Industrial pH measurement – Temperature influences on measuring uncertainty

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Summary
Reliability is the paramount requirement for industrial pH measurement followed by accuracy and temperature and pressure resistance. Automatically retractable probes, contactless connectors, and “intelligent electrodes” are typical developments of the last years to reach these goals. This article is to remind on the effects of temperature on the properties of electrodes, buffer and measuring solutions as well as on instrumentation and their influence on the measurement accuracy. The above mentioned development activities have no or only a little improving effect on these aspects.

Keywords
pH measurement, temperature influence, measurement uncertainty

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1 Introduction
Quality, production and operating costs are often determined by adherence to a specified pH value. A query of users with a total of 150 measuring stations showed that the reliability of a pH measuring was the top priority, even ahead of precision or temperature and pressure resistance [1]. The reliability of the measuring station should ensure a reproducible result for chemical production processes. The reproducibility of the measured values is thus more important than the accuracy.

In recent years, particularly in the biotechnical and pharmaceutical fields, the demands on accuracy have increased dramatically. The terms reliability, reproducibility and precision always come below the term measuring uncertainty. The pH electrode is always seen as the weak link in a PH measuring station here [2].

The source for the greatest contributor to uncertainty is generally the reference electrode or the diaphragm with the "liquid junction" [3]. The topic of diffusion potential was covered thoroughly [4]. The temperature should be treated as an additional source of uncertainty in pH measurement.

The temperature changes the properties of numerous components in a pH measuring station and must therefore be taken into account for measuring certainty. This is
particularly important if the calibration and measuring temperatures vary. The automatic temperature compensation only takes into account the change in theoretical slope. However, not all sources of error are eliminated by the influence of temperature. Many years ago in the chemical industry, the value $U_{is}$ represented the isothermal intersection on each measurement chain and was set to compensate on the pH meter. It is not easy to determine $U_{is}$. It requires expert knowledge and not an insignificant expense. Because $U_{is}$ can change in different ways depending on the usage conditions and length of use, there is always the question about the right time to determine and compensate the $U_{is}$.

Later, electrode manufacturers were required to produce and maintain $U_{is} < 30\text{mV}$, however, it only applied to new electrodes.

It would have been useful to have this $U_{is}$ determination of an electrode after "break in" during use for routine calibration. There was a suggestion for this [5], but it was not accepted by the users because calibration with an additional buffer for increased temperatures was seen as too costly.

Heavily loaded usage conditions can induce changes in both glass electrodes and reference electrodes, which can lead to less than ideal temperature behavior. In addition, factor in the occurrence of hystereses, which are often characterized as the memory effect. After a completely run hysteresis cycle, the memory effect often degenerates. The time until complete degeneration is dependent upon the load conditions.

Particularly with automatic changing probes, there is also a risk that the measured temperature is not that of the pH glass, reference system or buffer solution, if the electrode was withdrawn from a hot process for the purpose of calibration. In this case, there is often no measuring system equilibrium and the calibration process can cause systematic errors for the subsequent measurement.

The important and systematic influences of temperature on the pH measured value should be described here and its factors calculated for select examples.

2 pH value and temperature

The pH scale is given in an aqueous media at 0 to 14 because the ion product of the water in heavily diluted solutions for the reference temperature 25 °C is exactly $10^{-14}$ $(\text{mol/l})^2$. The ion product changes with the temperature and at 100 °C is approx. $10^{-12}$ $(\text{mol/l})^2$. Thus the neutrality changes with $[H^+]=[OH^-]$ from pH = 7.0 at 25 °C to pH = 6.15 at 100 °C.
2.1 Buffer solutions

Substances dissolved in water change pH values the most such that acids, bases or salt solutions result, which in special cases can have a buffering effect and can be used as calibration solutions. The practical pH scale is defined along a series of reference buffer solutions. Their compositions and pH values dependent on the temperature are described in detail in DIN 19266 [6]. pH measuring equipment is calibrated using such buffer solutions in order to trace back the measured values to the internationally recognized reference materials.

DIN 19267 [7] describes particularly stable buffer solutions for industrial use with their temperature progressions. Their measuring uncertainty is slightly higher than the reference buffer solutions per DIN 19266. The pH values of the buffers change significantly with the temperature; alkaline buffer solutions change more in general than acidic buffer solutions. This is attributed to the temperature dependence of the ionic product from the water. Figure 1 shows the temperature dependence of the pH value of a few common buffer solutions per DIN 19267 and of the ionic product of water.
2.2 Measurement solutions

Like with buffer solutions, the pH value of measurement solutions also changes with the temperature, particularly those in the high alkaline range. For most solutions, the temperature progress of the pH value is unknown because it has not been precisely studied how that would be done with great care for buffer solutions by metrological institutes. This frequently results in great variations between operational pH measurements at elevated temperatures and the measurement of the sample in the laboratory at ambient temperature. The magnitude of this difference cannot be checked for accuracy when information about the temperature progress is missing, which leads to unsatisfactory situations.

