

Application Note

Measuring to 0.001 pH

Denver Instrument's 200 Series Meters have a user selectable resolution of 0.1, 0.01 or 0.001 pH. Most measurements are reported to 0.01 pH units. Before switching to 0.001 pH there are some important points to consider.

1. Buffers – Typical buffers have a tolerance of +/- 0.02 pH. This means when you standardize using a pH 7 buffer at 25 °C the meter will display 7.00 pH but this could actually be 6.98 or 7.02 pH. Obviously this error is more significant when reading in 3 decimals. You can purchase buffers with a better tolerance such as the ones from Ricca Chemical Company with a +/- 0.002 pH tolerance.
2. Electrodes – You won't find an accuracy specification on a pH electrode. It is meant to be calibrated as part of a system (on a meter with buffers). Electrodes do perform differently not only from type to type but batch to batch.
 - Response time - Most electrodes get to 95% of their reading within 10 seconds. However as the probe ages this value changes. The value also changes with the matrix of the sample. For example, pH buffers stabilize quickly while low ionic strength samples (such as water) never truly stabilize. When reading to 0.001 pH it is important to reach a stable reading before standardizing and before recording a pH value for samples.
 - Reproducibility – A reproducibility study will be useful to see the variation of measurement in the last digit of the pH value. A good test is to standardize using a pH 4 and pH 7 buffer. Then measure a pH 6 buffer (or any other buffer between pH 4 – 7) taking 5 measurements. The same test should then be performed on your sample due to matrix differences explained above. These results will help you understand the accuracy of the electrode.
3. Meter – According to Nernst, there are 59.16 mV/pH at 25 °C. The accuracy of the 200 Series Meters is 0.05 mV which translates to 0.0008 pH units.
4. Temperature – Several times you've read "at 25 °C" above. Temperature is an important part of pH measurement. First, it is important that you use a temperature probe, or combination pH/ATC probe, as well as standardize using the "auto-enter" standardization in the meter. The alternative is to heat or cool your samples to 25 °C. This will assure that the temperature of the buffer is taken in to consideration. Beyond this temperature compensation our meters also apply the laws of Nernst. In summary, Nernst says that as temperature changes the slope of the electrode changes. For example the slope of an electrode at 25 °C is 59.16 mV/pH. However at 50 °C the slope changes to 64.12 mV/pH. The problem is that no electrode perfectly follows these laws. So you will have some error always due to temperature.

Many customers see great benefit in reading to 0.001 pH. They feel they are able to more quickly respond to the changes in pH. Our goal is to allow customers to make their own choices as to how they use our meters. But we also feel the necessity of informing you of some of the errors and possible dangers of reading in 0.001 pH. As long as you understand the results you are seeing you can best react to the pH readings.