



How to Check pH Electrode Health Using mV

Instrument used:



Milwaukee MW103 PRO+ 2-in-1 pH/pHmV/ Temperature Meter with ATC

1. Check the electrode offset

Place the clean electrode into fresh **pH 7.00/7.01 buffer**, select mV mode and allow the reading to stabilize.

The mV reading at pH 7 is the electrode's **offset**. Ideally, this value would be **0 mV**, but some deviation is normal. Milwaukee's general guideline is that the offset should remain within approximately:
–30 mV to +30 mV

An offset outside this range can indicate a problem with the electrode, including contamination, aging or problems with the reference system.

OFFSET AND SLOPE CAN TELL YOU MORE THAN A SUCCESSFUL CALIBRATION

A pH meter may complete calibration successfully, but that does not necessarily mean the electrode is performing at its best. As pH electrodes age, become contaminated or dry out, their electrical response can change.

If your pH meter has an **mV measurement mode**, you can use two fresh calibration buffers to check two important indicators of electrode performance: **offset** and **slope**.

These values provide a practical way to determine whether an electrode is responding normally, needs cleaning or conditioning, or may be approaching the end of its useful life.

WHAT DOES A PH ELECTRODE ACTUALLY MEASURE?

A pH electrode does not directly generate a pH number. It produces an electrical potential measured in **millivolts (mV)**, and the meter converts that signal into a pH value.

At **25 °C**, an ideal pH electrode produces approximately:

- **0 mV at pH 7**
- **+177.48 mV at pH 4**
- **–177.48 mV at pH 10**

This corresponds to a theoretical response of approximately **59.16 mV for each pH unit**.

Real electrodes rarely behave exactly like the theoretical ideal. Manufacturing tolerances, electrode age, hydration, contamination and maintenance can all affect the response.

Now that we know what the electrode is actually measuring, we can use its mV response to assess its condition. The check is simple and requires only two fresh calibration buffers and a pH meter with mV mode. Start with the electrode offset, then use a second buffer to evaluate the slope.

2. Check the electrode slope

Next, rinse the electrode and place it into a second fresh buffer – typically **pH 4.00/4.01** for acidic applications or **pH 10.00/10.01** for alkaline applications.

At 25 °C, the theoretical slope is: **59.16 mV per pH unit**

Between pH 7 and pH 4 there are three pH units, so an ideal electrode would generate approximately: **$59.16 \times 3 = 177.48$ mV** of potential difference between the two buffers.

The slope percentage can therefore be calculated as:

$$\text{Slope (\%)} = \text{measured mV difference} \div 177.48 \times 100$$

or more generally:

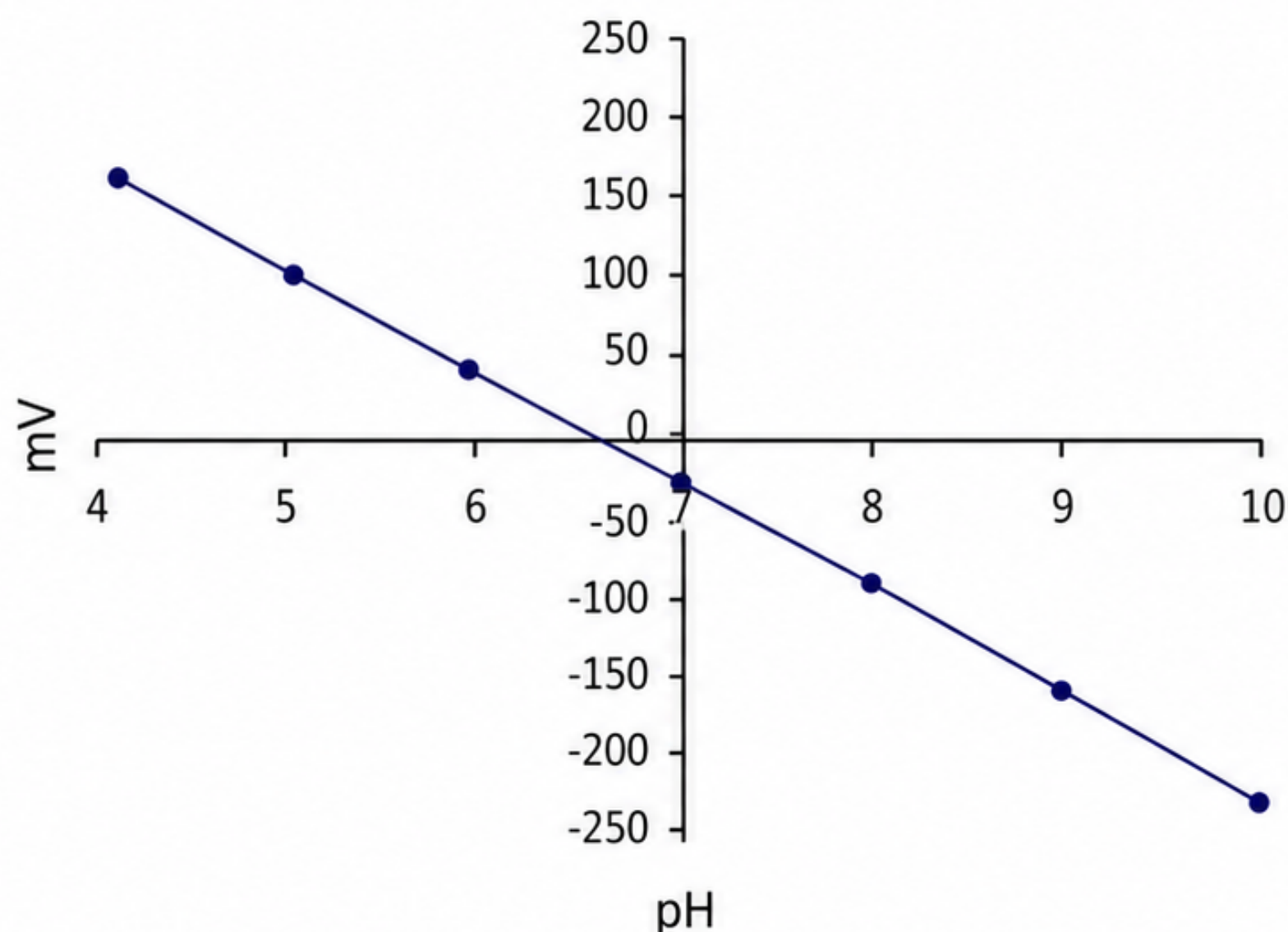
$$\text{Slope (\%)} = (\Delta \text{mV} \div \Delta \text{pH}) \div 59.16 \times 100$$



