

Critical Factors Affecting pH Measurement

Dr. Jan Bösche, Dr. Jürgen Schleicher

The pH is one of the most commonly measured physical chemical measurands: wherever water is used or treated, the pH value is measured. Applications include swimming pools, waterworks, sewage treatment plants, and the production of beverages/food/pharmaceuticals.

The reasons for this vary. On the one hand, regulatory requirements (swimming pool water regulations or DIN 19643 for water treatment) stipulate continuous pH measurement and documentation of the measuring point. On the other hand, pH measurement serves as a quality-determining parameter in the chemical and pharmaceutical industries. Staying within narrow limits for the pH value guarantees the desired product quality, increases the yield of the desired final product, and reduces the amount of undesired byproducts. At the same time, however, several aspects require attention during the pH measurement, namely, selection of the sensor as well as its regular calibration and maintenance. This article provides important practical information regarding selection as well as use of pH sensors and discusses a variety of critical factors.

To understand pH measurement and the critical factors that affect it, a look at the principle underlying the measurement is helpful. The pH measurement is a voltage measurement between two electrodes. The two individual electrodes – namely, the reference electrode and the pH electrode – are combined into a single unit in a so-called combination electrode. Each of the two individual electrodes generates a potential which on its own cannot be measured. An electrical voltage that can be detected by a measuring device is created only when the two potentials are measured against one another. To measure this voltage, a pH meter is needed (i.e. a "voltmeter" with an especially high input impedance). The input impedance of the pH meter must be several orders of magnitude greater than the internal resistance of the pH electrode to prevent "voltage divider effects" during the measurement.

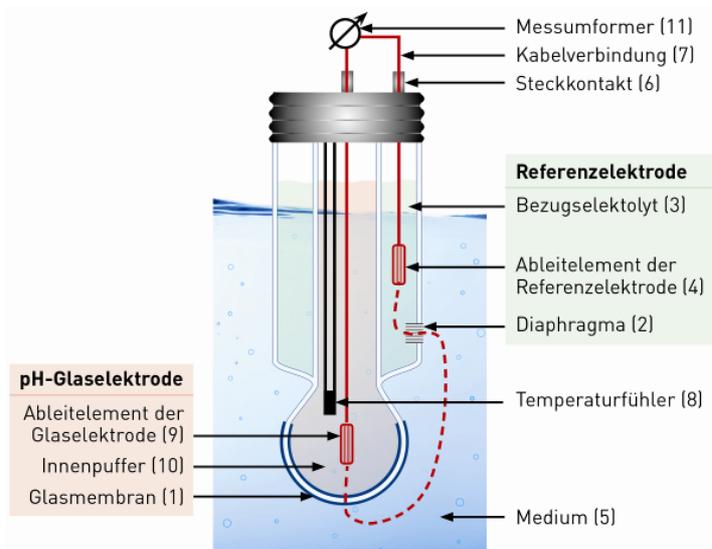


Figure 1: Components of the pH measurement and the pH electrode

Figure 1 shows the components of the pH measurement and the pH electrode in detail. The red line represents the electrical connection between the two individual electrodes. The solid portion of the electrical connection in the upper area above the electrode head between the combination electrode and pH meter is provided by the pH connecting cable and contacts. The dashed portion of the red line marks an invisible electrical connection without which a pH measurement is not possible. The "dashed connection" from the internal contact of the pH electrode to the contact element of the reference electrode is created by the internal buffer (internal reference solution), the glass membrane, the measurement medium, the diaphragm, and the reference electrolyte. Frequently, problems arise during pH measurement from an increase of the resistance or even complete interruption of electrical contact at one spot in this measurement circuit. The areas where measurement problems might occur can be seen clearly in Figure 1. Ways to solve these problems are discussed hereinafter (see Table 1). The corresponding numbers designate the location in Figure 1 at which the particular measurement problems occur:

