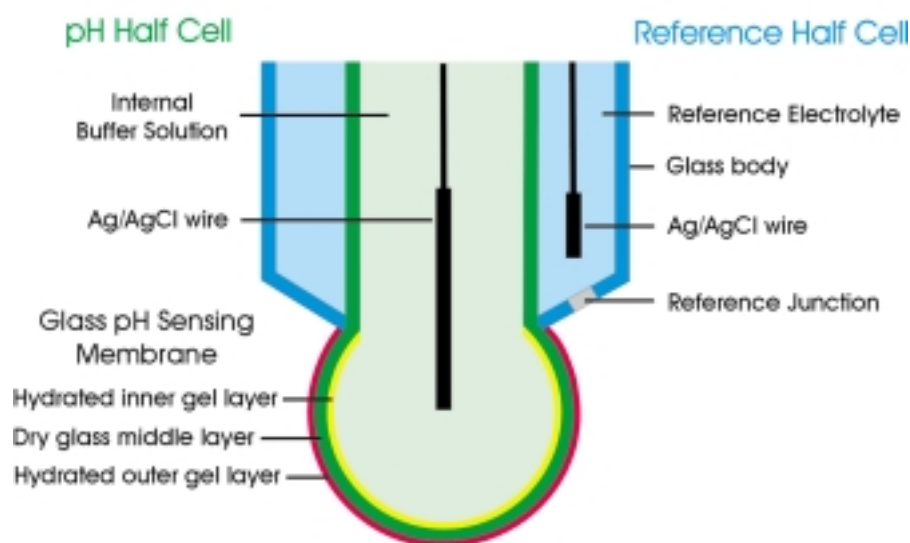


Figure 1 Typical combination pH electrode.

Ideally, all of the potentials are constant, except for one generated on the outer hydrated gel layer that depends on the pH of the sample according to the Nernst equation:

$$E_{obs} = E_c - \frac{2.303RT}{F} \text{pH}$$

where E_{obs} is the observed potential; E_c is the sum of all constant potentials, R is the gas constant, T is the temperature in K, and F is Faraday's constant.

Real electrodes differ from an ideal electrode due to various factors, including 1) manufacturing tolerances, 2) electrode aging, and 3) electrode conditioning and cleaning. All pH meters allow for calibration or standardization of the electrode to compensate for the above effects. A standard calibration involves measuring the response of the electrode in two pH buffer solutions with well-known pH values and creating a linear map of the electrode response to these two points. This results in offset and slope correction factors, where the offset is the mV reading at pH 7 and the slope is the change in mV response per pH unit, usually expressed in mV/pH as a percentage of the ideal slope of the electrode (59.16 mV/pH at 25 °C).

Calibration pitfalls

Errors can result following calibration because it is unknown which of the effects noted above are being compensated for, and the effects vary widely with time. For example, Figures 2 and 3 show the offset and slope, respectively, of four types of laboratory-grade electrodes (two of each type) that have been kept in milk 24/7 for more than four months. The electrodes were thoroughly cleaned before measuring the offset and slope over time. The graphs show that there is a systematic change in offset but the change is very small, whereas the slope is virtually unaffected with time.

The same tests were done in other solutions, such as orange juice, two solutions at pH 1 and pH 13, and a solution with a high content of veg-

