



pH handbook

HELPFUL GUIDE FOR PRACTICAL APPLICATION AND USE

SI Analytics

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Welcome to SI Analytics!

We express our core competence, namely the production of analytical instruments, with our company name SI Analytics. SI also stands for the main products of our company: sensors and instruments.

As part of the history of SCHOTT® AG, SI Analytics has more than 75 years experience in glass technology and in the development of analytical equipment. As always, our products are manufactured in Mainz with a high level of innovation and quality. Our electrodes, titrators and capillary viscometers will continue to be the right tools in any location where expertise in analytical measurement technology is required.

In 2011 SI Analytics became part of the listed company Xylem Inc., headquartered in Rye Brook / N.Y., USA. Xylem is a leading international provider of water solutions.

We look forward to presenting the pH handbook to you!

The previous publication "Interesting facts about pH measurement" has been restructured, made clearer and more engaging, and extra information has been added.

The focus has been consciously put on linking general information with our lab findings and making this accessible to you in a practical format. Complemented by the reference to our range of products and with practical recommendations for use with specific applications, the pH primer is an indispensable accompaniment for everyday lab work.

We at SI Analytics would be happy to work successfully together with you in the future.

SI Analytics GmbH

Dr. Robert Reining
CEO

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SECTION 1

BASIC CONCEPTS OF POTENTIOMETRY AND pH MEASUREMENT

This section explains basic concepts and contexts. The pH value plays a significant role in many areas of daily life. For food, the association of certain properties such as taste (acid = fresh, neutral = bland, alkaline = inedible) and shelf life (the reproduction of harmful bacteria) depend on the pH value.

The natural acid level of the skin lies somewhere between pH 4.2 - 6.7, and plays an important role in the manufacturing of soaps. Fresh milk has a pH value of 6.6 - 6.8. If the pH value falls to 4.7, it becomes sour and clotting begins. In cheeses, the pH value in the first few hours determines its firmness, color and flavor. Bread dough manufacturing only rises properly at low pH values, as CO_2 will only form under this condition.

Figure 1 contains a diagram showing various examples of the pH values of well-known, everyday items compared to an acid and a base.

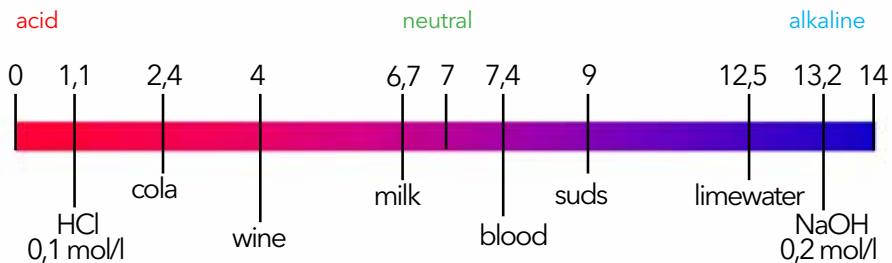


Fig. 1 pH values of a range of goods compared to an acid and a base

1.1 Definition of acid and base

Whether an aqueous solution reacts as an acid or a base depends on its hydrogen ion content. Even chemically pure, neutral water contains hydrogen ions, because some of the water molecules are always dissociated:



In chemical terms, the positive H^+ ion, the "proton", is usually referred to as the "hydrogen ion". The negative OH^- ion was previously known as the "hydroxyl ion", but now the term "hydroxide ion" is prescribed internationally. [1]

Strictly speaking, the hydrogen ion in aqueous solution is not present as a free proton, but is hydrated by at least one water molecule. The equation for the dissociation of the water is accordingly:



The hydrated proton was previously known as a "hydronium ion". Today the term "oxonium ion" is prescribed. [1]

However, because the concentration of oxonium ions corresponds to the concentration of hydrogen ions, in many cases the first equation can be used.

Ionic product of water

The equilibrium of dissociation of water under standard conditions is on the far left side. In 1 l of pure, neutral water at 10^5 Pa and 25°C there are only 10^{-7} mol H^+ - and 10^{-7} mol OH^- ions. In accordance with the law of mass action, the equilibrium constant K_D may be formulated for the dissociation:

$$K_D = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The virtually constant concentration of undissociated water H_2O as a result of its extremely low dissociation is combined with K_D of the dissociation constants to give K_W the "ionic product":

$$K_W = K_D \cdot [\text{H}_2\text{O}]$$

$$K_W = [\text{H}^+] \cdot [\text{OH}^-] = 10^{-7}\text{mol/l} \cdot 10^{-7}\text{mol/l} = 10^{-14} (\text{mol/l})^2$$

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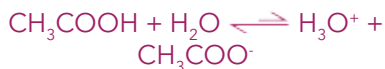
The ionic product of water changes with the temperature. This is because, like all equilibrium constants, the dissociation constant is also dependent on temperature. The ionic product of water at 0 °C for example is $0.11 \cdot 10^{-14}$ [mol/l]², but at 100 °C it is $54.0 \cdot 10^{-14}$ [mol/l]².

Instead of $1 \cdot 10^{-7}$ mol/l at 25 °C, the concentration of hydrogen ions at 0 °C is therefore only $0.34 \cdot 10^{-7}$ mol/l, but at 100 °C it is $7.4 \cdot 10^{-7}$ mol/l. This temperature dependency must also be taken into account in measuring the pH.

Acids and Bases

Acids are substances which release hydrogen ions in aqueous solution. Acidic solutions therefore contain more hydrogen ions than neutral water. Depending on their effect, a distinction is made between strong and weak acids. Hydrochloric acid, for example, is a strong acid, as HCl dissociates almost completely in water, thereby releasing a large number of hydrogen ions. Acetic acid (CH₃COOH) for example, is a weak acid, as it only dissociates partially when dissolved in water.

An acetic acid solution therefore contains significantly fewer hydrogen ions than a hydrochloric acid solution of the same molarity.



Some acids can release more than one hydrogen ion per molecule. Depending on the number of hydrogen ions which can be released, acids are classified as either monovalent, bivalent, trivalent etc. Hydrochloric acid (HCl) for example is monovalent, sulphuric acid (H₂SO₄) is bivalent and phosphoric acid (H₃PO₄) is trivalent:



In order to take account of the valency of the acids, their concentration is not expressed as molarity, but as a ratio of valency and molarity referred to as the normality. So 1n HCl is 1.0 molar and 1n H₂SO₄ 0.5 molar.

The dissociation constants (K_D) for the different stages of dissociation of a multivalent acid are often markedly different. This varying level of dissociation at the different stages plays an important role, for example in the use of phosphoric acid and phosphates in buffer solutions.

Bases are substances which accept hydrogen ions. When bases are dissolved in water, they bind to some of the hydrogen ions from the dissociation of the water. Basic solutions therefore contain fewer hydrogen ions than neutral water. Accordingly, the concentration of hydroxyl ions in basic solutions is greater than in neutral water. As with acids, a distinction is made between strong and weak bases. So for example sodium hydroxide (NaOH) is a strong base, while ammonia (NH_3) is a weak base.

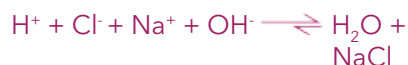


Basic solutions were traditionally known as "alkalis". Today however the umbrella term is "base". Even the characterization of basic solutions as "alkaline" is misleading. After all, it is not just the oxides and hydroxides of the alkaline metals which have the property of forming basic solutions.

Aqueous solutions are acidic if they contain more than 10^{-7}mol/l of hydrogen ions at 25°C , they are basic, if they contain fewer than 10^{-7}mol/l of hydrogen ions.

Acids and bases neutralize each other, resulting in the formation of water and salt. [2]

For example, hydrochloric acid and sodium hydroxide



Consideration must be given to whether strong acids are being neutralized with strong bases, weak bases with strong acids or weak acids with strong bases. In the first instance, e.g. in the neutralization of hydrochloric acid with sodium hydroxide, neutral table salt is formed (NaCl).

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If a salt like this, which has been formed from a strong acid and base is dissolved in water, the solution reacts neutrally. On the other hand, if the salt of a strong base and a weak acid, such as sodium carbonate (Na_2CO_3) is dissolved, the resulting solution is basic. If the salt of a strong acid and a weak base, such as ammonium chloride (NH_4Cl) is dissolved, the resulting solution is acidic.



1.2 Definition of pH value

The concentration of hydrogen ions in an aqueous solution is a measure of how acidic or basic it is. Accordingly, a scale can be created for acidity which starts with the concentration of hydrogen ions of 1 mol/l and ends with 10^{-14} mol/l (Fig. 2). The endpoints of the scale correspond on one side to the ideal solution of a 100% dissociated 1N acid and on the other side the ideal solution of a 100% dissociated 1N base.

	pH	H+ Activity		OH- activity
	0	1.E+00	1	0.00000000000001
	1	1.E-01	0.1	0.0000000000001
	2	1.E-02	0.01	0.000000000001
acid	3	1.E-03	0.001	0.00000000001
	4	1.E-04	0.0001	0.0000000001
	5	1.E-05	0.00001	0.000000001
	6	1.E-06	0.000001	0.00000001
neutral	7	1.E-07	0.0000001	0.0000001
	8	1.E-08	0.00000001	0.000001
	9	1.E-09	0.000000001	0.00001
	10	1.E-10	0.0000000001	0.0001
base	11	1.E-11	0.00000000001	0.001
	12	1.E-12	0.000000000001	0.01
	13	1.E-13	0.0000000000001	0.1
	14	1.E-14	0.00000000000001	1

Fig. 2 Table of H^+ / OH^- activity depending on pH value

However, concentration is not used as the measure of acidity. A logarithmic scale, the "pH value" is used. The pH value is directly proportional to the negative log base 10 of the hydrogen ion concentration. (The term "pH" comes from Latin and is an acronym for "potentia hydrogenii" - the power of hydrogen.)

$$\text{pH} \sim -\lg [\text{H}^+]$$

In practice that means that a change in the concentration of hydrogen ions by a factor of 10 creates a change of 1.0 on the pH scale.

Concentration and activity

Dissolved ions exert electrical forces as charge carriers on the medium surrounding them. While the solution is electrically neutral on a macroscopic scale, on the micro scale the effects can be drastic. The mobility of the ions is limited by the reciprocal influence, meaning that significant deviations from ideal behavior may occur. So as to take account of this fact, the activity of the ions must be considered, rather than the concentration.

Therefore instead of concentration $[\text{H}^+]$, the activity of the hydrogen ions is measured. The activity comprises an individual activity coefficient (f) and the concentration together.

$$a_{\text{H}^+} = f \cdot [\text{H}^+]$$

The pH value measured in practice is therefore the negative log base 10 of the hydrogen ion activity.

$$\text{pH} = -\lg a_{\text{H}^+}$$

Conventional pH values

Because of the difference between concentration and activity, the measurement of pH values cannot be directly based on the concentration of hydrogen ions in solutions. Conversely, it is not possible to achieve an absolute calibration of the pH scale against the concentration of hydrogen ions. Such a calibration would always be an approximation only.

Therefore the pH measurement in practice is based on a conventional pH scale.

The pH values measured in practice relate to a series of standard buffer solutions created by the NBS (National Bureau of Standards) and adopted by the Deutsche Institut für Normung (DIN).

Conventional pH values are therefore measured in comparison to the pH values of these standard buffer solutions. Provided that calibration and measurement is done carefully, this makes all pH values comparable, regardless of the probe or measuring equipment used to record them.

In determining the pH value of aqueous solutions, the reciprocal influence of the ions must not be ignored. A distinction must be made between the effective and therefore measurable concentration and the nominal concentration. This effective concentration is the activity. The pH value is therefore the log base 10 of the hydrogen ion activity.

All pH values are temperature dependent, so a comparison is only permissible if the temperatures are the same or similar.

The temperature dependence is specific to each probe and non-linear, so it is not possible to convert the pH value from one temperature to another.

Temperature dependence of the pH value

The neutral point of the scale is pH 7.00 at 25 °C. The dissociation equilibrium and ionic product of water are temperature dependent and therefore the neutral point is greater or less than 7.00 depending on the temperature. A measurement result of e.g. pH 6.82 at 50 °C in no way means that the solution is acidic. The temperature dependence of the pH value of acidic and basic solutions differs from that of neutral water, as the activity is temperature dependent.

Strongly acidic solutions display virtually no temperature dependence, as in acidic solutions the concentration of hydrogen ions is no longer determined by the auto-dissociation of water, but by the dissociation of the acid.

The change in the dissociation of the acid with the temperature is so slight that it is not recorded in the pH measurement.

On the other hand, the pH value of basic solutions is quite strongly temperature dependent. This is because in basic solutions the hydrogen ion activity is determined by the temperature-dependent ionic product, i.e. the auto-dissociation of water. The pH value of basic solutions generally decreases noticeably with increasing temperature (Fig. 3).

pH value and temperature reading

Comparing pH values without simultaneously stating the measuring temperatures is virtually meaningless. A synthesis such as "The reaction occurs at a pH value of 10.50 +/- 0.25 with a satisfactory yield", is also of little use.

temperature	0 °C	25 °C	50 °C
pH of water	7.47	7.00	6.63
pH of 0.001n HCl	3.00	3.00	3.00
pH of 0.001n NaOH	11.94	11.00	10.26

Fig. 3 pH value of three solutions depending on temperature

This provides no information as to whether the pH value of the reaction mixture was at room temperature before the start of the reaction or even if the pH value during the reaction was at 80 °C.

1.3 Electrochemical potential

Electrochemical potential is the basic measurement value on which pH measurement is based. In the next section, the theoretical principles will be explored in further detail.

Chemical reactions take place in accordance with the laws of thermodynamics. Thermodynamics describes the relationships between different forms of energy and can be relied upon to answer the question of whether a reaction is energetically favorable, in other words whether it can proceed in terms of energy.

In this respect the decisive factor is the Gibbs energy G , also known as free enthalpy. For changes ΔG during a reaction the following applies:

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- $\Delta G < 0$: an exergonic reaction, which under the specified conditions (concentrations) proceeds spontaneously;
- $\Delta G = 0$: Equilibrium, no reaction;
- $\Delta G > 0$: endergonic reaction, which would require energy to be added to proceed in the specified direction.

The change in free enthalpy of one mole of a substance during transition from one concentration to another concentration can be compared to the compression of an ideal gas from one pressure p_1 to another pressure p_2 . This process can be described with the following equation:

$$\Delta G = n \cdot R \cdot T \cdot \ln(p_2/p_1)$$

In very dilute solutions, the dissolved particles behave like those of an ideal gas, so that a similar formula can be created for the transition from one concentration c_1 to another concentration c_2 :

$$\Delta G = n \cdot R \cdot T \cdot \ln(c_2/c_1)$$

When considering mid-range concentrations, the activities must be used instead of the concentrations.

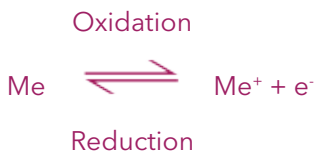
$$\Delta G = n \cdot R \cdot T \cdot \ln(a_2/a_1)$$

The differential change in free enthalpy according to the amount of substance under constant pressure, constant temperature and constant concentration is called chemical potential. Chemical reactions can only proceed if they are associated with a change in chemical potential. Absolute values for chemical potentials are unknown, and so it is only possible to observe changes in relation to an initial state. [2][3][4]

If a transition occurs from uncharged particles to ions, this can be compared with the functions of an electrode. The electrode system is a two-phase system (metal/solution) in which positive ions from the metal immersed in the solution can be dissolved. In accordance with the number of ions dissolved, the metal becomes negatively charged. The result is an electrical potential between the negatively charged metal and the positive solution.

The solution process continues until the electrical potential is so great that no further metal atoms are released. Strictly speaking, equilibrium is then achieved: For each unit of time, exactly as many metal atoms are dissolved as ions on the one hand as ions are discharged and deposited again as metal atoms on the other hand. This state of equilibrium corresponds to a potential of a quite specific voltage, which is typical for the metal and ion concentration in question.

A metal which is in contact with a solution of its own ions is a reduction / oxidation system ("redox" system for short). The donation of electrons by a metal atom corresponds to an oxidation; the acceptance of an electron by a metal ion is a reduction:



If a metal is in contact with an aqueous salt solution, this combination is therefore an "electrode". The aqueous salt solution is an "electrolyte". The electrode metal is a conductor of first order and the electrolyte a conductor of second order. If the metal is in contact with a solution of its own ions, an electrical potential (u) is formed, the so-called "galvanic voltage".

Electrodes of the first kind

Metal which is immersed in the solution of its own salt is referred to as an electrode of the first kind. For example a silver wire (Ag) which is immersed in a solution of silver nitrate (AgNO_3), is a typical electrode of the first kind. It is referred to as an Ag/AgNO_3 electrode (Fig. 4).

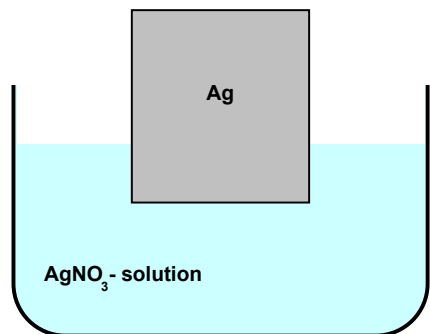


Fig. 4 Electrode of the first kind

Electrodes of the second kind

With electrodes of the second kind, a metal coated with a slightly soluble metal salt is immersed in an aqueous solution, which contains a readily soluble, chemically inert salt with the same anion. In addition, the solution also contains the same slightly soluble metal salt as a precipitate (Fig. 5).

