Understanding pH Probes rev 1.1

Have you experienced pH probe problems in measurement, calibration or installation?

This article has been compiled from various sources of information within the water treatment industry. It is intended to inform the reader of the various anomalies associated with pH probes, possible solutions, and most importantly, **cost-saving**.

- Problems with your pH readings may not always mean replacing your pH probe.

What are pH Probes?

PH probes are mysterious creatures compared to many of the other similar devices commonly used in industry. Most end users are not specialists and that's fine if everything is running smoothly. But if something goes wrong with a pH reading, the subtleties of electrochemistry mean that many engineers are not confident about diagnosing possible problems.
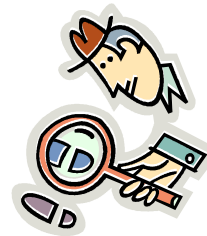
But there are general guidelines that can help users diagnose some of the most common faults, and it's sometimes possible to fix them without resorting to new equipment.
pH measurements need three elements: a pH electrode, a reference electrode and sometimes a temperature compensation element.

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These may be separate, but are generally integrated into a single combination electrode, which can be purchased from CWC. Problems can arise with any of the elements, or may be caused by other aspects of the installation, such as faulty cables or connections.

Perhaps the most useful approach is to look at some typical faults and highlighting their most likely causes:

Short scaling

This occurs where the sensor doesn't register the pH expected, or a has a slow, sluggish response.

Why: This results from contamination of the pH electrode, as the response of the probe to pH depends on the diffusion of ions from the sample to a pH-sensitive glass where ion exchange takes place.

Cause: The usual suspects are deposits of grease, proteins or scale, depending on the particular situation.
For example, a manufacturing process involving machinery will often result in oil in the wash water, while food production raises the possibility of protein deposits.
Scale problems are more likely in hard water areas.

Short scaling can also be caused by problems with the cable termination. The high-impedance signal from the pH probe means that the wire from the probe must be coated in an anti-microphonic layer to prevent interference from other electrical signals. This anti-microphonic layer must be completely removed at the termination. Of course, this should not be a problem for electrodes that are supplied ready-terminated. (usually with a BNC connector)

Solution: If grease is the problem, a good wash with an organic solvent such as isopropanol is the answer. Alternatively, the probe might need an overnight soak in acid to remove scale, while an enzyme such as pepsin can digest protein deposits.

Although deposits from the sample are the primary cause of contamination, they are not the only possibility. Be sure that dirty fingers have not left deposits on the glass, for example during installation.

Erratic readings

Why: Readings that bounce around and will not settle are usually the result of contamination or poisoning of the reference electrode.
In fact, reference poisoning lies behind
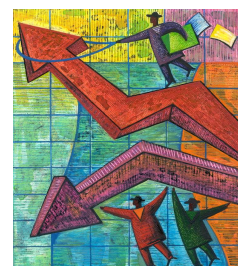
more than 95 per cent of the problems with pH sensors. The reference must be connected to the sample so eventual contamination is inevitable, though this may take years.

Cause: The most common poisons are sulphides, which are present in biogas and in many power generation applications. Bromides can also be a problem. Once poisoning occurs, the reference electrode must be replaced.

Solution: As with most probes, these are combination electrodes, where the reference electrode as well as measuring electrode are incorporated into one, so the whole probe needs to be replaced.
If not a combination electrode, where appropriate, a reference probe top up, or even a gentle shake might solve the problem.
A visual check on the liquid junction in transparent probes, to see that it is clean is also advisable.

Calibration issues

pH probes are dynamic systems and must be calibrated regularly.
Just how regularly will depend on the application, and a suitable interval could be anything from a week to a year.
For a typical, non-critical process applications such as effluent monitoring, three to six month intervals will usually suffice.
Of course, it's inevitable that some problems will show up during calibration, even though everything seemed fine during normal operations.

Science: The slope of a pH probe from 7ph to 10pH or 4pH, has an equivalent voltage associated with the pH value. 7pH is represented by 0V, 4pH is +177mV (milli-volts), and 10pH is -177mV. Approximately ±59mV per pH point is the slope mV for equivalent pH valve. However, pH probes are never perfect, and there will always be a deviation between different probes, normally expressed as a % accuracy or measurement error in the manufacturer's data sheets.