To avoid all doubt, the measuring temperature for the result of a pH measurement must always be given along with the type of measurement chain and calibration conditions used. Only then is a reproducible pH measurement with complete documentation ensured [8].

3 Measuring chain voltage and temperature

pH measuring chains with glass electrodes give off a voltage, which is linear and proportionate to the pH value until the sodium ion error is used.

\[ E_{x1} = (pH_{x1} - pH_{01}) \times S_1. \]

\( E_{x1} \) is the voltage in mV in a solution \( x \) with the pH value \( pH_{x1} \), \( pH_{01} \) is the measuring chain zero point and \( S_1 \) is the practical measuring chain slope in the mV/pH each at temperature \( T_1 \).

To determine the pH value, the measured voltage is converted in the pH measuring transducer or the pH meter in the measured value \( pH_{x1} \) and output according to

\[ pH_{x1} = pH_{01} + E_{x1}/S_1 \]

The zero point \( pH_{01} \) is the pH value at \( T_1 \), for which the measurement chain 0mV is output. It is mostly at approx. \( pH = 7 \), the nominal zero point.

The practical slope \( S \) is the reduced theoretical slope, mostly reduced by only a few percent. It is often shown as a percentage slope. The theoretical slope has the value, multiplied by -1, of the so-called Nernst voltage \( S_N \) and is calculated as follows:

\[ S_N = 2.303 \times \log \left( \frac{RT}{nF} \right) \]

with the general gas constants \( R = 8.314472 \text{ J/} (\text{K} \times \text{mol}) \), of the absolute temperature \( T \) in K, the number \( n \) of the electron transmissions where \( n = 1 \) for the pH measurement and the Faraday constants \( F = 96,485.3415 \text{ C/mol} \). At 25 °C, \( S_N = 0.05916 \text{ V} \) or \( S_N = 59.16 \text{ mV} \).

The Nernst voltage \( S_N \) is a positive voltage. With use in the pH measuring technology, a negative practical slope \( S \) in mV/pH results during calibration as can be derived from the potential-pH diagram (Figure 2). Here, the mathematically
correct pH is handled as a unit, which is not scientifically correct.

Eq. (3) shows that the slope changes with the temperature and thus must be considered when calculating the pH value from the measured voltage.

![Figure 2](potential-pH-diagram.png)

**Figure 2**
Potential-pH diagram of measurement chain with ideal ($U_{is} = 0$ mV) and non-ideal ($U_{is} = 30$ mV) characteristic curves.

### 3.1 Calibration

The practical slope $S_1$ as well as the zero point $pH_{01}$ are determined during calibration at $T_1$, so that the "correct pH value" can be output after adjustment. When calibrating in two buffer solutions, you receive

$$S_1 = (E_1 - E'_1)/(pH_1 - pH'_1) \quad (4)$$
$$pH_{01} = pH_1 - E_1/S_1 \quad (5)$$

with the measured voltages $E_1$ and $E'_1$ in the buffer solutions with the pH values $pH_1$ and $pH'_1$.

At the calibration temperature $T_1$ only one correct pH measurement can be taken. Measurement uncertainties are caused essentially by "liquid junction potentials" (LJPs).
3.2 Temperature compensation

If the measuring and calibration temperature differ, then the slope must be calculated using the current measurement temperature according to Eq. (3). The integrated temperature measurement in the pH meter ensures that the temperature-compensated slope is taken into account according to Eq. (6).

\[ S_2 = S_1 \times \left( \frac{T_2}{T_1} \right), \]

wherein the temperatures \( T_2 \) for measuring and \( T_1 \) for calibration are used as absolute temperatures in K.

The pH value is calculated according to Eq. (2).

\[ \text{pH}_{x2} = \text{pH}_{02} + \frac{E_{x2}}{S_2} = \text{pH}_{02} + \frac{E_{x2}}{S_1 \times \frac{T_2}{T_1}}. \] (2a)

This presupposes that for \( T_2 \) the zero point \( \text{pH}_{02} = \text{pH}_{01} \) for \( T_1 \) and also the percentage slope is the same for all temperatures. This applies mostly to new measurement chains as was already indicated in the introduction.

After longer use, particularly at high temperatures and extreme pH values or in highly diluted solutions, both values change frequently.