For example, a silver wire coated with slightly soluble AgCl and immersed in a solution of KCl is an electrode of the second kind, the Ag/AgCl/KCl electrode. The potential of an electrode of the second kind does not depend on the concentration of metal ions, but on the anion concentration or activity (a_x) in the solution.

$$u = u_{0(\text{Me/MeX})} - U_N \cdot \lg a_x.$$

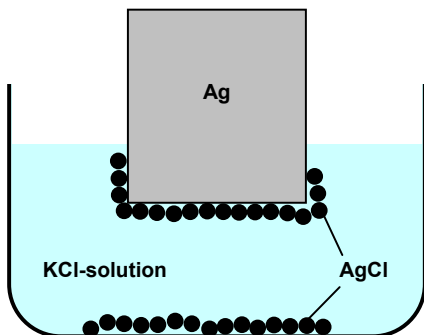


Fig. 5 Electrode of the second kind

Measuring and reference electrodes

Electrodes of the second kind generally display low polarizability. Their potential is very constant, because the anion concentration can be kept constant quite easily. Electrodes of the second kind are therefore widely used as "reference electrodes" in potentiometric measurements. If however a metal is immersed in a solution of unknown ion activity, this arrangement functions as a measuring electrode when measured against a reference electrode.

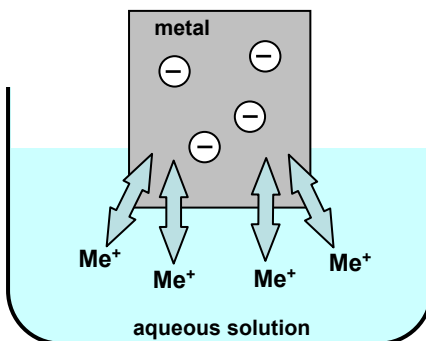
After calibration with solutions of known ion activity, the unknown activity can be determined from the voltage measured. Today the silver/silver chloride system is most often used for reference electrodes. Not only are they universally applicable, they also have no harmful effects on health or the environment.

In addition, SI Analytics offers reference electrodes for specific applications using the mercury/mercury chloride and mercury/mercury sulfate and iodine/iodide systems.

1.4 Nernst equation

In accordance with the theoretical principles set out above, it is possible to come up with an equation which describes the relationship between the potentials measured by the electrode and the pH value of the solution into which the electrode is immersed. This is the Nernst equation.

If a galvanic cell is observed in which two metals are immersed in the electrolyte solution, two electrochemical potentials are formed at the phase boundary which is in equilibrium when their amounts are equal (Fig. 6). For redox (ORP) systems, the Nernst equation is used to calculate the voltages of an electrode which occur. [2]



In accordance with Nernst, the galvanic voltage depends on the constants u_0 and the variables a_{Me^+} and T . U_0 is the standard potential of the metal, a_{Me^+} is the activity of the metal ions and T is the absolute temperature.

$$u = u_0 + \frac{R \cdot T}{n \cdot F} \cdot \ln a_{Me^+}$$

The standard potential u_0 has a typical value for each metal. It can be derived from the so-called "electrochemical series" of the metals. The galvanic voltage (u) measured corresponds exactly to u_0 if the activity of the metal ions in the solution is 1 mol/l (as $\ln 1 = 0$). The expression $(R \cdot T) / (n \cdot F)$ contains the gas constant (R), the oxidation number and valence of the metal ions (n), the Faraday constant (F) and the absolute temperature (T) in Kelvin.

Fig. 6 Development of the redox (ORP) potential by the dissolution and deposition of a metal in aqueous solution.

Nernst factor

For redox (ORP) reactions in which a single charge is exchanged per atom or ion ($n = 1$) and at a standard temperature of 25°C ($T = 298\text{K}$), the entire expression can be summarized in a single constant. This constant is then multiplied by 2.303, so that $\ln a_{\text{Me}^+}$ can be substituted by $\lg a_{\text{Me}^+}$. The resulting factor has a value of 59.16mV at 25°C . It is known as the "Nernst voltage" (U_N) or simply the "Nernst factor". The equation for the electrode potential is therefore greatly simplified:

$$u = u_0 + U_N \cdot \lg a_{\text{Me}^+}$$

Temperature dependence of the electrode potential

The Nernst factor is not a constant because it contains the absolute temperature as a multiplier. The electrode potential changes in accordance with this temperature dependence of U_N . Compared to the standard temperature of 25°C , the Nernst factor is approximately 8% smaller at 0°C and approximately 25% greater at 100°C (Fig. 7).

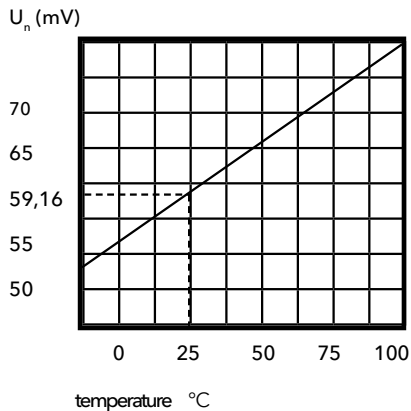


Fig. 7 Temperature dependence of the Nernst factor

1.5 Methods of pH measurement

There are potentiometric and optical methods for determining the pH value. The potentiometric methods relate to the measurement of electrical voltages on pH-sensitive electrodes. Optical methods involve the visual and photometric analysis of pH-dependent color changes.

Optical methods

These methods use pH-dependent color changes of specific organic pigments, so-called color indicators. So for example as the pH value increases, the color of methyl red in an aqueous solution changes from red to yellow at a pH of 4.9. Phenolphthalein for example turns reddish at a pH of 9.5. The best known of these is the pH indicator paper or pH test strips, which are prepared with indicator solutions of these organic pigments. The pH value is estimated by means of a visual comparison of the color against a color scale. However the precision is only sufficient to provide a rough estimate.

Photometric pH measurement

The color change of the indicator pigments can also be photometrically determined by shining a light and measuring the absorbance. These methods are referred to either as colorimetric or spectrophotometric, depending on the equipment and light source used. In theory it is possible to take pH measurements in this way. However the method is very prone to interference and the equipment needed is large. [2]

Disadvantages of the optical methods

The area of application for optical pH measurement, be it visual or photometric, is very limited. If the solution to be measured is cloudy or has an inherent color, the measurements will be unreliable. Some measurement solutions also contain chemical bonds which destroy the color indicators through oxidation or reduction and produce incorrect results.

Potentiometric determination of the pH value

This method uses the electrical potential of pH-sensitive electrodes as a measurement signal. A distinction is made between hydrogen, metal and glass electrodes. The glass electrode is the most commonly used sensor today. Not having the disadvantages of the optical methods, it can be used almost universally. It is one of the most sensitive and at the same time most selective sensors there is and has an unmatched measurement of pH 0 to 14, means from percent to ppq (= parts per quadrillion = one molecule in one quadrillion other molecules).

pH measurement with the antimony electrode

On some metals there are redox processes which depend directly on the hydrogen ion activity of the solution. For example, the oxidation or reduction of antimony (Sb), which depends on hydrogen ion activity, can be used as a measurement of pH.



The potential (u) of the antimony electrode ($\text{Sb}/\text{Sb}_2\text{O}_3$) is directly linked to the pH value:

$$U = U_{0(\text{Sb})} - U_N \cdot \text{pH}$$

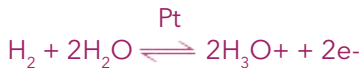
Essentially, the potential of the antimony electrode is measured against the constant potential of a reference electrode. The simple linear relationship between pH and measurement voltage however only applies in the range between pH 3 and pH 11. [5]

Reductive or oxidizing components in the measuring solution also interfere with pH values measured using the antimony electrode.

Consequently the antimony electrode is only used in special cases, if for example the use of glass electrodes in fluoride-containing solutions is not possible. It should be noted that on the antimony electrode the zero point is approximately pH 1 and these days can often only be used with corresponding process measuring amplifiers.

Functional principle of the hydrogen electrode

If a fine platinum mesh bathed with hydrogen gas is immersed in an aqueous solution, this arrangement represents an electrode of the first kind, the so-called "hydrogen electrode". Some of the hydrogen molecules donate electrons to the platinum and are released as hydrogen ions in solution:



The hydrogen electrode is an electrode of the first kind, whose potential at constant hydrogen pressure (1 bar) depends solely on the activity of the hydrogen ions in the solution. The hydrogen potential is measured on the platinum, a first-order conductor. For the actual redox process of the hydrogen electrode the platinum is chemically inert. It functions solely as an intermediate: depending on the direction of the current, hydrogen can be deposited as a metal or converted to ions.

$$U = U_N \cdot \lg a_{\text{H}^+} = U_N \cdot \text{pH}$$

Applications of the hydrogen electrode

Theoretically, pH value can be identified very precisely with the hydrogen electrode. In practice, however, working with the hydrogen electrode is expensive and cumbersome. High-purity hydrogen and constant hydrogen pressure are conditions which are hard to create in a practical setting. The hydrogen electrode will also fail if the solution contains heavy metal ions which contaminate the platinum surface. Reductive or oxidizing components in the measuring solution also lead to undesired side reactions and therefore to errors in measurement.

The hydrogen electrode is consequently only used today under very specific defined conditions for more scientific purposes. The same applies to the so-called quinhydrone electrode. As a special form of hydrogen electrode, today it is seldom used.

1.6 Summary

According to the theory of Brønstedt [6], acids are substances which are capable of separating hydrogen ions. Bases on the other hand enable the deposition of hydrogen ions.

A distinction is made between weak and strong acids and bases. Strong acids and bases are generally almost completely dissociated, weak ones on the other hand are only incompletely dissociated. In addition, a distinction is made between the molar concentration (previously: molarity) and the equivalent concentration (previously: normality). The molar concentration means moles per liter and the number of dissociable hydrogen ions is still included in the definition of equivalent concentration, i.e. mol/liter divided by the number of dissociable hydrogen ions. [4]

The electrode potential can be determined on the basis of the Nernst equation. The measurement voltage is the difference between two electrode potentials. Whether a reaction can proceed depends on the thermodynamic requirements. The decisive factor is the change in free enthalpy ΔG .

SECTION 2

STRUCTURE OF pH ELECTRODES

2.1 The glass electrode

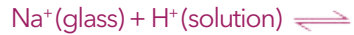
What is meant by glass, is an amorphous, i.e. solidified without crystallization, super-cooled liquid which softens only gradually when heated, whose atoms have a short-range order but no directional long-range order. [7]

The properties of the glass change depending on its composition. The oldest pH membrane glass is the MacInnes glass with the composition $\text{Na}_2\text{O} : \text{CaO} : \text{SiO}_2$ in the proportion 22 : 6 : 72. [3]

The glass membrane as a pH sensor

Under the action of water, alkali ions are released from the surface of the glass and the oxide bridges of the silicate structure are partially converted from H_2O to OH^- groups. This leads to the creation of a "gel layer" of approximately 500 nm thick. This gel layer acts as an ion exchanger of hydrogen ions:

alkali ions from the gel layer are exchanged for hydrogen ions from the water. [3]



If the alkali concentration of the aqueous solution is small, with certain types of glass a reproducible equilibrium is created between the solution and the surface of the glass, which depends only on the concentrations of hydrogen ions in the solution and in the gel layer.



If two solutions with hydrogen activities $a_{1(\text{H}^+)}$ and $a_{2(\text{H}^+)}$ are separated from each other by this type of glass membrane, a surface potential is created on both sides of the glass membrane.

Both surfaces of the membrane are in electrical contact with each other. Due to its ionic structure glass is a second-order conductor. A total potential of the membrane is created which can then be described using the Nernst equation.

This potential is directly proportional to the difference of the logarithmic hydrogen ion activities. If the hydrogen activity on one side of the membrane changes, a new equilibrium is reached between the gel layer and the solution and consequently a new potential. It takes just a few seconds to reach the new equilibrium.

The total time it takes to measure the changed potential however depends not only on the gel layer but also on the resistance of the measuring solution and the electronics in the measuring equipment. To measure this membrane potential, an electrode of the second kind is placed in each of the two solutions as a reference electrode. If the potentials of both reference electrodes are exactly equal, they cancel each other out and the measured voltage (U) now corresponds only to the total potential of the glass membrane.

$$U = U_N \cdot \lg \frac{a_{1(\text{H}^+)}}{a_{2(\text{H}^+)}} =$$

$$U_N \cdot (\lg a_{1(\text{H}^+)} - \lg a_{2(\text{H}^+)})$$

Structure of the glass electrode

The glass electrode profits from the dependence of the potential of the glass membrane on the activity of the hydrogen ions. At the end of a glass tube, a glass membrane is fused on as a pH sensor. This membrane is filled with a buffer solution of a known pH value. Into this buffer solution, the reference electrode is immersed. To measure the pH, the potential difference between the inner and outer surface of the glass membrane is used (see Fig. 8).

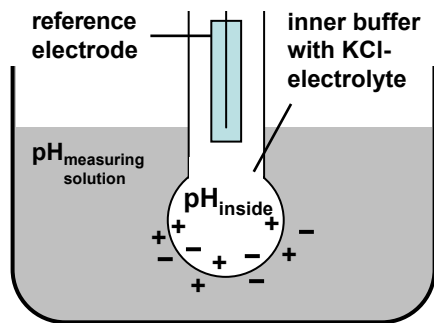
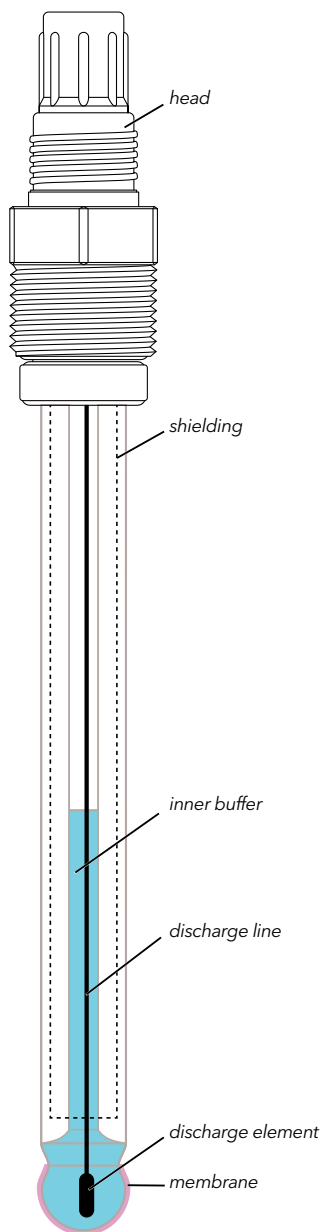


Fig. 8 Theoretical design of a glass electrode



This potential of the glass electrode (u) is directly proportional to the pH difference between the internal buffer and the measuring solution:

$$u = U_N \cdot (\text{pH}_{\text{in}} - \text{pH}_{\text{solution}})$$

Figure 9 shows a cross-section of a typical glass electrode. At the tip of the internal glass tube made from chemically inert, highly-resistive glass is a spherical membrane made from a special pH-sensitive type of glass. The internal tube and sphere contain the internal buffer, e.g. a 3.0 molar KCl solution buffered at pH 7, which simultaneously acts as the electrolyte for the reference system. The reference system in the example shown consists of Ag/AgCl. The electrical connection to the plug-in head consists of metal wire. The inner tube is covered in a film of metal, which operates as a shield against stray electrical fields. This shield is connected to the measurement connection shield via the plug-in head. The outer sheath of the electrode consists of a chemically inert glass tube.

Fig. 9 Cross-section of a glass electrode

Membrane glass and pH range

The membrane of modern glass electrodes consists of highly-advanced lithium silicate glass. Compared to conventional sodium glass, it has fewer alkali errors and better resistance to wear due to its improved chemical resistance. [3]

However there are no electrodes which are equally suitable at every temperature over the entire pH range. The membrane glass of the glass electrodes is better optimized either to the acid or the basic range, which greatly depends on the temperature.

The corrosion resistance of the membrane glass also plays an important role. Like all glass, the membranes of glass electrodes corrode under certain conditions. In the basic range, for example, the disintegration of the gel layer accelerates very quickly with increases in temperature. In the acid range, fluoride-containing solutions increasingly attack the glass membrane at pH levels greater than 6.

At higher temperatures the fluoride attack is accelerated even further. Higher phosphate ion concentrations have a very aggressive effect in conjunction with high temperatures.

Membrane resistance and temperature range

At a sphere diameter of approximately 10 mm, the wall thickness of the sphere membrane is approximately 0.5 to 1.0 mm. Its nominal resistance is between 100 and 400 M Ω at 25 °C. The resistance increases as the temperature falls, therefore attention must be paid to the membrane glass with measurements with low resistance at 0 °C.

Membrane glass type and shape

SI Analytics offers glass electrodes with three different types of membrane glass. This means that an exact measurement is possible at virtually every temperature and pH range.

Glass of type **A** is suitable for almost the entire pH range and every type of material for analysis at normal temperatures.

Membrane glass of type **H** optimized for the basic range has significantly fewer alkali errors (i.e. Na^+ errors) and is suitable for temperatures up to $+140\text{ }^\circ\text{C}$. They are used in particular in the basic range where there are high levels of sodium and lithium ions and for high-temperature measurements.

Membrane glass of type **S** is resistant to sudden, large changes in temperature and produces very consistent measurement values in hot alkaline solutions with a fast response time.

H Optimized for the basic range and for higher temperatures of up to $140\text{ }^\circ\text{C}$, also precise in very alkaline ranges.

S Resistant to sudden, large changes in temperature, such as during sterilization; very consistent measurement values in hot alkaline solutions with a fast response time.

A Fast response time in drinking, domestic, and waste water and for general use

In order to ensure optimal moistening of the glass membrane with the probe, the membrane shape must be optimized for the particular application. So for example a pH measurement of a flat surface should not be conducted using a spherical membrane, but with a flat membrane.

The different types of membranes and their features are shown in Fig. 10.

