Application Bulletin 188/4 e

pH measurement technique

Branch

General analytical chemistry; water, wastewater, environmental protection; pharmaceutical industry; plastics, photographic industry; food, stimulants, beverages, flavors; biochemistry, biology; metals, electroplating; detergents, surfactants, cosmetics; textiles, paper, ceramics

Keywords

pH; electrodes; branch 1; branch 2; branch 4; branch 6; branch 7; branch 8; branch 10; branch 12; branch 13

Summary

Using practical examples, this bulletin indicates how the user can achieve optimum pH measurements. As this Bulletin is intended for actual practice, the fundamentals – which can be found in numerous books and publications – are treated only briefly.

Instruments

- pH meter
- Magnetic stirrer

Electrodes

pH glass electrode, The choice depends on the sample

Reagents

- Buffer solution pH 4.00, e.g. 6.2307.200
- Buffer solution pH 7.00, e.g. 6.2307.210
- Buffer solution pH 9.00, e.g. 6.2307.220
- pHit kit care set for electrodes with liquid electrolyte, 6.2325.000
- Storage solution, 6.2323.000
- Electrolyte solution KCl 3 mol/L, 6.2308.020
- Electrolyte solution KCl sat. 6.2308.000 (for storage of gel electrodes)

Theoretical considerations

Theoretical slope

According to Nernst, the theoretical slope U_N of a pH electrode assembly is:

$$U_N = \frac{2.303 \times R \times T}{z \times F}$$

R: Ideal gas constant, 8.31441 $J \cdot K^{-1} \cdot mol^{-1}$
T: Temperature in K
z: number of electrons transferred
F: Faraday constant, 96484.56 $C \cdot mol^{-1}$

The slope is therefore temperature dependent and a change of 1 °C corresponds to 0.2 mV or a pH difference of 0.01 corresponds to 0.6 mV.

Table 1: Voltage difference for ΔpH 1 at different temperatures

Temperature / °C	Slope / mV
10	56.18
20	58.17
25	59.16
30	60.15

Explanations concerning pH calibration

In pH calibration the measured voltage in mV is plotted against the specified pH value of the buffer solution. A straight line is obtained. The intersection point of this straight line with the pH axis yields $pH_{(0)}$ (offset pH). Metrohm pH electrodes are constructed according to DIN 19263 to have their 0 mV potential reading (zero point) around pH 7. The slope of the straight line at 25 °C is theoretically 59.16 mV per pH unit. This value corresponds to a relative slope of 1 or 100%. The straight lines resulting from actual pH calibrations usually have slightly lower slopes.

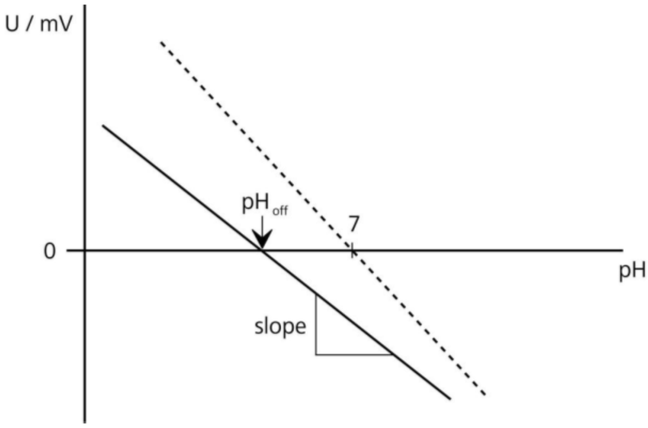

Fig. 1: Relation of ideal and real pH calibration line (dotted = ideal calibration line, straight = real calibration line)

Error sources at the diaphragm

These have different causes (diffusion potential, contamination, …) and can lead to considerable error of the measurement results. The measurement error can assume considerable proportions if measurements are performed

- with contaminated diaphragms.
- in ion-deficient solutions with unsuitable diaphragms.
- in strong acids and bases with unsuitable diaphragms.
- in colloidal solutions.
- with an unsuitable electrolyte solution

In such cases, errors more than 0.2 pH units, in extreme cases up to 1.5 pH units can appear! This is why the right choice of electrode for the application is of high importance.

Buffer solutions for calibration

Buffer solutions for calibration exist with the following specifications:

- measured value guaranteed to ± 0.02 pH (technical buffers, e.g. Metrohm buffers, traceable to NIST)
- measured value guaranteed to ± 0.005 pH (primary buffers, e.g. NIST buffers)

Precision buffers must be prepared very carefully and cannot be kept for long. The CO_2 input is more critical.

More information about measurement accuracy and buffer influence can be found in DIN 19268 (German only).

Technical buffers (like Metrohm buffers) are less critical, easier to handle and more user friendly. Definitions of technical buffers can be found in DIN 19266.