Process medium	Effect on component	Countermeasure
Pollutants, deposits		
<ul style="list-style-type: none"> • Lime, poorly soluble deposits • Oils, greases • Biofilms 	Coating on glass membrane (1), blockage of the diaphragm (2)	Maintenance, special electrodes, retractable holder with cleaning provision
Chemical attack		
<ul style="list-style-type: none"> • Hydrofluoric acid, alkaline solutions, complexing agents • Sparingly soluble compounds of Ag⁺ • Electrode poisons: metal ions, cyanides, ... 	Corrosion of the glass membrane (1) Reactions on the diaphragm (2) Diffusion in the reference electrode (3), (4)	Selection of special electrodes
Special media		

• Water with a low conductivity	High resistance between the pH glass electrode (1), (10), (9) and the reference electrode (2), (3), (4)	Selection of special electrodes
• Highly acidic media	Acid error at the glass membrane (1)	
• Highly alkaline media	Alkaline error at the glass membrane (1), glass corrosion	
Environmental conditions	Effect on component	Countermeasure
Physical		
• Extreme temp. / temp. change	Material stress, especially at joints, reduces the service life	Selection of special electrodes
• Extreme pressures / pressure change		
• Drying out	Glass membrane (1)	Soaking of the glass membrane, special fitting
• Inflow	Signal influence on diaphragm (2)	Select electrode with 3 diaphragms
Electrical		
• Fields	Electrical faults (7)	Check of installation
• Potentials	Falsification of measured signal (7)	Grounding, shielding
• Current flow, polarization	Damage to the reference electrode (3), (4)	Check of installation
• Moisture	Short-circuit between the contacts (6) and cable connection (7) results in loss of slope, possibly damage to the reference electrode	Replace cable and connector
Mechanical		
• Particles	Abrasive action on the glass membrane (1) reduces service life	Special design of glass membrane (flat membrane)
• Vibrations, shocks	Material stress reduces service life	Select different installation location

Table 1: Critical factors

(1) Glass membrane: Coatings on the pH-sensitive membrane glass can disrupt the pH measurement significantly or even make measurement impossible. If pollutants, solids, biofilms, poorly soluble deposits, lime, or even oils collect there, the measuring surface is no longer exposed to the measurement medium. This increases the electrical resistance at this location and incorrect measurements can result. The glass membrane should be cleaned regularly during the periodic calibration that is required anyway.

Any coating that may be present should be removed "chemically" instead of "mechanically" whenever possible. A coarse "mechanical cleaning" with the aid of scouring powder or hard brushes damages the surface of the glass membrane, reducing its slope. Instead, users should attempt to loosen lime or metal hydroxides, for instance, with the aid of dilute acids (by applying one-percent hydrochloric acid for a few minutes). Biofilms, greases, and oils can

be removed with tenside-containing cleaning solutions. Proteins can be removed with a pepsin/hydrochloric acid solution. Silver sulfide deposits in the diaphragm can be dissolved with a thiourea solution. When problems occur at short intervals at the measuring point as the result of external pollutants on the pH electrode, use of a retractable holder with an automatic cleaning provision should be considered.

(2) Diaphragms: The diaphragm of the pH electrode, which can consist of porous ceramic, a porous Teflon ring, a small hole, or a gap, needs to fulfill "contradictory functions". On the one hand, the diaphragm provides electrolytic contact between the reference electrolyte and the measurement through outflow of electrolyte (usually potassium chloride) and on the other hand, the diaphragm must prevent overly fast leaching of the electrolyte. If parts of the diaphragm are blocked by sparingly soluble compounds, the pH measurement is low due to increased resistance and even the zero point of the pH electrode can be shifted. A poorly soluble deposit forms in the diaphragm when anions from the measurement medium encounter silver ions from the reference electrolyte and form a sparingly soluble salt. This is the case, for instance, for sulfides, bromides, and iodides. This problem can be avoided by using a high-quality electrode with a cartridge reference system as the contact element (4). In this case, the reference electrolyte (3) is silver-ion free.

