

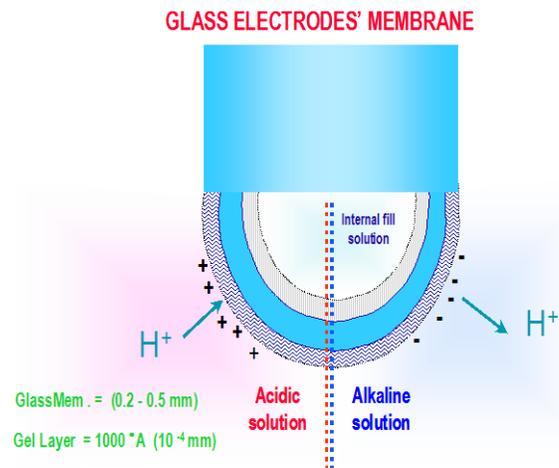
Wet vs. Dry Electrodes ~ Problems and Solutions~

pH electrodes (measure and reference) are designed to function in aqueous solutions and will be adversely affected if they are allowed to 'dry-out' and remain so for an extended period of time. Nearly all pH electrodes are packaged and shipped in a 'wet boot' to avoid problems, from time to time the solution in these boots will leak out. Also, some applications (especially batch processes) will drain away the process and leave an exposed pH electrode to dry out.

Glass (Measuring) Electrode

The glass electrode is composed of a glass body with a pH sensitive glass tip or bulb attached. The ability of the pH sensitive glass to form or hydrate a gel layer on its surface when it is exposed to water, is what makes glass *pH sensitive* glass is capable of sensing the hydrogen ion (H^+) concentration. The Hydrogen ions (H^+) in the process will establish equilibrium with the gel layer creating a potential.

pH glass is typically composed of alkali metal ions. The body has a buffered electrolyte fill with a constant pH value. A silver-silver chloride wire (most common), is immersed in the electrolyte to measure the potential created by the electrode. The pH electrode's potential is created by the sum of the potentials created by the outer gel layer and the inner gel layer and the silver-silver chloride wire.



Effects of Drying

When a pH electrode is allowed to dry out either in storage or in a process line or tank electrode's performance characteristics are affected. The gel's ability to conduct the electrical potential through the glass is affected negatively causing the pH reading itself may become slow and erratic if dehydration is severe enough. If the drying is allowed to continue, the pH measurement can shift upscale and a shortened span can result.

A dry pH electrode can have its gel layer rejuvenated. The good news is that short exposures to "dry conditions" (i.e. calibration, troubleshooting routines, or a batch refill of a process tank) usually requires no extra handling to regain a fully functional electrode.

Electrodes subjected to longer exposures of “dry conditions” such as being exposed in an empty tank overnight or left sitting on a bench can be treated in several ways. The electrode can be soaked in a 4.01 or 7.00 pH Buffer solution, a reference fill solution or regular tap water. The length of time required varies in relationship with the amount of time the electrode was left dry. Typically, from 30 minutes for short dry periods, to 24 hours for more severe instances. Or the electrode can be placed immediately into service *with the understanding that some measurement uncertainty will exist*. It can take up to eight hours for an electrode to fully recover from prolonged “dry conditions”. During this recovery period, measurement accuracy and response time will continue to improve up to, optimum values.

Also during this recovery period, a pH calibration will be marginally helpful. Accuracy is improved during the immediate period following the calibration. It must be recognized however, that the gel layer is changing with exposure to process fluids and a second calibration will be required for best accuracy within the next 8 to 24 hours.

Effects of Improper Storage

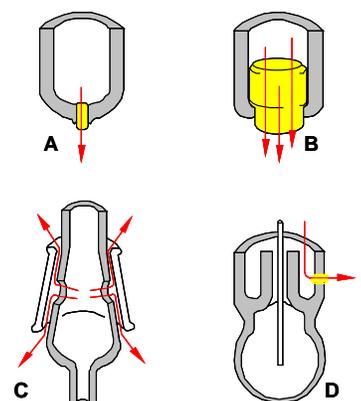
pH measuring electrodes, which are stored improperly, can also experience a similar recovery period. An air space or bubble is left inside most pH electrodes to allow for thermal expansion of the solution fill. The air bubble necessitates that the electrode be stored and used in a vertical position, with tip facing down. When stored flat, it is common for the air bubble to migrate to the upper surface of the inside of the bulb tip. Realistically however, it is difficult to store pH electrodes in an upright manner with the measuring tip facing down.



