

Top 10 Mistakes in pH Measurement

Are you making errors when measuring pH?

Here are the top 10 mistakes that our technical staff see most often.



[Proper technique in pH measurement](#) is a matter that is a bit hazy among some of our users. Questions like “how often should I calibrate?,” and “how often should I replace my electrode?” are commonplace for anyone starting a pH measurement process.

The team at Hanna has seen a lot of good (and bad) pH measurement practices throughout the company's 38 years of experience.

We've compiled a list of the top 10 mistakes in pH measurement, as well as advice on what to do instead.

Mistake #1: Storing the electrode dry

Improper electrode storage is something we see come up from time to time. Occasionally we'll encounter an electrode stored dry. Typically the incorrect rationale behind this is that the dry storage will keep the electrode inert and viable longer.

What is actually happening is that the electrode is drying out, possibly permanently if stored dry long enough. A pH electrode's sensing glass is actually composed of three discrete glass layers: a hydrated outer glass gel layer, a dry middle layer, and a hydrated inner layer. The hydrated layer is responsible for providing the electrode the sensitivity to changes in the pH.

By drying out the electrode, you severely reduce the sensitivity of your electrode.

This leads to drifting pH values, slow response times, and incorrect values. Fortunately, you can “revive” an electrode that has been stored dry in most cases by submerging the bulb and junction in [pH storage solution](#) for at least an hour. After that, you may calibrate the electrode and be back in business.



Mistake #2: Wiping the sensing glass

We get it. You want to make sure your pH sensing glass is nice and clean for the next measurement, so you thoroughly wipe your electrode with a paper towel. However, this can cause more problems than a little bit of residual buffer in your sample.

In order to understand the problem, it is important to know how the pH electrode works.

The electrode sends a voltage to the meter that is based on the pH of the sample it is submerged in. Wiping the pH glass can produce a static charge (think of it like rubbing a balloon and observing the static charge that builds on it). The static charge interferes with the voltage reading of the electrode. When the voltage reading is wrong, the pH value that the voltage is interpreted to is thrown off too. What's more, the hydrated layer of glass that you have worked to develop by proper storage is interrupted by wiping the sensing glass with a paper towel.

Instead of wiping the electrode sensing glass, simply rinse the electrode with distilled or deionized water.

If necessary, you may blot the electrode with a lint-free paper towel to remove excess moisture, taking care not to rub the surface of the glass (e.g. Kleenex®).



Mistake #3: Storing the electrode in DI water

Storage in pure water (such as deionized, distilled, or reverse osmosis) is also a major mistake in storing the pH electrode. This happens most often when a user runs out of storage solution but wants to keep the electrode hydrated. This presents another, far worse problem.

Deionized water contains virtually no ions. The pH electrode is full of ions, both in the filling solution and interacting in the hydrated portion of the pH sensing glass. So, when an electrode is submerged in a solution containing no ions, the ions in the electrode will want to move out into the solution with the intention of eventually establishing an equilibrium. With most of the ions gone from the electrode due to repeated deionized water storage, the electrode will be rendered inoperable. The glass also degrades much more quickly, leading to shorter electrode lifespans.

If you ever encounter an electrode stored in deionized or distilled water, immediately remove the electrode. If the electrode is refillable, replace the [fill solution](#) with fresh solution. Once the fill solution is changed, store the electrode in the storage solution and calibrate the electrode.

It's always best practice to use [storage solution](#) for storage.

If storage solution is absent or unavailable, pH 4 or pH 7 buffer can be used as an alternative.



Mistake #4: Not Cleaning the Electrode

We've seen a lot of interesting applications since we first released the pHep back in the 1980's. With its launch, pH measurement was opened up to applications beyond the laboratory as a variety of samples and substances were being measured, from soil to wine and everything in between.



With so many different samples, it makes sense to have cleaning solutions developed specifically for these applications.

Cleaning is just as important as calibration in attaining accurate pH measurements.

This is because deposits that form on the electrode coat the sensing glass. For example, fats in oils or foods can coat the electrode. As a result, you will be measuring the deposits and the sample, rather than just the sample. A

slow response time can also be seen from dirty electrodes. You might even record the value when it appears stable, but, in reality, it is drifting very slowly to the “real” value. This can happen even if the electrode “appears” clean; a very thin coating of oil or scale may still be on the electrode.

The best way to clean the electrode is to use a specially formulated [cleaning solution](#) for pH electrodes. Even better would be to use one that is developed for the application you are using the electrode for. For example, cleaning solutions are available that are ideal for removing wine deposits/stains from electrodes. This way, you can be sure that residues are completely removed from the electrode.



Mistake #5: Calibration Errors

[Calibration](#) is definitely one of the most common processes we get asked about. Frequency (or infrequency) of calibration is a major concern. We also have a lot of questions about which buffers to use for their application. Sometimes the frustration is so real, that users stop calibrating altogether. Fortunately, all of the questions (and frustrations) can be answered by understanding how calibration works.

All pH electrodes rely on a principle known as the Nernst equation. The Nernst equation takes a voltage (mV) reading and correlates it to ion concentration (or pH). This correlation forms a straight line. For pH electrodes, the theoretical mV value at pH 7 is 0 mV (neutral) and the slope of the line is 59.16mV. This means that in theory the electrode will change its output by 59.16mV for every pH unit you go (e.g. pH 6 to pH 7 would be 59.16mV/pH unit). All of this is in theory since electrodes will change their slope and offset as they age.

In reality, the electrode might behave slightly different than the theoretical behavior (e.g. 58.2 mV slope and 8mV offset). Calibration compensates for this by determining the actual slope and offset of your electrode by using known buffers and updating the algorithm in the meter accordingly.

