pH
Theory and Practice

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Guide to Reliable pH, Ion and Conductivity Measurements

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It describes our range of buffers and standards for pH and conductivity measurements as well as electrode maintenance and filling solutions. You will also find practical advice on how to achieve reliable pH, ion and conductivity measurements.

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Preface

The importance of pH

Many of nature's processes are highly dependent on pH. This is also the case for the chemical reactions which take place in industry or in a laboratory. In 1909, the founder of the modern pH concept, S.P.L. Sørensen, proved that pH is essential for many enzymatic processes. One example is the cleavage of cane sugar using invertase.

pH can also have an influence on the colour of certain dyestuffs. For example, although cyanidin chloride gives the cornflower its blue hue, it is the same dyestuff which gives a rose its red colour. The explanation is that cyanidin chloride is blue at a high pH while it is red at a low pH.

It is essential as regards living organisms that the pH of the biological fluids is maintained within a narrow pH range.

Swimming pool water is disinfected using a chlorine compound. The chlorine's optimal effectiveness and the avoidance of eye irritation can only be assured at a specific pH level.

In galvanic baths, quality and current efficiency is critically dependent on the correct pH. When the residual metals in the rinse water from such baths are precipitated, pH also plays a very important role.

These few though wide-ranging examples illustrate the importance of pH. It is appropriate to mention at this point that it is the pH value which is of significance and therefore not the total concentration of acid or alkaline species.

The booklet

The subject of this booklet is the potentiometric measurement of pH. This is the way in which pH is defined and is the optimal method for obtaining precise results. Reliable and accurate measurements depend on a number of factors: the quality of the equipment used, the electrode type, the accuracy of the calibration, the maintenance level, good laboratory practice and so forth.

The scope of this booklet is to discuss these various factors and their importance. Hints and recommendations are given and short theoretical sections are included. All the necessary information is therefore at hand to help you to obtain precision results in practice.

Contents

Definition of pH

pH is an abbreviation of "pondus hydrogenii" and was proposed by the Danish scientist S.P.L. Sørensen in 1909 in order to express the very small concentrations of hydrogen ions.

In 1909, pH was defined as the negative base 10 logarithm of the hydrogen *ion concentration*. However, as most chemical and biological reactions are governed by the hydrogen *ion activity*, the definition was quickly changed. As a matter of fact, the first potentiometric methods used actually resulted in measurements of ion activity.

The definition based on hydrogen ion activity is the definition we use today:

$$pH = -\log_{10} a_{H^+}$$

This definition is closely related to the operational pH definition which is currently defined using a standardised hydrogen electrode setup and buffers standardised in accordance with IUPAC recommendations.

Fig. 1. MeterLab® - the complete pH measuring setup

pH measurements

The electrode chain

pH is measured using a setup with two electrodes: the indicator electrode and the reference electrode. These two electrodes are often combined into one - a combined electrode.

When the two electrodes are immersed in a solution, a small galvanic cell is established. The potential developed is dependent on both electrodes.

Ideal measuring conditions exist when only the potential of the indicator electrode changes in response to varying pH, while the potential of the reference electrode remains constant.

The measured voltage can be expressed by the Nernst equation in the following way:

$$E = E_{ind} - E_{ref} = E'_T + R \bullet T/F \bullet \ln a_{H^+}$$

where

E = Measured voltage (mV)

E_{ind} = Voltage of indicator electrode (mV)

E_{ref} = Voltage of reference electrode (mV)

E'_T = Temperature dependent constant (mV)

R = Gas Constant (8.3144 J/K)

T = Absolute Temperature (K)

F = Faraday's constant (96485 C)

By using the base ten logarithm, the formula can be written as:

$$E = E'_T + 2.303 \bullet R \bullet T/F \bullet \log a_{H^+}$$

By introducing the pH definition as $pH = -\log a_{H^+}$, pH can be expressed at the temperature T as follows:

$$pH_T = pH_T^\circ - \frac{E}{R' \bullet S \bullet T}$$

where

R' = constant = 0.1984 mV/K

S = sensitivity, a correction factor which takes into account that the electrode response may differ from the theoretical value.

pH° = zero pH which is defined as the pH value at which the measured potential is zero. Figure 2 illustrates that the pH° will change with temperature and that another slope will be observed.

