New pH Measuring Probes for Laboratory and Process Applications

Determination of the pH value is one of the most important and frequently used measuring procedures in the laboratory and in processes. The pH value of aqueous media is frequently the decisive value for chemical and biological processes. Determination of the pH value can be accomplished economically and quickly. One single sensor is capable of covering the entire pH scale with 14 decades.

Manufacturers offer users a wide variety of sensors. The A 162 new combined pH electrode from Schott Instruments simplifies handling in the laboratory through the use of an integrated temperature sensor and quickly supplies reproducible and precise readings. It is suitable for highly differing areas of application including pH titration.

Continuous pH measurements in laboratory reactors and in processes are frequently subject to highly varying application conditions and require pH sensors which are designed accordingly. It is frequently necessary for the sensors to also withstand high pressure in the installed state. The newly developed, low-maintenance SteamLine Series of pH electrodes, also with integrated temperature sensor, is fast-acting and ensures long-term stability even under the most severe conditions.

The pH Measuring Probe

The most common pH measuring probe still consists of the two function elements pH glass electrode and reference electrode, which are usually located together in a rod-shaped shaft as a so-called combination electrode.

When the electrode with pH-sensitive glass is immersed in the solution, an electrical potential in the mV range is generated, where the magnitude is dependent on the pH value of the solution. Since this single potential cannot be measured alone, a second electrode is used as a reference. The so-named reference electrode should provide the same, constant potential in all measuring solutions. pH measurement is therefore a voltage measurement in the mV range [1].

pH Glass Electrode as Measuring Electrode

Electrode manufacturers offer a selection of different types of glass for the pH glass electrode for different applications in the laboratory and in process applications. Unfortunately, there is no universal pH glass which provides optimum results under all conditions. For measurements in low-ion media and/or at low temperatures, pH glass with the lowest possible membrane resistance is best.
Such glass, however, has a measurable error in the highly alkaline range and is not recommended for use at extremely high temperatures. The pH glass electrodes are optimized for ranges, with a magnitude depending on the pH value of the solution. Since this single potential cannot be measured at high temperatures and/or high pH values, are not well suitable for measurements in low-ion media or at low temperatures.

Extremely fast reacting pH glass is required especially for titration. Qualified manufacturers develop different types of pH glass to cover the widest possible bandwidth of applications using specialized calculation software and comprehensive testing.

Reference Electrode as Stable Reference

The most common pH measuring probe still consists of the two function elements pH glass electrode and reference electrode, which are usually located together in a rod-shaped shaft as a combined electrode.

(1) pH measuring probes A 162 and SL 82 „Location of temperature sensor and new geometry together with diaphragm ensure high measuring quality“

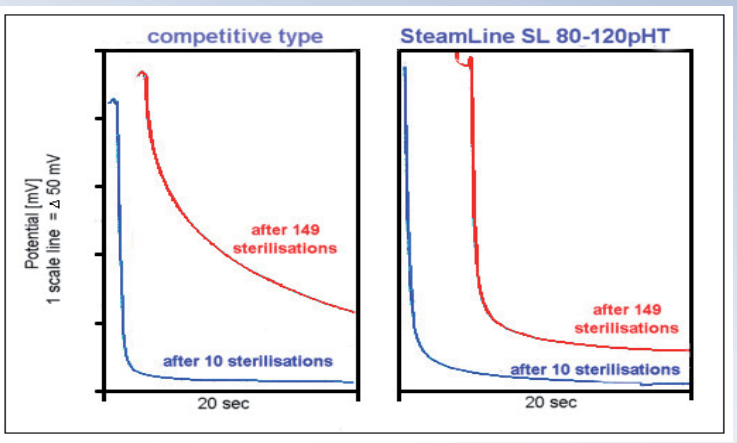
SCHOTT Instruments

An electrolytically conductive connection between the reference electrode and solution to be measured is required for measurement of the change in the voltage between the glass and reference electrode. This connection is created by a defined opening in the electrode shaft, the so-called diaphragm. This diaphragm is available in different versions for highly varying applications.

The reliability of this contact between the reference system of the electrode and the solution to be measured is a decisive criterion for the quality of the readings. Without this connecting opening, pH measurement is not possible. On the other hand, it is necessary to avoid excessively high exchange of fluid between the measuring media and reference electrolyte.

A commonly used version is the ceramic diaphragm. This ceramic pin is robust, however, has a non-uniform pore cross-section. Therefore, it is possible for areas to exist in which the measuring material diffuses into the reference system leading to errors. The ceramic diaphragm is thus more suitable in the laboratory for applications in clear aqueous solutions with medium salt contents. In process applications, the ceramic diaphragm is also used for reference electrodes subject to pressure and also preferred for low-maintenance versions capable of sterilization.

Another familiar alternative is the ground joint diaphragm. It can be used for liquids with high quantities of solids and is easy to clean. Handling of this diaphragm is more complicated and the filigrane shape results in higher procurement costs.



(2) Adjustement characterictis for SteamLine in comparison to conventional version.

