

Simple-to-use pH electrodes with platinum diaphragms for reliable, stable measurement results

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The determination of pH value is one of the most important and most frequently used electrochemical measuring procedures. The pH value of aqueous media is often a crucial figure for the course of chemical and biological processes. It is an important test criterion for production, quality control, and in environmental analysis.

The determination of pH value can be carried out very economically and very quickly (within the space of a few seconds). A single, suitably calibrated sensor can cover the whole pH range over 14 decades. The selection of sensors that are currently available on the market cover the full range of application areas. Thus, selection of the right sensor is critical to the quality of the measurement result obtained for each individual application. The benefits that can be achieved through the selection and use of the correct pH sensor can be demonstrated by means of a practical example.

Fruit processing

In a medium-sized fruit-processing company, hundreds of tons of different types of fruit preparations are produced annually for the food industry. In this situation, a reliable quality assurance system is essential. The fruit preparations are produced in batches. An important test criterion is the maintenance of specified pH values for the preparations, which are measured in the batches on-site, and then rechecked in the quality assurance laboratory.

pH sensor

For measurements in the laboratory, the requirement profile of the suitable pH sensor is determined mainly by the properties of the samples to be measured. The common pH sensor used in the laboratory consists of two electrodes that are housed together in a rod-shaped shaft. Immersion of the sensor into a solution results in the creation of a potential (in the mV range) at the electrode produced with pH-sensitive glass. This potential is dependent on the pH value of the solution. Since this single potential is not measurable, a second electrode must be used as a reference. This so-called reference electrode should produce an equal and constant potential as far as possible in all measured solutions. Therefore, the pH measurement is a measurement of the voltage in the mV range. Undesirable changes in potential at the reference electrode would cause measurement errors, thus giving rise to the question of how the resulting uncertainty of the measurement can be reduced to a minimum.

Reference electrode: An important part of the pH measuring chain

In order to measure the voltage differential between the glass electrode and reference electrode, an electrolytically conductive connection is required between the reference electrode and the solution to be measured. A defined aperture in the electrode shaft, the so-called diaphragm, creates this connection.

By means of the diaphragm, the reference electrode, usually a potassium chloride solution, is connected electrolytically to the measuring medium. The reliability of this contact between the reference system of the electrode and the measurement solution is a decisive criterion for the quality of the measurement result. pH measurement is impossible without this connecting aperture. On the other hand, too great a fluid exchange between the measuring medium and the reference electrolyte must also be avoided.

One common junction is the ceramic diaphragm. Although the ceramic pin is robust, it has an uneven pore cross-section, which leads to poorly defined flow ratios. This can give rise to areas where measurement solutions diffuse into the reference system, and contamination of the electrolyte then leads to false measurements or damage to the electrodes. This porous ceramic compound is also susceptible to contamination with dirt, and is difficult to clean. Solid particles in the measuring solution can lodge in the pores, thus blocking the connection. Therefore, the ceramic diaphragm is more suitable for applications in clear, aqueous solutions with medium salt content.

Another well-known alternative is the ground dia-

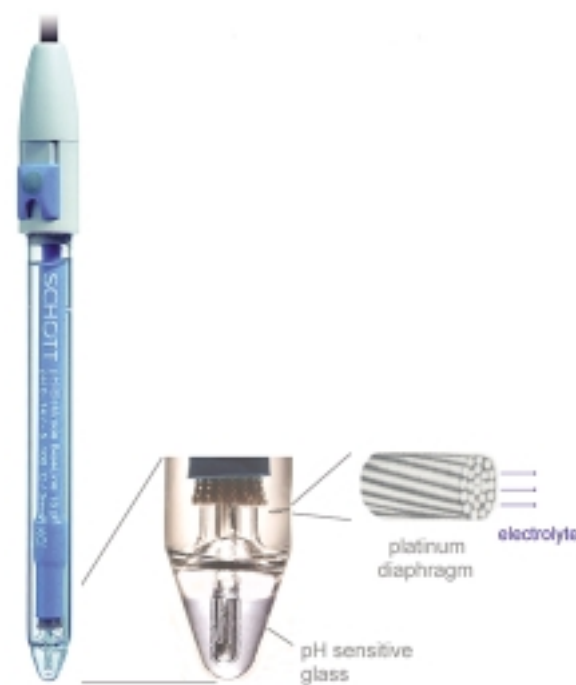


Figure 1 pH combination electrode.

phragm. This is used for liquids with a high content of solid particles, and is easy to clean. The use of this type of diaphragm is somewhat more complicated and the delicate and more complex design entails a higher purchase cost.