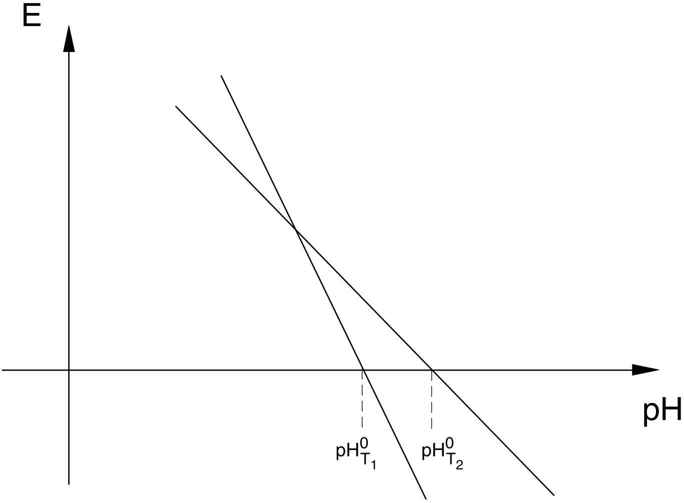


Fig. 2. The mV/pH relation at two different temperatures

Electrode construction

The construction of glass indicator electrodes and reference electrodes can be made in various ways. A typical glass electrode and a typical Ag/AgCl (Red Rod) reference electrode are shown below.