Gel layer and response behavior

pH values can only be measured accurately if the hydrated gel layer on the glass membrane of the pH electrode is present. Membrane glasses form such a gel layer in contact with an aqueous solution. In the absence of such a layer, e.g. due to dry storage of the electrode, the electrode exhibits a sluggish response and/or a shift in $pH_{(0)}$. Moreover, erroneous measurements may result.

Metrohm electrodes are supplied ready to use, i.e. the gel or hydrated layer is already present and remains intact thanks to “wet” storage. The following chemical or physical effects lead to disintegration of the gel layer:

- measurements in fluoride and HF solutions below pH 4
- long-term measurements in highly hygroscopic or completely non-aqueous solutions
- measurements in strongly alkaline solutions at elevated temperatures
- measurements with stirring in suspensions that contain abrasive substances (SiO_2, Al_2O_3, soil samples, etc.)
- cleaning of the membrane with abrasive powder or hard brushes
- dry storage of the electrodes

If the membrane is only dried out and not damaged, the electrode can usually be regenerated by storing in storage solution over night.

Heavily scratched membranes cannot be regenerated.

Long-term storage in KCl can result in ever-increasing response times. If a combined pH glass electrode is kept in the patented potassium-free storage solution 6.2323.000, then the performance of the glass membrane does not change with respect to the response time and the alkali error.

For combined electrodes filled with KCl 3 mol/L or Porolyte, the storage in storage solution is recommended.

Gel electrodes should be stored in KCl sat. Storage in less concentrated solutions will leach out the gel and reduce the life-time of the sensor.

Other combined electrodes with a different electrolyte or with a bridge electrolyte are stored in the electrolyte of the outer electrolyte compartment. Separate pH electrodes are stored in distilled water.

Electrode tests

Automatic electrode test

The Metrohm 867 pH Module or any Titrando with 900 Touch Control or ***tiamo***™ and the 781/780 pH Meters have a built-in, automatic electrode test. This tests the electrode under objective conditions and provides an overall assessment of the condition of the electrode (response time, drift behavior, zero point, slope, etc.). All pH glass electrodes from Metrohm are subjected to an equally demanding electrode test after manufacture and supplied with a certificate.

Manual electrode test

Slope and offset potential

1. Rinse the electrode with demineralized water and place in pH 7 buffer solution.
2. Measure temperature of the buffer solution and record.
3. When the measured value is constant, read off the voltage value in mV on the measuring instrument and record (offset potential).
4. Remove the electrode from the first buffer solution, rinse with demineralized water and immerse in the second buffer solution, e.g. pH 4.
5. When the measured value is constant, read off the voltage value and record.
6. Calculate the slope by dividing the measured voltage difference by the theoretical voltage difference.

Example:

Temperature	20 °C
1st buffer solution pH 7	-2 mV, (buffer table: pH value at 20°C is 7.02)
2nd buffer solution pH 4	+169 mV (buffer table: pH value at 20°C is 3.99)
measured slope	ΔU/pH = 171 mV / 3.03 = 56.44 mV
relative slope	measured slope / theoretical slope at 20°C = 56.44 mV / 58.16 mV = 0.970 (97.0%)
electrode data	offset potential -2 mV

Modern pH meters can not only recognize the buffers but also calculate the calibration data automatically.

Diaphragm

Unsatisfactory slopes can often be traced to a partially or completely clogged diaphragm or lack of electrolyte solution. The following test provides information:

1. Check that the electrode is filled with a sufficient amount of the appropriate electrolyte solution and that the plug is open for measurement. The electrolyte solution recommended by Metrohm is indicated on the label of the electrode head. The electrolyte filling level must be higher than the sample solution level.
2. Rinse the electrode well and immerse it in a pH 9 buffer solution.
3. Stir vigorously and read off or record the measured value.
4. Switch off the stirrer and again read off and record the measured value.

Good diaphragms show practically no difference between the two measured values ($\Delta U < 3$ mV). The greater the difference between the measured values is, the more extensive is the damage to the diaphragm. Treatment of the diaphragm depends on the type of damage (internal or external clogging) and is described in the electrode leaflet, which can be found on www.metrohm.com. Special electrodes may exhibit a higher stirring effect.

Glass membrane

If the diaphragm behaves normally in the above test, the unsatisfactory slope may be caused by damage to the gel layer of the glass membrane. If the membrane is only dried out and not damaged, the electrode might be regenerated by placing it into storage solution resp. the correct electrolyte solution overnight. Heavily scratched membranes cannot be regenerated.

Glass cracks, short circuits

With electrodes that have cracks in the glass membrane or short circuits in the cable, connector or inner parts, pH differences can no longer be measured. The electrode shows practically the same pH value in different buffer solutions (please test first whether the buffer has actually been changed). Electrodes with glass cracks cannot be repaired.

pHit Kit care set for electrodes

In the long term, only a preventive and regular care of the glass membrane and diaphragm guarantees reliable measurements. Cleaning by etching with toxic chemicals or mechanical treatment of the diaphragm is not only complicated and expensive, but also accelerates aging of the pH glass electrode. Metrohm developed a care set (Metrohm no 6.2325.000) for a simple and gentle cleaning of electrodes with liquid electrolyte. It contains KCl 3 mol/L, storage solution and a general purpose cleaning solution.

