

1. Temperature Compensation For pH
2. Tips For Optimizing pH Measurement



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Temperature Compensation For pH

Temperature affects the pH of buffers, samples and the pH electrode response.

If pH accuracy is important to you, the influence of temperature needs to be understood. In order to maximize the accuracy of pH readings, the following guide seeks to provide a better understanding of how temperature affects pH. There are two main concepts to grasp:

1) The pH of all liquids change with temperature

- a) The pH of common calibration standards (**buffers**) are known at various temperatures. When using a buffer which is recognized by the pH meter, the meter is able to read the temperature input and calibrate to the known pH value at that temperature. For example, when calibrating with a pH 10.00 buffer at 20 °C, the meter knows that the value for that buffer at that temperature is 10.06, and calibrates to this value. If ATC was not used, the meter would be off by 0.06 pH units at this pH level.

The Takeaway:

Always use an ATC probe. Understand that buffers will change with temperature too.

- b) Each solution behaves differently with respect to temperature and cannot be predicted by the pH meter. For this reason, always measure and include the temperature along with the pH reading. For example, pH 8.67 @ 35.4 °C is more meaningful than pH 8.67 alone – the pH at room temperature might be quite different.

The Takeaway:

Always use an ATC probe. Always express both temperature and pH measurement values together.

2) The pH electrode's property changes with temperature

- a) This is also predictable and is corrected by the meter. Note that when electrodes experience large temperature fluctuations, the pH electrode itself will require additional time to adjust to the new temperature (hot to room temperature, room temperature to cold, warm to cold, etc.)

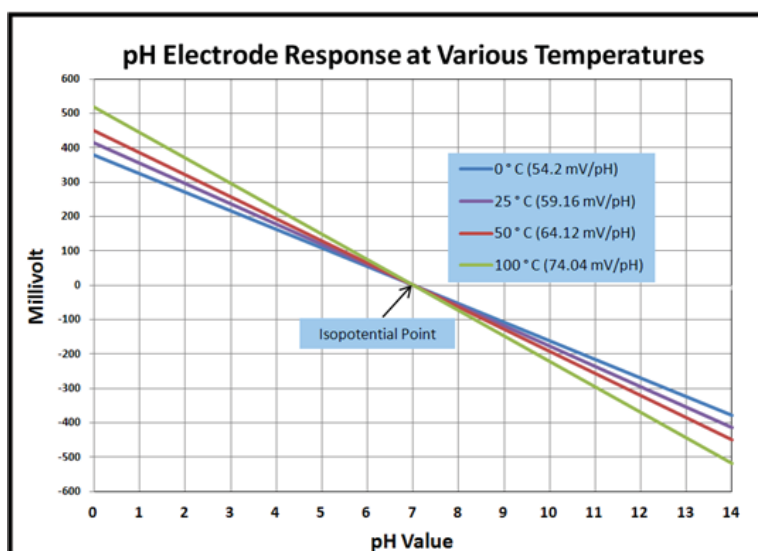
The Takeaway:

Always use an ATC probe. Other than allowing for additional time for the electrode to take a reading, no need to worry about this one – the pH meter will take care of this for me!

Temperature compensation correction does not account for pH change of **samples** that result from the effects of temperature on the sample itself. These effects are unknown for most samples and cannot be corrected for. For this reason, it is common to see methods which suggest that pH and temperature are measured and reported together. Alternatively, methods may specify that the pH must be measured at a specific temperature.



The **pH electrode response** changes by 0.2 mV/°C or ~0.003 pH units/°C. The pH at which the reading for the electrode does not vary with temperature is known as the isopotential point. For an ideal glass pH electrode, the isopotential point is pH 7. The further the sample pH is from pH 7, the more the reading changes when temperature changes and the larger the temperature compensation correction applied. The correction applied to a sample pH reading is approximately 0.003 pH/°C/pH units difference from pH 7. Consider the reverse – if temperature is NOT compensated for, this will be the approximate error. For best results, be sure to compensate your pH readings for temperature!



There are two methods to approach temperature compensation during calibration and measurement. Both methods require temperature input into the instrument; manually or automatically which is preferred and more common. Automatic temperature compensation (ATC) may come from a pH electrode that has a built-in temperature sensor, (3-in-1, triode, All-In-One, etc.), or from a separate temperature only probe – often stainless steel.