For best results, you should make sure you are calibrating using buffers that “bracket” your sample.

pH 7 buffer should always be included to obtain the offset (neutral) point. This means that if your sample is pH 8.6, then pH 7 and pH 10 buffers should be used.

The frequency of calibration ultimately depends on how accurate you like your numbers. Daily calibration is ideal; however, we get that calibration takes some extra time out of what might be a crazy schedule.

If you can tolerate a little bit of error in your measurement, daily calibration is not completely necessary (but highly recommended!)

Knowledge Base: How to check the slope and offset of a pH meter



[Download Hanna's pH Measurement Best Practices Cheat Sheet](#)

Mistake #6: Electrode Selection

All [pH electrodes](#) are not created equal. Even with the best technique you may still not be getting the best measurements. This is because some electrodes are better suited to certain applications than others. Using the less-than-ideal electrode can result in a longer response time and a shorter electrode lifespan.

Consider the “standard” pH electrode. It is typically glass-bodied with a large spherical bulb at the end which makes up the sensing glass portion. There is usually a small ceramic junction that allows electrolyte flow from the reference portion of the electrode. This electrode is functional for a wide variety of applications, but not ideal for all samples. Problems arise when the pH is measured in samples that are semisolid/solid or have solids suspended in the solution. These kinds of samples include wine, wastewater, and food. Samples low in ions can also pose problems with response time and stability (like drinking water).

In these cases, it may be ideal to use an electrode that is especially suited for these different kinds of samples. Conical sensing tips with open junctions allow direct measurement of solid and semisolid samples, eliminating

the need to make a slurry. Electrodes with multiple ceramic junctions allow electrolyte to diffuse into the sample faster, allowing more stability in pH measurements of samples with low-conductivity.

Ensuring that your electrode is best suited for the job is crucial to a good measurement.



Mistake #7: Not loosening (or removing) the fill hole cap

The fill hole screwcap seems like such a minor detail in the whole construction of a refillable pH electrode. After all, it just prevents the electrolyte from drying out, right? Yes, but if it is screwed on as tight as when you first receive the electrode, you might be in for some problems.

Most modern pH electrodes are technically two electrodes in one: a sensing electrode and a reference electrode.

The reference electrode requires a slow but steady flow of electrolyte out of the electrode and into the solution.

When the electrode fill hole cap is screwed on tightly, electrolyte cannot easily diffuse out of the electrode and into the solution. This phenomenon is just like covering one end of a straw with your finger; even if there's a hole in the bottom, liquid won't escape as long as your finger is covering the hole. This results in an erratic reading that might not ever stabilize in a reasonable amount of time.

Fortunately, the fix for this mistake is simply loosening or removing the fill hole cap. It's that easy.

Watch Our Knowledge Base Video: [Why keep the Reference Fill Hole open during a pH measurement?](#)



8. Electrolyte fill level

Refillable electrodes allow you to replenish the electrolyte in the reference compartment once it begins to run low. However, if you do not replenish the electrolyte from time to time, your pH measurements can be impacted.

Erratic electrode response is the most common problem with inadequate electrolyte levels.

Electrolyte flow from the reference junction permits the completion of the measuring cell. This ultimately allows you to take the mV value from the pH electrode and convert it to an adequate pH value.



Ensure that your electrode is replenished and functional by maintaining the fill solution level less than a half-inch from the fill hole cap.

[Watch our Knowledge Base Video: Filling the Electrode](#)



Mistake #9: Inadequate probe submersion

It's easy to think that as long as the pH electrode is touching the sample, then the value that appears on the screen is going to be the pH. The reality is that the pH sensing portion and reference junction needs to be completely immersed in order to properly function.

Let's refer back to the reference electrode and sensing electrode. A pH sensor works because the sensing glass interacts with the sample and produces a voltage that gets compared with the reference electrode (which is stable in all samples). Without one of these portions in complete contact with the sample, the measuring system is incomplete, leading to erroneous values.

Submersion problems are simply corrected by adding enough sample to submerge both the junction and sensing glass.

The position of the reference junction changes based on the electrode design, so be sure to check the manual to determine where the junction is located.



Mistake #10: Using an old/expired electrode

Just like any piece of equipment, pH electrodes need to be replaced from time to time as part of regular maintenance. As electrodes age, the sensing portion of the glass will break down and become less responsive than it was when it was first made. Eventually, the electrode will stop responding adequately to changes in pH.

There are some numbers associated with properly functioning electrodes. Slope and offset are familiar metrics that you can measure your electrode's functionality. These numbers can be determined during calibration. Offset is simply the mV reading in pH 7 buffer and slope is the mV change per pH unit. On many meters, these values can be viewed automatically through the Good Laboratory Practice (GLP) screen. Functional electrodes have a slope between 85-105% of the ideal value. The offset should be ± 30 mV.

Sometimes, despite all of your best efforts, the electrode still does not perform like you would like it to. If the electrode is old, it might just be time to replace it. By all means, though, try cleaning and soaking the electrode in storage solution first; it could just be one of the above problems after all.

Although this seems like a lot of steps to keep track of in order to take measurements, many Hanna Instruments meters like the [HI5221 Research Grade pH meter](#) offer CAL Check™.



Hanna's CAL Check™ compares electrode slope and offset data from calibrations made over time.

It immediately identifies potential problems with the electrode and/or buffers using built-in diagnostics.

These diagnostics will alert you of possible errors associated with dirty electrodes and contaminated buffers, as well as determine overall electrode condition after each calibration. CAL Check takes the guess work out of pH calibration, allowing you to be confident that your electrode is in good working condition and ready to take accurate measurements.

[Download Hanna's pH Measurement Best Practices Cheat Sheet](#)

[Find out more about our range of pH meters, electrodes and other pH related products.](#)