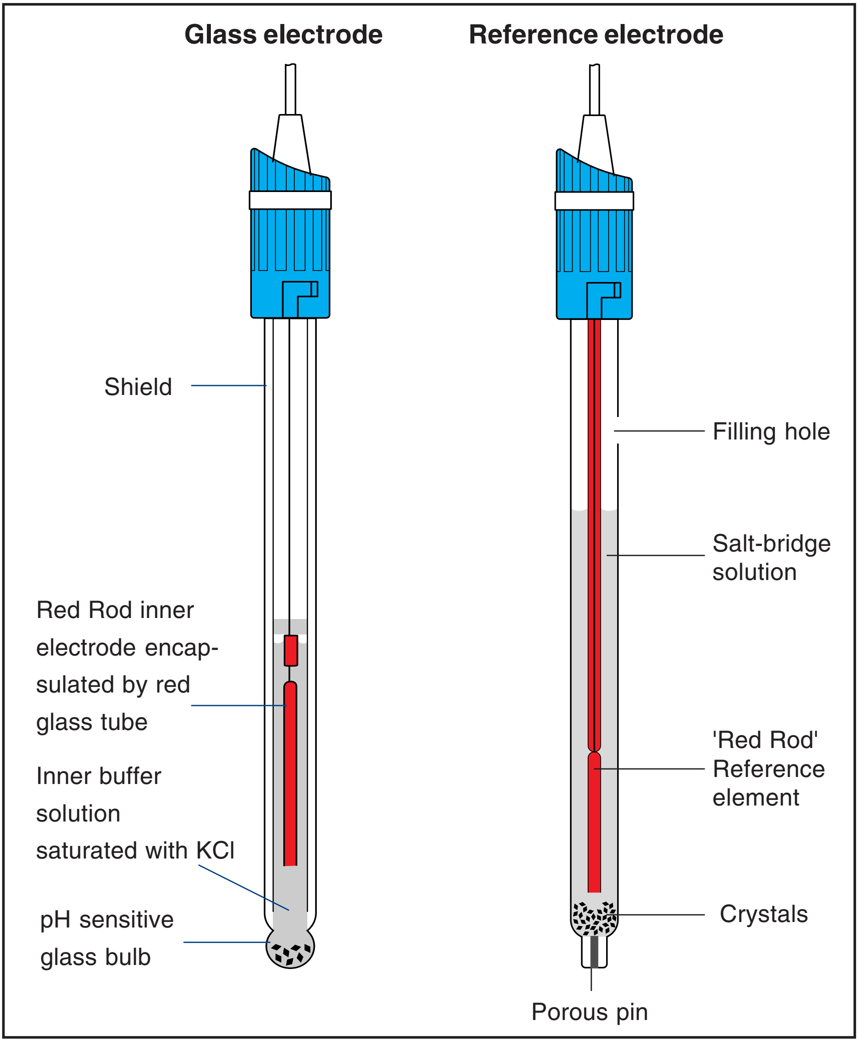


Fig. 3. Typical electrode constructions

Both the composition of the **glass electrode's** pH-sensitive glass and the composition of the glass electrode's inner solution have an influence on the potential which will develop.

The response of the electrode is the voltage developed between the inside and outside of the membrane. This voltage is proportional to the difference in pH in the inner solution and in the sample. The response is caused by an exchange at both surfaces of the swollen membrane between the ions of the glass and the H^+ ions of the solution - an ion exchange which is controlled by the concentration of H^+ in both solutions. As the structure of the glass membrane may not be uniform, an asymmetry potential may develop even if pH is the same on both sides.

The **reference electrode** shown on the previous page is a saturated silver/silver chloride electrode (Ag/AgCl) where the two components and the KCl are encapsulated in a red tube which is surrounded by a saturated solution of KCl. The red tubing affords protection from the harmful effects of light. The liquid junction, i.e. contact to the measuring solution, is achieved through a porous ceramic pin. The potential which occurs is determined by the solubility product of the silver chloride and the concentration of the KCl solution and is therefore constant.

A similar electrode construction can be made using mercury and mercurous chloride (calomel) instead. Such electrodes are not suitable for varying temperatures or temperatures above 60°C.

The potential of the reference electrode should be independent of the sample solution. This ideal situation will occur if all transport in the porous pin only involves the K^+ and Cl^- ions, and if they move at the same speed. This is the case in most samples in the pH range 1 to 13 and when a saturated or 3 M KCl salt-bridge solution is used. Deviation from this optimal situation creates the so-called liquid junction potential.

Red Rod electrodes should always used saturated KCl.

Table 1 lists the liquid junction potentials in different samples obtained with saturated KCl as the salt-bridge solution. The liquid junction potential's dependence on sample composition and especially on pH is obvious.

Sample	Liquid Junction Potential
1M HCl	14.1 mV
0.1M HCl	4.6 mV
0.01M HCl	3.0 mV
0.1M KCl	1.8 mV
pH 1.68 buffer	3.3 mV
pH 4.01 buffer	2.6 mV
pH 4.65 buffer	3.1 mV
pH 7.00 buffer	1.9 mV
pH 10.01 buffer	1.8 mV
0.01M NaOH	2.3 mV
0.1M NaOH	-0.4 mV
1M NaOH	-8.6 mV

Table 1. Liquid junction potentials in different samples

The table below shows the equivalent conductivity in infinitely diluted solutions (λ) of the ions commonly used in salt-bridge solutions. Equal conductivity of the cation and anion, used as a measure of their mobility, results in the lowest liquid junction potentials.

Cation	λ	Anion	λ
Li^+	38.7	CH_3COO^-	40.9
Na^+	50.1	ClO_4^-	67.4
K^+	73.5	NO_3^-	71.5
NH_4^+	73.6	Cl^-	76.4
		Br^-	78.1
		$^1/_2\ SO_4^{--}$	80.0
H^+	349.8	OH^-	198.3

Table 2. Equivalent conductivity of ions in infinite dilutions (S • cm^2/equivalent) at 25°C

Electrode types

Fig. 4. Different glass electrodes for different applications

Glass electrodes

The types shown in Figure 4 are examples of glass electrodes. However, glass electrodes are available in a number of different shapes and lengths to fit a wide range of applications. There are very thin electrodes, spear types, electrodes with a flat membrane for surface measurements and so forth. The shape, size and type of the inner electrode can vary, as can the glass composition of the membrane. The composition of the pH-sensitive glass will, to a large extent, determine the electrode's response time and its sensitivity to ions other than H^+. Sodium and lithium ions and, to a lesser extent, potassium ions, may interfere at high pH values (> pH 11). This is normally called the salt or alkaline error. If there is an abundance of sodium ions and few hydrogen ions, they may penetrate into the swollen glass surface layer. This means that the electrode will sense a higher ion concentration and therefore a pH value which is too low will be obtained by the pH meter.

