Webinars: pH Measurement Made Easy

Even though pH measurement is one of the most often used analytical methods in chemistry and is considered rather simple to perform, several factors have to be taken into account to obtain accurate and precise measuring results. If only an approximate value is required, a test with pH test stripes might already be good enough. However, if a more accurate result is required, a potentiometric measurement is a must. Depending on the requirements on the measurement precision, a lot of different pH meters are available on the market. The same is true for pH electrodes. And yet it is difficult for the user to find the right electrode for his application. The right diaphragm and/or glass membrane type have to be used for its field of application, otherwise low reproducibility or even incorrect results are likely.

The electrode has to be cleaned and maintained regularly to guarantee a long lifetime. But also, calibration and sample preparation can have a crucial influence on accuracy and precision of pH measurements.

Sensitive pH Glass Membrane

As soon as the glass membrane of a pH electrode is dipped into an aqueous medium, it will build up a hydration layer. If the concentration of protons in the solution is changing, there will be an ion exchange in this hydration layer and therefore a change in potential on the glass membrane. The response time for a stable potential is therefore also dependent on the thickness of the hydration layer. This layer will continuously grow when in contact with aqueous solution, resulting in longer response times. Damage to the hydration layer by inappropriate handling of the electrode increases its growth. The most frequent causes are incorrect storage, e.g. drying out of the glass membrane, wiping off the glass membrane and therefore building up electrostatic charge, or if the electrode is used as a stirrer hitting the wall of the measuring beaker. Sometimes it is possible to regenerate the hydration layer, however, often it is irreversibly destroyed and the electrode has to be replaced. With the selection of an appropriate glass membrane for the application as well as an optimal treatment, maintenance and storage of the glass membrane this growth can be minimized.

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One of the most often used reference electrolytes in pH measurements is potassium chloride. Therefore, pH electrodes are often stored in c(KCl) = 3 mol L^{-1} to omit a conditioning of the diaphragm and still have the electrode ready for use. The storage in KCl, however, will harm the glass membrane over time; alkali ions will penetrate into the hydration layer causing it to swell and therefore, increase the response time. That is why Metrohm has developed a special storage solution which is free of alkali ions. By using this storage solution for the storage of the electrode, the response time remains unchanged and the diaphragm does not need to be pre-conditioned.

Another effect which is caused by alkali ions is the so called alkali error. Thereby, a lower pH value is measured than theoretically calculated. Alkali ions, which may be present in the sample behave more or less like protons, penetrating into the hydration layer and changing the potential at the glass membrane. They suggest a higher proton concentration than actually present and therefore a lower pH value is measured. This effect can be minimized by the right choice of the glass membrane type.

To Stir or Not to Stir?

In the past it was said that calibration and measurement should be performed under the same stirring conditions. If the solution was stirred, it would have to be with the same speed in a beaker with the same geometry, or it should not be stirred at all. With a new generation of diaphragm type, the so called ground-joint diaphragm, the influence of stirring on the pH measurement is much smaller. This diaphragm enables a continuous, controlled outflow of the electrolyte and

Webinar I: Basics of Potentiometric pH Measurements

30.10.2018

In this first webinar, the focus lies on the basics of pH measurement. It gives further insights on which parameters have a direct influence on pH measurement and how to control them as well as electrode selection, maintenance and storage.

Key learning objectives:
- Understand the basics of pH measurement and influencing factors
- Understand why a proper pH calibration is important for correct pH measurement
- Know how to select the best-suited electrode for the application and how to maintain it

Who should attend?
Everybody who is interested in pH measurement and would like to learn more about:
- pH measurement basics
- Maintenance and storage of pH electrodes

Webinar II: pH Measurements in Difficult Matrices and Troubleshooting

06.11.2018

The second webinar targets troubleshooting of common errors, and tips and tricks for a correct pH measurement in matrices other than simple aqueous solutions.

Key learning objectives:
- Know how sample preparation can influence results
- How to reduce errors
- Learn how different ionic strengths as well as high acid or base concentrations can affect the electrode
- How to determine pH value in media other than water

Who should attend?
Everybody who already knows the basics of pH measurement and would like to get more information on:
- Troubleshooting of most common errors
- The effect of low or high ion concentrations in the sample
- pH measurement in difficult matrices, such as non-aqueous solvents

therefore a steady signal with only small streaming dependency. That means, streaming potentials, which can occur when solutions are stirred, remain negligible. Furthermore, the risk of a diaphragm blockage is quite small due to its large surface.

pH and Temperature Belong Together

If the temperature of the sample in which pH is measured deviates from the calibration temperature of the electrode, an exact determination of the temperature of the sample and the calibration is essential.

Temperature affects pH measurements in two different ways:

The slope of the electrode depends on the temperature according to the Nernst equation. This temperature behavior can be mathematically compensated. Most modern pH meter perform this compensation automatically. However, this requires a connected temperature sensor.

Furthermore, temperature influences the pH value of the sample itself. This temperature related change of the pH value cannot be compensated. Therefore, the pH of a particular sample should always be measured at a defined temperature to obtain comparable pH values. Most pH electrodes do have a temperature sensor integrated, otherwise you might also work with an additionally connected temperature sensor or the temperature value might be entered manually into the pH meter.

Calibration as Basis

Not only the selection of the electrode may have a decisive effect on the measurement. It is also important that the electrode is correctly calibrated on a regular basis. Depending on the requested accuracy of the pH measurement the electrode should be calibrated at least daily or even more often. Additionally, a calibration is necessary after maintenance of the electrode or if the electrode was stored for a longer period of time.

The electrode zero potential and the slope are determined by a calibration. It is recommended to perform at least a 2-point calibration. The larger the range that is calibrated, the more buffers should be measured. Furthermore, the pH value of the measured sample should lie within the calibration range. A calibration always enables a check of the measuring electrode. If the slope and/or zero potential are outside the rated range (e.g. 95-103%, or pH 6.8-7.2, respectively), cleaning or even a replacement of the electrode is necessary.

Buffer solutions that are used for calibration are very accurate solutions with a guaranteed value and precision. To ensure that this value remains unchanged, any contamination of the solution has to be avoided, the uptake of CO_2 minimized, and the buffer must not be used after the expiry date as specified by the manufacturer.

Possible Influences of the Sample

Additionally, sample preparation and sample measurement should be kept in mind. Stability of the sample, i.e. the changing of the sample over time or its tendency for taking up CO_2 (which leads to a reduction of the pH value), can have a huge influence on precision and accuracy of the results. Therefore, samples should be analyzed as quickly as possible after sampling. The homogeneity of the sample as well as its subsamples throughout the measurement has to be guaranteed, e.g. through stirring.

In short: Many factors that influence pH measurements can in fact be controlled by the choice of a suitable electrode (ideally with an integrated temperature sensor) for the particular sample at hand. However, the human factor must never be disregarded. Different habits of different users regarding the handling of hardware and samples can play a major role and may have a big impact on the results of pH measurements. Despite that, only minor attention is usually paid to this fact and its influences are even often neglected.

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