Lower-cost electrodes with "wire contact elements" work with a reference electrolyte that is saturated with silver chloride. In especially problematic situations that cannot be handled in any other way, it is also possible to use a reference electrode that is supplied continuously with liquid potassium chloride solution. The continuous outflow of potassium chloride solution through the porous diaphragm prevents components of the measurement medium from reaching the diaphragm. In such a system, an adequate amount of potassium chloride solution must always be present and the pressure on the reference electrolyte must be somewhat higher (a few tenths of a bar) than the pressure of the medium.

Continuous measurements almost always take place in flowing water. Every measuring change responds more or less strongly to the motion of the water. The variations in measured value caused by the approaching flow and agitation effects can be up to 40 mV (H. Galster, pH-Messung, Grundlagen, Anwendungen, Methoden, Geräte; VCH Weinheim, 1990, p. 92). While new measuring chains are relatively impervious to changes in the approaching flow, the effect can cause considerable variations in measured value for depleted measuring chains. The orientation of the diaphragm with respect to the flow direction is a major factor in this regard. For instance, electrodes with only one ceramic diaphragm exhibit greater flow sensitivity than an electrode with three diaphragms, a Teflon ring, or split diaphragm. A regular check of the sensitivity to the approaching flow provides information about the state of the

measuring chain. If the sensitivity to the approaching flow is too great, replacing the measuring chain becomes necessary.

(3) Reference electrolyte and contact element of the reference electrode

(4): In unfavorable situations, the measurement medium can contain electrode poisons that can reach the contact element via the diaphragm and the reference electrolyte. There, they destroy the silver/silver-chloride reference electrode, as a result of which its potential shifts. In low-maintenance electrodes with a gel or solid reference electrolyte, access to the reference electrode can be slowed through various measures: for instance, a so-called two-chamber electrode (Fig. 2) where the reference electrode chamber contains an additional barrier can be used. Such problems can be prevented entirely if the solution with a continuous supply of liquid potassium chloride solution as already mentioned above is used.



Figure 2: Two-chamber electrode

(5) Measurement medium: Special problems with pH measurement can arise in certain media. In water with a low conductivity (for example, deionized, distilled, fully demineralized water), the electrical resistance of the connection through the measurement medium is especially high. The consequence is a slow, drift and trouble prone pH measurement. Special electrodes that have a supply of solid potassium chloride in the reference electrolyte and release an especially large amount of potassium chloride (KCl) through three diaphragms provide a solution to this problem.

If the conductivity of the water is below 50 $\mu\text{S}/\text{cm}$, it is better to resort to the above-mentioned solution with a continuous supply of liquid potassium chloride solution. Moreover, the amount of KCl released close to the diaphragm can be controlled by means of the pressure on the KCl reservoir. The "KCl cloud" formed around the diaphragm and membrane glass increases the conductivity of the measurement medium locally, making problem-free pH measurement possible at all. With such water quality, the measurement should be made in a

flow-fitting shielded from the external surroundings in any case, since the pH value of the water can otherwise change due to absorption of carbon dioxide from the air.

If the resulting increase in salinity of the water by the KCl from the reference electrolyte is disruptive, the measured water must be discarded. In the case of extreme pH values, deviations can arise as the result of the so-called "alkaline error" or "acid error". Today's membrane glass is optimized with regard to the acid error in such a way so that deviations are negligibly small. The alkaline error becomes noticeable when large amounts of lithium or sodium ions are contained in the measurement medium at high pH values. At high pH values, the alkaline error leads to values that are too low. For such applications, pH electrodes with a special membrane glass that causes extremely little deviation are available.

Media that contain fluoride ions and have a pH value below 4 can attack the membrane glass chemically and ultimately dissolve it. Membrane glasses that are more resistant to hydrofluoric acid have been developed for measuring in media containing hydrofluoric acid, but these glasses will also be attacked at some point. If a measurement medium has overly high concentrations of fluoride ions (> 1 g/l) and a pH value below 4, an antimony electrode and a KCl reservoir with a separate reference electrode represent the better choice.