3.3 Non-ideal behavior at zero point and slope

When the zero point varies with the temperature, a measurement error occurs, which is proportional to the difference between the calibration and measured temperature, but is constantly above the entire pH range. If this temperature drift of the zero point is known, the error can be avoided using the correction according to eq. (7):

\[ \text{pH}_{x2} = \text{pH}_{01} + (T_2 - T_1) \text{pH}_{0is} + \frac{E_{x2}}{S_2}. \] (7)

where

\[ \text{pH}_{0is} = \frac{(\text{pH}_{02} - \text{pH}_{01})}{(T_2 - T_1)} \] (8)

the change in the zero point per K. This correction of the zero point drift corresponds to the correction of the isothermal intersection by entering \( U_{is} \) in the pH meter, as was once standard. Some pH meters still allow the entry and correction of \( U_{is} \), however this function is used extremely rarely.

The potential pH diagram in fig. 2 shows different electrode characteristic curves.

For the pH value \( \text{pH}_{is} \) of the isothermal intersection, the measurement chain voltage at all temperatures is \( U_{is} \). All isotherms "revolve" around this point. In practice, this is usually not a point but rather a range. As a first approximation, however, an intersection is assumed here. To determine the isothermal intersection, the electrode curves must be recorded at two different temperatures \( T_1 \) and \( T_2 \). The following is true for the isothermal intersection:

\[ \text{pH}_{is} = \frac{(S_2 \times \text{pH}_{02} - S_1 \times \text{pH}_{01})}{(S_2 - S_1)}, \] (9)

\[ U_{is} = (\text{pH}_{is} - \text{pH}_{01}) \times S_1 = (\text{pH}_{is} - \text{pH}_{02}) \times S_2. \] (10)

If \( U_{is} \) is known, \( \text{pH}_{is} \) can be calculated using eq. (11):
\[ pH_{1s} = pH_{01} + U_{is}/S_1 = pH_{02} + U_{is}/S_2. \]

11. In practice it can be that not only the zero point, but also the percentage of the practical slope can vary with the temperature. This is not considered by any pH meter, however. Unlike with the zero point, the result of the percentage slope varying with the temperature is an error, which is zero at the isothermal intersection and becomes greater proportionately with the distance from the isothermal intersection.

If, for example, the factor of the practical slope at \( T_1 \) \( f_1 = 98\% \) and at \( T_2 \) \( f_2 = 96\% \), then, with a linear correlation, factor \( f_3 \) at \( T_3 \) is calculated as a percentage variation in slope per K.

\[ f_3 = f_1 + f_{is} \ast (T_3 - T_1) \quad (12) \]

where

\[ f_{is} = (f_2 - f_1)/(T_2 - T_1) \quad (13) \]

The usual temperature compensation for the slope according to eq. (6) must then be expanded to

\[ S_3 = S_1 \ast (T_3/T_1) \ast f_3/f_1 = S_1 \ast T_3 \ast f_3/(T_1 \ast f_1). \quad (14) \]

A correction of the percentage slope variation and the zero point brings about the complete correction of these temperature influences:

\[ pH_{x3} = pH_{01} + (T_3 - T_1) \ast pH_{ois} + E_{x3}/(S_1 \ast T_3 \ast f_3/(T_1 \ast f_1)). \]

3.4 Measurement errors due to non-ideal measurement chains

Measurement chain zero point and slope can thus exhibit deviations in practice from the ideal behavior. Below we will consider what the permissible value given above for \( U_{is} = 30\text{mV} \) means for new measurement chains and how great the measurement errors thus caused can be.

Figure 3 shows the measurement error resulting from the measurement chain curves with \( U_{is} = 30\text{mV} \) from Fig. 2 with and without corrections of the isothermal intersection. Calibration values at 25 °C always correspond in the examples given to characteristic curve A from Fig. 2 where \( pH_{01} = 7.00 \) and \( S_1 = 98\% \) or \( S_1 = -57.98 \text{mV/pH} \).

It can be seen from characteristic curve F that the conventional correction of the isothermal intersection does not correct the slope and that a measurement error of, for example, \( \Delta pH = 0.1 \) at \( pH = 2 \) and 80°C remains due to the percentage variation of the practical slope of 98% to 96%.

The measurement deviations in Gig. 3 are calculated for 80 °C measurement temperature for different measurement chain parameters. The measurement errors vary with the difference between measurement and calibration temperature. Figure 4 shows the maximum measurement error of measurement chains where \( U_{is} = 30\text{mV} \) and slope variations of 98±2% corresponding to the characteristic curves D and E at 25 °C calibration temperature as a function of the measurement temperature.
Measurement deviations with the characteristic curves from fig. 2 without correction of the isothermal intersection for the ideal characteristic curve B and characteristic curve C where $S_2 = 98\%$ and $pH_{02} = 6.92$, D where $S_2 = 96\%$ and $pH_{02} = 6.928$, E where $S_2 = 100\%$ and $pH_{02} = 6.91$, F like D, but where $U_{is}$ compensation.

Figure 3
Errors similar to those shown in fig. 4 can occur when an electrode with ideal behavior is used, but the wrong parameters are set on the pH meter for $U_{is}$. After calibration, the measurement at the calibration temperature appears to be correct, but at a different temperature, measurement errors occur as shown above.