Two disadvantages of glass electrodes are that measuring solutions can damage the glass membrane and that the glass membrane is easily broken. Alternatives to the glass electrode are available but are seldom used as they have other drawbacks, e.g. a long response time. The antimony electrode is the most widely used alternative. The thin oxide layer formed on the surface of the antimony metal is sensitive to pH.

Reference electrodes

A number of different reference electrodes are available. These variations relate to:

- the physical construction of the liquid junction
- the composition of the salt-bridge solution
- the electrode's electrochemical composition

The most common type of liquid junction is formed by a porous pin. However, depending on the application, other types can be used: circular ceramic junctions, sleeve junctions or an open junction through a thin glass tube. These will ensure a higher outflow of salt-bridge solution which is beneficial when measuring in solutions of very high or very low ionic strength. Certain buffers and samples, for example, tris buffer and slurry also require these types of liquid junctions.

Four different liquid junctions are shown in Fig. 5. The typical outflow of KCl salt-bridge solution for each type is also stated.

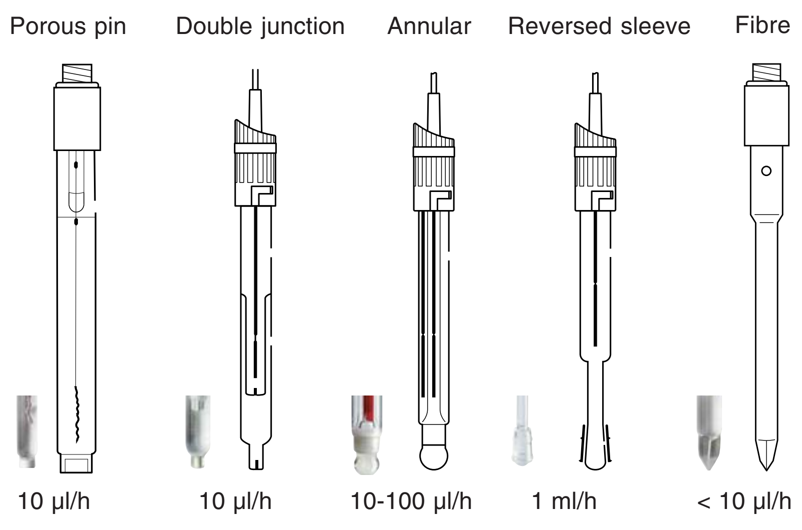


Fig. 5. Liquid junction constructions with typical KCl outflow

KCl should not be used as the salt-bridge solution if:

- it will interfere with the measuring solution
- if there is a risk that the liquid junction will become blocked due to precipitation
- if it is immiscible with the sample.

Two alternatives are available: a double junction system, i.e. with a second salt-bridge which does not contain KCl, or a modified electrode system can be used. A system with mercurous sulfate and potassium sulfate is one example. An overview of some of the combinations is provided in Table 3.

Type of reference electrode	Salt-bridge solution(s)	Potential vs. standard H_2 electrode	Potential vs. sat. calomel electrode
Hg/Hg_2Cl_2	sat. KCl	244 mV	0 mV
Ag/AgCl	sat. KCl	200 mV	- 44 mV
Hg/Hg_2SO_4	sat. K_2SO_4	640 mV	408 mV
Calomel	1 M LiCl	~ 285 mV	~ 40 mV
Hg/Hg_2Cl_2	sat. KCl/KNO_3	244 mV	~ 0 mV
Hg/HgO	0.1 M KOH	~ 175 mV	~ - 70 mV

Table 3. Potentials for different reference electrodes

Combined electrodes

Since it is easier to handle one electrode instead of two, combined electrodes (single stem) are very popular. The indicating glass electrode and the reference electrode are simply built into a single physical entity. This helps to ensure that the two electrodes have the same temperature during operation.

