# Smart Notes

## My samples read pH 13-14, but my highest pH calibration standard buffer only goes to pH 12.46. Will my sample readings be accurate if the calibration buffers don't bracket the sample pH?

Good quality pH standard buffers are traceable to National Institute of Standards and Technology (NIST) primary or secondary standard buffer solutions. NIST standard solutions have rigorous requirements for purity, stability, and other properties that make them suitable for calibration*. Values for NIST standard solutions range from pH 1.68 to pH 12.46. When calibrating a pH meter, it is good practice to choose pH calibration buffers that bracket the expected pH of the sample. However, an extreme pH sample (e.g., an acidic sample with a pH < 1.68 or a basic/alkaline sample with a pH > 12.46) cannot be bracketed by these pH calibration buffers. In that case, it is natural to be concerned about the accuracy of low or high pH readings that fall outside the range of the calibration curve.

**When testing extreme pH samples, we recommend a two-step calibration verification process:**

1. Perform a routine multipoint calibration with 2 or more NIST-traceable pH standard buffers, using the buffers closest in value to the sample pH;

2. Measure the pH of a technical pH standard that is similar to the sample pH. This allows for determination of accuracy for readings beyond the calibration curve.

ThermoFisher SCIENTIFIC

thermo scientific

# How can I optimize my pH calibration for extreme pH sample testing?

In this case, when measuring a pH 13-14 sampe, a 2-point calibration at pH 10.01 and 12.46 or a 3-point calibration at pH 7.00, 10.01, and 12.46 would be suitable. If the slope of the calibration is good, verify the performance beyond the curve by measuring a known pH buffer with a value in the range of pH 13 - 14. pH 13 buffers are available commercially. A pH 14 solution of 1M sodium hydroxide can be expected to read near 14.05**. While neither of these solutions may be perfectly suited for calibration, either can be used as a verification standard. The difference between the verification standard reading and its expected value gives an estimation of the error associated with sample readings in that range.


Thermo Scientific™ Orion™ pH Buffer Bottles

## When testing extreme pH samples, we recommend these three steps to optimize pH equipment:

- **Use a suitable electrode.** Choose an electrode that covers the full pH range, 0 – 14. A double junction electrode with a refillable, high flow junction will reduce drift, stabilize more quickly, and protect the reference from the extreme pH of the sample. Maintain your electrode. Top up the fill solution daily and change it biweekly or more frequently to assure good performance. Before storing the electrode, rinse off all traces of sample and place into specially formulated electrode storage solution. Change the electrode storage solution regularly.

- **Choose good quality, NIST-traceable calibration buffers.** Store them properly at room temperature and out of the sunlight. Ensure the containers are closed tightly to prevent contamination and evaporation. Never pour used buffer solution back into the buffer container. Discard it. Every day or every shift, pour a fresh portion of each buffer for calibration. Discard expired buffers.

- **Use an appropriate measurement technique.** When measuring extreme pH samples, drift and a slower response of the pH electrode is often observed. Allow extra time for the pH reading to stabilize. Stirring the sample will speed the electrode response and make for quicker readings. Do not leave the pH electrode in the strong acid or base sample for extended periods of time. Rinse the electrode thoroughly with reagent grade water to remove all traces of sample, then store in electrode storage solution. If readings are too slow or drifty, perform maintenance on the electrode as noted above and clean it per instructions. If the issue persists, consider replacing the electrode, choosing a different model electrode, or using a consistent timed-reading approach (e.g., where the reading is collected at 1 minute or 2 minutes for all extreme pH samples).

When testing extreme pH samples, calibrate with high or low level NIST-traceable pH buffers and verify with a high or low level technical pH standard. Use a suitable electrode and an appropriate measurement technique to achieve faster, more accurate results.

**Figure 1. pH Calibration Buffers, NIST-Traceable**

| Nominal pH value at 25 °C | 0 °C | 5 °C | 10 °C | 20 °C | 30 °C | 40 °C | 50 °C | 60 °C |
|---|---|---|---|---|---|---|---|---|
| 1.68 | 1.67 | 1.67 | 1.67 | 1.68 | 1.68 | 1.69 | 1.71 | 1.72 |
| 4.01 | 4.00 | 4.00 | 4.00 | 4.00 | 4.02 | 4.03 | 4.06 | 4.09 |
| 6.86 | 6.98 | 6.95 | 6.92 | 6.87 | 6.85 | 6.84 | 6.83 | 6.84 |
| 7.00 | 7.11 | 7.08 | 7.06 | 7.01 | 6.98 | 6.97 | 6.96 | 6.97 |
| 9.18 | 9.46 | 9.40 | 9.33 | 9.23 | 9.14 | 9.07 | 9.01 | 8.96 |
| 10.01 | 10.32 | 10.25 | 10.18 | 10.06 | 9.97 | 9.89 | 9.83 | 9.79 |
| 12.46 | 13.47 | 13.24 | 13.03 | 12.64 | 12.29 | 11.99 | 11.73 | 11.50 |

* Measurement of pH. Definition, Standards, and Procedures. IUPAC Recommendations 2002. Pure Appl.Chem., Vol. 74, No. 11, pp 2169-2200, 2002.

** The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, 11th ed. Budavari, S., Ed.; Merck & Co.: Rahway, NJ, 1989; pH Values of Standard Solutions, p. MISC-113.

Find out more at **thermofisher.com/electrochemistry**

ThermoFisher SCIENTIFIC