Milwaukee Meters Makes Reliable pH Measurement Easy

If you use a pH meter then you most likely you rely on it to provide an accurate measurement that you will then use to make a decision whether an adjustment is needed or not.

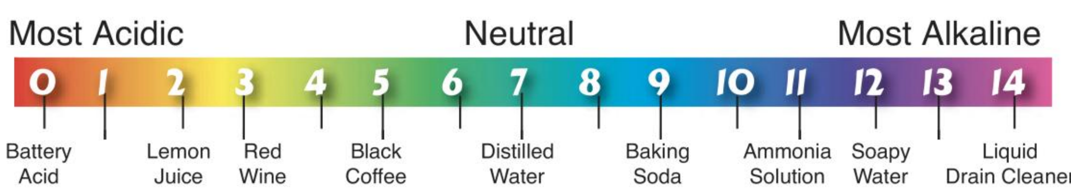
• In agriculture, whether in soil or soilless media, the pH impacts optimum plant growth
• In brewing, the conversion of starch to sugars by enzymes in the mash, has an ideal pH between 5.2 and 5.5.
• In saltwater reef aquarium, the pH impacts the growth of coral.
• In food products, to prevent microbial growth and increase shelf stability, the pH is lowered to a pH 4.

Many industries rely on pH measurement including water treatment plants, wastewater treatment plants, chemical plants, paper mills, surface finishing including plating, textile mills, automotive plants, power plants and more need to measure and control pH.

The pH can impact the speed or rate of chemical reactions, solubility, ability for a living organism to survive are pH dependent.

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 1 to 2 years for standard probes and 6 months to 1 year for a tester probe. How long an electrode actually lasts is dependent upon its maintenance, types of solutions measured, and the temperatures used at. 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**:

$$E^{obs} = E^{c} + 2.303\ (RT/nF)\ (\log a_{H+})$$

E^{obs} = Observed Potential
E^{c} = Reference and all other fixed potentials
a_{H+} = The Hydrogen ion activity
T = Temperature in Kelvin (^{o}C +273.15)
n = Valence of the ion of interest (i.e. H^{+} = +1)
F = Faraday's constant (9.6485 x 10^{4} C/mol)
R = Gas constant (8.31432 J/mol*K)

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 actual 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 normalize the response to 25 ^{o}C.