If the electrodes are installed in pipes or closed reactors, the effect of pressure on the individual component also needs to be taken into consideration. It has an effect on both the reference electrode and the pH value. The effect on the reference system can be taken into account by selecting an appropriate pressure resistant measuring chain. Pressure-resistant or low-maintenance electrodes are those with a solid reference electrolyte. The advantage here is that no measurement medium can reach the reference electrode chamber through the diaphragm, since the "solid" reference electrolyte presents a physical resistance to the incoming measurement medium.

Alternatively, when making measurements under pressure, it is of course also possible to use an electrode with a liquid reference electrolyte under somewhat higher pressure than that applied to the measurement medium. This ensures that reference electrolyte is always forced through the diaphragm. It goes without saying that depletion of the reference electrolyte fluid in the reservoir must be topped up regularly. This maintenance activity can be eliminated by using the already mentioned low-maintenance electrodes. In addition to effects on the pH electrode, the pressure can also give rise to physical processes in the measurement medium that manifest themselves in pH fluctuations:

In process media containing pH-active gases such as ammonia, carbon dioxide or hydrogen sulfide, the pressure changes the pH value. In basic solutions, the pH value increases with increasing pressure (e.g. NH₃ in water) and in acidic solutions it decreases (e.g. SO₂ in water). If a reference measurement is made under normal pressure conditions, the measurement result will be correspondingly higher or lower. Frequently, outgassing of dissolved gases increases this effect at low pressure.

(6) Contacts: pH combination electrodes are supplied with potted connecting cables (primarily for laboratory use) or with a connection system consisting of a plug head with a corresponding connecting socket with connecting cable (process measurement equipment). Various connector systems are available (cable socket N for electrodes with a temperature sensor) or Variopin (VP) for electrodes with an integrated temperature sensor). Since pH measuring chains are consumable items, whether versions with an integrated temperature sensors should be used needs to be given careful consideration. After all, the temperature sensor is then also discarded with each change of the measuring chain and must be purchased anew. Another problem, however, is that most manufacturers have developed their own connection systems, resulting in incompatibility of the measuring equipment among different manufacturers.

The connection between the electrode and cable is usually secured mechanically by screws in the connection systems. An O-ring prevents ingress of moisture. The protection rating stated for the connector system (usually IP65, IP67 or IP68) applies when plugged in.

(7) pH connection cable: pH combination electrodes represent a high-impedance electrical voltage source. For this reason, the signals are susceptible to electromagnetic interference. For the measurement, this means that both the pH meter or the pH transmitter/controller and all electrical connections must have a very high input or insulation resistance ($R_{input} > 1 \text{ T}\Omega$, $R_{ISO} > 1 \text{ G}\Omega/\text{km}$). Every short-circuit (whether from moisture or incorrect wiring) causes a measurement error or can damage the measuring chain. To ensure proper transmission of the measurement signal, only special coaxial cables are used in pH measuring equipment. They provide the electrical connection between the sensor and the transmitter. The pH cables have a special construction. In addition to copper shielding, there is also a semiconducting layer.

Because of the high impedance of the pH measuring chain, the cables cannot be connected via terminals. If the shielding between the combination electrode and transmitter is interrupted at one spot, so-called "hand sensitivity of the measurement" can occur. It is common practice to ground the shield of the measuring chain. An electrical current can flow in the process medium itself

(e.g. in electrochemical systems). In addition, corrosion currents can arise from use of different metal components in the system and falsify the measured value. In industrial systems, the process medium is typically grounded via the pipeline. If, however, the ground for the measuring device and the ground for the measuring point are at different potentials, the equalizing current that then flows can falsify the measured values or even lead to destruction of the reference electrode.

A special ground line is a remedy in this case. If the process medium has only a low conductivity or the pipelines are made from a nonconductive material, grounding is achieved through use of a so-called ground rod made of a noble metal that is screwed into the pipeline and connected electrically to the transmitter. Furthermore, the cable length should be kept as short as possible – if for no other reason than the need to calibrate the measuring chain. In the case of cable lengths exceeding 15 meters, for instance, an impedance converter that screws onto the electrode is used. These are usually battery-operated and lower the internal resistance of the pH electrode to such a point that trouble-free transmission of the pH signal is assured.