Combined electrodes with symmetrical electrode chains are the optimal construction for obtaining temperature equality in the two electrodes. In these electrodes the inner electrode of the glass electrode is the same type (Ag/AgCl) and has the same dimensions as the reference electrode, and the inner solutions are as identical as possible (saturated with KCl).

Choosing the right electrode

Choosing the right physical dimensions is straightforward as the sample size and sample vessel will dictate the type you should use. If the electrodes are to be used under harsh conditions, types with a plastic stem and protection cap will be suitable. Measurements which are to be performed directly on a surface require a flat electrode and so forth.

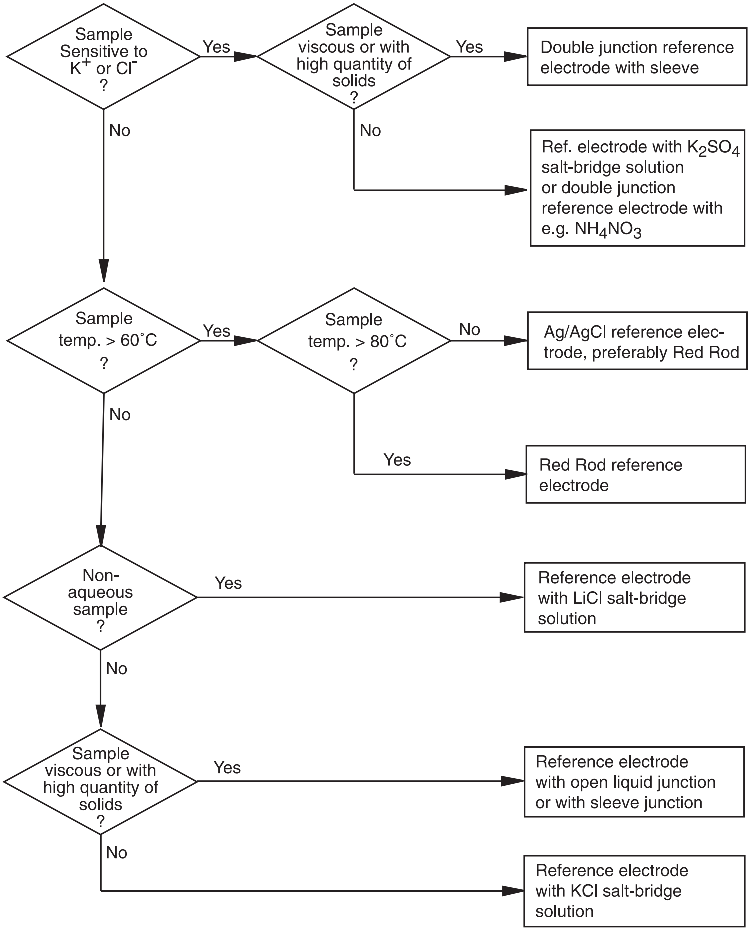


Fig. 6. Selection of the correct reference electrode for different measuring conditions

Measurements at high temperatures restrict your choice of electrodes as only certain electrochemical systems can withstand higher temperatures. Calomel electrodes, for example, cannot withstand temperatures above 60°C. However, certain Ag/AgCl reference electrodes can be used instead. The temperature range used may also be restricted depending on what the electrode is made of. *Low temperature* prolongs the response time of the electrodes. Long response times are often caused by membranes with high electric resistance which occurs in small or thick membranes and in glass compositions which are alkali-resistant.

High pH and high salt concentrations call for electrodes with alkali-resistant glass membranes. In all other cases, an electrode with a standard glass composition should be used.

When measuring in *emulsions* or *fatty solutions*, it is important to select the correct type of liquid junction. It is also important that the junction is easy to renew and clean. Open liquid junctions or sleeve junctions can therefore be recommended. These types can in some cases also be used for measurements in non-aqueous solutions. However, a salt-bridge solution containing lithium chloride is often preferable. LiCl is soluble in many organic media whereas KCl has a very limited solubility.

