

pH Electrodes

Designed and Manufactured by Hanna

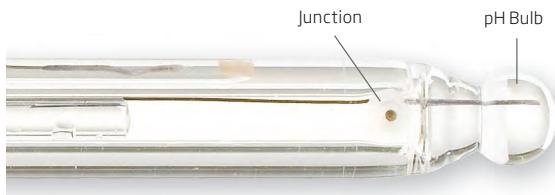
Calibration

pH Electrode Preparation Procedure

A clean, conditioned Hanna pH electrode will provide the best measurements possible. When using a new electrode, remove the protective bulb cap and inspect the electrode.

As water may have evaporated during shipping or storage, salt crystals may be found in and around the protective cap or on the pH bulb, this is normal.

Rinse off with water. During transport, air bubbles may have formed inside the glass bulb. Shake down the electrode as you would with a spirit filled thermometer. Condition the sensing tip; soak the pH bulb and junction in HI70300 storage solution for at least one hour or longer. If possible, an overnight soak is best. This will hydrate a dehydrated glass sensor and thoroughly wet a dried reference junction.



Rinse Electrode with Purified Water

Prior to placing the electrode in calibration solution, it should be thoroughly rinsed with clean, purified water to prevent any contamination to the pH buffer. The electrode should always be rinsed with purified water after placing it in any solution.

Use Fresh pH Buffer for Calibration

The calibration of the pH electrode is only as good as the buffer used. Once a bottle of buffer is open, it should be discarded after six months of use. To prevent cross-contamination, never pour buffer back into the bottle. If the same buffer is to be used for multiple calibrations, it is better to pour a small amount of buffer in a separate container that can be sealed. If using a separate container, the buffer should be changed frequently (i.e. daily, weekly).

It is important to note that pH buffers at higher values (i.e. pH 10.01) are less stable than lower values, this is due to atmospheric CO₂ diffusing into the buffer, forming carbonic acid. If the buffer is old, the actual value might be less than stated on the bottle, resulting a low slope.

Open Reference Fill Cap on Refillable Electrodes

If using a refillable pH electrode, the fill cap should be removed prior to calibration and measurement. Removing the cap creates positive head pressure in the reference cell allowing for higher flow rate of electrolyte through the outer junction. A higher flow rate will result in a faster and more stable reading.

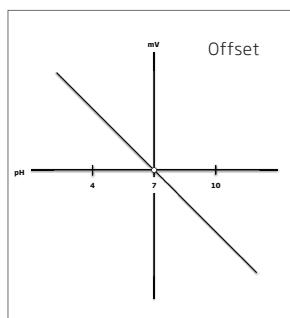
Submerge Electrode Past Junction

It is critical that the junction of the electrode be completely submerged in the pH buffer or sample. Failure to do so will result in erratic readings.



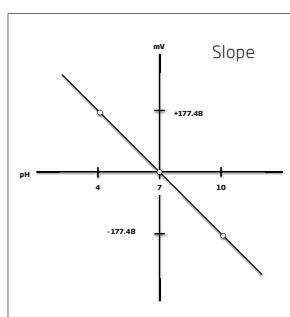
Use a Magnetic Stirrer

For benchtop meters, it is beneficial to use a magnetic stirrer. A magnetic stirrer will ensure that the pH buffer or sample is homogenous. The movement of the solution will also increase the response time of the electrode in the solution.



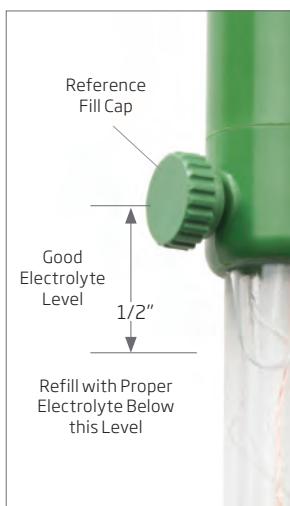
One-point Calibration

For one-point calibration it is important to calibrate the pH electrode in pH 7.0. This calibration determines the offset value. The mV value at pH 7.00 ideally should be 0.0.