Miniaturization of powerful electronics has advanced significantly in recent years. Today, it permits the pH electrode to be equipped directly with processing electronics. Processing of the high-impedance pH signal and signal conditioning take place directly in the head of the electrode. The signal can be transmitted to a supervisory control system digitally (e.g. via Modbus or HART protocol) or in analog form (4 to 20 mA current signal). A major benefit is the improved signal transmission compared to high-impedance analog original signals from sensors. Moreover, this intelligence in the sensor head makes it possible to store calibration data directly in the sensor. This permits simple startup of new measuring points even by untrained personnel. These benefits are offset, however, by the fact that at the end of the electrode's service life the entire electrode, including electronics, must be discarded. Recycling of the permanently integrated electronics is thus not possible.

(8) + (1) + (5) Effect of temperature (p / T change / extreme temperature):

The temperature value provides basic information for the temperature compensation of the transmitter (11); it is also frequently documented in addition to the pH value. Measuring chains in which a temperature sensor (8) is already integrated are thus especially practical. In this case, only one installation location and one connection cable are needed for both sensors (pH measuring chain and temperature sensor). The temperature represents a major factor in two regards: On the one hand, all chemical processes are temperature-dependent equilibrium reactions, including the pH value of the measurement medium.

On the other hand, the pH measuring chain provides a temperature-dependent voltage signal. The Nernst equation describes the relationship between the pH value, temperature, and voltage:

$$\Delta E = E_0 + \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

ΔE : Measuring chain voltage

E_0 : Standard voltage of the reference system

R: General gas constant (= 8.314 J k⁻¹ mol⁻¹)

T: Absolute temperature [K]

n: Charge of the hydrogen ion: n = 1

F: Faraday constant (= 96485 C mol⁻¹)

a_1 : Activity of the hydrogen ions in the measurement medium

a_2 : Activity of the hydrogen ions in the internal buffer (constant)

The expression RT/nF is usually called the Nernst voltage (k) and represents the theoretical slope of a pH measuring chain (Fig. 3).