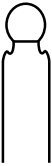

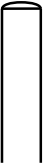

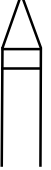

	form	property / application
	sphere	constant quality, low resistance because of large surface, for most applications
	dome	high resistance, shock-proof, easy to clean and therefore applicable in measuring points with automatic cleaning
	flat	high resistance, shock-proof, easy to clean, especially for pH surface measurements
	cylinder	high resistance, shock-proof, for general application, especially usual for fermenter electrodes
	spear	high resistance, suitable for penetrating semi - solid media and for measuring points with automatic ultrasonic cleaning
	cone	robust, smooth, easy to clean, universally applicable

Fig. 10 Types of membrane

Inner buffer

Glass electrodes manufactured today generally have an inner buffer at pH 7. For special cases, there are electrodes with inner buffers at other pH values, e.g. 4.6, in order to quickly identify a short-circuit fault in probes that frequently have a pH of 7. The exact pH value of the inner buffer is not relevant, so pH 6.86 is not worse than pH 7.00. These differences are easily compensated for during calibration. What is important is the long-term stability and above all the consistency of this pH value at all temperatures in the proposed measurement range.

The electrodes from SI Analytics also meet stringent requirements in this regard. At temperatures below 0 °C, normal inner buffers are unsuitable, as the electrolyte begins to freeze below 0 °C. In these cases, electrodes with inner buffers which contain "frost protection" additives such as e.g. glycerin are used.

2.2 The reference electrode

Measuring chains

The potential of an individual electrode cannot be measured. All that can be measured is a voltage as the difference between two electrode potentials in a closed circuit. If for example two electrodes of the same metal are immersed in solutions of their own salts at various concentrations, the voltage between these two redox electrodes can be measured. The measuring device is simply interconnected between the electrodes. These combined electrodes are termed an "electrode chain" or "measuring chain", when used to measure potentials.

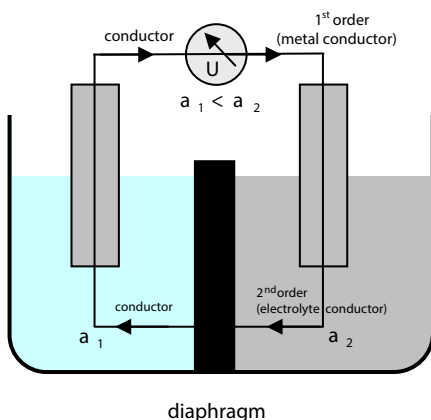
Circuit in the measuring chain

The outer circuit corresponds to a first order conductor, because it consists of an electrode metal, connection cable and measuring device - all ohmic conductors. The inner circuit corresponds to a second order conductor, it consists of the electrolytes in the measurement solution and the diaphragm - all ionic conductors.

The voltage measured by the voltmeter results from the difference between the two electrode potentials. If both solutions in the example shown (Fig. 11) have the same concentration, the voltage of the electrode chain is zero ($U = u_1 - u_2 = 0$).

However if both solutions have different concentrations or activities a_1 and a_2 , metal atoms will be dissolved in the dilute solution, while metal ions will be deposited in the concentrated solution. Electrons will therefore flow from the electrode of the lower concentration via the measurement device to the electrode of higher concentration. The voltage of such a measuring chain can be formulated in accordance with the Nernst equation:

$$U = U_N \cdot \lg a_1/a_2$$



pH measuring chain

To measure the pH value, a chain consisting of one glass electrode (= the measurement electrode) and a reference electrode. The reference electrode is in electrical contact with the measurement solution, so that the circuit is closed through the measurement solution.

Structure of the reference electrode

The reference electrode is an electrode of the second kind. Under normal circumstances an Ag/AgCl system is immersed in an electrolyte made from a concentrated KCl solution (3.0 mol/l). The diaphragm creates the electrical contact with the measurement solution. It is only slightly permeable, so that the electrolyte does not escape too quickly in the case of a liquid electrolyte. Figure 12 shows a schematic diagram of a typical reference electrode. 1st

Fig. 11 Circuit in the measuring chain

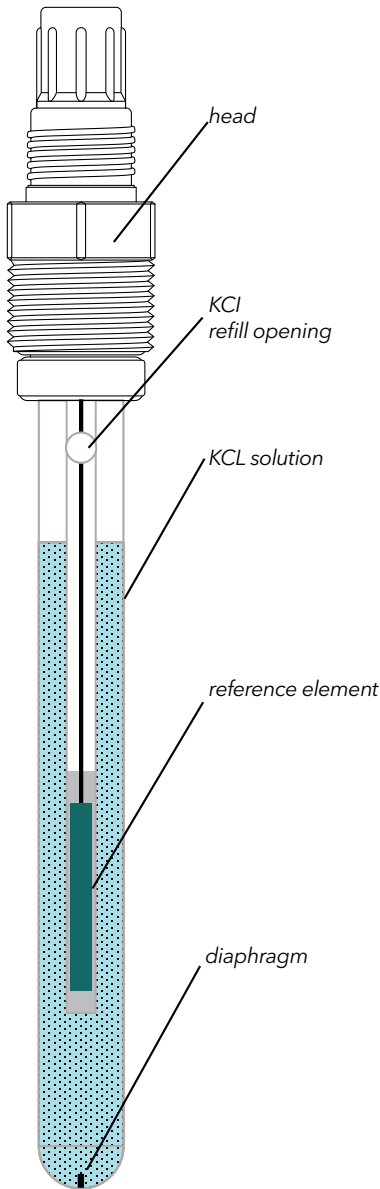


Fig. 12 Cross-section of a reference electrode

Discharge systems

One type is used above all else for the conduction system of the glass electrode and the reference electrode: silver/silver chloride ($\text{Ag}/\text{AgCl}/3.0 \text{ mol/l KCl}$). Mercury chloride is very rarely used these days. Thalamid is no longer produced due to the toxicity of thallium. The iodine/iodide system was developed as a new conduction system. This system combines the advantage of being free from silver ions, with the low temperature curve of the redox potential. There is therefore a new reference system available for potentiometric measuring chains.

Silver/silver chloride system

The silver/silver chloride system is the conduction system universally used today. As silver is non-toxic for humans, Ag/AgCl electrodes can also be used in medicine and food technology, where the poisonous mercury and thallium systems are prohibited!

Disposal is less critical with Ag/AgCl than with the "poisons" thallium and mercury. Ag/AgCl has a wide range of application with respect to temperature (up to 140 °C) and is therefore also suitable for sterilizable electrodes. The sensitivity of the Ag/AgCl electrode to chelating agents can be compensated for with an electrolyte key or double electrolyte electrodes.

Mercury chloride system

The mercury chloride system Hg/Hg₂Cl₂ is the conduction system in use for the longest time. Today however it is only used in exceptional cases, and not only due to the toxicity of mercury. The reliable temperature range when using mercury chloride is relatively narrow, and at temperatures above 60 °C the Hg₂Cl₂ begins to degrade.

Mercury chloride displays strong temperature hysteresis, meaning that during sudden changes in temperature it takes a relatively long time until the electrode regains the original potential value. Resistance to chelating agents (cyanide, thiocyanate, organic chelating agents) in the measurement solution is low.

When these effects are excluded and at room temperature, the mercury chloride system again displays the most stable potential in the presence of KCl saturation. Today the mercury chloride system is only used for academic purposes.

Iodine/iodide

The redox pair iodine/iodide exhibits important advantages versus other systems, specifically low temperature dependence, fast response behavior and freedom from contaminated metal ions. The iodine/iodide system has an additional interesting feature versus other redox systems, such as silver/silver chloride or mercury/mercury chloride. The temperature dependence, or more specifically the temperature coefficient of this reference system, is almost zero. [3]

A new reference system for potentiometric measuring chains with the advantages of being silver ion free and having the low temperature curve of the redox potential is therefore available. It offers a good alternative in the presence of fluctuating temperatures and is free from silver ions and other possibly disruptive metal ions.

Electrolytes

The reference electrolyte should have good electrical conductivity, be chemically neutral, not react with the measurement solution, and its ions should be as equally mobile as possible, as otherwise a perturbation potential may be created, a diffusion potential, due to the differing speeds of diffusion.

Potassium chloride (KCl) meets these requirements. As the temperature behavior of the electrodes is the closest to ideal at high electrolyte concentrations, concentrated KCl solutions are used. [3]

In the Hg/Hg₂Cl₂ system, the electrolyte generally consists of a saturated KCl solution, in the Ti/TiCl system a 3.5 mol/l KCl solution. For the Ag/AgCl electrode a 3 mol/l KCl solution is generally used. For measurements at low temperatures, electrolytes of lower KCl concentrations are used with a glycerin additive. For precise pH measurements, it is important not only that the discharge and reference system, but also its electrolyte concentration, are identical.

If the KCl concentrations in the reference electrode and the measurement electrode are in fact different, an additional potential is created. This potential has a temperature dependence which cannot be compensated for during room temperature calibration or for measurements at significantly different temperatures. The concentration of the reference electrolytes changes over time due to the diffusion of water and evaporation. This effect can be balanced out by calibration if the changes are minor and the measurement is being conducted at normal temperatures.

In the event of bigger changes in concentration, it is recommended that the electrolyte be changed if there is a great need for precision in measurement.

Gelatinous and polymer electrolytes

The use of gelatinous or polymer electrolytes has the advantage that no electrolyte can leak out during storage. Even in use there is virtually no loss of electrolyte.

Because the traditional diaphragm is no longer required, with the solid interface instead acting as a "diaphragm", electrodes with polymer electrolytes and KPG diaphragms are less susceptible to contamination.

These features mean electrodes with polymer electrolytes are largely maintenance-free.

Polymer electrolytes, such as REFERID® and DURALID® developed by SI Analytics, have the advantage of high pressure and resistance to changes in pressure.

The difference between the DURALID® and the REFERID® system is that the REFERID® system contains a visible KCl reserve. The DURALID® system contains finely-dispersed, solid KCl in gel.

This means it can be used without special pressure compensation. The disadvantage of gelatinous and polymer electrolytes is their lower resistance to temperature and changes in temperature, which can limit their range of use. In addition, the low or vanishingly small rate of outflow in strongly acid and basic test materials, as well as in those that are low in ions, can lead to diffusion potentials (see section 3.1) and consequently to errors in measurement.

On the other hand, the polymer electrolyte also has advantages due to the absence of a traditional rate of outflow. Due to the greatly limited "mobility" of all the ions, there is no precipitation of silver at the "diaphragm", and the diffusion in of foreign ions ("electron toxins") is virtually impossible. All in all, electrodes with gelatinous or polymeric electrolytes are strongly recommended for a whole range of precisely-defined fields of use. On the other hand, electrodes with liquid electrolytes, while they are more time-consuming in terms of handling, in many cases offer better measurement reliability.

Types of diaphragms

The diaphragm of the reference electrode is of great importance for the measurement precision of the pH chain. Diffusion voltages at the diaphragm are a common measurement error. To keep these small, the diaphragm must guarantee a relatively large and consistent outflow of KCl. Its electrical resistance should be as low as possible and it must be chemically inert. A decision must be made for liquid electrolytes in accordance with these criteria as to whether a ceramic, ground-joint, plastic or platinum diaphragm best fits the measurement conditions. Figure 13 (see page 37) gives an overview of the various diaphragms and their features.

Ceramic diaphragm

The ceramic diaphragm uses the porosity of unglazed ceramic. Its KCl outflow rate is approximately 0.2 ml / 24 h ($p = 1\text{ m}$ water column). Its electrical resistance is relatively high at 1 k Ω . In measurement solutions with greater ionic strength, the concentration gradient at the diaphragm is very large, meaning diffusion potentials are very easily created.

At lower ionic strengths the resistance of the test material may be too high for exact measurements. Both effects are amplified by low outflow rates, and so ceramic diaphragms are less suitable in such cases. Due to the high risk of blockage of its pores, it is also not suitable for solutions containing suspended particles. Only in measurement solutions that contain oxidizing substances is it clearly superior to the platinum diaphragm.

Ground-joint diaphragm

The ground-joint diaphragm works with the thin gap of the unlubricated ground glass as an outflow opening for the electrolyte. The outflow rate is 3 ml/24 h ($p = 1\text{ m}$ water column) and greater. Its electrical resistance is very low at 0.1 k Ω . It is suitable for measurements in contaminated solutions, as it is easy to clean. Due to the high outflow rate, it is suitable for both high and low-ion solutions. In versions without a screw connection, the ground gap must be manually adjusted in order to set a consistent flow rate.

Plastic diaphragm

For special applications there are also diaphragms made from plastic fibers. For example, single-rod measuring chains with a plastic shaft often have diaphragms made from nylon fibers so as to avoid contamination of the connection hole. For process measurements in solutions that contain fluoride, electrolyte keys with PTFE diaphragms are used.

Platinum diaphragm

The platinum diaphragm is an SI Analytics development. It consists of fine, twisted platinum filaments between which the electrolyte flows out along precisely defined channels. The platinum diaphragm does not easily become blocked and therefore features a very constant outflow. With approximately 1 ml/24 h ($p = 1\text{m}$ water column) and approximately 0.5 k Ω electrical resistance, it has advantages over ceramic diaphragms. However it is more sensitive to mechanical stress. It is also less than optimal for strongly oxidizing or reducing solutions due to the occurrence of disruptive potentials.

KPG or annular gap diaphragm

For solid-state electrodes a conventional diaphragm is superfluous, as the surface of the solid acts as an interface. In single-rod measuring chains, this is capitalized on in the form of the "KPG diaphragm". It consists of an annular interface wrapped around the sensor between the membrane and the outer tube. Due to the relatively large interface between the electrolyte and the test material and their small distance from the sensor, a relatively low resistance is achieved. The annular arrangement around the sensor rules out any disruptive effects based on the geometry.






	type	resistance	flow out	applications / properties
	ceramic	1 k	0.2 ml/d	<ul style="list-style-type: none"> + general applications, robust, low-priced - universally, short response time, constant insensible against dirt and chemical reactions, tend to pollution/blockage
	platinum	0.5 k	1 ml/d	<ul style="list-style-type: none"> + universally, short response time, constant, insensible againsts dirt, clean and defined flow channels, less diffusion potentials - cleaning only chemically, not mechanically
	ground joint	0.2 k	3 ml/d	<ul style="list-style-type: none"> + emulsion, paste, ultrapure water, easy cleaning - flowing-out deviations by not reproducible handling; in case of pressure overload loosening of ground joint, filigree
	annular gap	0.1 k	none	<ul style="list-style-type: none"> + symmetrical annular gap, easy handling, insensible against dirt - sample can reach into reference system, no cleaning of reference system
	fibre	1 k	none	<ul style="list-style-type: none"> + short response time, easy handling - sample can reach into reference system, no cleaning of reference system

Fig. 13 Types of diaphragm

2.3 Combined measurement chains

Single-rod measuring chain

The conduction system of the glass electrode and the reference electrode system must be coordinated. It makes sense to combine the measurement electrode and the reference electrode into a combined electrode ("single-rod measuring chain"). This significantly reduces the space required to make measurements. Figure 14 shows a schematic diagram of a typical single-rod measuring chain.

The glass electrode of the single-rod measuring chain no longer requires a metal shield, as the low-resistance electrolyte of the reference electrode surrounds the inner tube with the glass electrode as a sheath.

The Ag/AgCl system is suitable for all pH uses and for temperatures of up to 140 °C. Silamid® from SI Analytics is increasingly being used as the conduction system. Silamid is a glass tube coated with silver, which is half-filled with silver chloride. The connection to the reference electrolyte is made via a fiber wick.

Silamid® is a double-diaphragm system which provides low measurement errors from disruptive currents as well as a stable display of values under critical conditions. Long diffusion routes mean there is no need for an additional heavy metal as a silver ion barrier.

Measuring chains with electrolyte key

For measurements in solutions which could attack or contaminate the reference electrode system, measurements are taken with a so-called electrolyte key.

This means that the reference electrode is not immersed in the measurement solution, but instead in a container with the electrolyte solution which is in contact with the measurement solution via an additional diaphragm. If the electrolyte in the electrolyte key is changed frequently, there should be no risk of disruption to the reference electrode. For special cases there are reference electrodes with an integrated electrolyte key, so-called "double electrolyte" electrodes.

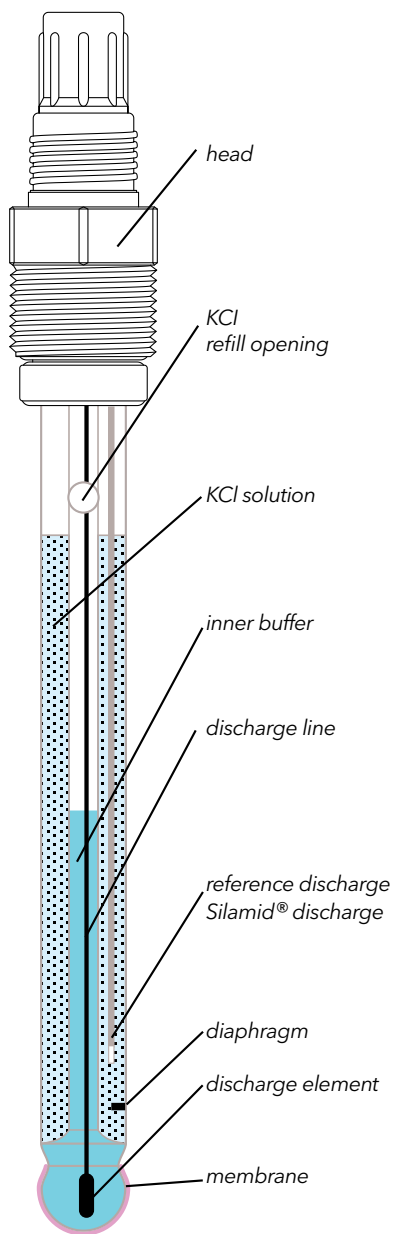


Fig. 14 Cross-section of a single-rod measuring chain

2.4 Summary

The principal components of a single-rod measuring chain are the pH-sensitive membrane, the reference electrode (reference system) and the diaphragm. All components must be appropriately adapted to the application. For example, a measurement in which the medium must be pierced must not be measured with an electrode with a spherical membrane. In this case a spear membrane must be used.

The use of the different diaphragms depends on the particular application. The selection of the right diaphragm for the respective application will also be decisive in obtaining good, reproducible measurement values. A platinum diaphragm can be used almost universally.

