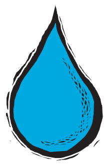
Reliable pH Measurement

If you use water or chemicals, you probably need reliable pH measurement for

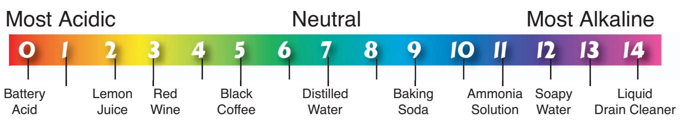
- Quality Control
- EPA compliance
- Safety
- Maximum productivity



Water treatment plants, wastewater treatment plants, chemical plants, paper mills, metal processing plants, textile mills, automotive plants, food processing plants, power plants and more need to measure and control pH.

The speed or rate of chemical reactions and degree of solubility are directly related to pH. Living organisms survive in a very specific pH range.

So what is pH?
pH represents the amount of available Hydrogen ions in a solution. It is defined as the negative log of the activity of Hydrogen ions. The scale ranges from 1 to 14 with 7 being neutral.



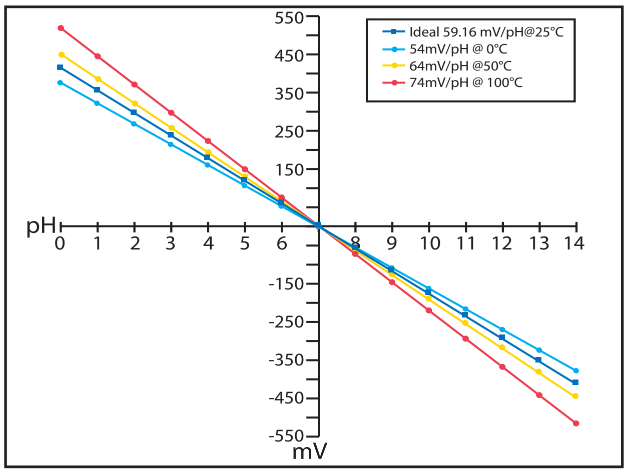
Even though this measurement is heavily relied upon there is little attention paid to the acceptable tolerances for a properly functioning pH electrode. In fact, many do not realize that the typical electrode life is between 6 months to 1 year. How long an electrode actually lasts is dependent upon its maintenance, types of solutions measured, and the temperatures. It is the intention of this article to explain a method to determine if an electrode is operating within acceptable tolerances in an effort to avoid potentially erroneous measurements.

The pH measurement of a solution is based upon the potential developed by a pH electrode and can be determined by the Nerst equation:

$$E_{obs} = \frac{Ec - 2.303RT}{F}$$

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

Theoretically according to the Nerst equation, at 25°C an electrode in pH 7.0 solution will generate 0 mV potential and for each pH unit away there will be an increase of 59.16 mV. A pH of 4.0 will generate +177.48 mV while a pH of 10.0 will generate –177.48 mV. The potential generated is dependent on the temperature of the solution. Figure 1 shows the impact of temperature on what mV will be observed at various pH values. Note that the impact of temperature is greater at the extremes. Most pH meters have automatic temperature compensation (ATC) to correct for this effect.

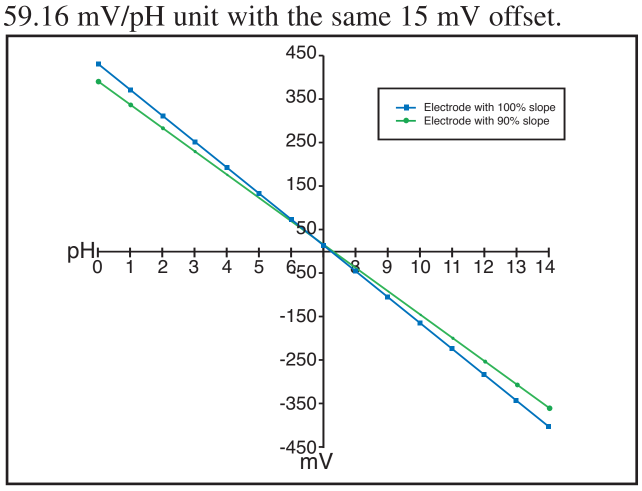


Figrue 1. Theorectical mV potential for a pH electrode in a solution at different temperatures.