In most cases, electrodes with platinum diaphragms operate with extreme reliability. The platinum diaphragm consists of a number of platinum wires entwined with one another. The reasons for the reliability of the platinum diaphragm are based on the layout [2,3]. Smooth hollow chambers are located between the individual platinum wires. These channels connect the reference electrode chamber with the medium to be measured. The electrolyte flows at uniform speed through these clearly defined hollow chambers. In this manner, the diaphragm rinses itself at the contact point with the solution to be measured. The results of these characteristics are impressive capabilities in nearly all situations:

- Extremely short adjustment time for readings
- High measuring accuracy
- Insensitive to effects of stirring and flow

In addition to being excellently suited for standard applications, platinum diaphragms are therefore particularly advantageous for highly demanding applications such: Precision measurement, titration, low-ion and aggressive media. With their reliable and uniform electrolyte flow, they also provide a good conductive connection between the reference electrode and medium to be measured even in specimens which previously described difficulties.

(tab. 1) „Selection of membrane glass“

pH Glass Type	Character
A	for general applications, wide application area, short response time also for the drinking, waste and sewage water
S	tolerates wide temperature range and prompt temperature changes; also for hot, alkaline solutions very constant measuring values with fast response time, for sterilizing applications
H	wide pH and temperature range, high accuracy also for intense alkaline areas

(tab. 2) „Selection of common diaphragms“

Diaphragm Type	Application Characters	
	advantages	disadvantes
Ceramic	general applications robust	without overpressure tends to contamination and blockage
Platinum	universal, fast, constant, non-sensitive to contamination, stirring and flow	no mechanical cleaning
Ground joint	non-sensitive to contamination	filigree handling
Fibre	easy handling	cleaning almost not possible

pH Measurement in the Laboratory

In laboratories, highly differing types of specimens are usually analyzed. It is desirable to be able to determine the pH value with one single type of electrode wherever possible independent of the specimen matrix or measuring instrument.

The A 162 pH combination electrode was developed for this purpose. It consists of the nearly universal Type A pH glass and is equipped with the proven platinum diaphragm. The A 162 contains a temperature sensor for automatic temperature compensation and indication of the measuring temperature, because the pH value is meaningful only when the temperature is specified. The electrode has a SMEK plug head to fit practically all pH measuring instruments in the laboratory. The electrode can easily be plugged into pH meters from different manufacturers using a suitable connection cable of desired length.

pH Measurement in Laboratory Reactors and Fermenters

Laboratory reactors are used for many types of applications. The wide spectrum ranges from mixing cosmetic products to chemical reactions under all imaginable conditions. For pH electrodes, applications in the cosmetic field usually mean higher viscosity and extremely high conductivity values. For applications in the chemical sector, the electrodes must be capable of withstanding an entire spectrum of measuring media in a wide variations in temperature over the entire pH range.

Fermenters serve for controlled growth of microorganisms and mammal cells. Maintenance of the specified pH value is important because the pH has an inhibiting effect on the growth of the cells when certain limits are exceeded. Sterile operation is absolutely necessary.

Usually, the CIP and SIP capability of the electrodes used for such applications is important. CIP stands for „Clean In Place“ and can mean treatment for one hour in a hot soda solution at 95 °C. SIP stands for „Sterilize In Place“ and describes the sterilization method used particularly in the pharmaceutical industry for boilers and pipelines at approx. 135 °C for at least one half hour.

For such applications, pH sensors are required with a pH glass withstanding such stress and where the diaphragms do not fail, particularly from contamination. The new low maintenance SteamLine electrode series was developed specially for such applications.

The S glass which has proven itself over an extremely long period, is used for the pH glass electrode in the SteamLine series. It ensures rapid and stable adjustment characteristics.

The low-maintenance reference electrode is pressurized and filled with a new developed gel electrolyte. The electrolyte is optimized in terms of its viscosity so that it flows out of the diaphragm so slowly that its pores are kept free. In the pharmaceutical industry, the number of sterilization operations which an electrode can withstand is an important quality criterion. Numerous endurance tests and practical tests prove that these excellent measuring characteristics are ensured over a long period.

Conclusion

Selection of suitable sensors is important for laboratory measurements as well as continuous measurements in reactors and fermenters.

Sensors with platinum diaphragms can be used almost universally for highly differing applications in the laboratory. These economical sensors are simplier to use and the service life is usually significantly longer. They can be connected to all common measuring instruments using cables of different lengths.

Low-maintenance electrodes with pressurized reference electrodes are suitable for continuous measurement applications. With simplified installation, the pressure in the reference electrode provides virtually the same positive measuring characteristics as refillable reference systems in terms of reliability and adjustment time.

Literature

[1] Firmenschrift Schott-Geräte „Wissenswertes über die pH-Messung“, 1993

[2] Günter Tauber, „Das Platin-Diaphragma“, Chmie-Ingenieur-Technik plus, 1999

[3] Frank Honold, „Das Platin-Diaphragma in der pH-Messtechnik“, LaborPraxis, Dezember 1999

[4] Wolfgang Knappek, Jan Munk, „Qualität - auch eine Frage des pH-Wertes“ Labor-Praxis, November 2000

[5] Günter Tauber, „pH-Glaselektroden für den Einsatz in heißen alkalischen Medien“, Regelungstechnische Praxis 26 (1984), Heft 10

Author

Dipl.-Chem. Wolfgang Knappek
Sales Manager Electrodes and Meters

SCHOTT Instruments
Hattenbergstr. 10
55122 Mainz
Germany

Phone +49 (0)6131 665111
Fax +49 (0)6131 665001

SCHOTT Instruments