A ground-joint diaphragm is good for use suspended solids and in solutions of high and low ionic strengths. Due to the low outflow rate of ceramic diaphragms, contamination can occur quickly, for which reason it should only be used in non-critical applications. The outer layer of the membrane glass swells in the solution and H^+ ions can penetrate the gel layer from the

measurement solution. Sodium ions are forced into a type of ion exchange due to the higher affinity of H^+ ions for terminal silicate groups. The sodium ions can penetrate the gel layer, but the H^+ ions cannot move from the gel layer to the negative charges of the silicates. As a result a potential builds at the interface of the glass and the solution. The difference between the potential of the glass and the inner electrolyte is measured. The difference is proportional to the pH value of the solution and can be measured against the stable potential of a reference electrode.

In glass and reference electrodes, systems consisting of a metal and its salt are used to conduct the signal.

One popular system today is Ag/AgCl, which is marketed by SI Analytics in a special format called Silamid®.

SECTION 3

POTENTIOMETRY OF THE pH ELECTRODE

3.1 Potentials of the pH measurement chain

The voltage of a pH measuring chain (U) consists of six individual potentials together (cf. Fig. 15).

- the potential in the measurement system of the glass electrode (u_1),
- the potential on the inside of the membrane (u_2),
- the asymmetry potential of the glass membrane (u_3),
- the potential on the outside of the membrane (u_4),
- the diffusion potential of the diaphragm (u_5)
- and the potential of the reference element of the reference electrode (u_6).

$$U = u_1 + u_2 + u_3 + u_4 + u_5 + u_6$$

In order to determine the desired membrane potential for identifying the pH value ($u_2 + u_4$), the other potentials (u_1, u_3, u_5, u_6) must also be measured at the same time.

If it is possible to keep these potentials constant, they can be electrically compensated during measurement by calibration.

However as u_1, u_3, u_5 and u_6 are dependent on the temperature, electrolyte concentration and on the pH value itself, they may in some cases become "disruptive potentials". Reliable electrodes are designed in such a way that these potentials are very small. Any fluctuations in the potentials are consequently of little impact. Once the measuring chains are properly maintained and calibrated, the precision and reproducibility of the pH measurement is virtually unaffected.

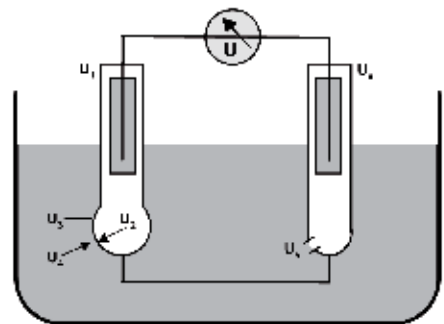


Fig. 15 Potentials in the measuring chain

Asymmetry potential

The cause of the asymmetry potential (u_3) is the difference between the two surfaces of the glass membrane. Their surface, shape and the distribution of the gel layer are not completely identical in each case. Even if the pH value on both sides of the membrane is exactly identical, the overall potential on the membrane is never exactly zero. However if the electrodes have been manufactured with close tolerances and have a well-designed gel layer, the asymmetry potential is only a few mV. This corresponds to a deviation of a few hundredths of a pH unit, which in principle can be corrected by the calibration of the electrode.

Diffusion potential

The diffusion potential can pose difficulties (u_5) [3]. This is the result of the difference in the speed of diffusion of different types of ions. If a hydrochloric acid solution adjoins with pure water, the H^+ and Cl^- - ions move into the pure water at different speeds. The H^+ ions diffuse significantly faster than the Cl^- - ions.

This creates a division between a positive and negative charge, in other words an electrical potential. With other types of ions, e.g. with K^+ and Cl^- - ions, the differences in diffusion speed are small, and consequently a much smaller diffusion potential is created.

At the diaphragm of the reference electrode there is also an interface between solutions of different ionic concentrations. Generally speaking, in electrodes with liquid electrolytes, some KCl electrolyte constantly flows through the diaphragm into the measurement solution due to the overpressure.

The ions in the measurement solution can therefore only diffuse against this KCl flow. As the electrolyte is constantly renewed by the outflow in the diaphragm, a greater diffusion potential of the measurement solution ions cannot form there.

The K^+ and Cl^- ions of the outflowing reference electrolyte diffuse between the ions of the measurement solutions directly in front of the diaphragm, thereby short-circuiting their diffusion potential.

If the measurement solution is hydrochloric acid, for example, the diffusion potential is greatly reduced by the KCl outflow. The diffusion in the opposite direction of K^+ ions that are also positively charged compensates to a large extent for the faster diffusion of the H^+ ions. Problems arise if, for example, the KCl outflow is too low due to a blocked diaphragm. The diffusion potential can then become so great that deviations of 0.1 pH units can arise. [8]

Chain voltage under ideal conditions

If electrodes with identical measurement and reference systems are used, their potentials u_1 and u_6 are virtually equal. As both potentials have opposite polarities, they cancel each other out. Potential u_3 can, as mentioned, be compensated for by calibration. U_5 can be kept negligibly small by ensuring sufficient KCl outflow. Under ideal conditions therefore, the chain voltage depends solely on the difference of the potentials between the inside of the membrane (u_2) and the outside (u_4).

$$U = u_2 - u_4 =$$

$$U_N \cdot (\text{pH}_{\text{inner}} - \text{pH}_{\text{of the measurement solution}})$$

Resistance ratios and polarization

The Nernst equation only applies when the processes at the electrodes are in chemical equilibrium. If too high a current flows through the measuring chain, it moves out of equilibrium and the measured voltage no longer matches the theoretical voltage calculated by the Nernst equation.

A measurable drop in voltage then occurs, the so-called "polarization" of the electrodes. Polarization can be caused by too low an internal resistance in the measuring device. Both disruptive effects, polarization and diffusion potential, can also play an unwelcome role in pH measurement!

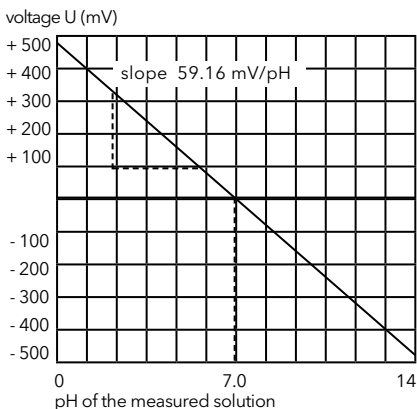


Fig. 16 Ideal line of the pH chain at 25 °C

Ideal characteristic curve of the measuring chain

The connection between the pH value of the measurement solution and the voltage (U) of the pH measuring chain can be shown in a U/pH diagram. Under ideal conditions, the voltage of the pH measuring chain follows a linear equation. The ideal characteristic curve is there a straight line in the U/pH diagram (Fig. 16). The incline of the ideal characteristic curve at 25 °C is 59.16 mV/pH, in accordance with the Nernst factor (U_N). The measurement voltage is therefore the product of U_N and the pH difference between the inner buffer and the measurement solution. If the pH value of the inner buffer is 7.00, then when measuring a solution of pH 7.00 at 25 °C the pH difference is also 0.00. The ideal characteristic curve in a measurement solution of pH 7.00 therefore moves through the 0 mV axis ($U = 59.16 (7.00 - 7.00) = 0.00$). If the measurement solution is at pH 13.00, the measurement voltage is -354.96 mV ($U = 59.16 (7.00 - 13.00)$). If the measurement solution is at pH 5.00, the measurement voltage is 118.32 mV ($U = 59.16 (7.00 - 5.00)$).

3.2 Characteristic curves of the pH measurement chain

Nonlinearity Acid and alkaline errors

Even measuring chains whose zero point and incline match the ideal characteristic curve will deviate from the linear course in strongly acidic and strongly basic ranges.

The so-called "acid error" causes greater pH values to be displayed at lower pH values and/or the voltage of the measuring chain is too negative (Fig. 17).

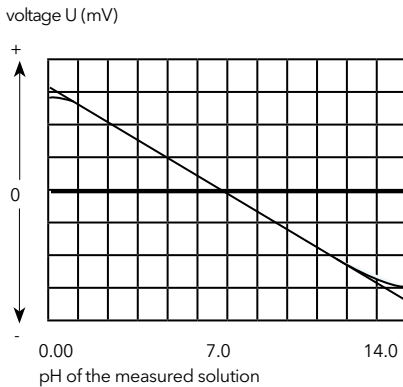


Fig. 17 Acid and alkaline errors

The cause of the acid error is the absorption of acid molecules into the gel layer and subsequent change in water activity [3].

The acid error in modern pH glasses is however in most cases negligible. The so-called alkaline error provides pH readings that are too low at high pH values or the measurement voltage is too positive. The cause of alkaline errors is the exchange of alkali ions between the gel layer and the measurement solution, which at values above pH 12 compete noticeably with the hydrogen ions. In modern membrane glasses, alkaline errors now only occur if the measurement solution at higher pH values contains large amounts of sodium or lithium ions.

Characteristic curve of actual pH measuring chains

Apart from acid and alkaline errors, the other ratios in actual measuring chains do not meet the theoretical requirements for the exact validity of the Nernst equation. Due to the non-negligible potentials u_1 , u_6 and u_3 , without calibration the zero point of the measuring chain is almost never exactly at the pH value of the inner buffer.

The slope of actual measuring chains also rarely corresponds exactly to the theoretical value of the Nernst factor. The zero point and slope of the characteristic curve of actual measuring chains therefore deviates to an extent from the ideal course. These deviations are compensated for by calibration. The position of the zero point and the slope of electrodes from SI Analytics which are properly stored are extremely stable over long periods of time. But even with good electrodes, it should be noted that they age, i.e. the zero point and the slope change due to storage and use.

Temperature dependence of the ideal characteristic curve

The voltage of the pH electrode changes with the temperature. This temperature dependence of the measurement voltage affects the Nernst factor (U_N) in particular. It varies between 54.20 mV/pH at 0°C and 74.04 mV/pH at 100°C. This change in the measuring chain slope caused by the temperature dependence of the Nernst factor is balanced out during measurement by so-called temperature compensation (cf. Fig. 18).

As pH measurement is a measurement of the activity of H^+ ions, and activity is a temperature-dependent thermodynamic value, pH values recorded at one temperature cannot therefore be converted to the pH value at another temperature by a simple calculation.

0 °C	= 54.20 mV/pH-unit
25 °C	= 59.16 mV/pH-unit
50 °C	= 64.12 mV/pH-unit
75 °C	= 69.08 mV/pH-unit
100 °C	= 74.04 mV/pH-unit

Fig. 18 Change in the Nernst factor with the temperature

Isotherms

In very worn electrodes, not only is the zero point not exactly at the pH value of the inner buffer, but even the position of the zero point is temperature dependent. In addition, the temperature dependence of the measuring chain slope does not exactly correspond to the temperature dependence of the Nernst factor (U_N). Consequently, if the voltage of a measuring chain is recorded at different temperatures, a different characteristic curve will be obtained for each temperature. These "isotherms" do not intersect with the ideal characteristic curve on the 0 mV axis, but at the so-called "isotherm intersection point". The isotherm intersection point therefore deviates noticeably from the zero point of the ideal characteristic curve (cf. Fig. 19).

3.3 Summary

The potential of the measuring chain consists of six individual potentials combined, with the asymmetry potential and the diffusion potential being of particular note. The asymmetry potential can be determined by calibration and the measurement assembly adjusted to the potential recorded.

The diffusion potential is more difficult. This builds up primarily on the diaphragm. It can be reduced by increasing the electrolyte flow at the diaphragm (e.g. using a platinum diaphragm).

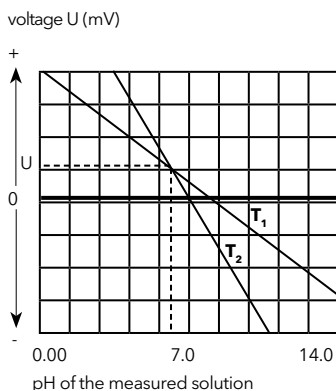


Fig. 19 Isotherms are the characteristic curves of actual measuring chains at various temperatures. They never intersect with the ideal zero point.

SECTION 4

BUFFER SOLUTIONS AND SAFETY IN pH MEASUREMENT

4.1 Definition of buffers

Buffers are the aqueous solutions whose pH remains virtually unaltered by the addition of small quantities of acids or bases. Buffer solutions are also capable of binding hydrogen ions with the addition of acids and releasing hydrogen ions with the addition of bases. The easiest way of understanding is to compare this to neutral water. If the same quantity of a strong acid is added to neutral water, to a weak acid and to a mixture of a weak acid and its salt, the pH value decreases very differently in each case.

Weak and strong buffers

The change in pH value with the addition of strong acids (e.g. HCl) to pure water directly corresponds to the amount of hydrogen ions added. The concentration of hydrogen ions increases in our example (Fig. 20) from 10^{-7} mol/l to 10^{-2} mol/l (corresponding to a Δ pH of 4.99).

With the addition of the strong acid to weakly dissociated acetic acid, its dissociation equilibrium is shifted and the concentration of hydrogen ions increases by a significantly smaller amount (this corresponds in our example to a change of just Δ pH 0.47). Likewise with the addition of a strong base (e.g. sodium hydroxide) to acetic acid, the decrease in the concentration of hydrogen ions due to the release of hydrogen ions through the dissociation of the acetic acid is less than when added to pure water. A buffer effect, occurs in the titration of acetic acid with sodium hydroxide.



tl	pH-value	after addition of 10ml 1nHCl	difference Δ pH
neutral water	pH 7.00	pH 2.01	Δ pH = 4.99
acetic acid 0.1n	pH 2.47	ph 2.00	Δ pH = 0.47
acetic acid 0.1n + 0.1m Na-Acetate	pH 4.75	pH 4.71	Δ pH = 0.04

Fig. 20 Buffer effect of different solutions and water with the addition of a strong acid

The buffer effect of mixtures of weak bases or weak acids with their salts is particularly strong, e.g. acetic acid with sodium acetate. If a strong acid is added to this buffer solution, its hydrogen ions will be absorbed by the acetate ions. On the other hand, if a strong base is added, its effect will be compensated for by the undissociated acetic acid. A simple formula can be derived from the law of mass action for the pH value of such a buffer solution of a weak acid and its salt. In this formula K_{HA} is the dissociation constant of the acid, $[HA]$ is its weighed concentration and $[salt]$ is the weighed salt concentration.

$$pH = -\lg K_{HA} + \lg \frac{[salt]}{[HA]}$$

This formula shows that the pH change is determined by the concentration ratio of salt and weak acid. Only when so much base or acid is added will this ratio change by a factor of 10 does the pH value change by a unit.

Buffer value and dilution effect

"Buffer value" and "dilution effect" specify how good the effect of a buffer solution is. The buffer value (β) is a measurement of the capacity of the buffer. It specifies how much the change in pH (dpH) will be for specified volumes (V_0) with the addition of a differential, gram-equivalent quantity (dn) of acid or base.

$$\beta = \frac{1}{V_0} \cdot \frac{dn}{dpH}$$

The dilution effect specifies by what amount (ΔpH) the pH value changes with the dilution of the buffer solution with pure water in the ratio 1:1.

Temperature dependence of the buffer

The pH values of buffer solutions are also temperature dependent. As a general rule, basic buffer solutions exhibit stronger temperature effects than acidic ones. This should not be overlooked during calibration. For example, if calibration is conducted with 0.01 m borax solution, an adjustment must be made to pH 9.18 at 25 °C, to pH 9.46 at 0 °C and pH 8.96 at 60 °C. Modern pH meters automatically adjust for the respective temperature profile once the buffer series used has been correctly set.

4.2 Standard buffers

Standard buffers in accordance with DIN 19266 are used for the calibration of pH measurements. The so-called technical buffers are governed by DIN 19267. DIN buffers are manufactured in accordance with DIN 19266 and can be traced back to primary or secondary reference material. The primary reference material (powder form) is manufactured by NIST (National Institute of Standards and Technology).

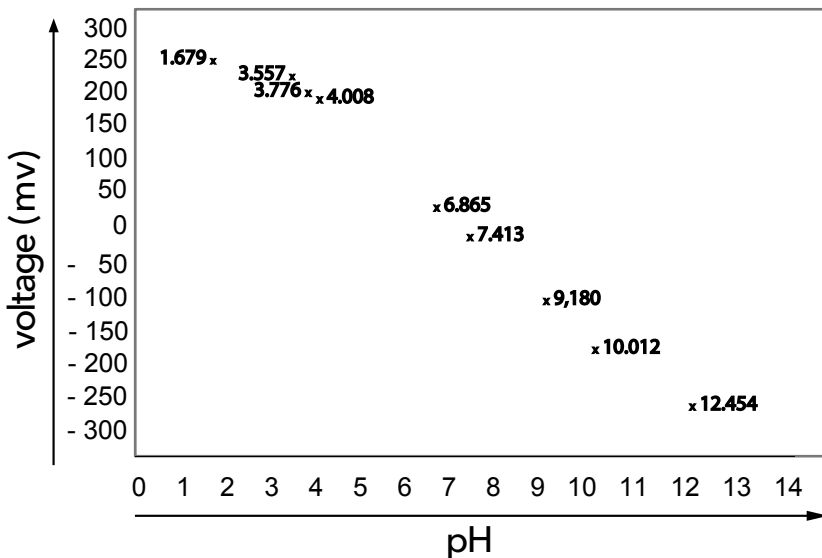


Fig. 21 DIN buffer solutions and their pH values at 25°C

The pH values of solutions should be very close to the theoretical pH values and be traceable to them. They are the basis of almost every practical pH measurement, because they represent the official reference system. The composition of these solutions is set by the NBS (National Bureau of Standards) and their pH values electrochemically determined.

The cells used for this purpose consist of a platinum/hydrogen and silver/silver chloride electrode. They are the pH values which most closely match the current thermodynamic definition of pH value and are fully traceable. They can be compared to a specification measured against the original meter in Paris.

Secondary reference material has an identical composition to primary reference material. It is produced exclusively by accredited manufacturers and the pH values are determined by an accredited laboratory (differential potentiometry as opposed to primary standard buffer solutions).