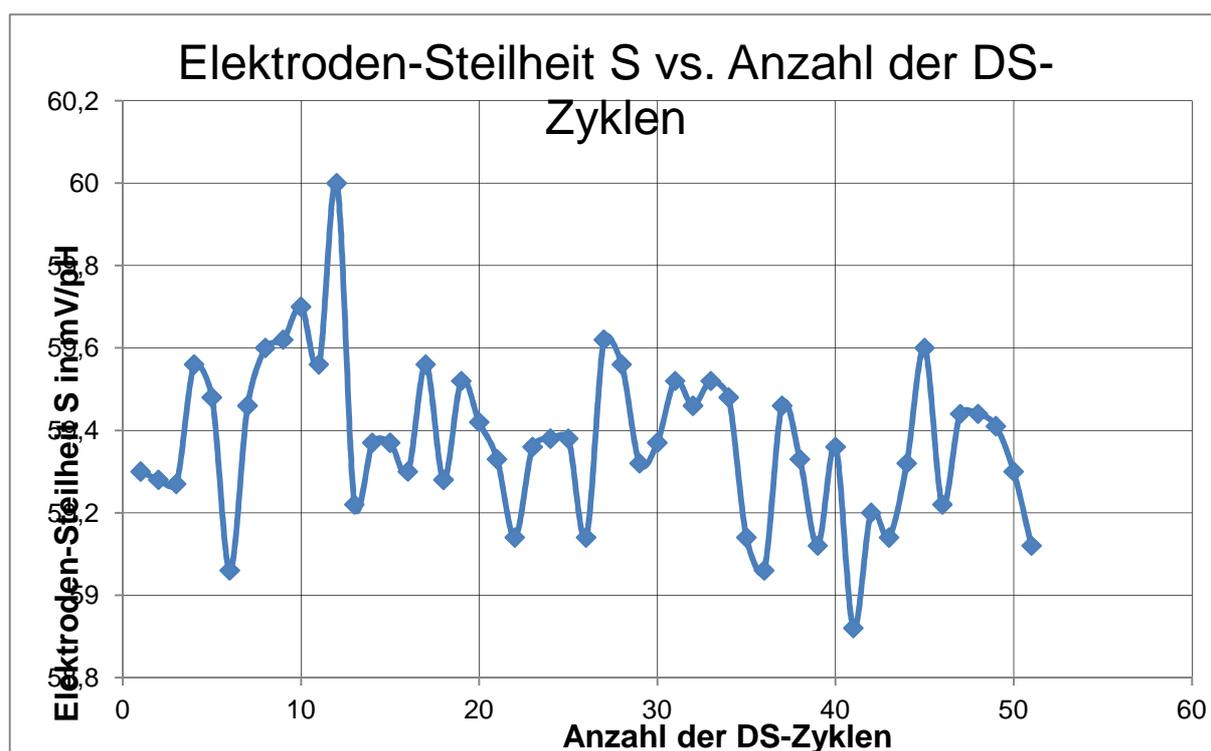


Figure 3: Electrode slope

A temperature of 25 °C corresponds to a voltage change of 59.16 mV per decimal logarithm (pH unit). While the measuring chain generates about -56 mV at 10 °C for a pH = 8, this already changes to -59 mV for the same value at 25 °C. The transmitter must know the temperature of the measuring chain to calculate the correct pH value. At a relatively constant temperature, entering

the temperature value in the transformer manually suffices (e.g. in swimming pools).

With variable temperature conditions, a measuring change with a temperature sensor is recommended. The transmitter automatically uses the temperature-corrected slope on the basis of the temperature information. In real measuring chains, the slope of the measuring chain usually deviates from the ideal value, the Nernst voltage. In addition, the zero point (Fig. 4) of real measuring chains is temperature-dependent. If the measuring chain voltage is determined as a function of the pH value for real pH electrodes at different temperatures (isotherms), the characteristic curves obtained for the electrode intersect at a point. This is called the isotherm intersection point. It can differ from the real zero point of the electrodes.