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TWO ELECTRODES - SIMILAR OFFSET, VERY DIFFERENT PERFORMANCE

Example 1

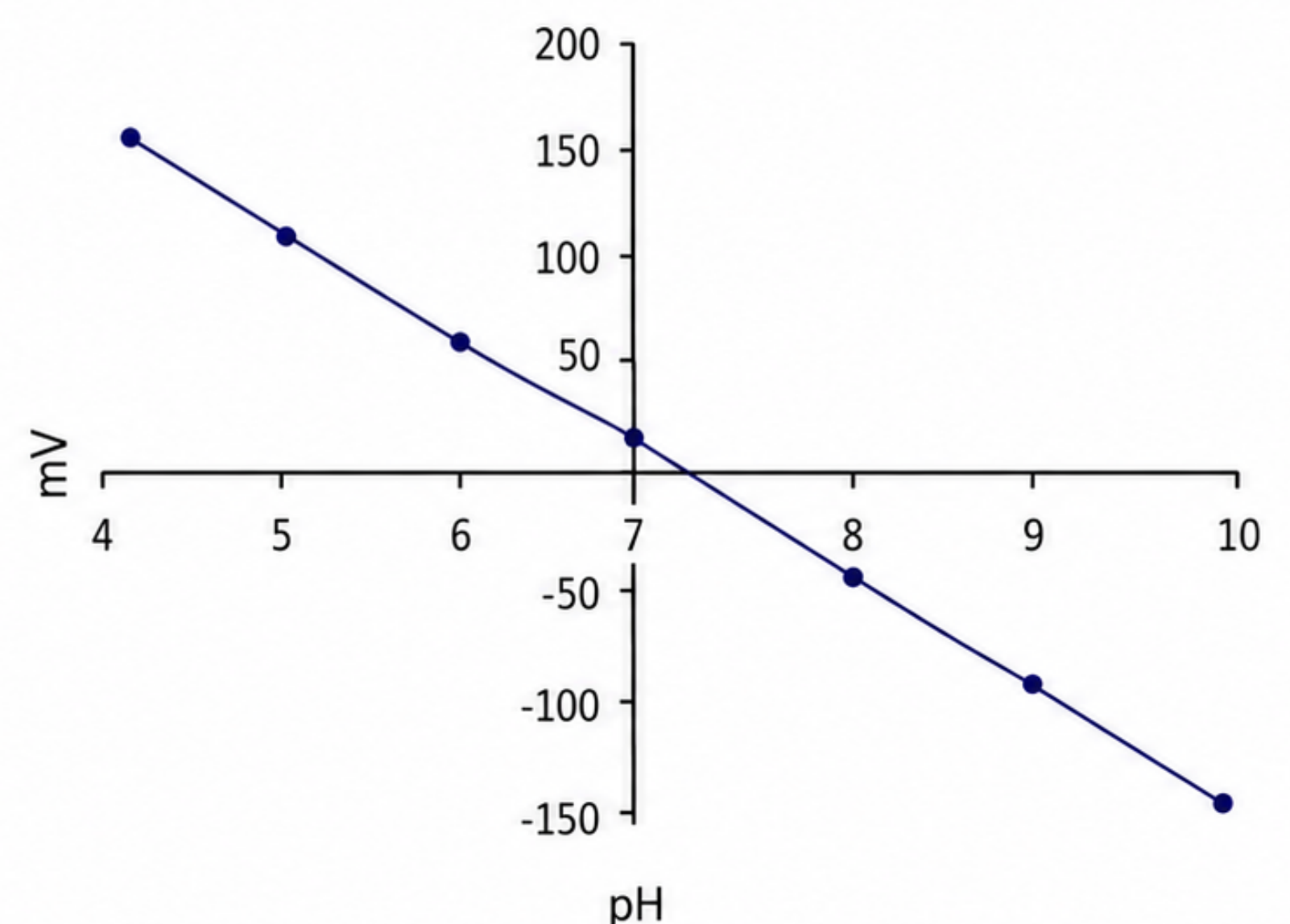


pH 7.0 = -15 mV and pH 4.0 = +160 mV

Offset = -15 mV

$$\begin{aligned}\text{Slope} &= \left[\frac{(160 - [-15])}{59.16 \times 3} \right] \\ &= 175 / 3 = 58.33 \\ &= 58.33 / 59.16 \times 100 = \mathbf{98.6\% \text{ slope}}\end{aligned}$$

Example 2



pH 7.0 = +15 mV and pH 4.0 = +160 mV

Offset = +15 mV

$$\begin{aligned}\text{Slope} &= \left[\frac{(160 - [+15])}{59.16 \times 3} \right] \\ &= 145 / 3 = 48.33 \\ &= 48.33 / 59.16 \times 100 = \mathbf{81.7\% \text{ slope}}\end{aligned}$$

Example 1

pH 7.0 = -15 mV

pH 4.0 = +160 mV

The electrode offset is -15 mV, which is within the expected range.

The potential difference is:

$$160 - (-15) = 175 \text{ mV}$$

Therefore:

$$175 \div 3 = 58.33 \text{ mV/pH}$$

and:

$$58.33 \div 59.16 \times 100 = 98.6\% \text{ slope}$$

This electrode is responding close to the theoretical Nernst response.

Example 2

pH 7.0 = +15 mV

pH 4.0 = +160 mV

The offset is still well within the expected range.

However:

$$160 - 15 = 145 \text{ mV}$$

$$145 \div 3 = 48.33 \text{ mV/pH}$$

and:

$$48.33 \div 59.16 \times 100 = 81.7\% \text{ slope}$$

The important point is that **both electrodes have acceptable offset values, but their slopes are very different.**

The second electrode therefore demonstrates why checking the pH 7 offset alone is not enough to evaluate electrode performance.



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WHAT IS A GOOD PH ELECTRODE SLOPE?

As a general Milwaukee guideline, a pH electrode with a slope of approximately: **90–105%** is considered to be performing within a normal range.

The offset should generally remain within: **±30 mV**