Technical buffer solutions are based on DIN 19267 and differ in several respects from DIN buffer solutions manufactured in accordance with DIN 19266.

They are often colored, so as not to be confused during every day use, are based on whole numbers and are more stable. The composition varies depending on the manufacturer.

Accordingly, the temperature responses of the buffers also vary from manufacturer to manufacturer. When using DIN buffers, these may be used regardless of manufacturer, as they are all based on an identical formula.

The values stored in the equipment in respect to technical buffers relate to a specific manufacturer. Use of other buffer solutions generally leads to errors in measurement.

In general, it should be noted which buffer has been set for the device and which one was actually used. This should also be done in the context of the reference temperature, as the pH value is not always given at 25 °C, but sometimes at 20 °C.

Referenz buffer solution	A	B	C	D	E	F	H	I
	Potassium- tetra- oxalate	Potassium- bitartrate	Potassium- hydrogen- phthalate	Phosphate (KH_2PO_4)	Phosphate (KH_2PO_4)	Borax	Potassium- hydrogen- citrate	Sodium- carbonate/ sodium- bi- carbonate
Molality mol kg^{-1}	0.05	saturated at 25°C	0.05	0.025 (KH_2PO_4) 0.025 (Na_2HPO_4)	0.009 (KH_2PO_4) 0.03 (Na_2HPO_4)	0.01	0.05	0.025 (Na_2CO_3) 0.025 (NaHCO_3)
PTB- label	PTB- 01-00	PTB- TA-00	PTB- PHT-00	PTB- PHOA-00	PTB- PHOB-00	PTB- BO-00B	PTB- CIT-00	PTB- CAR-00
Temperature °C	pH(pS)-values							
5	1.668	-	4.004	6.950	7.502	9.392	3.837	10.248
10	1.670	-	4.001	6.922	7.474	9.331	3.819	10.180
15	1.672	-	4.001	6.900	7.451	9.277	3.801	10.121
20	1.676	-	4.003	6.880	7.432	9.228	3.787	10.066
25	1.680	3.557	4.008	6.865	7.416	9.184	3.775	10.014
30	1.685	3.553	4.015	6.853	7.405	9.144	3.766	9.970
37	1.694	3.550	4.028	6.841	7.393	9.095	3.757	9.911
40	1.697	3.549	4.036	6.837	7.389	9.076	3.754	9.892
45	1.704	3.544	4.049	6.834	7.386	9.046	3.751	9.856
50	1.712	3.548	4.064	6.833	7.384	9.018	3.748	9.830

pH(pS) values can differ in the measuring uncertainty $U(\text{pH}) = 0.005$ between charges. Therefore they are only with the calibration certificate e.g. from PTB for a certain charge valid.

Fig. 22 Examples of pH values of reference buffer solutions depending on the temperature (cf. DIN 19266 [9]: For a better understanding this non-official document has been translated to English from the official German version).

4.3 Calibration

Why calibrate?

The precision of the measurement stands and falls with the calibration/adjustment.

Adjustment is the setting of the pH meter to the measuring chain data gathered through calibration (slope and zero point). During adjustment, the electrode functions obtained during calibration are balanced out. The current slope and zero point are identified from the measuring chain voltages in the reference solutions. However as the word calibration is more commonly used in everyday speech, it will also be used here. The pH meter must be aligned with the pH electrodes used, as the design, type of electrolyte (gel or liquid electrolyte) or the diaphragm (cf. section 2), the zero point and slope may differ from electrode to electrode. These properties also depend on the age and level of use of the electrode.

Precise and reproducible measurements are only possible if calibration has been carried out. How often it is necessary to calibrate depends on a number of factors. Firstly, the type and composition of the probe and secondly the frequency of measurement. Whether a calibration is necessary can easily be checked by recording the measurement value in a buffer solution. Some applications require daily calibration of the measuring equipment, such as measurement in low-ion water. For other applications, weekly or even monthly calibration may suffice. It is therefore not possible to give an exact specification. The principle on which calibration is based will be briefly explained below.

The slope of the electrode signifies the potential difference in mV when two pH values with a difference of one pH unit are considered. So in an ideal situation the pH value of a solution with pH 4 should provide a mV value which differs by 59.16 mV from a value recorded at pH 5 and 25° C. The slope is then stated to be 59.16 mV/pH. The zero point of the calibration line is the intersection of the lines with the y-axis and in an ideal situation should be pH 7.

Fig. 23 shows a graph of the calibration lines of an electrode exhibiting ideal behavior.

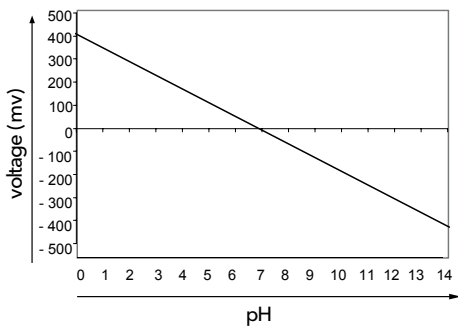


Fig. 23 Ideal characteristic curve

Calibration procedure

For analog measurement devices, the procedure is as follows:

- *Bring both measurement buffers to the same temperature*
- *Fill a small container with the measurement buffer*
- *Remove the protective cap from the electrode and open the fill opening, so that electrolyte can flow out of the diaphragm. For gel electrodes this is not necessary.*
- *Rinse the electrode briefly with distilled water.*
- *Measure the temperature of the calibration buffer.*
- *Adjust the temperature on the temperature regulator of the equipment. This is not necessary for measuring devices with automatic temperature compensation, when a measuring chain with a temperature sensor is being used.*
- *Immerse the electrode in the buffer and ensure that the whole of the tip of the electrode and the diaphragm is immersed in the solution.*

- *If after approximately 30 seconds there is no further change in the pH value, the pH value displayed is adjusted to the nominal pH value of the buffer solution using the zero point adjustment knob. Care is necessary, as pH values are temperature dependent and so must be adjusted to the pH value valid at the respective temperature.*
- *Remove the buffer from the electrode and rinse with distilled water and immerse in the second buffer.*
- *If after approximately 30 seconds there is no further change in the pH value, the pH value displayed is adjusted to the nominal pH value of the buffer solution using the slope adjustment knob.*
- *As a precaution, the buffer is checked again for the zero point, as the turning of the slope and zero point adjustment knobs on analog equipment can have an effect on readings.*

Modern pH meters are microprocessor controlled. The calibration procedure is in principle the same as with analog measurement equipment, however

the processes are begun and confirmed using buttons. The adjustment is calculated inside the device. It is not necessary to carry out the calibration procedure a second time. For safety, after calibration the value of a used or additional buffer can be measured.

The temperature dependences of the pH value of the buffers are stored in modern equipment and are calculated directly.

By using new ID electrodes, the electrodes can be recognized directly by the device. The calibration values recorded for this electrode are also stored directly in the electrode and not the device, so that when it is used the values can be referred to again. Therefore, when using several ID electrodes on the one device or one ID electrode on several devices with ID recognition, it is not necessary to recalibrate every time if these electrodes/devices are being exchanged.

Single point calibration

With pH measuring equipment, calibration may be finished after one buffer. This determines the zero point. For the slope, the theoretical slope is used. Slope = Nernst slop (- 59.16 mV/pH at 25 °C).

The range of use of single-point calibration is limited. It is possible to measure only within a range of + / - 0.5 pH units from the pH of the buffer solution used. The measurement probe should have the same properties as the buffer solution. The pH value obtained may be used to compare to previously obtained measurement results, but is not an absolute value.

Two-point calibration

With two-point calibration, asymmetry and slope are identified, thereby determining the slope and axis intercept of linear calibration lines. The pH value of the buffer used should ideally differ by two pH units. Basic buffers should not be used as their pH value changes by absorbing CO₂. For routine measurements the use of DIN buffer solutions with pH = 6.865 and pH = 4.008 is recommended.

Multi-point calibration

With multi-point calibration, the main difference to two-point calibration is that the calibration line is calculated by means of a linear regression.

The difference between the pH values of the reference buffer solutions should be $\Delta \text{pH} > 0.5$ if possible. The coefficient of determination (correlation coefficient) R^2 is used to assess this. R^2 is a dimensionless measure and can accept values between -1 and +1. At -1 there is a negative relationship between the values calculated, at +1 there is a positive relationship. The nearer the value is to 1, the better the match with the linear assumption.

4.4 Working with buffer solutions

When using buffer solutions, there are a few points to observe:

- *Has it reached its expiration date?*
- *Buffer solutions must not be reused*

- *Avoid basic buffer solutions. If this type of buffer solution is in contact with the air, a gas exchange takes place, which also affects the carbon dioxide in the air. In aqueous solutions, carbon dioxide is in equilibrium with carbonic acid. This has little effect on neutral and acidic buffers. In basic buffers however a neutralization reaction occurs, meaning that carbon dioxide is constantly removed from the air. As a result, the pH value of the buffer changes.*

- *If alkaline buffers are nonetheless used for calibration, a sealed container should be used and the storage bottle should only be opened briefly.*

- *Small container sizes are also recommended.*

- *Never immerse the measuring chain in the buffer solution containers, always take out the volumes required. That is the easiest way to avoid contamination!*

- *Always close the container immediately after use (carbon dioxide, contamination by dust particles!)*

- *Never pour quantities removed back into the container. Risk of contamination!*

- *Use opened containers of buffer as soon as possible (neutral and acidic buffers within the next month, basic buffers within the next few days).*

- *Use appropriate container sizes!*

Many of these problems can be avoided by using buffer vials produced by SI Analytics. If the measuring equipment displays a calibration error during calibration, this is frequently caused by a worn measuring chain. If the error message is not resolved by a new measuring chain, the pH meter is rarely defective. Usually the buffer solution used has become contaminated or too old. This applies especially to buffers with basic pH values. The pH is ultimately shifted. If a buffer of pH 10 is left open overnight, its pH value the next morning will be clearly lower than 10.

pH handbook

Figure 24 shows the actual pH values of an opened **technical buffer solution** (pH 10) and a **standard buffer solution** (pH 9). Over the course of 12 hours the pH of the pH 10 buffer changes by 0.22 pH units and that of the pH 9 buffer by 0.02 pH units. If buffers of 6.87 and 4.01 are used for calibration, pH values in the basic range can also be identified very well, as the linearity of the electrodes is excellent.

However there should first be a brief check of the pH value of the basic buffer solution of 9.18, in order to rule out any measurement errors. pH measurements are required in many applications and accordingly have different requirements. But in general the requirements of the response time and the stability of the signal are greater the more pure and clean the measuring medium is. With contaminated media the response time and stability is generally very good, although the service life of the electrode is very short. In these cases the frequency of calibration must also be increased.

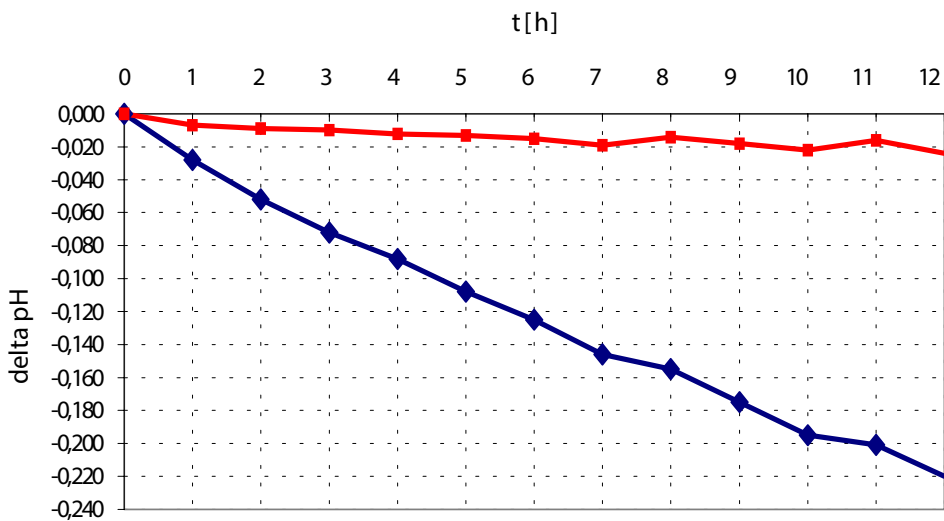


Fig. 24 Change in buffer solutions over time due to entry of CO_2

4.5 Measurement uncertainty

Measuring pH values

To take a measurement, the calibrated measuring chain is rinsed with distilled water and immersed in a sufficient quantity of the test material. It is important to ensure that no calibration buffer solution is introduced during the measurement. This would lead to serious measurement errors. When using a measuring chain without a temperature sensor, the temperature should be set on the pH measurement device. The measurement value should only be read when the display stops changing. The measuring time must in any event be longer than the response time. For intact measuring chains the response time should be about 30 seconds. If after 1 minute a stable measurement value cannot be read, this may point to a defective measuring chain.

A certain amount of time is required for the temperatures of the measuring chain and the test material to balance. If the temperature difference is a few degrees, the adjustment should take approximately 1 minute.

Greater differences in temperature may require some minutes to balance.

For high-precision measurements, care should be taken to ensure that the calibration temperature and measurement temperature are similar, as otherwise significant errors can occur due to the temperature dependence of the pH measurement.

Measurement uncertainty

Different measurement applications have different measurement uncertainties and consequently there are different requirements to ensure reliable measurement. These requirements include not only the equipment but also the type of calibration, buffer solutions used, electrodes used etc. Different measurement uncertainties are likewise associated with the different materials used, meaning that a general statement cannot be made as to how reproducible or difficult a measurement is. One reproducibility may be significantly better, as only random errors are identified. A systematic error can always provide easily reproducible measurement values which do not always match with reality.

pH handbook

Some examples should briefly explain what the possibilities of measurement uncertainty are and how to estimate these (Fig. 25). The term measurement uncertainty is defined in DIN V ENV 13005 [10]

Measurement uncertainty describes a parameter which is accorded to the measurement result and which characterizes the dispersion of the values.

The major factors affecting measurement uncertainty depend on the buffer solutions, measurement equipment and measurement solution used. Temperature plays a significant role in measurement uncertainty (Fig. 26).

Firstly, it affects the properties of the measuring chain during calibration and the adjustment of the measurement device, and secondly it affects the actual measurement itself.

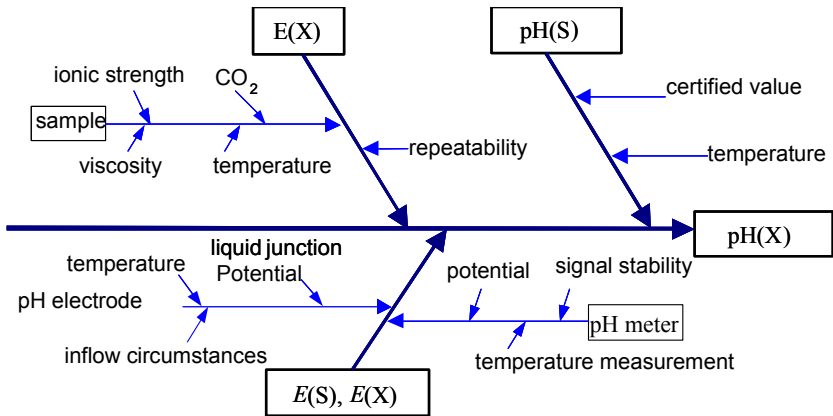
		Standard uncertainty of the components of U(k=2)			
component of the pH-measurement unit	dimension/ unit	0.3	0.1	0.03	< 0.03
referent solution	pH	0.05	0.03	0.01	< 0.01
pH-meter	pH	0.01	0.01	0.001	0.001
pH-meter	mV	1	1	0.1	0.1
pH-electrode, slope (25°C)	mV/pH	> 57	> 58	> 58	> 58.5
pH-electrode, setting time to $dE/dt < 0,1V/m/10s$	s	< 90	< 60	< 30	< 30
pH-electrode, stirring sensitivity	Δ mV	< 2	< 1	< 0.5	< 0.3
pH-electrode, repeatability	Δ mV	< 2	< 1	< 0.4	< 0.2
temperature measurement	°C	< 1	< 0.5	< 0.5	< 0.2
temperature consistency during calibration and measurement	°C	< 2	< 1	< 0.5	< 0.3

Fig. 25 Standard uncertainty in accordance with DIN 19268 [11]

The table shows the different uncertainties for the different components of the measuring equipment. If the overall calculated error is intended to be no more than 0.03 pH, then the reference solution must have an accuracy of +/-0.01 pH, the pH meter +/- 0.001 pH or +/- 0.1 mV, the electrode slope better than 58 mV/pH etc.

If the calibration and measurement temperature are different, the measurement device will only be adjusted to the slope of the calibration lines using the temperature dependence of the Nernst potential. There will be no adjustment for asymmetry. However temperature compensation is only possible if the temperature is disclosed to the measurement device. This is done either by using an integrated temperature sensor inside the pH electrode or

by manually inputting the temperature to the pH meter. If the temperature is manually entered, it must be recorded beforehand using a temperature sensor (thermometer, electric temperature sensor). These measurement devices have varying measurement uncertainty, however, which also influences the overall measurement uncertainty. The maximum achievable uncertainty is with the use of technical buffer solutions at 0.1 pH units.



- pH(S) pH value of the buffer solutions used for calibration
- pH(X) pH value of the sample solution
- E(S) potential of the buffer solution
- E(X) potential of the sample solution

Fig. 26 Components of measurement uncertainty

The stability control (drift control) function of the measurement device checks the stability of the measurement signal. The measurement signal is accepted as stable when the drift is < 0.02 pH units within 15 seconds. The stability has a significant effect on the reproducibility of the measurement value. In addition, the measuring chain must be adapted to the application. There are many different measuring chains which due to their design, the diaphragm used or the type of pH glass used can be used in a variety of different applications.

4.6 Summary

Buffers are solutions which can stabilize the pH value even with the addition of acids/bases. This effect is particularly pronounced with buffer mixtures of weak acids/bases and their salts e.g. acetic acid/acetate. The pH value of the buffer is temperature dependent. At this point, calibration is very important.