Method 1:

Perform pH calibration and measurement with calibration standards (buffers) and samples that are both at room temperature. This is most typical. Calibration standards and samples that are within 1 °C are adequate for most applications. Allow samples to cool or warm to room temperature before taking measurements.

Method 2:

Cool or warm the calibration standards (buffers) and electrode to match your expected sample temperature prior to performing calibration. Calibrating with standards at the same temperature as samples will minimize the correction that is applied. For example, if calibration is conducted with pH 7 buffer at 20 °C while the sample measures pH 8.5 (1.5 pH units higher than pH 7) at 38 °C (18 ° higher than calibration), the correction applied to the measurement will be $0.003 \text{ pH} \times (18 \text{ }^\circ\text{C}) \times (1.5 \text{ pH}) = 0.081 \text{ pH}$. If the calibration had been performed with pH 7 buffer at 38 °C, the potential error could be reduced. Samples can be measured at the actual temperature, without the need for cooling or warming to room temperature.

Many people measure pH, however most do not have a complete understanding of the influence of temperature on pH. Hopefully the explanation provided in this article will serve you well.









Tips For Optimizing pH Measurement

There are 100's of different applications for measuring pH. When you consider the number of available instruments, electrodes, calibration standards, and individual techniques, it might be hard to find two users that measure pH the exact same way. Needless to say some users are able to achieve the best possible results, while many more users struggle to get accurate and repeatable pH measurements. With that in mind, I've outlined some basic tips to help you get the most out of your pH system (meter + electrode + calibration standards), whether you have a pocket Testr or an advanced benchtop meter.

Part 1 Preparation

It should come as no surprise that choosing the proper equipment is an important first step for achieving good pH measurement results. However, if a mistake is made, it usually occurs when choosing the pH electrode, not the pH meter. Choose a pH meter based on features, form, and price range. Choose a pH electrode based on your sample type and application. A high-end electrode on a basic meter will almost always out perform a basic electrode on a high-end meter.

Electrode selection can be summarized in three decisions:
Glass or plastic, gel-filled or refillable, single or double junction.

	Plastic Electrodes: resistant to breakage (better for field use), won't last as long, harder to clean, less expensive	Vs.		Glass Electrodes: easier to maintain, high sample compatibility, high temperature tolerance (typically 100 °C), more expensive, more prone to breakage
	Gel (Non-Refillable) Electrodes: are non-refillable, slow response (poor choice if you need to measure 100 sample per day!), less expensive, lower maintenance, typically plastic, often include built-in temperature sensor, generally don't last as long as refillable electrodes	Vs.		Refillable Electrodes: require filling solution, higher maintenance than gel electrodes, faster response, increased performance is usually worth the extra maintenance!
	Single-Junction: less expensive, often will clog and respond slowly with many sample types. If you replace electrodes often, chances are it is single-junction electrode	Vs.		Double-Junction: if your samples have TRIS, sulfides, proteins, heavy metals or you aren't sure, don't take a chance – use a double-junction electrode!

- Become familiar with your equipment.
- Know the correct filling solutions, storage solutions, calibration solutions.
- To eliminate temperature errors associated with the electrode, take advantage of automatic temperature compensation (ATC) for best accuracy. You'll need a separate temperature probe if it one is not already built-into your pH electrode.
- Develop a realistic standard operating procedure (SOP) that can be maintained and followed as well as training for individuals that use the pH equipment.
- Electrodes perform best when they are sufficiently hydrated. Allowing electrodes to dry is not ideal, but they can typically be reconditioned to normal performance again. Soaking in electrode storage solution or warm pH buffer helps to optimize and re-establish the thin hydration layer on the sensing bulb that is critical to pH measurement. Rinsing with Demineralized or Deionized or Distilled water is fine for occasionally rinsing, but should **NEVER BE USED FOR STORAGE or SOAKING!** Doing so will de-hydrate and may irreversibly damage the electrode. Don't forget to add filling solution to refill electrodes before soaking.