Why is the air bubble an issue? The inner gel layer under the air bubble dries out. When placed into service in a normal upright position the inner gel layer will recover. Many end users will do a second calibration after 24 hours of run time to correct for the inner gel layer’s recovery.

Reference Electrodes

The purpose of the reference electrode is to complete the measuring circuit and provide a stable potential or reference line against which the pH electrode is compared. The reference electrode is designed to generate the same potential or reference voltage no matter what solution it is in, hence the name *reference electrode*. Reference electrodes; commonly use a saturated KCl solution with a surplus of KCl crystals. The excess KCl dissolves into the electrolyte as the potassium and chloride ions diffuse out through the liquid junction in normal use. This extra



safeguard of KCl extends the time before the reference cell starts to drift due to the depletion.

The reference electrolyte passes through some form of a liquid junction to make electrochemical contact with the process. As long as this electrolyte is flowing and in contact with the process a stable reference potential is possible. Junctions can be made from ground glass sleeves (C) with small holes (A, D), ceramic, porous Teflon® (B), polyester and wood fibers (B), etc.

Effects of Drying

The internal fill solution of the reference electrode is designed to leak out into the solution being measured. When in long term storage or a "dry condition" the KCl still slowly leaks out and is not being whisked away by the process fluid, the KCl can slowly build up on the junction of the reference electrode causing it to become clogged. When this happens the result will be an inaccurate pH reading due to the increased "resistance or impedance" of this junction. This KCl creep can be seen as a white crystalline substance.

If a clogged junction is suspected it is best to soak the electrode in some warm tap water to dissolve the KCl and clear the junction. When reference electrodes experience "dry conditions" in more prolonged occurrences, coating can occur. Coating will cause the pH measurement to drift upward. A totally coated reference junction, due to KCl creep, will drift *off scale* in an upward manner. In these advanced cases of creep a functional liquid junction can be more rapidly obtained by first carefully scrapping the KCl creep from the junction, and then cleaning.

KCl creep occurs more frequently with liquid filled reference electrodes rather than with gel filled or slurry filled electrodes. Nevertheless both gel filled and slurry filled reference electrodes can also experience creep.

Solutions to Prevent Drying

Simple as it sounds, the answer is *soaking the electrode*. Proper storage of pH electrodes is a key concern for assuring their effective life as well as how quickly they function when put on line. Soaking a pH measuring or a reference electrode overnight will solve most problems associated with drying.

4 Buffer is an excellent solution to soak a pH measuring electrode in. 7 Buffer is also good, but the more acidic buffer will regenerate the pH electrode faster.

Soaking time is dependent on three things:

- 1) Importance of the accuracy of the pH measurement.
- 2) How long the electrode was dry.
- 3) Can a delay in replacing the current in-line electrode be tolerated?

If the answer to 3) is "no time to wait", then the electrode is inspected, cleaned and placed into service. A new calibration should be done within the next 8-24 hours after the installation to correct for changes in the gel layer.

If the answer to 3) is "we have time", then a 4 hour soak will suffice for electrodes which were allowed to dry out for 3 to 5 hours. If extreme accuracy is required or the electrodes were dry for 8 hours or longer then an 8 hour soak is the minimum required soak. Overnight is better.

Reference electrodes can also be soaked in 4 or 7 Buffers with no ill effects. Still a warm water rinse and wash (to clean any KCl) from the junction may be all that is required.

In situations where a reference electrode or a combination electrode need to be kept wet during long term storage; a storage solution may provide more satisfactory results than Buffers. These Storage solutions are normally 7 Buffer with some amount of KCl and anti-growth agents added.

No Buffer? No storage solutions? Use clean tap water. Any electrode which has had sufficient time to soak will give a more accurate and reproducible measurement than an electrode placed into service from a "dry condition".