The buffer solutions are the basis of practical pH measurement, as they serve to calibrate the pH measurement unit and thereby match the measurement unit to the pH measuring chain used. In order to achieve the greatest possible measurement certainty, buffer solutions which meet DIN 19266 should be used, as these provide state of the art levels of certainty in calibration.

Temperature has a decisive influence on pH measurement. It is not possible to measure any more precisely than the precision of the buffer solutions used. Only the user can identify the appropriate time intervals for calibration.

SECTION 5

MEASURING EQUIPMENT AND MEASURING SET-UP

5.1 Function of the pH meter

Task of the measuring equipment

The pH measuring equipment must translate the voltage produced by the electrodes used into a pH value. This means that the measuring equipment must be adapted to the particular pH measuring chain used. In principle it is unimportant whether the display is analog with a dial instrument or digital with an LED or LCD. In certain circumstances the readability and precision of reading may be better with a digital display. What does make a significant difference, however, is whether the measurement voltage is processed by analog or digital means.

Why calibrate?

The necessity for calibration can be seen from the difference between the actual characteristic curve of the pH electrodes and the ideal characteristic curve. If the pH value displayed by the

measuring device must match the actual pH value of the measurement solution, the amplifier electronics of the measuring equipment must fulfill two conditions:

The electrical zero point and the amplification factor must be adjusted to the zero point and the slope of the characteristic curve of the respective pH measuring chain. For this calibration of the measurement electronics, a calibration buffer of a known pH value is used. After this calibration the electrode characteristics are adapted/adjusted.

Functional principle of the analog pH meter

Analog pH meters have a high-resistance amplifier, the characteristics of which can be adjusted with three potentiometers (variable resistances) to the characteristic curve of the measuring chain: for the zero point, the slope and the temperature compensation. With the "zero point potentiometer", the electrical zero point of the amplifier electronics is adjusted to the zero point of the measuring chain.

With the "slope potentiometer", the amplification factor of the amplifier is modified so that it matches the slope of the measuring chain.

With the "temperature potentiometer" the amplification factor is modified in accordance with the temperature-related change in the Nernst factor (U_N). In addition to this temperature compensation, a temperature-dependent resistance (e.g. Pt 100 or Pt 1000) with a corresponding adjustment may also be directly incorporated into the amplification circuit. This allows temperature compensation to take place fully automatically. A requirement for this is that the temperature of the measurement solution can be measured simultaneously with the pH value (Fig. 27).

Functional principle of the pH meter microprocessor

Modern microprocessors are designed with digital electronics. After a high-resistance input amplifier, there is an AD converter, which converts the analog measurement voltage to a digital value. The microprocessor sets off this digitized measurement voltage against the values for calibration and temperature compensation (also digitized). The result is then relayed to the digital display. While the amplifier is still "turned" on analog measuring equipment, the internal calibration of the microprocessor of the pH meter is completely different. The microcomputer carries out the calculation: the pH values of common calibration buffers including their temperature dependences are stored in it. Apart from the button to be pressed to carry out the calibration, the microprocessor device carries out the adjustment to the measuring chain automatically.

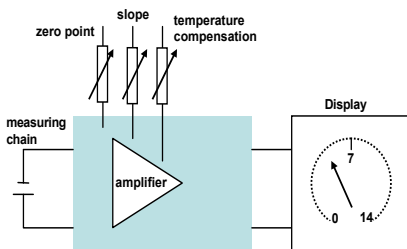


Fig. 27 Functional principle of the analog pH meter

The microcomputer calculates the course of the actual characteristic curve from the voltages of the measuring chain in the calibration buffers used, and compares these mathematically with the ideal characteristic curve which is stored in the form of the calibration buffer values.

During calibration the microprocessor identifies the typical difference between the ideal and actual course of the characteristic curve for the measuring chain used and offsets this automatically as a correction value during measurement. The adjustment to the measuring chain in a pH meter microprocessor is therefore not carried out electrically, but mathematically (Fig. 28).

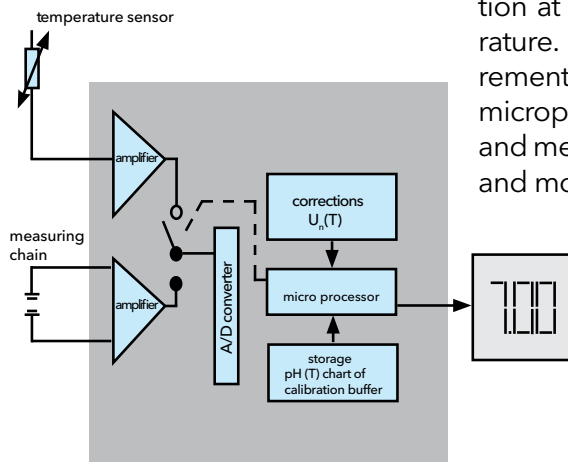


Fig. 28 Functional principle of the microprocessor pH meter

The microprocessor functions in exactly the same way for temperature compensation. It offsets the stored temperature dependence of the Nernst factor. In addition it should always be remembered that the microprocessor cannot take into account non-ideal temperature dependence which deviates from the Nernst equation in the characteristic curve, or disruptive potentials (cf. section 3). Therefore the disruptive potentials should be kept as small as possible through appropriate measuring conditions, even when working with a microprocessor based pH meter.

The deviation of the actual isotherms from their ideal course is best accounted for by calibration at the measurement temperature. Only when these requirements are fulfilled does the microprocessor make calibration and measurement quicker, easier and more certain.

5.2 The measuring circuit

Resistance ratios in the measuring circuit

The glass membrane of the measurement electrode has the greatest electrical resistance in the measuring chain at approximately 100 to 400 M Ω at 25 °C. For precise measurements, however, the chain voltage must not drop off at the electrode, but must be fully present at the measuring equipment. The input resistance of the pH measuring device must therefore be significantly higher than the resistance of the glass membrane. Modern pH measuring equipment has an input resistance of $> 10^{12} \Omega$. A guide value for pH measurement is that the input resistance of the measuring equipment should be at least 1,000 times greater than the resistance of the glass membrane. At a glass membrane resistance of e.g. 100 M Ω = 0.1 G Ω , the input resistance of the measuring equipment is approximately 10,000 times greater.

Modern pH meters therefore have more than adequate reserves. If this requirement is compared with the input resistance of modern voltmeters of approxi-

mately 10 M Ω , it is clear that connecting a pH glass electrode to such a measuring device would almost cause a short-circuit!

The electrical resistance of the measurement solution depends on its ion content. Chemically pure water has an extremely high resistance. However as long as there is not too great a distance between the diaphragm and the glass membrane as well as a sufficient KCl outflow, the measurement error caused by this, even in low-ion liquids, is less than 0.01 pH units. The diaphragm of a typical reference electrode has a resistance of up to 5 K Ω = $5 \cdot 10^3 \Omega$. When using glass electrodes with relatively low resistance and pH measuring equipment with a resistance greater than $>10^{12}$, the voltage drop in normal cases is negligible.

Fig. 29 shows a schematic representation of the resistances in the complete measuring circuit of electrode and measuring equipment.

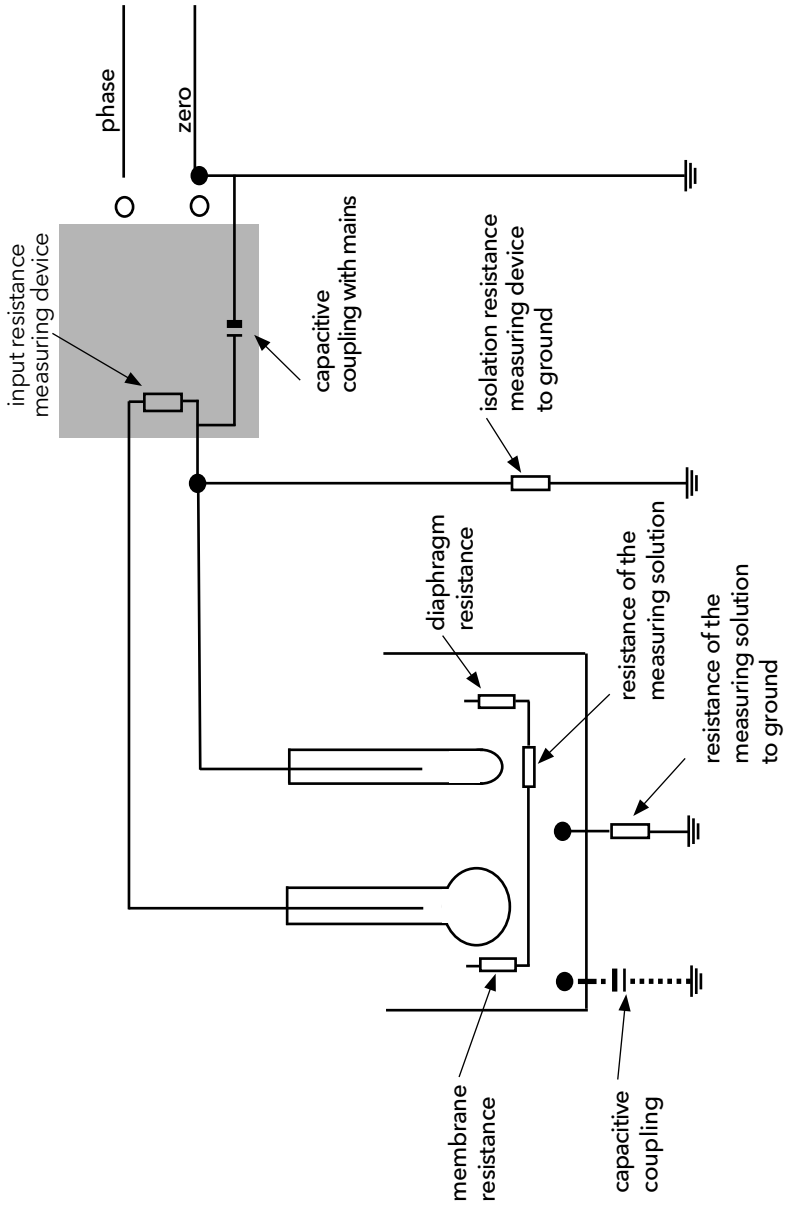


Fig. 29 Resistance ratios in the measurement circuit

Temperature dependence of the membrane resistance

The relatively strong temperature dependence of the membrane resistance must be taken into account. As an ion conductor, the resistance of glass reduces at higher temperatures and increases at lower temperatures. At 0 °C for example, the resistances of the glass membrane is approximately 10 times greater than at 25 °C.

Grounding

Closely related to the resistance ratios in the measuring circuit is the electromagnetic shielding and grounding.

Ideally, both the resistance of the measuring equipment and the resistance of the test material to ground would be limitless. For measurements in industrial plants, the test material is normally grounded using pipelines. If the measuring equipment is grounded in this way, significant measurement errors can occur due to the formation of a ground loop. Grounding the reference electrode line can even lead to a short circuit, which sooner or later can destroy the reference electrode.

Therefore if the measuring circuit is grounded via the test material, it must be galvanically separated from the actual measuring equipment by an isolation amplifier.

Shielding

Alternating currents can flow into the measuring circuit by capacitive or inductive coupling of the measurement lines with the grid or directly by irradiation of the test material (e.g. through a magnetic stirrer or a hot plate)

These alternating currents lead to a measurable proportion of direct current and unstable displays. The measurement errors thereby caused may be in the order of a few 100ths of a pH unit. In case of doubt, measurements must be taken without mains power, magnetic stirrer and hot plate, with a battery-operated or rechargeable pH meter. The high-resistance glass electrode acts as an antenna for stray electromagnetic fields of all kinds. Therefore it must be carefully shielded along with the associated measurement line.

Under no circumstances may the shielding be interrupted with "temporary fixes" or repairs.

Cables and plug contacts

As a result of the above, there are significant requirements on cables and plug contacts for pH measurement! The cables must be well shielded and short. If cables are connected on an ad hoc basis, there is a risk of undesired short circuits or interruptions to the shielding. It is therefore always recommended to use the original cables with the original plug connections of the manufacturer.

With longer cables, e.g. in industrial applications, there is a high risk of interference along the cable. Due to the high resistance and large capacity of longer cables, the response times during measurement are also unusually long. This effect is difficult to distinguish from errors in the electrodes. With longer measuring cables, an impedance converter should therefore be positioned directly behind the measuring chain.

Some of the SI Analytics electrodes are supplied with fixed-sealed connection cables. However many feature a plug-in head system to connect to the connection cable. The plug-in heads of the electrodes and the cables

must be of high quality to ensure reliable pH measurements. Mechanically loose connections, contact resistance due to corrosion, leakage currents from moisture etc. can not only cause errors in measurement but also destroy the electrode.

The original plug-in head system from SI Analytics prevents these errors. The contacts are gold-plated and corrosion resistant. The plug connection between the cable and electrode is mechanically secured by a screw connection and the screw connection is sealed against moisture by an O-ring. The electrical shield is seamlessly integrated into the plug-in head. The isolation from the inner contact consists of extremely water repellent PTFE.

5.3 Summary

Modern measuring equipment is microprocessor controlled. The input resistance of the measuring equipment should be approximately 10,000 times higher than the membrane resistance of the pH electrode. In the measuring equipment, the voltage value given by the measuring chain is converted to a pH value using the values obtained during calibration (zero point and slope).

SECTION 6

PRACTICAL pH MEASUREMENT

6.1 pH measurement in various applications

As previously mentioned, there are different requirements for different applications. The measurement requirements for waste water are clearly lower than those for the measurement of drinking water. There is essentially one reason for this: the pH value in strongly buffered solutions is easier to determine than in less buffered, low-ion media.

Some general points should be set out in advance:

1. The measuring chain used must be suitable for the application in question.
2. Unless otherwise specified, the test containers and calibration containers should be rinsed with the buffer solution and samples respectively.

3. Samples should not be transported and should be measured on location. If this cannot be avoided, the sample containers should be filled right up to the top, leaving no air.

4. Measurement should be carried out as quickly as possible, particularly with biological samples. By selecting the appropriate pH membrane glass and diaphragm, a selection for the application can be made in advance.

In the electrodes from SI Analytics there are four different types of membrane glass available.

A-glass has a fast response time in drinking, domestic and waste water. It is used in general applications and in low-ion media.

L-glass can be used at low temperatures and for general applications.

H-glass is well suited to high temperatures, in the acidic and alkaline range, and in high concentrations of sodium ions.

S-glass is particularly suitable for hot alkaline media and is therefore primarily used in process electrodes.

Measurements in beverages

For carbonated beverages (e.g. lemonade, beer) the carbon dioxide must first be expelled. To do this, the beverage is shaken in a closed container, vented at intervals and repeated until there is no more overpressure. It is then filtered through a fluted filter.

Our electrode recommendation
A7780, N62 or an electrode from the BlueLine 11 range.

Measurements in water-soluble paint

Gel measuring chains are not suitable for water-soluble paints, as they are difficult to clean. The ideal measuring chains have a high electrolyte outflow and an easy-to-clean diaphragm. Therefore measuring chains with a ground-joint diaphragm should be used. Depending on the type of sample, it may be useful to dilute the sample with distilled water. The immersion depth of the measuring chain should also be kept constant. The reference electrolyte solution should always be filled to the maximum, in order to avoid penetration of paint into the measuring chain due to the hydrostatic pressure.

Our electrode recommendation
ScienceLine range e.g. A164 or N64

Measurements in ground water, tap water, mineral and drinking water

Depending on the conductivity, it may be useful to take the measurement in the absence of air. Depending on the original and regional soil conditions, the buffer content of the sample may be very low. Calibration is conducted with buffer solutions of pH 6.87 and pH 4.01 or pH 9.18.

Our electrode recommendation
ScienceLine range e.g. N64 or N62

Measurements in low-ion spring water and rainwater

The sample bottle must be rinsed well. Ideally the measurement should be taken mid-flow. If this is not possible, the measurement must be taken in a closed container. The use of special measuring chains is usually necessary, ideally a measuring chain with a ground-joint or platinum diaphragm.

Our electrode recommendation
ScienceLine range e.g. N62 or N64 due to the increased demand for precision and the difficulty of the application

Measuring as a means of testing equipment

In contrast to the applications listed above, DIN buffer solutions must be used for calibration. Basic samples must be measured in the absence of air. The difference between the measurement temperature and the calibration temperature must not exceed 0.1 °C. The accessible measurement range is between 1.68 and 12.45, in accordance with the pH values of the DIN buffer solutions.

Our electrode recommendation
ScienceLine range e.g. N64 or N62

Strongly acidic solutions

For measurements in solutions with a pH value of less than pH 1, the acid error may occur, i.e. the pH values measured may be too great. In the acidic range there is also a risk of corrosion of the glass membrane by fluoride ions and phosphate ions, particularly at high temperatures.

Any possible changes in the membrane due to long-term measurement in the strongly-acidic range can often be reversed by thorough rinsing of the electrode between measurements.

Our electrode recommendation
N62 or IL-pH-A120 MF.

In internal tests, electrodes with A-glass have proven more resistant against small quantities of fluorides.

Strongly basic solutions

In the range above pH 11, the gel layer is rapidly changed or even destroyed, particularly at high temperatures. This causes strong asymmetry potentials and slows the response time. If the basic solutions contain sodium or lithium ions, then the so-called alkaline error may occur, i.e. the measurement will provide pH values which are actually too low. To keep these errors to a minimum, glass electrodes whose membrane glass has been optimized for the basic range are used (e.g. SI Analytics Type H or, for hot, basic solutions, Type S).

Our electrode recommendation
H62 or H64

High temperatures

For temperatures above 50 °C, a suitable discharge system for the electrodes must be ensured. Mercury chloride may only be used up to 50 °C. At temperatures above 100 °C, the electrolyte may boil. By the use of additives which raise the boiling point of the electrolytes, certain glass electrodes, reference electrodes and single-rod measuring chains can be used up to 110 °C. Pressurizing silver/silver chloride electrodes with overpressure in principle allows temperatures of up to 140 °C. However it should be noted that use at high temperatures shortens the service life of the electrodes.