General Hints

The accuracy of the pH measurement depends greatly on the correct choice of the electrode combination and the calibration buffers. Naturally, the condition of the electrode and the calibration buffers are also important.

Calibration of the pH electrode at regular intervals is important because the electrode zero point and slope may change as result of the aging of the glass membrane or contamination of the diaphragm. The pH meter must be adapted to the characteristics of the electrode by calibration.

Depending on the accuracy demands

- a one-point calibration can be performed (only check)
- a two- or multi-point calibration should be performed (recommended)

A calibration with two different calibration buffers is the rule.

Calibration of electrodes

- Use commercially available, freshly prepared or freshly diluted buffer solutions.
- Bear in mind the storage life of the buffers (attack by fungi, bacteria or algae change the measured value, as does CO_2 in alkaline buffers). Already opened bottles must be considered with care and known not to be open for too long (check for recommendations on product). Metrohm buffers are also available in convenient 30 mL portions sealed safely in a sachet which guarantees the best buffer quality for each calibration.
- Discard used buffer solutions; never pour them back into the bottle!
- Note the temperature behavior of the buffer solution. The temperature compensation function of the measuring instruments only takes into account the temperature variation of the measuring chain. Choose the right buffer table in your instrument. All Metrohm pH meters have stored lists of predefined buffer pH values for several different buffer systems. For highest accuracy is it recommended to calibrate and measure at the same temperature.
- Calibrate in the region of the pH value or the temperature expected in the sample (thermostat if need be). With the “Long Life” electrodes, accurate measured values are obtained even if the calibration and measurement temperature are not the same.
- Calibrate while stirring gently.
- Give preference to two-point or more-point calibrations. With instruments equipped with automatic buffer recognition and calibration, the order of the buffers is unimportant. With older or simpler instruments with no automatic features, calibration must first be performed with pH 7 buffer. Depending on the pH of the sample, pH 4 buffer or pH 9 buffer is used as the second buffer, whichever is closer to the expected pH of the sample.

During measurement

- It is important that the electrode is always filled with fresh electrolyte up to the hole. If the level of the electrolyte is below that of the sample, the sample will enter the sensor and contaminate and possibly even destroy it.
- To ensure free flow of electrolyte (which is important to obtain optimal results), the electrolyte refilling opening of the sensor must be open during the measurement. During storage it should be closed.
- If an electrolyte different from KCl 3 mol/L must be used, a double junction (DJ)-electrode (e.g. Profitrode) must be chosen. The inner electrolyte must always remain KCl 3 mol/L. An exception is Solvotrode which is used for titration in non-aqueous environment (only potential jump taken into account and not the absolute mV-value).
- Some substances, e.g. formaldehyde, hydrogen peroxide are toxic for the reference system of the electrode. In these cases, the use of a DJ-electrode with very regular replacement of the outer electrolyte is recommended to increase life time of the sensor.

Treatment of the electrodes following measurements

- Rinse electrodes well with demineralized water. Never touch with a cloth.
- Store combined electrodes in 6.2323.000 storage solution if the electrolyte is KCl 3 mol/L. Otherwise store in reference electrolyte solution (e.g. in Idrolyte if reference electrode is filled with Idrolyte). DJ-electrodes are stored in the bridge electrolyte. Gel electrodes are stored in KCl sat.
- With samples containing fat, first clean the electrode with ethanol/ether; then with demineralized water.
- The treatment of electrodes whose diaphragms are contaminated by AgCl or Ag_2S is described in the electrode leaflet that can be found under www.metrohm.com.

- With samples containing protein, immerse the electrode in pepsin-hydrochloric acid (5% pepsin in HCl 0.1 mol/L, freshly prepared) from time to time. Then rinse well and place for a few hours in storage solution 6.2323.000.
- Preventive, the pHit kit can be used regularly to extend the life-time of the electrode.
- Never clean electrodes in an ultrasonic bath (risk of glass breakages or mechanical damage of the internal system, possibly also of the reference system).

Disinfection of pH electrodes

pH electrodes can be disinfected by immersion in 70% ethanol. As this solution does not attack the electrode, it can be disinfected for some considerable time (1...2 h). A very effective method involves exposure to ethylene oxide gas.

Please note that the diaphragm is not a sterile filter!

The use of pure (>96%) ethanol and steam sterilization is not advisable.

pH measurement in different media

For pH measurements, Metrohm offers a wide range of different electrode types that differ in part in their length, the glass composition, the shape of the glass membrane and the type of diaphragm used.

Under www.metrohm.com there are two downloadable pdf documents that offer an overview which electrode to choose for which application. Additionally, a smart phone app is available as well. For further questions, please feel free to contact your Metrohm sales representative.

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