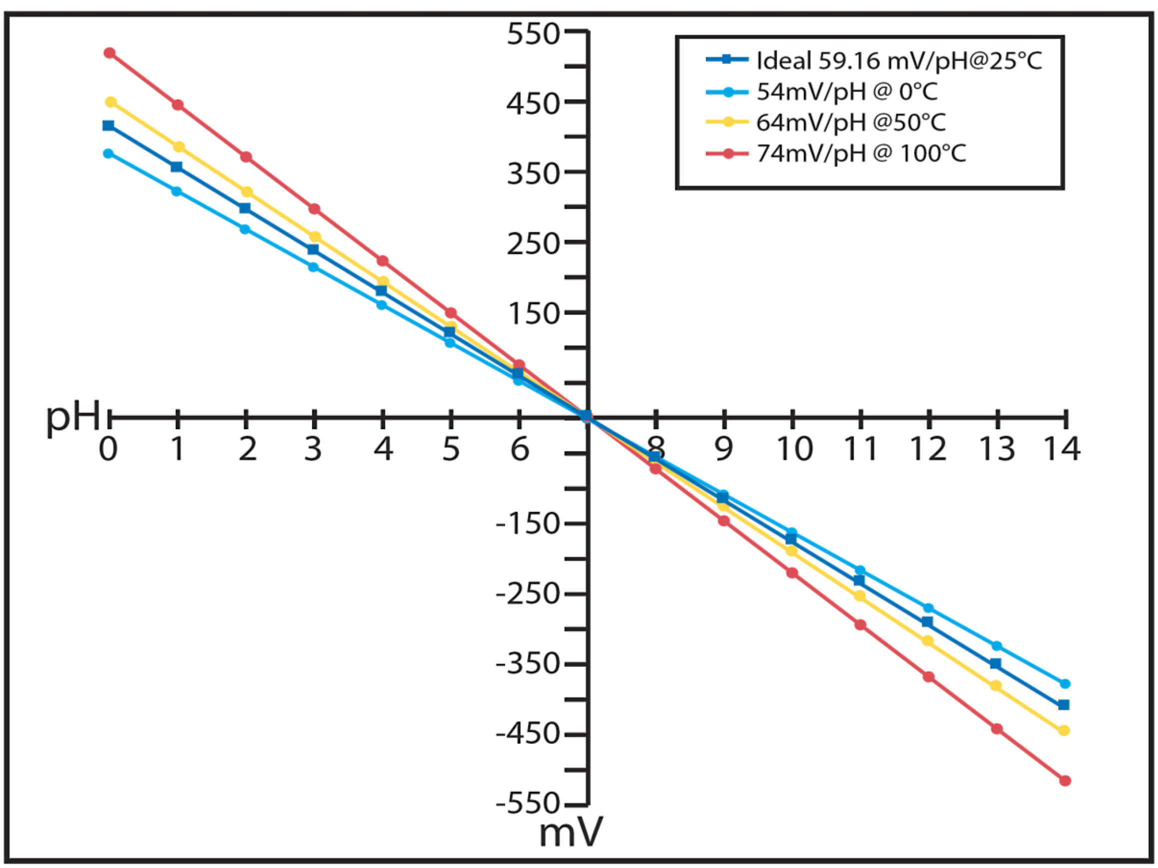


Figure 1. Theoretical mV potential for a pH electrode in a solution at different temperatures

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 +/- 30 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 +/- 160 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 90% 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 along with a line that is at the theoretical maximum of 59.16 mV/pH unit (100%) and having the same 15 mV offset.

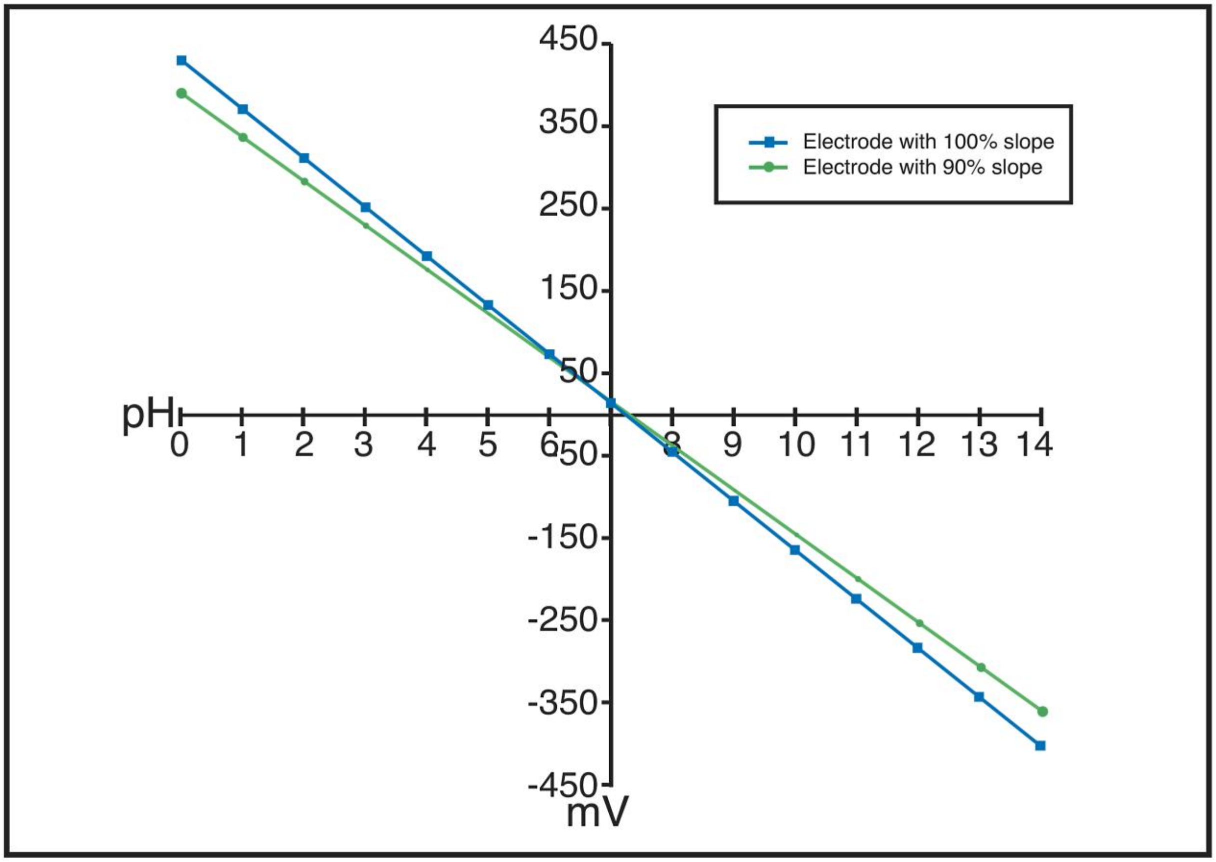


Figure 2. Graph showing a pH probe with a 90% and 100% slope percentage.

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 +75 mV offset value is outside the acceptable +/30 mV range for an offset but still has a good slope percentage. Graphically there is a complete shift of line of +60 mV and can be seen in figure 3.

