Understanding Calibration of Laboratory pH Systems

Achieve greater confidence in your measurements

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Summary

Have you ever wondered what is going on when you calibrate a pH system or what to do when something doesn't work as it should? Many labs often resort to external calibration of their pH meters to gain confidence in the measurements but is this necessary? In this document we will break down some of the myths and confusion over calibration, validation and verification. This will help you make informed choices in your lab and enable you to have greater confidence in your measurements.

How does a pH system work?

The entire pH measuring system consists of the meter, the electrode, the temperature sensor, and the calibration buffers. For high confidence in the accuracy of the pH measurement, the entire system must be working well together. The electrode picks up a signal from the sample in mV based on the activity of the hydrogen ion. This mV signal is passed down the cable of the electrode and is interpreted into a pH value based on the last calibration that was done on the meter. A meter is calibrated using high purity, known pH value buffers which allow the meter to assign a mV value to specific buffer values. The measurements are heavily temperature dependant, so a temperature measurement is always taken with a pH measurement.

Calibration, validation, verification - What do they mean?

Validation is ensuring all functional parts of the meter are working within specification. No adjustments are made. It is a process of determining if the system is capable to perform as per specific criteria. A validation usually follows a defined protocol which is provided by the manufacturer that covers aspects such as the products used and the application that they will be used for, the environment an instrument will operate in, temperature measurements are within a given tolerance, voltage checks, meter performance at calibration etc Calibration is an actual adjustment to the pH value that is assigned to a particular mV value. Assure accuracy by using fresh, high-quality pH standard buffers that are certified traceable to the regional or national metrology institute of choice. Examples include NIST (National Institute of Standards and Technology) in the USA or the PTB (Physikalisch-Technische Bundesanstalt) in Germany and many others around the globe. During a calibration, there is a change made within the meter where a mV value is assigned to a pH value using certified buffers, Afterall, your results depend on it. Verification is measuring a standard that does not form part of the calibration set to ensure that the calibration is accurate, and the standard reads within a given tolerance of its certified value. It is a way of verifying and providing confidence that all is as it should be. Read a buffer that is near the pH level or interest or falls within the calibration range but is not the calibration buffers. If the verification reads within the expected range (e.g., +/- 0.1 pH or 0.05 pH), then we have confidence in the entire measuring system.

Figure 1. pH meter system

Can I perform these processes myself in my lab?

All of the processes described in this document can be performed by the user. It makes sense to do these in-house since you can take action quickly and it will improve your understanding of your pH system and how it is used.

Should I calibrate with buffers or a mV simulator?

Meter accuracy is a quick check for the mV accuracy of the meter and can be done by attaching the shorting cap to the BNC connector for pH measurement on the meter. If the meter is working well, the meter will display 0.0 +/- 0.1 mV when the shorting cap is installed. If the reading is not within the expected range, contact your meter manufacturer technical service team to troubleshoot. It may just require a simple meter reset to restore performance.

Calibration check with a mV simulator requires disconnecting the electrode and connecting the simulator. This can then be used to mimic certain pH values and determine how accurate the meter is independently of the electrode & buffer solutions.

Calibration is better when done with buffers, since it is using the entire meter system including the electrode. If a calibration is done using only mV simulator then this is checking only the meter performance. Once an electrode is attached, it will need to be calibrated in buffers anyway since every electrode is different based on design, age, level of cleanliness, contamination etc.

When a sample is measured, the meter uses the most recent calibration that was done on the meter in order to generate the result. In this way, if a mV simulator is used for a calibration and then a user performs a calibration with buffers it will be the buffer calibration that the meter is using rendering the initial calibration superseded. Then every subsequent buffer calibration that is done on the meter is superseding the previous one in the same manner.

Is my calibration ok? The Orion tolerance window for mV values in buffers, it is +/- 60 mV, same as the E0. Also, if autocal correctly identifies the buffer, that is because it is reading within the expected range – so there's your verification that the buffer is within a certain tolerance. Stabilization time – in general, if the electrode stabilizes within 1-2 minutes, that is a good thing. If takes longer, electrode probably needs maintenance – pay attention to the junction, too. A poorly leaking junction will cause drift. When slope is 92 to 100% and the E0 is +/- 60 mV, the pH measuring system is working within expected parameters.
Should I use a verification buffer? It is recommended to verify a calibration to give confidence in measurements (since any measurements is only as good as the last calibration that was done!) however, it is not a compulsory part of the calibration protocol. This is normally stated in your site SOP if this would be required.