If there is a risk that chloride will interfere/contaminate, a reference electrode with a chloride-free reference system must be used (e.g. Hg/Hg_2SO_4 with K_2SO_4 salt-bridge), or a reference electrode with a double salt-bridge construction.

Measuring pH in pure water and other solutions with low ionic strength can pose problems. Although contamination of the measuring solution must be avoided, a fairly high outflow of KCl is necessary to minimise the liquid junction potential. Junctions with annular rings are therefore recommended. Sleeve junctions can also be used although their junction potential is less stable.

High ionic strength solutions and certain buffers also require a high outflow to ensure that the ionic transport in the junction is still dominated by the KCl ions. Open liquid junctions and sleeve junctions are recommended (see figure 5). High precision measurements can sometimes be facilitated by using open liquid junctions with a controlled and small outflow.

Electrode maintenance

Proper electrode maintenance ensures:

- a faster response
- more reliable measurements
- a longer lifetime.

The glass electrode and the reference electrode have different maintenance requirements and will therefore be described separately. The information concerning glass and reference electrodes also applies to combined electrodes.

The GK ANNEX Electrode Maintenance Kit from Radiometer Analytical contains all the items necessary for maintaining glass electrodes plus combined and reference electrodes with saturated KCl as the salt-bridge solution.

Glass electrode

The glass membrane must always be clean. For measurements in *aqueous solutions*, rinsing with distilled water will often suffice. Rinsing the electrode with a mild detergent solution once a week, such as Radiometer Analytical's RENOVO•N, will be beneficial. Measurements performed in *solutions containing fat or protein* require stronger cleaning agents, e.g. alkaline hypochlorite solution. RENOVO•X has been developed to meet these requirements.

The glass electrode should be stored in distilled water or in a weak acidic buffer between measurements. Prolonged use of strong alkaline solutions or even weak solutions of hydrofluoric acid will severely reduce the lifetime of the electrode as the glass membrane will gradually be dissolved. This occurs more rapidly at high temperatures.

For overnight storage, combined electrodes should be stored in refilling solution. If the electrode is not to be used for 2 weeks or more, dry storage is recommended. Remember to soak the electrode well before use.

No air bubbles must be trapped around the inner reference electrode as unstable readings may result. Tap the electrode gently or swing it in circles by its cable. If the air bubbles are trapped by KCl crystals, heating the electrode gently to max. 60°C in a water bath may be necessary.

To establish a stable, swollen, glass layer around the pH-sensitive glass, new or dry-stored glass electrodes have to be soaked in distilled water or an acidic buffer for some hours before use. Normal response times will be achieved after approx. 24 hours, although a longer soaking period may be needed for small electrodes. If measurements are needed before this time, calibrations should be repeated often due to drifting potentials.

If the response of a glass electrode has become sluggish, slight etching of the outer glass layer may help. The recommended treatment (which should only be performed when other measures have failed) consists of 1 minute in 20% ammonium bifluoride solution followed by 15 seconds in 6 M hydrochloric acid. *Care should be exercised when carrying out this treatment as the risk of the formation of hydrofluoric acid is present*. The electrode should then be thoroughly rinsed and soaked for 24 hours in water or in an acidic buffer solution.

In aqueous solutions, the function of the glass electrode depends on the hydration (swelling) of the glass layer which takes place on the surface of the pH-sensitive glass during soaking and measurement. However, measurements in non-aqueous or partly non-aqueous solutions are also possible as long as the electrode is frequently rehydrated, i.e. soaked in water or an acidic buffer. Between measurements in a non-aqueous solvent which is immiscible with water and before soaking, the electrode should first be rinsed with a solvent which is miscible with both water and the solvent before finally rinsing with water.

Because of the extremely small currents which pass through the glass electrode, *the cable, plug and connector must be kept clean and dry* if reliable measurements are to be obtained.

The lifetime of a glass electrode depends on a number of factors and is therefore highly individual. Good maintenance will prolong the lifetime whereas high temperatures, alkaline solutions, repeated etchings and improper maintenance will reduce the electrode's lifetime. However, the composition of the glass membrane will gradually deteriorate even during dry storage. As a guide, standard glass electrodes in normal use can last for a year or two.

