pH Probes
(Maintenance, Calibration, & Temp. Compensation)

Q: How do you maintain and calibrate a pH probe & what is temperature compensation?
A: pH instruments are great tools. However, unlike some measuring devices they require special handling and care to provide consistently accurate readings:
1) pH probes should NEVER be stored (or shipped) dry, or in distilled water.
2) New pH meters should be first calibrated using a two-point calibration method
3) After each use, the probe should be rinsed with plain water and stored in a "storage" solution.
4) Upon removal from the storage solution, the probe should be rinsed in plain water.
5) To ensure accuracy, pH probes should be calibrated before daily use.

Maintenance

The success (or failure) of pH measurement depends on the proper application of the probe and proper probe maintenance. The procedures described below apply to the most common pH probe in use today - the flat surface combination pH probe.

The most common failure mode associated with pH probes is breakage. The pH electrode is a very thin glass membrane that is easily damaged. Foreign object damage, or mechanical shock during calibration / use is often the cause. The next most common cause of failure is a plugged reference junction. The reference junction consists of a porous material, usually ceramic or Teflon, which must remain open. The junction creates a fluid interface between the reference material that is a liquid and the process fluid. A flow, albeit infinitesimally low, must exist from the reference electrode to the process fluid. In environments where there are high solids, oils or grease this junction can become plugged.

Probe Cleaning

Unlike flow sensors, temperature sensors, or just about any other type of commonly used industry sensor, the pH electrode is relatively unstable and maintenance intensive. pH Probes will normally require weekly or monthly cleanings and monthly calibrations. The actual frequency is a function of the installation environment but could be as often as a couple of times a day. When the reference junction becomes plugged, the probe will become sluggish and unresponsive. In many cases, the junction can be cleaned with aggressive alkaline cleaners (for oil plugging) or dilute acids (for salt deposits) or a combination of both. In most cases, for probes with large junction surface areas the junction material can be scraped away with a screwdriver revealing a new surface. Aggressive procedures are sometimes necessary to bring life back to a dead probe.

The glass pH sensing membrane may also require service in some applications. This membrane can become dehydrated or coated with a thin layer of deposits. The best procedure for cleaning or rehydrating the glass is to soak the probe in a pH buffer of 4.0 for several hours. If this does not work then immersing the probe in hot buffer 4.0 solution will usually work.

Calibration

pH Electrodes must be calibrated using a two-point method with the appropriate buffer standards. There are manufacturers who suggest a single point calibration, which is minimally effective. pH probe failure modes are numerous and can escape conventional single point checks. Therefore, a two-point calibration must be performed.

To perform a two-point calibration two buffer solutions are required, as the method implies. These buffers should be based upon the normal measurement range that probe operates in. An effluent monitoring probe or neutralization probe should use pH buffers 7.0 and 10.0. However, pH probes used for home brewing purposes should be calibrated with nominal 4.0 and a 7.0 buffer solutions.

Care must be taken not to cross contaminate the buffers. As the name implies pH buffers solutions are designed to be buffering at their advertised pH value. They can, however, become easily contaminated which, of course, renders them useless. The probe should be rinsed and wiped dry (if possible) when moving from one buffer to the next. As one might expect it is easy to drag out buffer from one beaker to the next. Therefore rinsing the probe (and wiping dry) is essential when moving between buffer solutions. Demineralized (DI) water is not required to rinse the probes. Any clean water source will suffice.

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It is important to point out that DI water **should not** be used to store a pH probe. This will actually shorten the probe's life. A pH probe should be stored in a solution with high ionic strength, preferably a pH buffer solution of 4.0.

- **Long-term storage**(More Than 24 hours): Store the electrode in a storage bottle containing a buffer pH-4/KCl solution [Storage Solution]. This keeps the reference electrode moist and adds to the longevity and response time. A small amount of a biocide added to the storage solution prevents mold growth, which plugs the membrane. Never store glass electrodes dry!
- **Short-term Storage**(Up To 24 Hours): Place the electrode in pH-4 or pH-7 buffer solution.

Temperature Compensation

There are two components to temperature compensation in pH measurements - changes in actual pH due to the solution temperature, and changes in the pH electrode's sensitivity.

- **Solution Temperature Effect** - When temperature changes, the actual pH of the solution being measured changes. pH electrodes measure the activity of the Hydrogen ions, which become more active with an increased sample temperature. As such, the pH of the sample will change with temperature. This change in pH is not an error. It is the true pH of the solution at the new temperature, and therefore, there is no need to correct or compensate for this effect. Consequently, both the pH and temperature of a sample should be recorded.

  > "Ever wonder why there is confusion over what the mash pH should be? It's often due to different sample temperatures. When measured at room temp. the nominal pH should read 5.4-5.8. But if measured at mash temperatures, the pH should read 5.1-5.4. The higher temperatures result in more hydrogen ions in solution, and the sample pH is lower. But the mash pH is fine in both instances."

- **Electrode Sensitivity** - There is only one major temperature effect in pH measurement that can cause errors in readings, and that is the change in the electrode's response (or sensitivity) to pH with changes in temperature. pH meters with temperature compensation correct for this effect.
  - The amount of this error is very close to 0.003 pH/oC/pH unit away from pH7. In a pH electrode, zeroed at exactly pH 7.0, there is no temperature effect on the electrode sensitivity no matter how much the temperature changes. Most pH electrodes are not perfect. Their temperature error is minute when near pH 7 (±0.01 pH) and can be disregarded. However, the further the solution is from pH 7, and the greater the temperature change, the greater is the electrode sensitivity measurement error.
  - Electrode sensitivity temperature compensation can be either automatic (ATC), or manual, where the user must set or enter the solution temperature by means of push buttons or a dial. Temperature compensation eliminates most of the temperature dependent measurement error from the electrode. Additional temperature related measurement error (in both compensating and non-compensating pH meters) can be made by calibrating the instrument in pH buffers that are close to the expected measurement values for the expected pH and at (or near) the same temperature as the solution to be measured. -HT (1/9/05)