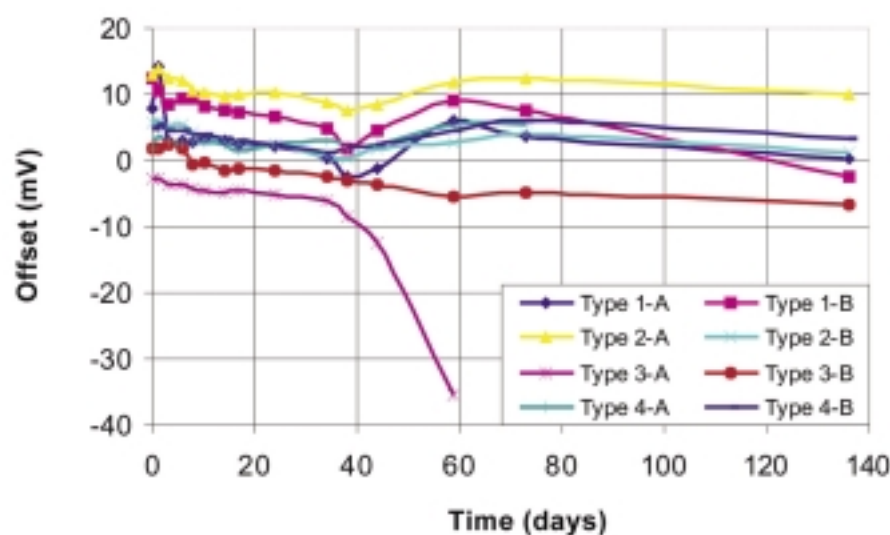


Figure 2 Long-term stability of offset in milk for typical pH electrodes.

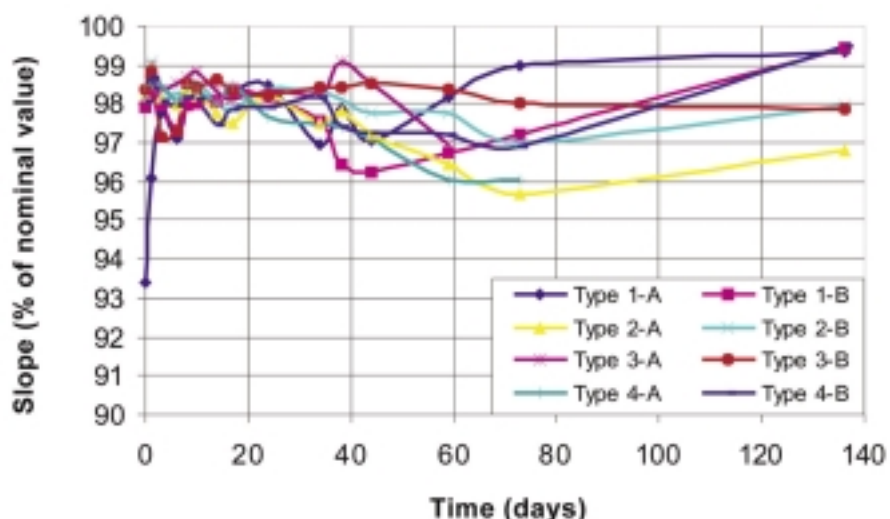


Figure 3 Long-term stability of slope in milk for typical pH electrodes.

etable oil. All the tests gave similar results. This shows that normal electrode aging is a slow process and that sudden changes in the electrode response are not likely due to aging.

Electrode 3-A in Figure 2 indicates a failure in the reference junction, which caused the milk to penetrate inside the reference electrode. Even though the electrode was clearly unusable, the calibration coefficients remained within an ac-

ceptable range. Conventional pH meters have a wide calibration window, and as long as the electrode falls within the range, they will calibrate, leading to potential problems.

Another common calibration pitfall is associated with improper electrode cleaning. To demonstrate the importance of proper cleaning, another test was performed. This test began with the proper conditioning of three new electrodes by immersion into a standard cleaning solution and then standard storage solution. This was followed by the immersion of two electrodes (test 1 and test 2) into a solution containing oil for a few minutes to simulate normal use. The electrodes were then removed and cleaned with a standard (rather than an oil-specific) electrode cleaning solution and again conditioned with storage solution. This was followed by calibration of all three electrodes using pH buffers 7.01 and 10.01. In order to assess the effects of using dirty electrodes, as opposed to clean, all three electrodes were then left in the 10.01 pH buffer solution and the readings were logged over time. (The slopes at calibration were 96%, 93%, and 91% for clean, test 1, and test 2 electrodes.) *Figure 4* shows what happens when calibrating with electrodes that, while seemingly clean to the eye, have a thin layer of material coating the electrode.