Multiple-point Calibration

For improved accuracy it is recommend to calibrate a minimum of two points. The second point determines the slope of the line. It is important to use buffers that bracket the expected value of the sample to be tested. For example, if the expected value is pH 8, the electrode should be calibrated using pH 7.01 and pH 10.01 buffer.



Electrode Fill Solutions

The electrolyte level in refillable electrodes should be checked before performing any calibration. If the level is low (<1 cm or ½" below fill hole), refill with the proper electrolyte solution to ensure the optimum electrode performance. This simple maintenance step helps guarantee adequate head pressure to promote efficient and precise reading.

Always use the appropriate fill solution for your pH electrode. Typically single junction pH electrodes use the HI7071 electrolyte solution (3.5M KCl + AgCl) while double junction pH electrodes use HI7082 electrolyte solution (3.5M KCl).

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Maintenance and Storage

General Maintenance Tips

Periodically check the offset and slope characteristic of the pH electrode.

If your meter does not have GLP (Good Laboratory Practice) capability to display this information, see below on how to use the mV function of a pH meter to determine offset and slope characteristics. A probe should have an offset (pH 7.01) voltage of ± 30 mV. Values outside this range could indicate that an electrode needs to be cleaned or the reference fill solution is contaminated. A probe should have a slope greater than 85% (50 mV/pH @ 25°C). Many Hanna meters will alert the user if the offset exceeds ± 8.0 mV or if the slope is less than 94%.

If it is not possible to check offset and slope of the electrode with your meter, it is recommended to change the pH electrode yearly to ensure that accurate readings are obtained.

How to calculate offset and slope

- Must have a pH meter that can be placed in mV mode
- Must use fresh buffers

The procedure below is based on calibration buffers at 25°C. At this temperature the theoretical 100% slope is 59.16 mV/pH change from pH 7.0. A pH electrode in calibration buffer at 50°C will generate 64 mV/pH, while at 0°C the response will be 54 mV/pH.

Step 1 measure mV of pH 7.01 buffer and record value

Step 2 measure mV value of pH 4.01 buffer and record value

Step 3 calculate the absolute mV difference (pH 4.01 value - pH 7.01 value)

Examples:

Electrode 1 pH 7.01 = -15 mV

pH 4.01 = +160 mV

Absolute mV difference is $+160\text{ mV} - (+15\text{ mV}) = +175\text{ mV}$

Electrode 2 pH 7.01 = +15 mV

pH 4.01 = +160 mV

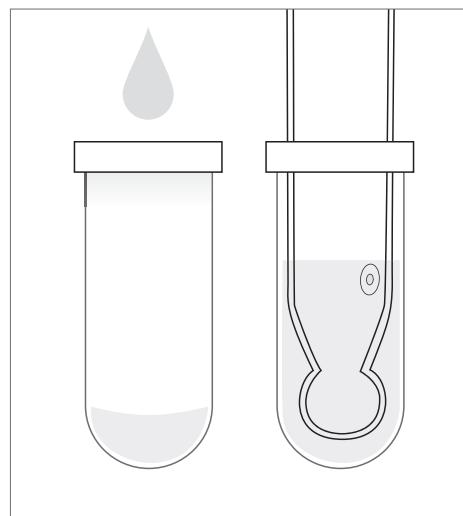
Absolute mV difference is $+160\text{ mV} - (-15\text{ mV}) = +145\text{ mV}$

At 25°C pH 7.01 (offset) = ± 30 mV.

The absolute mV difference should be 150 mV (85% slope) to 186 mV (105% slope).

Conclusion: Electrode 1 is working properly while electrode 2 has an unacceptable slope. Try cleaning and if possible replace fill solution. If slope is still low then replace the pH electrode.