Advantages of the platinum diaphragm

In most cases, reliable results can be obtained with electrodes using a so-called platinum diaphragm. This diaphragm consists of several platinum wires twisted together, which are smelted into the glass shaft of the electrode (Figure 1). The platinum diaphragm offers not only excellent measuring properties, but also has other advantages. The connection between the glass and the platinum offers high temperature stability due to the similar expansion coefficients. The platinum diaphragm is also chemically inert, and will work even in hot, caustic solutions where a ceramic diaphragm will often fail.

For measurements in the laboratory, the requirement profile of the suitable pH sensor is determined mainly by the properties of the samples to be measured.

The significant advantages of the platinum diaphragm over the ceramic diaphragm become clear when one compares their cross-sections. Between the individual platinum wires are smooth-walled cavities. These channels connect the reference electrode chamber with the measuring medium. The electrolyte flows through these clearly defined cavities at a constant speed. Thus, the diaphragm continually rinses itself clean at the contact point with the measuring solution. The result of these properties is an impressive measuring capability in almost all situations: very short setting times for measured values; high measurement accuracy due to the constant, low-diffusion potential; and insensitivity to stirring and incident flow effects (Figure 2).

The platinum diaphragm is not only very well suited for standard applications, but also demonstrates its advantages in particularly demanding measurements such as precision measurements, titrations, low-ion solutions, and aggressive media.

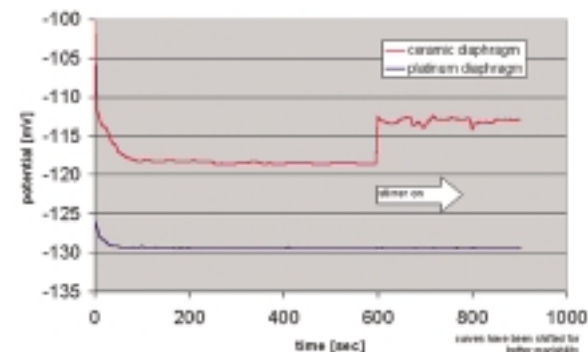


Figure 2 Response time and stirrer influence at the reference electrode.

pH measurement of fruit preparations

Typically, fruit preparations are rich in components such as fruit fibers and fruit sugars, and often contain oily components such as vanilla extracts. These viscous, fibrous media are usually low in ions, and hence represent a special challenge for pH measurement.

When fibers and other materials block the diaphragm, there is an increased maintenance/cleaning requirement; an additional effect may be the curtailed working life of the electrode. The low-ion test matrix also makes it more difficult to set the electrode quickly to a stable measuring value. Since the pH value in this case is a decisive quality criterion, this increased lack of reliability of the measurement is not acceptable.

For the measurement of these samples, a pH combination electrode from Schott Glas (Mainz, Germany) was selected using A-glass and a platinum diaphragm. Experience has shown that, as a pH-sensitive glass, A-glass quickly produces a stable potential in low-ion media. The platinum diaphragm, with its reliable and constant electrolyte flow, should also ensure a good connection in the low-ion media and keep the diaphragm clear.

The setting time of this electrode type was compared with other electrodes using other pH glass and different diaphragms. The working life of the various electrodes used was also calculated and compared in practice in the fruit company's quality laboratory.

Summary

pH sensors with platinum diaphragms at the reference electrode offer significant advantages without extra cost. The user obtains faster and more reproducible measuring results. In addition to the greater ease of use, the maintenance requirement is lower and, at practically identical purchase costs, the shelf life is generally much higher. Due to the flexibility of sensors with platinum diaphragms, the user can often use the same sensor for very different applications while still maintaining the high quality of the measured values.

As described in the application involving the fruit preparation company, not only has the working life of the electrodes increased since the use of electrodes with platinum diaphragms, but also widely varying preparations from the manufacturer's wide product range have been tested using the same electrode. This not only simplified the work in the quality laboratory, but also led to more reliable measurement results and reduction of costs.

Additional reading

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