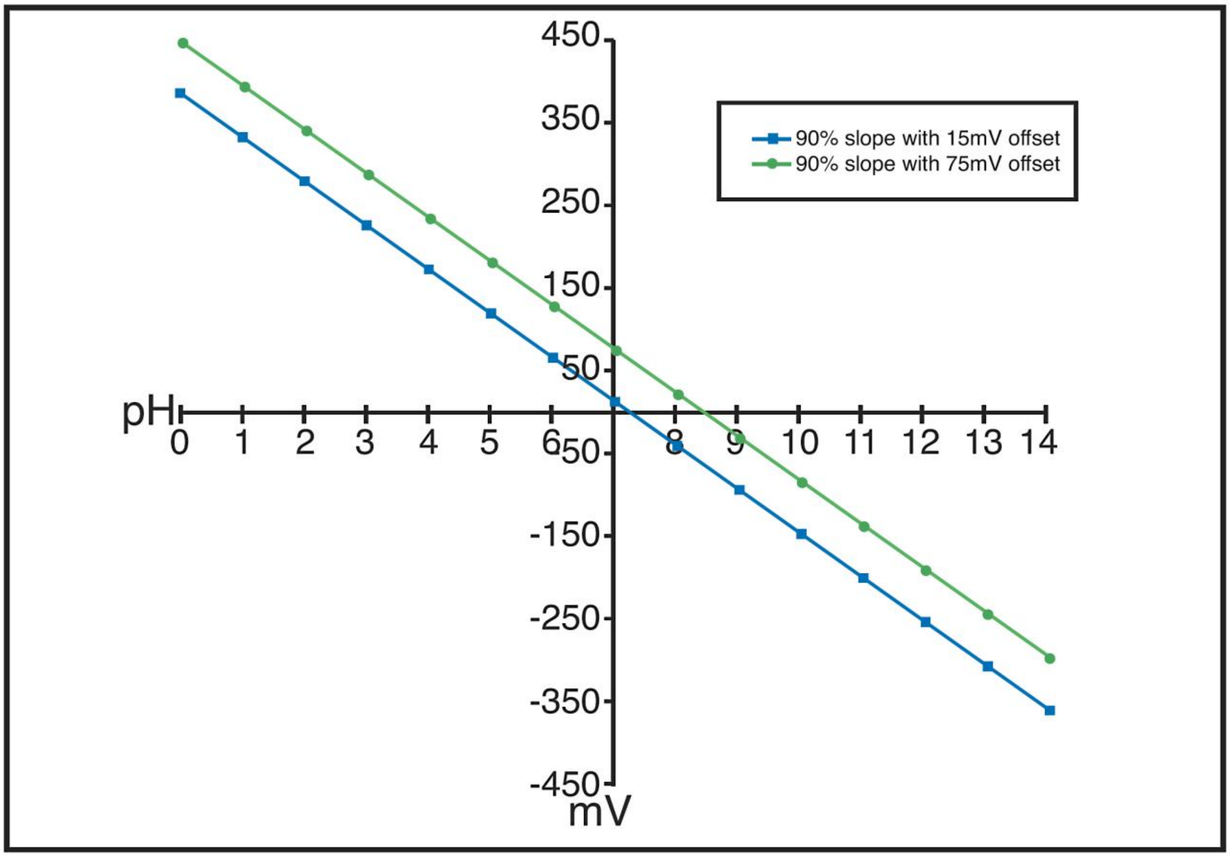


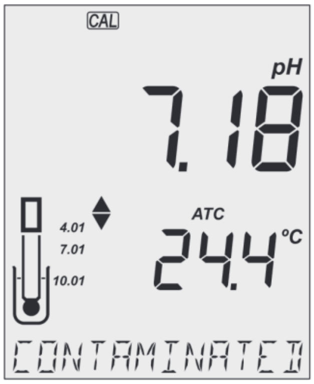
Figure 3. Two pH probes with the same 90% slope percentage but with different offset voltages.

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 then 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?

Milwaukee Instruments manufactures microprocessor based portable and benchtop meters that analyze the mV potential generated during the calibration process. The meters will alert you with, on-screen messages, to potential problems during the calibration process. These messages include:

The "clean" electrode message will appear when there is a significant change in offset voltage but little change in slope. This type of error was shown in Figure 3. Applications that are viscous, oily, or substances that can coat the glass bulb would benefit from knowing when to clean it.



The “contaminated buffer” message is displayed when there is a significant change in slope from one calibration to the next. Figure 2 is an example of a large slope change that would result in the meter displaying the message.

The probe condition indicator is displayed after calibration and indicates the overall health of the pH electrode.

The probe condition indicator has 5 segments (20% each) that is based on the offset and slope response.

5 bars	Excellent condition
4 bars	Very good condition
3 bars	Good condition
2 bars	Fair condition
1 bar	Poor condition
1 bar blinking	Very poor condition
no bar	Not calibrated

Both the MAX portables and benchtops also feature 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.