Why: A low slope where the pH value is not high (or low) enough, may mean that the electrode is lazy, which sometimes happens if it is being used in an application that normally operates across a very narrow pH range. For example, if a sensor is used in the final stage of effluent purification, it will only see samples that are almost exclusively pH neutral. If this is the case, challenging the probe by submerging it in acid will often reinvigorate it.

A check whether the pH returns to the reference (7pH) after a slope calibration is recommended. If this does not get close (within approx. 0.2 of a pH point) there may be a problem with the reference side of the system, and probe replacement may be required.

Solution: As pH probes age, the instrument used to measure the pH is normally re-calibrated many times. At some point the instrument will not be able to compensate for the error in measurement of the pH probe. This can be checked by simulating pH values from a pH simulator to the instrument itself. This can give the user an idea of how damaged the pH probe is. If after cleaning the probe (see probe cleaning methods below) the error is still great, it is time to replace the probe.

Expert's Opinion

Although end users should be able to diagnose and treat some of the common problems that arise with pH readings, the fact remains that pH sensors are complex, dynamic electrochemical systems. If you're still in doubt, it may be best to check with your supplier.

For probes with replaceable electrolyte -
How often does the electrolyte need replacing? This depends on the sample being measured, and is best determined by experience. Error can be determined by comparing readings before and after renewal of the electrolyte on the same sample. Normally, errors of less than a few hundredths of a pH can be expected after a full day's use and electrolyte need only require weekly replacement.

Summary:

- pH probes are dynamic systems and must be calibrated regularly. Try three- to six month intervals as a guide.
- Due to the nature of electro-chemistry devices, different pH measurement instruments and different probes will most likely give a different reading but should generally be within 0.2pH of each other.

Probe Cleaning Methods:

Before cleaning a pH electrode, it should be noted that distilled or deionized (DI) water should not be used for electrode storage or soaking. This can result in permanent damage to the electrode. However, it is recommended that DI water be used to rinse the electrode when cleaning and/or transferring to another solution. Also, it is preferable that pH electrodes be chemically, rather than mechanically, cleaned.

The following methods are taken from various manufacturers of pH probes, and hopefully one of them will work for you:

- Mild acid is best for scale - say hydrochloric acid diluted 1:10. However, the detergent "Jif" is an excellent all purpose cleaner. Use undiluted on a cotton bud.
- Prepare the following soaking solutions: 5% HCl, 4% NaOH, and 4 buffer saturated with KCl.
  Pour each solution into a separate beaker. Use enough solution, as required, to submerge the porous Teflon junction of the sensor.
  Soak each sensor in 5% HCl for 5 minutes while "swirling" the sensor to create agitation. Repeat this step in the 4% NaOH solution.
  Rinse in DI water for 2 minutes and visually inspect the porous Teflon. If the Teflon is not clean, or is still contaminated, repeat step 3 until clean. Rinse in DI water for 2 minutes.
  Place sensor in the beaker of 4 buffer saturated with KCL, and let soak for 48 – 72 hours and retest.

- Clean the electrode periodically dependent on the application. Remove the sleeve as in Preparation. Clean the membrane, ground glass stem and sleeve with solvents, detergents, or acid. DO NOT USE ABRASIVE MATERIALS!

  Alkaline samples and scale - Soak the electrode in 6M HCl (Hydrochloric acid), 3M sulphuric, or chromosulphuric acid for 15 minutes. Wash well with tap water and soak before use.
  Biological and protein samples - Soak the electrode in 0.1% pepsin / 0.1M HCl for 1 hour or overnight. Rinse the electrode and then soak in pH7 buffer which contains 0.5g KCl /100mL before use.
  Grease and oil - Wipe the membrane and ground stem with cotton or tissue soaked in acetone or methylated spirits. Wash with deionised water and soak before use.
  Dirt and organics - Wipe the tip with cotton or tissue soaked in a mild non-alkaline detergent (e.g. Palmolive). Wash with deionised water and soak before use.
  Rejuvenation of the response of aged pH electrodes may be obtained by immersing for 10 seconds (no longer) in 10% hydrofluoric acid and immediately washing well in tap water. This treatment should be used sparingly.

Storage:

When not in use, it is preferable to keep the electrode tip immersed in KCl (Potassium Chloride). If this is not available, pH 4 or 7 buffer is acceptable. This keeps the reference from drying out and the pH glass hydrated, so the electrode is ready for use immediately. If all else is not available, tap water will do.