Our electrode recommendation

SteamLine electrodes from the process product group.

Low temperatures

At low temperatures the resistance of the glass membrane increases, so that normal glass electrodes may only be used down to -5 °C. Below that, specific low temperature glass electrodes with membrane glass Type L are necessary.

Most reference electrodes and single-rod measuring chains are not suitable for use below +10 °C. At lower temperatures the KCl in the reference electrode crystallizes. These can be retrofitted by swapping the electrolytes when used at low temperatures (2.0 m KCl solution from 20 °C to -5 °C; in 1.5 m KCl with 50% glycerin up to -30 °C and/or pre-manufactured low-temperature electrolyte L 200 from SI Analytics.

Our electrode recommendation

Electrodes with L glass, e.g. L9180.

Extreme ion strengths

In very high-ion solutions, disruptive diffusion potentials can easily occur at the diaphragm. In very low-ion solutions the test material resistance is relatively high. Therefore diaphragms with a high outflow rate should be used, e.g. a ground-joint or platinum diaphragm.

Our electrode recommendation

ScienceLine range e.g. N64 or N62

Chemically-reactive solutions

Strongly basic, hydrofluoric acid and phosphoric acid-containing solutions attack the glass membrane, particularly at high temperatures. Regeneration by lengthy rinsing of the electrodes in 3 M KCl solution is recommended to a certain extent. Strongly oxidizing solutions (e.g. solutions with chlorine, bromine, iodine, chromate etc.) can also be problematic.

Platinum diaphragms cannot be used in them. Reference systems can also be destroyed. In such cases the reference electrode must be protected with an electrolyte key, or a double-electrolyte electrode used. Reference electrodes with the Ag/AgCl system are rarely used in sulfide-containing solutions. Chelating agents contaminate both Ag/AgCl and Hg/Hg₂Cl systems. In this case the use of a reference electrode with platinum diaphragm and an electrolyte key can help. In addition, the problems may be resolved by the use of the loLine electrodes, as the reference system of the loLine electrodes does not contain silver and therefore does not lead to the production of anti-soluble silver sulfide.

Our electrode recommendation
IL-pH-A120MF.

Suspensions and emulsions

In solutions with finely-distributed particles or substances with high viscosity, diaphragms can very easily become blocked. Diaphragms with high outflow rates which are not susceptible in this respect, such as the platinum diaphragm, can counteract this effect. After measurements in protein-containing solutions (milk, blood etc.) the diaphragm should be cleaned with a pepsin solution. Another option is the use of ground-joint diaphragms, which are easier to clean.

Our electrode recommendation
ScienceLine range e.g. N64 or N62

For use in the pharmaceutical sector, the loLine electrodes such as e.g. IL-pH-A120 MF are a good alternative.

Abrasive test material

Moving test material with solid, hard suspended matter can damage the surface of the glass electrode. This generally becomes noticeable due to longer response times.

This can be compensated for to a certain extent by frequent regeneration of the glass membrane and repeated calibration.

Our electrode recommendation
ScienceLine range N64

Solid test material

Solid test material, such as dough or soil samples, is not suitable for the determination of pH value without further adaptation. Compliance with precisely defined measurement specifications is crucial, so that the test results are comparable. Soil for example are suspended in a specified quantity of water, which must be in a precisely-defined ration to the mass of the test material. Then a suspension additive is used (e.g. CaCl_2 solution). The pH value is only measured after a certain settling period. In such cases the exact DIN standard must be followed (e.g. for soil samples DIN 19684).

Our electrode recommendation
ScienceLine range e.g. N64 or N62

6.2 pH measurement in an organic solution

Relevance of the transfer of the pH measurement to non-aqueous systems

The demands, particularly of the pharmaceutical industry, on the feasibility and precision of pH measurements and titrations in non-aqueous media for the purpose of process and quality control are constantly growing. These analyses are necessary as many of the substances do not dissolve in water.

It is therefore important to examine to what extent one can speak at all of a classic pH-measurement in such analyses and how the electrodes respond in such a medium. An optimum response time, that is as short as possible, is the basis for achieving a reproducible and precise analysis. That means as short a period as possible until a stable measurement value is obtained.

Theoretical considerations in the measurement of pH in non-aqueous systems

The main difference from classic pH measurement in aqueous solutions is that the pH value in accordance with DIN 19260 is only defined in aqueous media. [12]

Statements on the H^+ activity of the pH in water are therefore not applicable to other solvents. However similar observations for aqueous solvents may be made and the following equation can be employed:



Aprotic solvents such as e.g. DMSO or benzene do not dissociate in accordance with this equation and are not considered in this analysis. H_2Ly^+ is the protonated solvent molecule and is called the lyonium ion. Ly^- is the deprotonated solvent molecule and is called the lyate ion. Water-like solvents are autodissociative, which allows a pH scale for this solvent to be introduced. Fig. 30 provides some values for common solvents.

solvent	Lyonium-ion	Lyat-ion	pK _{Ly}
sulfuric acid	H ₃ SO ₄ ⁺	HSO ₄ ⁻	3.6
water	H ₃ O ⁺	OH ⁻	14.0
methanol	CH ₃ OH ₂ ⁺	CH ₃ O ⁻	16.7
ethanol	C ₂ H ₅ OH ₂ ⁺	C ₂ H ₅ O ⁻	19.1

Fig. 30 Common solvents with the resulting ions and the pK_{Ly} value at 25 °C [13]

The length of the pH scale is based on the pK_{Ly} value. In water it is 14 and for ammonia the scale is 22 units long. The neutral point of the scale is located at half of the pK_{Ly} value and describes the point at which the lyonium and lyate ion activities are equal. For water for example this is 7 at 25 °C.

As the determination of the pH value relates to a conventional aqueous pH scale, a pH scale must be created for each solvent to ensure correct measurements. Due to the lack of reference buffer solutions based on the particular solvent, it is therefore not possible to convert the actual measured mV value as reported by pH electrodes into a pH value.

If the pH electrode is calibrated with the usual aqueous buffer solutions and a pH measurement is then performed in an aqueous medium, this corresponds to the proverbial comparison of apples and oranges.

At this point it is necessary to distinguish between the two options of pH measurement and titration.

In titrations, what is considered is not the exact pH value, but a pH jump. The equivalence point is used to calculate the content. What matters is not the absolute pH- value, but only the consumption observed during the jump. In non-aqueous media, only a direct mV measurement can be taken. The main reason for non-comparability and conversion of the measured mV- value to a pH- value in non-aqueous solvents is that the activity of the hydrogen ions is not known. The measurement is made more difficult by the existence of a phase boundary voltage at the diaphragm during contact of the non-aqueous solution with the reference electrolyte of the electrode. [3]

In addition, the measurement is made more difficult by the low conductivity in organic solvents. The effects of lower conductivity in terms of very unstable measurement values can be felt even in pH measurements in distilled or demineralized water.

The electrodes and/or their membranes should therefore be conditioned, i.e. reformed, before measurement.

The resistance of the glass membrane in the corresponding solvent is thereby reduced ensuring a better and faster response time of the electrode. The electrode is already adjusted to the non-aqueous medium and a faster measurement can be taken. [3]

So for example before each measurement the electrode is first conditioned in water for 30 seconds and then in a buffer of pH 7.00 for 30 seconds, and subsequently in the non-aqueous medium such as isopropanol (100%) or isopropanol/toluene mixtures (50%: 50%).

Practical experiments in the isopropanol and isopropanol/toluene system

For measurement in non-aqueous solvents, the use of electrodes with reference electrolytes similar to the test medium is recommended. In order to investigate two common solvents in more detail and decide whether an electrolyte similar to the solvent would make measurement easier, or whether the usual 3 molar KCl solution could be used, the response times of two electrodes (N64, N6480eth) are analyzed in acidic or basic isopropanol and isopropanol/toluene mixtures. The only difference between the electrodes is the reference electrolytes. With the N6480eth, this consists of an ethanol solution saturated with LiCl, while the N64 is a 3 molar KCl solution.

The configuration of both electrodes is shown in Figure 31.



Fig. 31 N6480

Measurement of response time behavior depending on the water content of the sample

Measurements are conducted with a variety of water content proportions. For each measurement, 3 ml of aqueous 0.01 molar HCl or 0.01 molar NaOH is added to 30 ml of isopropanol/water or isopropanol/toluene mixtures. The ratios of the isopropanol/toluene mixtures in the measurement solutions were always 50% : 50%.

Figures 32 - 36 show the response time behavior of the single-rod measuring chains N64 and N6480eth depending on the content of water and at three different times (0 sec (directly after introduction of the electrode), after 30 seconds and after 60 seconds).

In the present case, no pH measurements can be taken in non-aqueous medium with a water content of less than 30%, only mV measurements. Only with a water content greater than this is it possible to speak of a classic pH measurement.

If the electrode is pretreated, i.e. reformed, a response time in a non-aqueous solvent of at least 30 seconds is to be expected. A reference electrolyte of a 3 molar KCl can also be used for the measurement.

These statements should be reviewed again by determining the mV curve for different water contents in non-aqueous solvents with both electrodes. The response times of N6480eth in pure aqueous systems and N64 in non-aqueous systems is 30 seconds. The situation is different for N64 in pure aqueous and N6480eth in a non-aqueous system. Here the response times are less than 10 seconds for N64 and approximately 10 seconds for N6480eth. In the isopropanol-toluene system the mV curves are more unstable.

Figures 36 - 39 show the results in this system with both electrodes and varying water contents.

This experiment shows that the water content is also important for the response behavior of the electrode, whether measured in HCl or NaOH. In pure non-aqueous solutions using HCl the N6480eth is preferred, as it has a faster response time (~ 40 seconds). A very unstable curve is produced with water content in the range of 30 - 40%. For measurement in acidic solutions, there is a fast adjustment to a stable measurement value due to the increased H^+ ion activity.

Measurements in the alkaline range are more difficult. A response time of approximately 80 seconds should be expected in pure non-aqueous systems using the N64. In pure aqueous systems a stable final value for the N64 will be reached after approximately 20 seconds. With the N6480eth, a response time of approximately 60 seconds for a pure non-aqueous system should be expected. In pure aqueous systems a waiting time of approximately 50 seconds should be expected for the N6480eth.

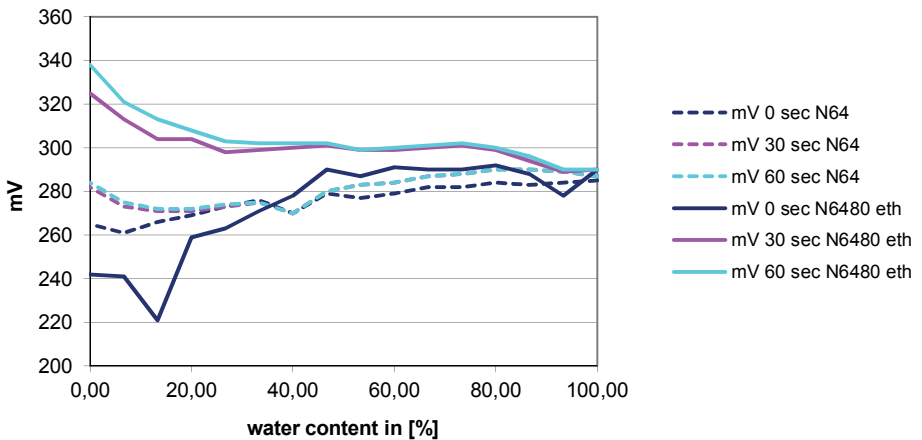


Fig. 32 mV curve of both electrodes in isopropanol/water mixtures, after the addition of HCl

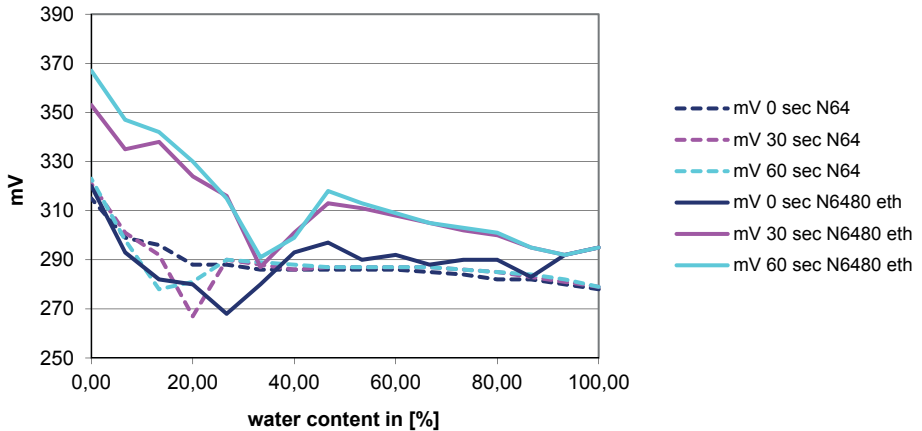


Fig. 33 mV curve of both electrodes in isopropanol/toluene mixtures, after the addition of HCl

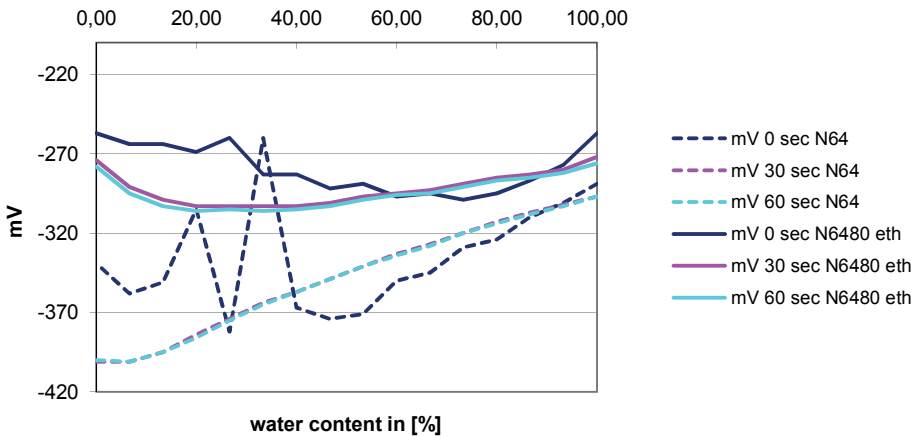


Fig. 34 mV curve of both electrodes depending on the water content in isopropanol/toluene mixtures, after the addition of HCl

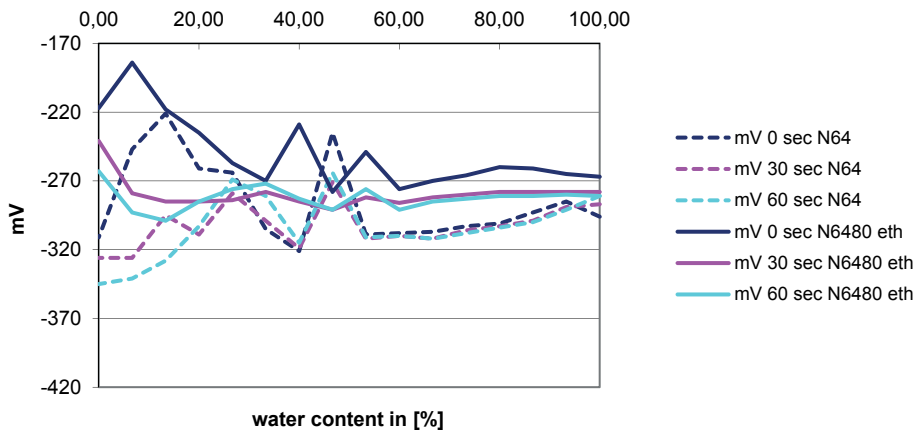


Fig. 35 mV curve of both electrodes in isopropanol/toluene mixtures, after the addition of NaOH

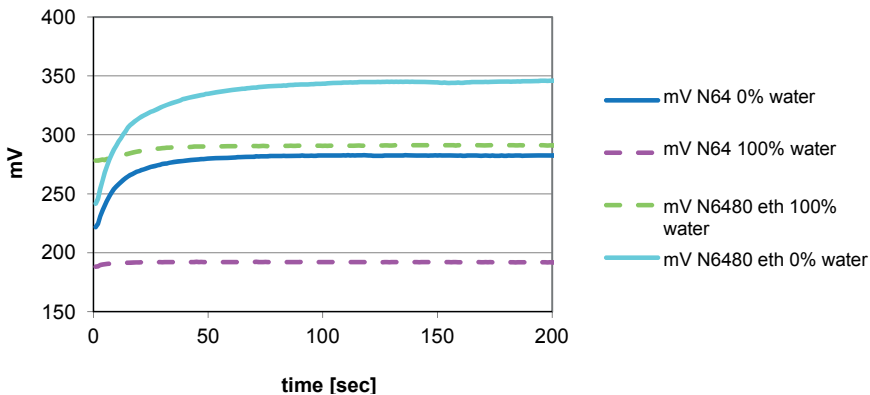


Fig. 36 mV curve of both electrodes depending on the water content in isopropanol/toluene mixtures, after the addition of HCl

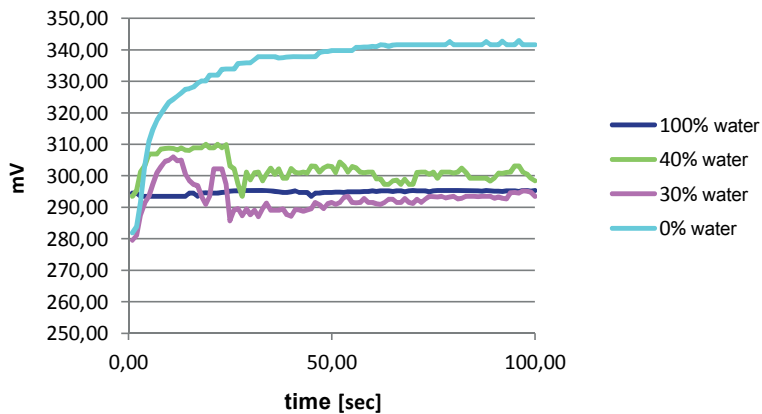


Fig. 37 mV curve of the N6480eth electrode in isopropanol/toluene mixtures, after the addition of HCl