Part 2

Standardization

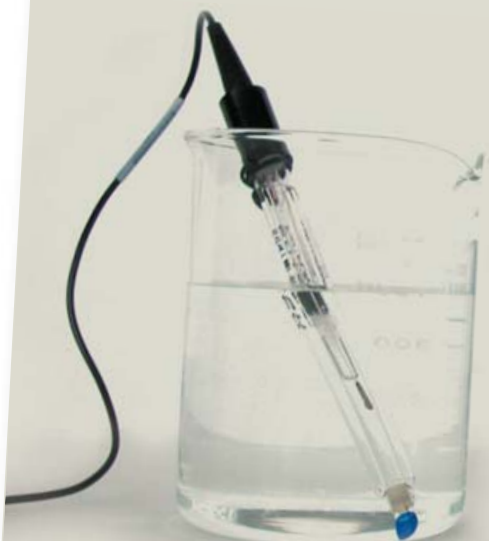


A pH system is only as accurate as the calibration buffers that are used for standardization. Avoid the most common mistake of using expired calibration standards. Performing calibration at pre-determined and regular intervals is essential.

For best accuracy, use a minimum of two-point standardization; first with a buffer value close to the electrode systems zero potential (typically pH 7); and next with an acid or base buffer whose value brackets the expected pH value of the sample(s).

Microprocessor-based meters may permit additional calibrations – up to five points in some models. If your samples are never above pH 7, performing calibration with values above pH 7 won't typically help your accuracy and can be avoided.

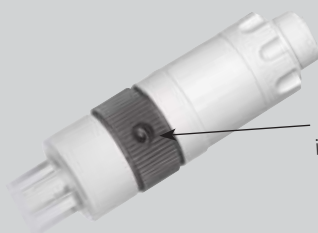
- Always use fresh calibration standards. Do not re-use standards. Standards can change rapidly with exposure to air – especially pH 10 buffer which can drift in a matter of hours. Discard and use new calibration standards frequently.
- Use an adequate volume of standards that will allow moderate stirring and movement. Test tubes and vials are not recommended for calibration for this reason.
- Periodically check your system by measuring calibration standards as if they were unknown samples. Compare the value at the actual sample temperature – for example, at 20°C, pH 7 and pH 10 buffers actually measure 7.02 and 10.06 respectively.



Now that you've managed to get the right electrode and calibrate your equipment, you should be well on your way to getting great results. Remember these common mistakes:

Part 3
Measurement

- In my humble opinion, the biggest mistake is drying the electrode between measurements. Please don't wipe, blot, or otherwise dry your pH electrode bulb in any way. Instead, rinse the electrode then gently shake excess rinse water without using any paper towel, cloth, lab wipe, or anything else. All that work to hydrate the electrode sensor may be reversed in an instant. If several drops of your rinse solution somehow enter your sample, it will not affect the pH reading. A dry pH electrode bulb can cause many problems however. Imagine what would happen if you were to dry off a goldfish after removing it from one bowl before placing it into another.
- Allow adequate time for the reading to stabilize. Don't rely solely on the meter for determination when the measurement is ready. A slow responding electrode (gel filled, single-junction electrode that is dry for example), will often appear to be ready, only to change again. Response time is often a good indication of overall electrode health. If a slow-responding electrode cannot be fixed it should be replaced.
- Since temperature changes pH values of solutions, the corresponding sample temperature should always be recorded along with the pH readings. A proper result might be shown as "pH 8.43 @ 23.2 °C", instead of "pH 8.43" without a temperature.
- If samples will be measured significantly far away from room temperature, allow extra time for the pH electrode itself to equilibrate to the sample temperature. It will continue to drift until the electrode itself is the same temperature at the sample – regardless of the ATC reading.
- If you utilize a refillable electrode, keep the filling hole in the OPEN position during measurement to allow best electrode response.



Refilling hole in open position

- Stirring samples is beneficial to maintain a uniform sample pH, however excess mixing can introduce carbon dioxide from the air, which can introduce error to samples with low ionic strength.

Part 4
Storage

Follow these simple tips to help ensure that your next measurement is just as good as the one you just completed:

- Discard old calibration standards and non-working pH electrodes.
- If you utilize a refillable electrode, close the filling hole.
- As mentioned previously, electrode hydration is vital. Keeping your electrode bulb wet will reduce start-up time and keep the electrode active. If you don't plan on using the electrode again soon, dry storage is acceptable. Electrode storage solution is best, but pH 4 or 7 buffer will do – just don't use deionized water! Keep the electrode upright if possible to eliminate the formation of air bubbles.
- pH instruments can typically be turned off as the calibration setting will be retained.

Still having trouble optimizing your pH system? Contact us and we can help you today!