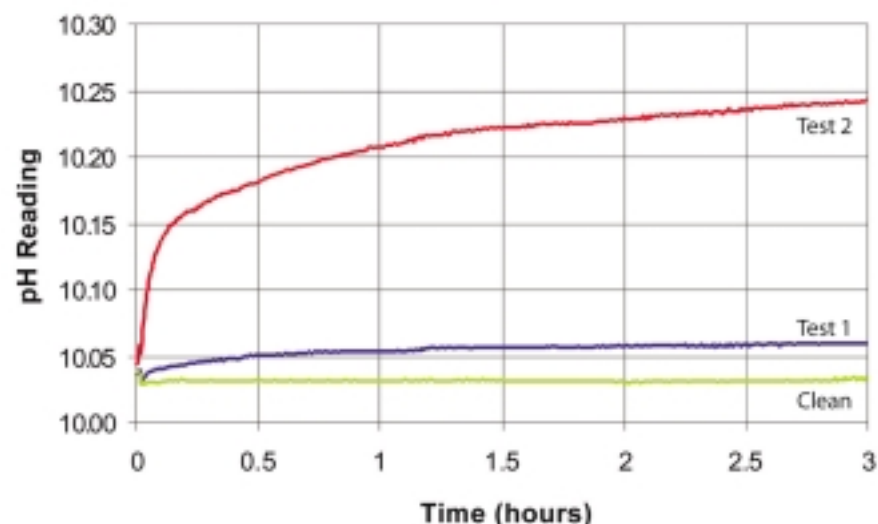


Figure 4 Reading in pH 10 (10.04 at 22 °C) for one clean and two test electrodes.

Following calibration, the readings of all electrodes were equal. However, the reading of the test 1 and test 2 electrodes then drifted away from the correct value. There were no further changes in the readings of clean and test 1, and the reading of test 2 finally stabilized at pH 10.27 after about 12 hrs. This test shows that the readings can change quickly and become unreliable as the state of the electrode is changing while the calibration is compensating incorrectly. The results above demonstrate that a seemingly clean electrode can produce undesirable results and that proper cleaning is essential for accurate pH readings.

Enhanced calibration messages

The problem is addressed with Calibration Check™, which is built into the HI 221 and HI 223 line of bench meters (Hanna Instruments, Woonsocket, RI). In conjunction with a specially designed series of electrodes, the meters perform a set of diagnostic checks during each calibration.

The meters store the calibration history and compare new calibrations with previous ones. Since the electrodes are not expected to age suddenly, the user is informed of any significant changes in the offset and slope of the electrode, so that the problem can be confronted. Messages are tailored to the situation and include electrode (“clean electrode” and “check electrode”) messages as well as buffer (“wrong buffer” and “contaminated buffer”) messages. In most cases, a problem in the electrode is identified and corrected during calibration, significantly reducing the possibility of erroneous measurements. The user is even reminded to clear the previously stored calibration history if the electrode has been replaced with a new one so that the diagnostic tests can be restarted.

Electrode condition and response

Apart from the enhanced calibration messages, it is also useful to have an indication of the condition and response time of the electrode. This is because even if the electrode is properly cleaned

and maintained, natural aging inevitably occurs. The HI 221 and HI 223 meters provide two digital indicators on the meter display. One indicator shows the value of condition, which is based on the slope and offset of the electrode rather than simply on slope alone. Both offset and slope are important, as illustrated in Figures 2 and 3, where electrode 3-A was within an acceptable slope range, while the offset indicated a problem with the electrode.

The same idea has been used for the response time, another important indicator of the electrode status. The response time is calculated from the transition between the first and second calibration buffers. Monitoring the values of condition and response offers the user a clear indication of the status of the electrode. This improves confidence in the measurement and provides an advance warning of necessary electrode replacement.

Summary

For the conscientious user, electrode maintenance and troubleshooting is a routine part of the measurement process. A properly maintained electrode

can be expected to have consistent readings for a long time. The challenge is in understanding exactly when the usage, aggressive measurement environments, or improper cleaning begin to negatively affect the pH measurement. A conventional pH measurement system can still calibrate without showing error messages, even though major problems may exist. It is important to note that standard cleaning solution may not be appropriate for all types of deposits, as shown (deliberately) in Figure 4. Users should take care in matching the appropriate cleaning solution to the type of sample being measured.

Compromised measurements may be close enough to the expected results to seem plausible. For the user, knowing the operating condition of the electrode will bring a high level of confidence in the results. The Calibration Check™ system indicates an electrode that needs attention before measurements are compromised. This technology streamlines the task of properly maintaining the pH measurement system and dovetails smoothly into existing GLP procedures.

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