What should I do when something goes wrong?

Calibration failure / low slope – Usually when a calibration fails it is due to the slope value being outside of the set acceptance which is set within the meter. This can be due to buffer contamination (replace buffer with fresh), electrode is fouled (clean electrode with an appropriate solution depending on application), electrolyte is contaminated (replace refillable electrode fill solution, if gel-filled then replace electrode). Also verify that fill hole is open on liquid fill electrodes and buffer volume used is sufficient to cover the bulb and the junction (e.g., the lower 2 cm) of the electrode.

Buffer not recognised – If only 1 buffer from a 3-part set is not recognised it is most likely due to buffer contamination / degradation. Check buffer is not past the expiry date (shelf life and opened), pour fresh and / or open a new bottle.

Verification failure – Check calibration is ok or not. If it is not, then repeat the calibration and then re-verify. If calibration was ok, pour fresh verification standard. Check that the tolerance you are applying to the verification buffer is realistic and within the accuracy of the buffers and meter.

Other topics:

Custom buffers – Custom buffers are standards that are not auto-recognised by the meter and should only be used in cases where there is not a standard value that sufficiently brackets the measurements. Custom buffers may be bought in or selfprepared. If they are self-prepared then particular attention needs to be given to the purity of chemicals used, reagent grade water and analytical technique for preparation. If they are bought, then they should be accompanied by a temperature table to allow adjustments to be made and the calibration be accurate.

Noisy / unstable readings – A badly performing electrode junction can cause unstable readings and is often due to clogging (see cleaning steps below). Also, could be dirty/coated pH glass sensing bulb (see cleaning steps below). Can be caused by electrode damage (visually check for cracks or other damage but note that not all damages can be seen), damage to the electrode cable (visually check but note that not all damages can be seen), perform meter self-test to satisfy yourself that that the meter is ok. If the electrode calibrates ok but becomes noisy / unstable in samples then check that the electrode is compatible with the sample (i.e., semi-solid, non-aqueous etc).

Electrode cleaning – Soak in dil. HCl for general purpose, pepsin in HCl for proteins etc.

Figure 2. Electrode in cleaning solution

When to replace electrode – Reference failure is the inevitable end for all pH electrodes. Afterall, pH electrodes are a consumable item and won't last forever. Having said that, there are ways to extend the life of your electrode. Ensuring you are using the right electrode for your application, handling it carefully, cleaning as needed and storing in storage solution will all help to get the maximum lifetime. For liquid fill electrodes, you can drain & replace the electrolyte when readings become sluggish or slope drops. In the case of gel-filled electrodes though, this is not possible due to the solid-state electrolyte.

If using a gel-filled electrode, then it must be replaced if cleaning no longer proves effective at restoring performance.

Daily calibration – Assure the system is working well now. – A pH measurement is only ever as good as the last calibration so performing regular calibrations is important to have confidence in your measurements.

Autocal – The meter will autocal when the mV value measured during pH calibration falls within expected ranges – this helps provide confidence that the entire pH measuring system is working within expected parameters. – Autocal works by being able to know which buffer the electrode is in using a window of tolerance around a buffer value. When using a meter with autocal function, it is important to use the buffer values within the calibration protocol to help ensure it works as it should. It is not necessary to present the buffers to the meter in any particular order and even if you accidentally re-read the same buffer twice, this is ok since the meter will know which buffer it is in.

Figure 3. pH calibration buffers

Repeatability – Two portions of the sample tested under the same conditions (usually sequentially) will give the same pH readings within an accepted uncertainty range. For real world samples (rather than standard calibration buffers) that value may be 0.1 pH or more.

Check your reference method of choice – Generally accepted reference methods for pH will usually define good performance of the pH measuring system as meeting some or all the following criteria: slope value, E0 value, calibration verification reading, and/or repeatability. A good method or SOP (Standard Operating procedure) will consider the accuracy that is needed for the result, the electrode & meter capabilities, calibration protocol that brackets the expected results as well as how temperature is handled during calibration & measurements.

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