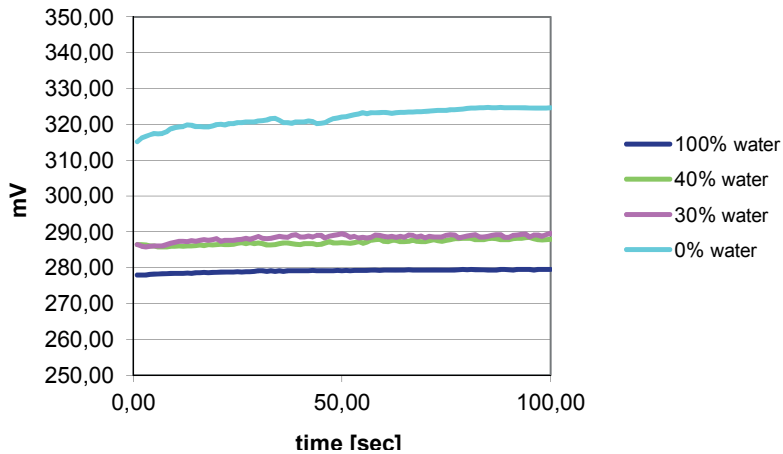


Fig. 38 mV curve of the N64 electrode in isopropanol/toluene mixtures, after the addition of HCl

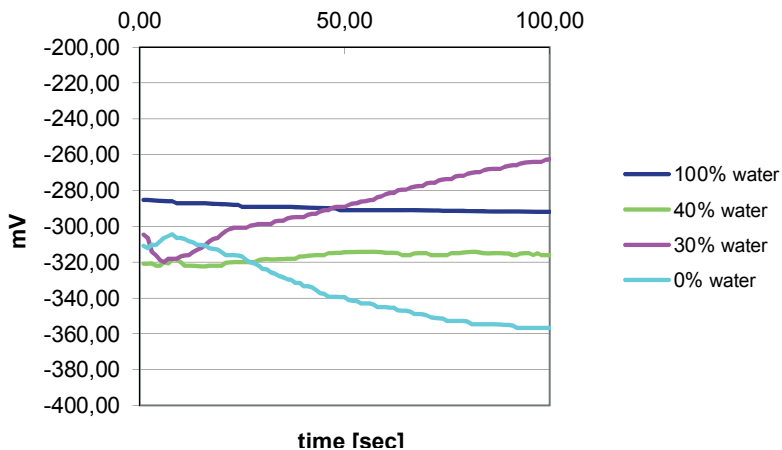


Fig. 39 mV curve of the N64 electrode in isopropanol/toluene mixtures, after the addition of NaOH

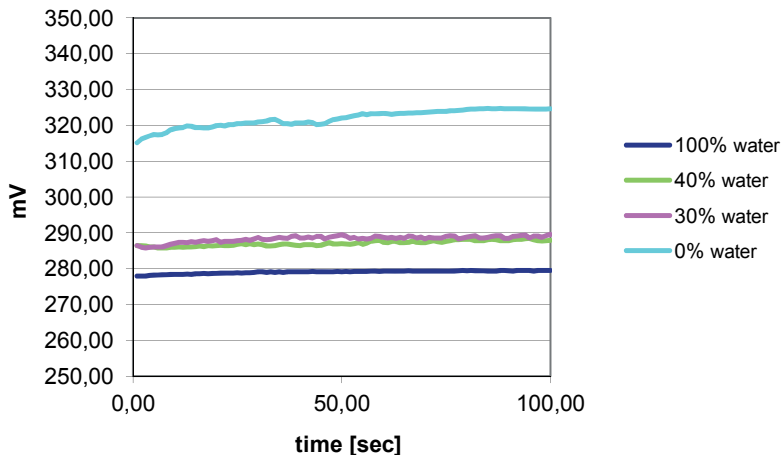


Fig. 40 mV curve of the N6480eth electrode in isopropanol/toluene mixtures, after the addition of NaOH

6.3 Summary

In the systems investigated here, no pH measurements can be taken in a non-aqueous medium with a water content of less than 30 %, only mV measurements.

Only with a water content greater than this is it possible to speak of a classic pH measurement. In the isopropanol/water system, a response time of 30 seconds should be expected, in the isopropanol/toluene system a response time of 60 seconds should be expected at 0 % water, even when the electrode has been pre-treated, (reformed).

A reference electrolyte of a 3 molar KCl can also be used in measurements with a water content of >30%. It can therefore be said that the water content of the sample and the H⁺ ion activity are the determining factors in the selection of the most suitable electrode.

Particular emphasis must be placed on the maintenance and care of electrodes, in order to optimize the useful life.

SECTION 7

RECOMMENDATIONS FOR USE, MAINTENANCE AND CARE OF ELECTRODES

7.1 Electrode recommendations

Due to the large range of electrodes we offer, the following table provides a few representative examples of the different measurement technologies and the recommended areas of use in each case.

Accordingly, the BlueLine 11 pH electrode is representative of the versions 12, 14, 15, 17, 18 and 19 pH. For the ScienceLine and IoLine pH electrodes, in the versions N62 and H62 as well as ILpHA120MF and ILpHH120MF it should be noted that these are also available with longer shaft lengths, which provide a faster and more stable measurement result under the same test conditions, as well as a longer service life for the electrodes.

The higher electrolyte column and the associated greater electrolyte outflow reduce undesired diffusion potentials at the diaphragm and rinse it clear. For some applications, other electrode recommendations may be advisable due to the specific test conditions, as even identical applications can vary significantly due to differences in concentrations or temperatures.

Please also take note of the resistance of the sensor material in respect to test medium.

pH handbook

Application area	Electrode series		pH measurement														ORP		Conductivity			
	toLine	BlueLine	ScienceLine	BlueLine	ScienceLine	BlueLine	ScienceLine	BlueLine	ScienceLine	BlueLine	ScienceLine	BlueLine	ScienceLine	BlueLine	ScienceLine	BlueLine	ScienceLine					
Sensor example	IL-pH-A120MF	IL-pH-H120MF	A 7780	H 62	H 64	L 32	L 8280	N 62	N 64	11 pH	22 pH	13 pH	Ag 6280	Pt 62	Pt 8280	31 RX	32 RX	LF 313 T NFCT	LF 413 T	LF 613 T	LF 713 T	
	Application																					
Chemistry	Etching and degreasing baths	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Bleach and dyeing solutions	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Cutting oil emulsions	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Cyanide detoxification	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Dispersion paint	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Emulsions, water-based	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Emulsions, partly water-based	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Paint/varnish, water-soluble	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Fixing bath	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Varnish, water-based	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Varnish, partly water-based	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Lye, extreme	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Oil/water-emulsions	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Organic percentile high	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Paper extract	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Acid, extreme	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Sulphide containing liquid	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Suspension, water-based	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Ink	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	Viscose samples	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Field measurements	Beck	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Ground water	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Lake water	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Seawater	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Rain water	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
Beverage production	Beer	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Fruit juice	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Vegetable juice	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Lemonades/soda	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Mineral water	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Juice	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Spirits	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
	Wine	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	

Application area	Electrode series	pH measurement										ORP		Conductivity											
		toLine	ScienceLine					BlueLine			ScienceLine	BlueLine	ScienceLine	Conductivity											
Sensor example		IL-pH-A120MF	IL-SP-pH-A	A 7780	N 1048 A	L 32	L 39	L 6880	L 8280	N 62	N 64	11 pH	22 pH	13 pH	21 pH	27 pH	Pt 62	Pt 6140	Pt 8280	31 RX	32 RX	LF 313 TNFTC	LF 413 T	LF 613 T	LF 713 T
Application																									
Cosmetics	Creme	■	■		■		■	■		■	■	■					■					■	■	■	
	Hair dye	■								■	■			■			■					■	■	■	
	Hair gel	■	■		■		■																■	■	
	Hair mousse	■																					■	■	
	Lotions	■																					■	■	
	Make-up	■																					■	■	
	Mouth wash	■																					■	■	
	Shaving cream	■																					■	■	
	Sun lotion	■																					■	■	
	Tooth paste	■	■				■	■															■	■	
Agriculture	Ground (extract/slug)	■		■					■														■	■	
	Fertilizer solution	■			■				■														■	■	
	Vegetables	■			■		■	■															■	■	
	Liquid manure	■		■		■			■														■	■	
	Fruit	■	■						■														■	■	
Food production	Bread/dough/pastry	■			■			■																	
	Vinegar	■		■																				■	■
	Grease	■																					■	■	
	Fish	■		■																			■	■	
	Meat	■		■				■															■	■	
	Honey	■		■				■															■	■	
	Margarine	■																					■	■	
	Coffee extract	■																					■	■	
	Jam/marmelade	■																					■	■	
	Mayonnaise	■																					■	■	
Dairy	Sausage	■																					■	■	
	Butter	■	■																				■	■	
	Yoghurt	■		■		■																	■	■	
	Cheese	■	■		■		■																■	■	
	Milk	■		■		■																	■	■	
Surface	Cream	■																					■	■	
	Skin																								
	Leather																								
	Paper																								
Textiles																									

pH handbook

Application area	Electrode series		pH measurement										ORP		Conductivity		
	IoLine	ScienceLine	ScienceLine					BlueLine					ScienceLine	BL*	ScienceLine		
Sensor example	IL-pH-A120MF IL-pH-H120MF IL-Micro-pH-A IL-SP-pH-A	A 157 A 7780 H 62 H 64 N 1048 A L 32 L 39 L 6880 L 8280 N 62 N 64 N 6000 A N 6003											PL 62 PL 6140 PL 8280 PL 5900 A	31 RX 32 RX	LF 213 T LF 313 T LF 313 T N/FC LF 413 T LF 613 T LF 713 T		
Application																	
Pharmacy, biology, biotechnology, medicine, microbiology	Agar-agar gel																
	Enzyme solution																
	Infusion solutions																
	Small vessels/sample quantity																
	Bacteria cultures																
	Gastric juice																
	NMR tubes																
	Precision measurement																
	Protein containing liquid																
	Serum																
	Tris puffer																
	Urine																
	Vials																
Technical	Cooling water																
	Lye, hot																
	Acid, hot																
Washing agents	Detergents																
	Disinfectant																
	Cleaning agent																
	Soap solution																
	Dishwashing liquid																
	Surfactant solution																
Water	Waste water, general																
	Aquarium water																
	Demineralization/ion exchanger																
	pH values, extreme																
	Media containing low ions																
	Boiler feed water																
	Condensate																
	Purity water																
	Salt solution																
	Drinking water																
Drops																	

* BL = BlueLine

7.2 Maintenance and care of the electrodes

Particular emphasis must be placed on the maintenance and care of electrodes in order to optimize useful life.

We can make the following recommendations with respect to handling and care:

- *If a watering cap is located above the membrane and diaphragm, it should be removed. It contains electrolyte solution L300 (potassium chloride solution 3 mol/l). The electrode is ready for measuring.*
- *Dry-stored electrodes are soaked for 24 hours in electrolyte solution.*
- *In the electrolyte space of the reference system, any missing potassium chloride solution should be refilled.*
- *The fill level of the electrolyte solutions should always be at least 5 cm above the level of the test medium.*
- *To calibrate and measure liquid electrolyte electrodes, the cap of the refill opening must be opened.*

- *The diaphragm must be immersed in the measurement solution.*
- *For low-maintenance electrodes with gel filling, such as DURALID® or REFERID®, there is no need to refill.*
- *Soaking with electrolyte solution is particularly important with these electrodes.*

Measuring the pH value

Please also observe the user instructions of the measuring equipment when calibrating and measuring. In order to minimize distortions in the results, electrodes that are used under extreme conditions or at the limits of the specified application ranges must be calibrated more frequently. For precise calibrations, we recommend the use of our hot vaporsterilized buffer vials certified according to DIN 19266 . Use only fresh buffer solutions at all times.

Storage and maintenance

- *Electrodes must be stored between 0 and 40°C. Depending on storage conditions (temperature and humidity), the liquid in the watering cap can dry out prematurely. In this case, the electrode must be soaked for at least 24 hours in a potassium chloride solution of 3 mol/l, before it is ready for use.*
- *In pH measuring chains and reference electrodes with liquid electrolytes, the electrolyte must occasionally be topped off or changed.*
- *Crystals in the electrolyte space of liquid electrolyte electrodes can be dissolved by gently warming in a water bath. The electrolyte solutions should then be changed and the electrode calibrated.*

Cleaning

- *Contamination on the membrane, PT sensor and diaphragm result in measurement deviations. Depositions can be removed with thinned mineral acids (e.g. hydrochloric acid 1:1), organic contamination can be dissolved with suitable solvents, fats can be removed with surfactant solutions, and protein can be dissolved with pepsin solution (cleaning solution L510). Rinse the electrode with distilled water after cleaning, do not rub dry.*
- *Ceramic diaphragms clogged from the outside become usable again after careful rubbing with fine sandpaper or a diamond file. The pH glass membrane must not be scratched!*
- *Platinum diaphragms must not be mechanically cleaned. Chemical cleaning (e.g. with diluted hydrochloric acid) can be carried out after unblocking (e.g. by vacuuming).*

- *Ground-joint diaphragms can be made functional again before measurement by gently raising and then pushing up the ground socket to the ground core. The refill opening should be open during this procedure. Warning: electrolyte will flow out more quickly when doing so, enabling thorough wetting of the ground surface. The glass membrane can be cleaned by wiping with an ethanol-soaked, lint-free cloth.*

Quality

Each electrode must meet the quality requirements of our final inspection in order to provide the best measurement reliability, response speed and service life. It is not possible to make a general statement as to the service life of the electrode. The service life is very dependent on the operating conditions. Extreme conditions such as high or frequently changing temperatures, strong acids and alkalis, protein-containing or very contaminated solutions or electrode poisons such as sulfide, bromide and iodide reduce the service life of the electrode. Hydrofluoric acid and hot phosphoric acid adversely affect the glass.

7.3 Summary

The recommendations made here with respect to cleaning and maintenance should be followed in order to obtain the most reliable measurements possible and achieve the longest service life for the electrodes. The electrode must always be matched to the particular application in order to achieve the best test results.

INDEX OF TECHNICAL TERMS

Resolution: smallest difference between two measurement values that the display of a measurement device is capable of displaying.

Diaphragm: a body in the wall of the reference electrode or electrolyte key housing which can be permeated by solutions. It transmits the electrical contact between the two solutions and hampers the exchange of electrolytes. The term diaphragm is also used for ground-joint and diaphragmless transfer.

Adjustment: to intervene in a measurement device so that the output values (e.g. the display) deviate as little as possible from the correct value or a value deemed to be correct, or so that deviations remain within tolerances.

Calibrate: comparison of the output values in a measurement device (e.g. the display) with the correct value or a value deemed to be correct. The term is also commonly used when the measurement equipment is adjusted at the same time (see adjustment).

Chain zero point: The zero point of a pH electrode is the pH value at which the pH electrode chain voltage is zero for a given temperature. Unless otherwise noted, this is at 25 °C.

Chain voltage: the electrode voltage U is the measurable voltage of an electrode in a solution. It is the same as the sum of all galvanic voltages in the electrode. Its dependence on pH is produced by the electrode function, which is characterized by the slope and zero point parameters.

Measured property: the measured property is the physical property identified by the measurement, i.e. pH or conductivity.

Measurement solution: Term for the sample ready to be measured. A measurement sample is usually obtained by preparation from the analysis sample (original sample). Measurement solution and analysis sample are therefore identical if no preparation takes place.

Measurement value: is the specific value of a measured property to be identified. It is specified as the product of a numerical value and a unit (e.g. 3 m; 0.5 s; 5.2 A; 373.15 K).

Molality: is the amount (in moles) of a dissolved substance in 1000g of solvent.

Zero point: Term for the offset voltage of a pH electrode. It is the measurable chain voltage of a symmetrical electrode whose membrane is immersed in a solution with the pH of the nominal electrode zero point (pH = 7).

Offset voltage: the measurable chain voltage of a symmetrical electrode whose membrane is immersed in a solution with the pH of the nominal electrode zero point. The zero point is a component of the offset voltage.

pH value: is a measurement for the acidic or basic effect of an aqueous solution. It corresponds to the negative log base 10 of the molal hydrogen ion activity divided by the unit of molality. The actual pH value is the measurement value of a pH measurement.

Potentiometry: Term for a form of measurement technology. The signal of the electrode used that depends on the measurement property is the electrical voltage. The electrical current remains constant.

Redox voltage: is caused by oxidizing or reducing substances dissolved in the water, if these become effective at the surface of an electrode (e.g. one made from platinum or gold).

Reference temperature: specified temperature for comparison of temperature dependent measurement values. In measurements of conductivity, the measurement value is converted to a conductivity value at 20 °C or 25 °C reference temperature.

Standard solution: is a solution whose measurement value is by definition known. It is used to calibrate measurement equipment.

Slope: the incline of a linear calibration function.

Temperature function: term for a mathematical function which provides the temperature behavior e.g. of a measurement sample, a sensor or a part of a sensor.

Temperature coefficient: Value of the slope of a linear temperature function.

Temperature compensation: Term for a function which calculates the effect of temperature on the measured property. The method of temperature compensation varies depending on the measured property to be determined. For potentiometric measurements, the slope value is adjusted to the temperature of the measurement probe, however the measurement value is not converted.

Resistance: Short term for specific electrolytic resistance. It corresponds to the inverse of electrical conductivity.

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SI Analytics GmbH

Hattenbergstr. 10
55122 Mainz
Germany

Phone: +49.(0)6131.66.5111
Fax: +49.(0)6131.66.5001
E-Mail: si-analytics@xyleminc.com
Internet: www.si-analytics.com

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