Important note: A pH 7.01 mV value outside ± 30 mV is an indicator of a build up/coating on the pH bulb. The electrode should be cleaned.



Electrode Storage Solutions

To minimize junction clogging and ensure fast response time, always keep the glass bulb and the junction of your pH electrode hydrated. For benchtop meters used in the lab pour a small amount of the HI70300 storage solution in a small beaker and lower the electrode into it making sure that the junction is covered. For portable meters, store the electrode with a few drops of HI70300 storage solution in the protective cap.

Storage solutions are designed to keep the pH electrode hydrated while minimizing growth on the electrode from bacteria and algae. Placing a probe in water will result in a growth on the electrode that might not be visible to the naked eye. This growth will affect the performance and accuracy. To minimize growth it is recommended to use pH 4 buffer if storage solution is not available. Solutions with lower pH values can inhibit growth. If pH 4 buffer is not available, it is advisable to use pH 7 buffer.

Never store a pH electrode in purified water as it will dehydrate the bulb. The concentration of the fill solution is 3.5M KCl. The reference cell with this concentration generates a specific voltage. Placing a probe in purified water will have an osmotic effect causing water to move into the reference cell. There will also be a higher rate of diffusion of electrolyte from the reference cell into the water due to a concentration gradient. Both will result in a different reference electrolyte concentration, which will result in a change in the reference potential. If using a non-refillable probe in which the reference electrolyte cannot be changed, storage in purified water may result in premature failure and ultimately replacement of the electrode.

Inspect the electrode for any scratches or cracks on the bulb or stem.
If any are present, replace the electrode.

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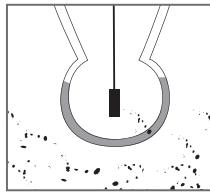
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Electrode Cleaning

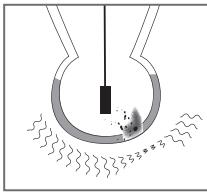
Cleaning Procedure

The most common cause for pH measurement inaccuracies is an unclean or improperly cleaned electrode. This is very important to note, because during calibration, the instrument assumes that the electrode is clean and that the standardization curve created during the calibration process will remain a valid reference until the next calibration. pH meters on the market today will allow an offset voltage of approximately ± 60 mV. The deviation from 0 mV is not unusual but ideally should be no greater than ± 30 mV. The calibration process compensates for the change in offset voltage.

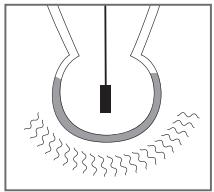
Calibrating a meter with a dirty electrode will result in inaccurate readings. If the mV offset continues to deviate with a properly cleaned electrode, it is a good indication that the electrode may need to be replaced.



In time, particles during routine measurement can contaminate the sensor tip. Mishandled and aged solutions can also be affected.



Your meter can still be calibrated even if the electrode sensor tip is not properly cleaned before calibration. If the contamination dissipates, the calibration is no longer valid and the readings are inaccurate.



A proper cleaning and fresh solution ensures the whole surface of the sensor tip is reading correctly, ensuring an accurate calibration.

General Cleaning

Soak in Hanna HI7061 General Cleaning Solution for approximately 30 minutes to dissolve mineral deposits and other general coatings.

Protein Coating

Soak in Hanna HI7073 Protein Cleaning Solution for 15 minutes to enzymatically dissolve deposits from protein sources.

Inorganic Soak

Soak in Hanna HI7074 Inorganic Cleaning Solution for 15 minutes. This cleaner is especially effective at removal of precipitates caused by reaction with the silver in the filling solution that may form on a ceramic junction.

Oil and Grease Rinse

Oil and grease removal require the correct chemicals to solubilize the coating, but are mild enough to leave the electrode unaffected. Use Hanna HI7077 Oil and Fat Cleaning Solution.

After performing any of the cleaning procedures, rinse the electrode thoroughly with purified water and then soak the electrode in HI70300 or HI80300 storage solution for at least 1 hour before taking measurements.