Reference electrode

It is also important that the reference electrode is kept clean. As a matter of fact, most electrode problems can be traced to the reference electrode. It can be rinsed in the same solutions as those used for the glass electrode.

The reference electrode must always be nearly filled with salt-bridge solution. Potassium chloride in a high concentration is normally used.
Calomel and red rod electrodes from Radiometer Analytical require saturated potassium chloride solution (KCl•L). This means that *KCl crystals should always be present* in the salt-bridge solution.

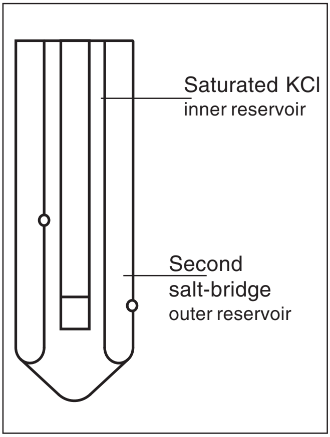


Fig. 7. Double junction reference electrode

The *special reference electrodes for chloride-free solutions or for non-aqueous solutions* should, of course, be filled with the appropriate solution. This will normally be potassium sulfate and lithium chloride respectively. Reference electrodes with a double salt-bridge contain potassium chloride in the inner one and a suitable salt in the outer one (high concentrations of KNO_3, NH_4NO_3 and Li-Acetate are some of the most often used solutions).

If the reference electrode is not capped and stored dry, it should preferably be stored in a beaker containing salt-bridge solution. The ability of concentrated KCl solutions to creep should, however, be kept in mind.

The *direction of flow* in the reference electrode should always be from the electrode to the measuring solution. As this one-way flow can only be partly achieved, the salt-bridge solution should be changed regularly, e.g. once a month.

Liquid junctions with fibres or ceramic pins can occasionally become blocked due to crystallisation (e.g. of KCl). If soaking in KCl solution does not solve the problem, raising the temperature to the maximum allowable for the reference system will often help. Other types of blockage can also occur, for example, in the form of a precipitate (black) of silver chloride or mercury sulfide in the porous pin. Gentle use of abrasive paper can sometimes remove the precipitate.

In other cases, chemical procedures such as soaking the electrode for a few hours in an acidic solution of thiourea (1 M thiourea in 0.1 M HCl) can be used.

A malfunction can also be caused by trapped air bubbles. These bubbles can be removed by gently tapping the electrode. If this does not alleviate the problem, the electrode shaft should be dipped in salt-bridge solution and heated to 60°C.

The lifetime of reference electrodes also depends on maintenance and especially on the liquid junction zone not becoming blocked. The electrode must never dry out and should therefore always be filled with the proper and uncontaminated, salt-bridge solution. A lifetime of 2 years or more is, in most cases, obtainable.

If the above recommendations have been followed, a proper calibration should be able to be performed easily. If this is not the case, the electrodes should be exchanged or examined more closely. The response time of the electrodes can be checked during a calibration.

The pH reading obtained in each of the two buffers should be stable within approx. one minute, otherwise the electrode's condition is poor.

It is strongly recommended that the zero pH and sensitivity are noted down after each calibration since a large deviation from one calibration to the next indicates that there is a problem. Radiometer Analytical recommends the use of the GLP•LOGBOOK for this purpose. It is part of the GK ANNEX kit.

The pH meter

A pH meter measures the potential difference (in mV) between the electrodes and converts it to a display of pH.

In order to obtain a correct measurement, the input amplifier and the converting circuit must meet certain requirements. The principal construction of a pH meter can be seen in the simplified diagram below.

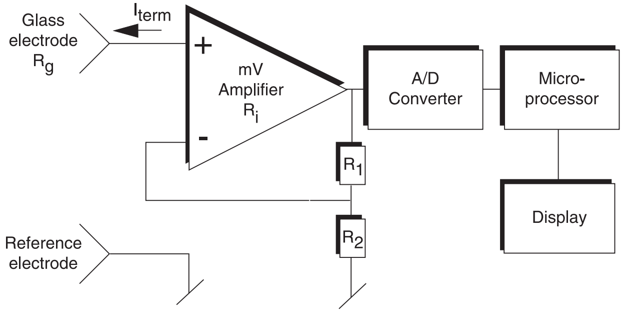


Fig. 8. Simplified pH meter diagram.