3.5 Causes of changes in characteristic curves

The causes of non-ideal behavior can be many. If one assumes that a pH measurement chain was correctly completed and exhibits ideal values in the new state, different changes can appear after load. Extreme pH values can change the pH glass electrode, the reference electrode and the "liquid junction" very sharply. Particularly on "low-maintenance" electrodes with gel or polymer electrolytes, LJPs can occur with very different sizes and opposite signs, so that no generally applicable systematic correction is possible.
There are no known practical values for the LJPs of used electrodes. They lead to deviations in the zero point and slope during calibration and thus to systematic errors which are unacceptable in demanding pH measuring stations. However, the resulting measurement errors are not detected because they cannot be seen from the measured value display.

The literature contains no experimental data on LJPs as a factor of temperature, so that this too must be viewed as a further source of measurement uncertainty.

4 Kinetics with temperature jumps

With fast jumps in temperature, irregular adjustments of the new temperature in time and space can occur on glass and reference electrodes as well as in the solutions and on integrated temperature sensors. The slowest step caused by the temperature change determines the adjustment time of the changed pH display. Such kinetically related problems with respect to the adjustment time occur on electrodes in automatic quick-change fittings, which are drawn from a hot process medium and flushed through with cold buffer solutions, for example.

A time delay of the measured value setting also occurs when the change in temperature and/or composition of the material for analysis bring about a change in the electrode parameters. Such hysteresis effects can occur under extreme conditions both on pH glass and on reference electrodes.

5 Measuring transducers and temperature

Measuring transducers or pH meters are generally the least weak point in the system. In case of incorrect operation or specialized applications in industrial pH measurement, however, operating conditions can arise in which the measuring transducer and the connecting unit must also be considered possible sources of error.

According to the standard DIN 19265:2007 [9], the measurement error of the pH measuring transducer must be $\Delta pH < 0.02$. This error is mainly eliminated by the adjustment during calibration. However, if the ambient conditions change, the measurement error can be greater. The measurement uncertainty rises with the ambient conditions by a temperature coefficient of up to 0.002 pH/K. Therefore if the ambient temperature, and thus the temperature of the pH meter, changes by 20 K due to a SIP process, the measurement error can be up to $\Delta pH = 0.04$.

According to DIN 19265, the input resistance of the measuring transducer must be greater than $5 \times 10^{11}$ $\Omega$. This is generally altogether sufficient, as the glass electrode resistance is generally less than $10^9$ $\Omega$. Parallel to the input resistance of the measuring transducer, however, the cable with the connecting plug is located on the electrode head and the connecting terminals for the measuring
transducer, whose insulation resistance values must be correspondingly high.

At low temperatures and high humidity, water vapor can condense from the air so that the input resistance is lowered and measurement errors occur.

If the temperature is lowered by 30 K, the membrane resistance rises by a factor of 10. A glass electrode with a membrane resistance of $100\,\text{M}\Omega$ at $25\,^\circ\text{C}$ at $-5\,^\circ\text{C}$ $10^9\,\Omega$ and at $-35\,^\circ\text{C}$ $10^{10}\,\Omega$. With a membrane resistance of $10^{10}\,\Omega$ and an input resistance of $5\times10^{11}\,\Omega$, the voltage measurement error is approximately 5%.

Such conditions occur rather rarely and lead to complete failure or changes that do not compute. It is sufficient merely to note the possibility of such errors at this point.

6 Summary

As quality demands on products in the chemical and pharmaceutical industry rise, higher demands are also placed on the accuracy of pH measurement.

This article sets out to explain the influence of temperature on the uncertainty in industrial pH measuring stations. Most theoretical contexts can be found in many textbooks. The consequences of "slight deviations from the ideal" temperature behavior of electrodes for the resulting measurement error only become clear with calculations and graphs.

It must be considered that the error observations demonstrated here are purely mathematical contexts for electrodes with the deviations from ideal behavior that are given and permitted by the user. Electrode characteristic curves can be better in practice, but also worse.

The values assumed here for non-ideal behavior can be observed in practice according to greater stress, with clear differences existing for various electrode types and manufacturers.

More recent developments such as automatic quick-change fittings, non-contact signal transfer and "intelligent sensors" with stored electrode characteristic data and usage history are doubtless helpful and practical. However it must be noted [10] that there remains room for improvement.

In industrial pH measuring stations, with their large application areas with regard to pH, temperature and pressure, the sensor signal is delivered exclusively by the pH electrode. If the electrode characteristic curve is reproducible and the temperature behavior is known, reliability and accuracy in industrial pH measurement can be significantly improved. For this, the measuring transducer must have access to the complete and correct electrode characteristic data. The method of signal transmission, whether analog or digital, is unimportant.
Literature


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