These values should be treated as general electrode-health guidelines. Individual instruments may apply their own calibration acceptance criteria, so the specifications and manual for the meter being used should always take precedence.

WHAT IF THE SLOPE OR OFFSET IS OUT OF RANGE?

A poor result does not automatically mean the electrode must be replaced.

Before replacing it:

1. **Use fresh, uncontaminated calibration buffers.**
2. **Clean the electrode using the appropriate cleaning solution.**
3. **Make sure the sensing bulb is properly hydrated.**
4. **Check the electrode for visible damage or contamination.**
5. **Recondition the electrode if appropriate.**
6. **Repeat the test and recalibrate.**

If the offset or slope remains outside the acceptable range after cleaning and conditioning, electrode replacement may be necessary. Milwaukee's own guidance specifically notes that electrode aging, conditioning and cleaning can affect the measured response.

WHY THIS CHECK MATTERS

Calibration compensates for differences between an actual electrode and the theoretical pH response. But checking the underlying mV response gives you additional information about **how well the electrode itself is functioning**.

Monitoring offset and slope can help you identify:

- electrode aging,
- contamination or coating of the sensing surface,
- inadequate hydration,
- deteriorating response,
- and electrodes that may soon require replacement.

That can be particularly useful when pH results begin to drift, stabilization becomes slower, or repeated calibration does not solve measurement problems.

A NOTE ON TEMPERATURE

The theoretical value of **59.16 mV/pH applies at 25 °C**.

The **Nernst slope** changes with temperature, which is why this simple calculation should be performed with buffers at or close to 25 °C if 59.16 mV/pH is used as the reference value.