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Precision Sensor News

In This Issue

- Temperature Effects on pH Measurements
- Should the RTD be built into a Steam Sterilizable pH Sensor?
- Nernst Temperature Dependence
- Who is Nernst?
- Temperature Compensation for Nernst Temperature Dependence
- The Nernst Temperature Dependence is Minimal Near 7 pH
- Pointers for Manual Temperature Compensation
- Pointers for Automatic Temperature Compensation
- What is Solution Temperature Dependence?

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Temperature Effects on pH Measurements

In order to obtain the best precision from your pH measurement system, it is important to understand the effects that temperature has on pH measurement. Not only does the pH electrode output change with temperature, but also the pH of the media being measured will change with temperature. The first effect, the change in electrode output, is the Nernst temperature dependence. The second, the change in media pH, is referred to as the solution temperature dependence. These two effects, either together or separately, can lead to errors in calibration, measurement and control. When properly understood, it is possible to minimize errors caused by these temperature effects.

PT100 TEMPERATURE SENSOR IN UNGUARDED HOUSING

Broadley-James Corporation offers a selection of temperature compensators with T-Pull handles to fit most standard 25 mm housings. These temperature sensors are available in a variety of values such as Pt100 and Pt1000. Call us to determine which sensor is best for a particular application.

Should the RTD be built into a Steam Sterilizable pH Sensor?

The RTD sensor (Resistive Temperature Device) is commonly used to measure the on-line temperature of an industrial process. The most common RTD elements are the Pt100 ohm and Pt1000 ohm platinum resistance chips.

Internal RTD's are routinely used in industrial pH sensors for purposes of Nernst temperature compensation. The RTD is built into a glass or polymer tube within the pH sensor. The majority of these pH sensors are used at ambient temperature for water and wastewater monitoring. However, in industrial processes demanding tight temperature control and more precise pH measurements, a separate in-line RTD sensor is utilized for both temperature monitoring, control, and Nernst temperature compensation of the pH sensor.

Traditionally in fermentation and cell culture applications, the precision and accuracy demands of the process have led to the use of a separate RTD sensor that has its own thermowell through the vessel wall. This RTD sensor is routinely validated and then used for all temperature monitoring, control, and pH sensor compensation.

Recently, sterilizable pH sensors with built-in RTD's immersed in the electrode's reference salt bridge have appeared on the market. There are a number of concerns with this approach to Nernst temperature compensation in a sterilizable pH sensor.

(1) It is inherently unsound to immerse the RTD into the corrosive KCl salt bridge of a sterilizable pH electrode that is subsequently steam sterilized at temperatures up to 130°C. While there are a number of immersible encapsulated RTD elements on the market today, none of them have a performance rating in 130°C KCl solutions and none of them were designed to work in such a corrosive environment. By building the RTD into the pH sensor's salt bridge, the overall reliability of the pH sensor is lowered.

(2) The makers of these sterilizable pH sensors with the built-in RTD's place a warning within their own sensor instructions stating the RTD should not be used for temperature measurement. This is a step backwards for precise pH temperature compensation.

(3) The validation task is greatly complicated. Instead of validating one RTD sensor per vessel on a routine basis the validation engineer must now think about validating the RTD in each pH sensor before each and every run. There is no other way to insure that each RTD is still working after a steam cycle in concentrated KCl. Additionally, there is no way to validate the RTD's functionality after the steam cycle and during the run. While a grab sample can be taken to verify that the pH sensor is functioning during a run, a grab sample measurement will not detect a defective RTD.

Bioprocess applications have the most demanding requirements for sensor precision and accuracy of any industrial process. Built-in RTD's jeopardize the precision and reliability of sterilizable pH sensors. There is no more reliable and precise way of measuring bioprocess temperature than the current practice of using a separate RTD sensor in its own thermowell. Given the importance of correct temperature feedback to the pH transmitter to insure precise temperature compensation, the separate RTD is recommended.

Nernst Temperature Dependence

The pH electrode's output is temperature dependent. Even at constant pH, the electrode output will change a little with temperature. Every 1°C increase or decrease in temperature will change the electrode output by approximately 0.2 mV/pH unit. Unless compensated, this mV change can result in an error of 2.5% to 3.5% over a range of just 10°C. The table above illustrates how the electrode output per pH unit changes from 0°C to 100°C.

pH Electrode Output versus Temperature

°C	mV/pH unit	°C	mV/pH unit
0	54.20	50	64.12
10	56.18	60	66.10
20	58.17	70	68.09
25	59.16	80	70.07
30	61.14	90	72.05
40	62.13	100	74.04

Who is Nernst?

Walter Nernst (1864-1941) was the first person to derive an equation that models the output of electrochemical half-cells such as the pH electrode. The Nernst equation, which describes the half-cell's output and behavior, is temperature dependent. Most modern pH instrumentation uses a form of the Nernst equation to convert the mV output from the pH electrode to the displayed pH units.