Electrodes in use differ from the theoretical maximums obtained by the Nerst equation. Differences can be due to many factors including manufacturing tolerances, electrode aging, conditioning, and cleaning. The calibration process allows for the standardization of the electrode to compensate for these factors but does so with little regard to its optimal functionality. A method to determine the status of an electrode is to look at the mV readings rather than pH. From a mV reading a slope percentage can be calculated. Electrodes with slope percentages of 90-105% are generally said to be in good condition. It is important to perform the analysis with fresh uncontaminated buffers. It is always important to clean the electrode and store it properly when not in use. The following calculations described are based on using buffers that are at ambient room temperature of 25°C.

Calculating the slope percentage is relatively easy to do. First, the mV generated from an electrode in pH 7.0 buffer is recorded. This reading is known as the offset and should fall within +/- 25 mV. Readings outside this range indicate a problem. Second, the mV reading generated by the electrode in a pH 4.0 or 10.0 buffer is recorded. This reading is known as the slope adjustment and generally should fall between +/- 150 mV to +/- 186 mV. Again outside these ranges indicates a problem. To calculate the slope percentage the offset reading is subtracted from the slope reading. This number is then divided by the theoretical maximum +/- 177.48. To change to a percentage simply multiply by 100. Acceptable slope percentages should fall within the 85% to 105% range.

Example 1: An electrode in pH 7.0 buffer generated 15 mV while in pH 4.0 buffer it generated +175 mV. The net difference of +160 mV is then divided by +177.48 mV. The result, 0.901 is then multiplied by 100 to give a slope percentage of 90.1%. Figure 2 shows a graph of this line and compares the change to an electrode operating at the theoretical maximum of 59.16 mV/pH unit with the same 15 mV offset.



Figrue 2. Graph of an electrode with a 90% and 100% slope percentage.

Again, an electrode having a slope percentage of 90% is generally thought to be in good condition. It is still possible to have a good slope percentage but not have an electrode within acceptable tolerances.

Example 2: An electrode in pH 7.0 buffer generated 75 mV while in pH 4.0 buffer it generated +235 mV. The net difference of +160 mV is then divided by +177.48 mV. The result, 0.901 is then multiplied by 100 to give a slope percentage of 90.1%.

Note that the offset and slope values are outside the acceptable ranges stated earlier but still generate a good slope percentage. Graphically there is a complete shift of line of 60 mV and can be seen in figure 3.

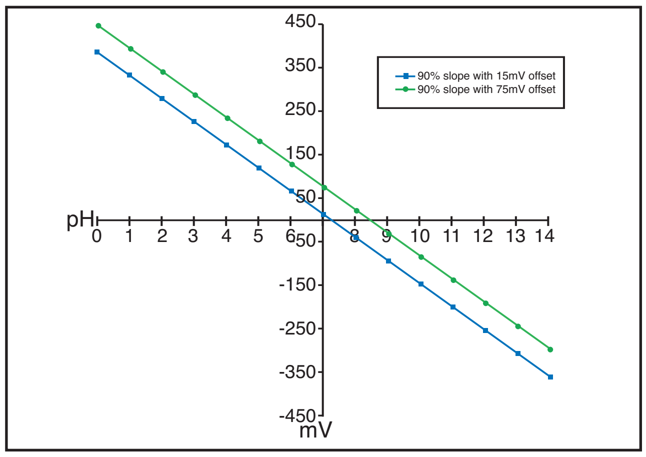


Figure 3. Two electrodes with a 90% slope percentage but one having a15 mV offset and the other on having a 75 mV offset.

If this shift is due to an electrode being "dirty" then this can lead to a potential problem. As the contaminants come off the electrode during use the electrode characteristics will change. This change will result in a calibration that is no longer valid and any readings obtained will be inaccurate.

How do you determine the reliability of your pH electrodes?

Hanna instruments manufactures a microprocessor-based instrument that analyzes the mV generated by the offset and slope measurements. The bench-top HI221 and HI223 are designed to alert you to the condition of the electrode during the calibration process. These indicators include probe condition, response time, "clean" electrode, and contaminated buffers. Built in GLP features allow the user to review calibration data including time, date, buffers used, and the slope of the electrode. Calibration time-out feature can be enabled to notify the user when it is time to recalibrate. The HI 221 can log up to 100 points and has a resolution/accuracy of 0.01/±0.01 pH. The HI 223 can log up to 500 measurements and has a resolution/accuracy of 0.001/±0.002 pH. Both can download data to a computer through an RS232 connection.

Contributed by
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The bench-top HI221 and HI223 are designed to alert you to the condition of the electrode during the calibration process.