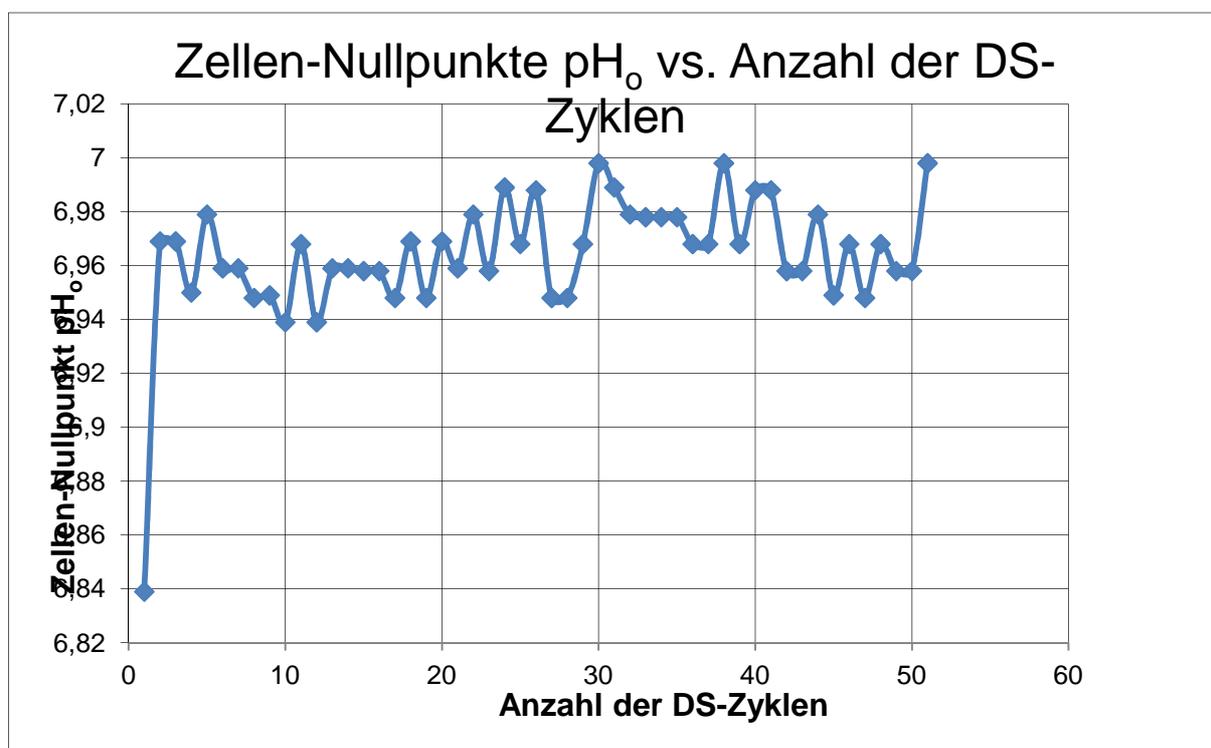


Figure 4: Curve for the cell zero point

However, good pH measuring chains are designed in such a way so that the isotherm intersection point falls at the measuring chain zero point of pH 7. For a high-accuracy measurement, it is recommended that the measurement and calibration be performed at the same temperature. It is necessary to ensure that the temperature compensation described above considers only the temperature-dependent change of the Nernst voltage. The temperature compensation in the transmitter cannot compensate for any possible temperature-dependent shift of the chemical equilibrium. Furthermore, it is necessary to consider that the process temperature also has an effect on the

individual components of the measuring chain. It has a significant effect on the operating life of the electrode.

For instance, with a combination of high pH value and high temperature, the source layer of the glass membrane (1) is attacked faster, lowering the operating life as a result. The chemical attack of the glass membrane by hydrofluoric acid (HF) mentioned above also occurs faster at a higher temperature. Every pH electrode manufacturer has special membrane glasses optimized for continuous use at high temperature in their product line. Membrane glasses that can withstand sudden temperature changes such as those encountered in SIP (sterilize in place) processes present a special challenge. It must also be taken into account that the reference system needs to be matched to the temperature conditions. Solid electrolyte gels with a fixed matrix typically find use here. The solid gel prevents the ingress of measurement medium as the result of pumping effects especially in applications with changing temperatures and pressures. In summary, the critical factors and countermeasures described above are presented in Table 1.

Summary:

When making a pH measurement, considering the various critical influencing factors and the effects on the individual components of the measuring chain is necessary. With exact knowledge of these quantities, it is possible to match the electrode optimally to the desired process conditions through skillful selection of appropriate electrode components such as the membrane glass or diaphragm and thereby minimize the undesirable effects.

Upon consideration of all influencing factors, it becomes clear that the reference electrode can often be the source of most problems and frequently causes failure of the measuring chain. From many years of practical experience, the authors estimate that in about 80 percent of cases the reference electrode is the reason for failure of a pH electrode. Alone the leaching of the reference electrode through the diaphragm will sooner or later lead to "normal" electrode failure from potential drift. Here, electrodes with a potassium chloride reservoir (e.g. in the form of salt rings) clearly have an advantage.

However, even when electrode poisons are present in the measurement medium, the two-chamber electrode represents an option for extending the service life of the measuring chain. Unfortunately, so-called digital sensors with integrated electronics or non-contact connector systems do not offer any advantages here – the permanent integration of electronic parts only increases the mountain of trash and makes the pH sensor more expensive as a consumable.

The pH is a universal measurand which nevertheless requires experience when it comes to selecting appropriate components. To cover the entire

spectrum of process measurement technology available for pH measurement, a manufacturer of pH measuring equipment must offer a comprehensive range of combination pH electrodes, fittings, accessories, and special solutions. As a manufacturer of high-quality electrochemical sensors for over 40 years, JUMO regularly examines its own pH measuring chains and tests them against electrodes from other market participants. The knowledge gained is used for continuous improvement of the electrodes.