Temperature Compensation for Nernst Temperature Dependence

In order to perform this correction the instrument needs to know the temperature of the sample solution to be measured. Two types of compensation are commonly available: manual and automatic. With manual temperature compensation the operator inputs the correct temperature by hand. With automatic temperature compensation the instrument is connected to a temperature sensor that continuously measures the sample temperature. Regardless of which method is used, there are a few rules to follow for optimal temperature compensation.

(1) Confirm that the instrument is programmed for the desired method of compensation, manual or automatic, prior to calibration and use.

(2) Calibrate and validate the temperature sensor on a regular basis. The precision and accuracy of the pH measurement data depends on precise temperature measurements.

The Nernst Temperature Dependence is Minimal Near 7 pH

By design, the output of the pH electrode is nearly independent of the need for Nernst temperature compensation at pH 7.00. Most pH electrodes are formulated to have an output of 0 mV at 7.00 pH. As the sample media goes alkaline the electrode output goes negative, such that -59 mV = pH 8 and -118 mV = pH 9, and so forth. As the sample media goes acidic the electrode output goes positive such that +59 mV = pH 6 and +118 mV = pH 5 and so forth. However, with the electrode output at 0 mV at 7.00 pH the Nernst temperature compensation is also at or very near 0. The need for compensation grows as the media pH gets further away from 7.00. The table below shows the electrode output at various pH's at both 25°C and 37°C. If calibration buffers are at 25°, while the pH instrument is adjusted for 37°C, then the last row of the table shows the magnitude of the resulting error that will be made during the calibration. As the table below illustrates, the error increases significantly as the media pH gets further from 7.00.

pH electrode mV output at 25°C and 37°C							
Sample pH	4	5	6	7	8	9	10
mV at 25°C	177.5	118.3	59.2	0	-59.2	-118.3	-177.5
mV at 37°C	184.5	123	61.5	0	-61.5	-123	-184.5
Possible error in pH units	0.12	0.08	0.04	0	-0.04	-0.08	-0.12

Pointers for Manual Temperature Compensation

If the process temperature is nearly constant (such as 37°±1°C for bioprocesses) *and* the sample media is between 6 and 8 pH, then manual temperature compensation is a distinct option. Most pH transmitters have this functionality and allow the operator to manually input the process temperature through a keypad. There is one caution. If the pH sensor is calibrated with buffers at room temperature, the pH transmitter must also be set to that temperature (such as 23°C) before calibration. After calibration the pH transmitter can be set back to the process temperature (such as 37°C); the transmitter will then display the correct pH for the process at that process temperature. Sometimes the standard operating procedure (SOP) will call for the calibration to be carried out with buffers in a temperature bath at 37°. This procedure precludes the need to manually change the transmitter's temperature setting before or after calibration.

Pointers for Automatic Temperature Compensation

If the process temperature fluctuates excessively over a wide range *or* the sample media is lower than 6 pH or higher than 8 pH, it may be best to use automatic temperature compensation (ATC). With this option, an on-line temperature sensor is connected to the pH transmitter. The transmitter then uses the continuous input from this temperature sensor to correct the pH reading for the Nernst temperature dependence. Again there is a caution: the pH transmitter must know the temperature of the buffers during calibration. There are two options:

(1) If the temperature sensor in the wall of the process tank or vessel is at the same temperature as the calibration buffers (room temperature), then the calibration can proceed with no further consideration of temperature.

(2) If the temperature sensor is at a different temperature than the calibration buffer, the pH transmitter must be switched back to manual mode and then set to the calibration buffer's true temperature. After the calibration is complete the transmitter must be reset to automatic temperature compensation.

What is Solution Temperature Dependence?

The pH of the media can change with a change in temperature. This is the solution temperature dependence. The pH change is real and not a measurement error. The table below displays some common buffers and solutions and their corresponding pH values at 20°C, 30°C and 37°C. One should always assume that a temperature change will result in a pH change. It is not uncommon for the media or buffer to show real pH changes of 0.01 to 0.03 pH units per °C.

Solution	20°C	30°C	37°C
Pure Water	7.08	6.92	6.81
NBS Phosphate Buffer	6.88	6.85	6.84
Tris Buffer	8.30	7.99	7.77
HEPES Buffer	7.55	7.41	7.31
Blood Plasma	7.60	7.50	7.40

This pH change is important to consider, particularly when using a grab sample (off-line pH measurement of the media) to verify the process pH inside the tank or vessel. Many SOPs call for a grab sample to be used for validation and, if necessary, for correction of on-line measurements. For a more accurate comparison of on-line and off-line pH data, both measurements should be taken at the same temperature to eliminate solution temperature errors. ■

A temperature probe is sometimes necessary as an independent temperature input. When using automatic temperature compensation, the temperature sensor should be calibrated to the transmitter prior to calibrating the pH electrode.

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