Troubleshooting

Drifting/Erratic Readings

Potential problems include:

Build up on glass electrode - Clean electrode

Clogged junction - Depending on the material clogging the electrode, use application specific cleaning solutions. It may be possible to dissolve in high purity water or place in an acid such as 0.1M HCl or 0.1M HNO₃ at elevated temperature (50°C) for about an hour to clear the clog.

If the junction is constantly clogging due to measuring in semi solids or viscous samples, use a pH electrode that has an open junction design or cloth junction. The open junction design of the FC200 resists clogging, while those with a cloth junction can have the junction extracted, effectively renewing the junction.

Low conductivity solution - Use an electrode that has a high flow rate or add high purity KCl to sample to increase EC.

Electrode is not properly hydrated - Soak in storage solution for at least 1 hour, if not longer.

Frozen pH Reading

Broken electrode - Possible short between internal pH electrode and reference. pH meter displays the same value when placed in different buffers. The electrode should then be replaced.

Inaccurate Reading:

Improper calibration - Make sure that pH electrode was rinsed with purified water between buffers to prevent cross-contamination and the electrode is at thermal equilibrium with the buffer.

Check offset and slope of electrode. Offset mV value in pH 7.0 should be ± 30 mV; if outside of this range, try cleaning the electrode. Slope (difference in mV from pH 7.0 to pH 4.0) must be greater than 150 mV (85%). If the slope is less than 85% then use fresh buffers, change fill solution, and clean electrode. If the slope cannot be increased to an acceptable value, replace electrode.

Important note: A low slope can be due to a bad buffer. If calibrating to pH 7 and 10, it is possible that pH 10 buffer is no longer valid. pH 10 buffer is susceptible to diffusion of CO₂ from the air. When this happens, the pH 10 buffer will have a lower pH value and result in a low slope percentage value. Tracking the mV values of the buffer by writing the value on the bottle when opened is a way to have a reference point of a good buffer.

85% slope is the absolute threshold of an acceptable slope percentage. There are industries that require a slope of 90% or higher.

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Calibrating and measuring at different temperatures—Either use a meter that has automatic temperature compensation or calibrate and measure at same temperature. Note that the buffer pH at various temperatures is noted on the bottle.

Measuring at high pH (>pH 10.0) introduces alkaline error—

Use a pH electrode that has HT glass to minimize alkaline error.

Calibration with an electrode that was not clean—Any coating that comes off the electrode during use will alter the electrode characteristic, resulting in the calibration being no longer valid.

Electrical noise interference can interfere with obtaining an accurate pH measurement—Noise from rectifiers in plating baths, motors or pumps can interfere with the high impedance measuring circuit.

pH Electrode has a Short Life Span (< 6 months)

Elevated temperatures reduce the life span of pH electrodes. At room temperature (25°C) a pH electrode will typically last 1 to 2 years. A general rule is that for every 25°C increase the electrode life will decrease by ½. Temperature cycling has the most detrimental effect.

Operating Temperature	Average Lifespan
25°C	1-2 years
50°C	6 to 12 months
75°C	3 to 6 months
100°C	<1 month

If measuring samples at temperatures greater than 50 °C, use a pH electrode with high temperature (HT) glass such as the HI1043.

Storing a pH electrode in purified water will shorten the life span of pH electrode—If using a refillable pH electrode, replace fill solution; if using a gel-filled electrode, the electrode will have to be replaced. Store in storage solution.

Wiping a pH electrode with tissue will harm an electrode—It is important to blot a pH electrode. Wiping the electrode can produce a static charge on the sensor that will destabilize the measurement thus requiring additional time before stable measurements can be obtained..

Solutions with hydrofluoric acid will dissolve the glass at a pH less than pH 5. Use electrodes with HF resistant glass. The HI1143 will resist HF up to 2 g/L @ pH 2 and temperatures less than 60°C.

pH

electrodes