The potential difference between the reference electrode and the glass electrode is amplified in the mV amplifier before the A/D converter feeds the signal to the microprocessor for result calculation.

As the glass electrode typically has an inner resistance of the order of $10^8\Omega$, the amplifier's input resistance, R_i, must be considerably higher. A value of 10^{12} is required. For the same reason it is also important that the amplifier does not send any current through the glass electrode as this will give an error potential and could even disturb the electrode. The so-called terminal or bias current, I_{term},should therefore be below 10^{-12}A.

When $R_i >> R_g$, $I_{term} = 10^{-12}$ A and $R_g = 10^8\Omega$, the error introduced can be calculated according to Ohm's Law:

$$V_{error} = 10^{-12}\text{A} \bullet 10^8\Omega = 10^{-4}\text{V} = 0.1 \text{ mV}$$

To attain reliable and consistent results, the amplifier and other circuits must have a small temperature coefficient, i.e. the influence of temperature variations must be under control.

Normally, the result is displayed in numeric form although a few pH meters with needles are still available. The term analog or digital pH meter is often used to distinguish between these two forms of display.

However, it is also used to differentiate between control/conversion circuitry in *analog* or *digital* form.

In an analog pH meter, the adjustment of zero pH and sensitivity is carried out using adjustable resistances (dials) and the amplification factor is under direct manual control. The signal is then sent through an A/D converter. The output is a digital signal for the numeric display. *In a digital pH meter,* the amplifier works under the same conditions all the time and is directly connected to an A/D converter. The converter's output is then manipulated by digital circuitry (microprocessor-based) and the calculated pH is then displayed. Use of a temperature sensor provides both temperature correction and a temperature display. For microprocessor systems, the software will often provide automatic recognition of the calibration buffers and even automatic stability control of the electrode signal. To avoid interference, the following points should be checked:

Fig. 9. The PHM240 pH/Ion Meter for high-precision pH measurements

- Proper grounding of all types of pH meters will alleviate a lot of problems related to noisy electrode signals.
- If the pH meter is part of a larger measuring system, all the instruments should be connected to the same point.
- If the wall power outlet does not include a proper ground, a separate grounding lead must be used.
- The electrode cables should not run parallel to power lines as they may pick up noise.
- If the measuring solution is grounded (e.g. through pipes or stirrers), the pH meter circuitry must be isolated from ground and connection to other instruments (e.g. recorders or printers) should be performed with great care (galvanic insulation is required). Otherwise there is a great risk of current being passed through the reference electrode, disturbing the measurement and causing irreparable damage.

Alternatively, a differential measurement, in which the glass and reference electrode are connected to two high-impedance inputs, should be performed. In this case, the PHM250 Ion Analyser is the ideal instrument.

Buffers

A calibration is required to match the pH meter to the electrodes. For this purpose *a solution with a precisely known pH* has to be used. Such a solution must have a certain insensitivity to being lightly contaminated with acid or alkaline species, i.e. it must have a buffering capacity. This is where the terms buffer solution or buffer originate from.

The chemicals used in buffer solutions must be pure and stable, the pH values should be well-defined and the liquid junction potential should be the same size as the one for the unknown sample solutions. As these requirements partly contradict each other, two kinds of buffer solutions have been developed: the so-called technical buffers with a high buffer capacity and IUPAC/NIST buffers with a lower buffer capacity. The latter ones are, however, directly in accordance with the pH definition thus ensuring better accuracy, and the different buffers in the series have a high degree of consistency.

Fig. 10. IUPAC Series certified standards in thick, plastic bottles placed in tins assure long shelf life

The problem of varying liquid junction potentials is minimal as regards normal, diluted sample solutions. Radiometer Analytical buffers are therefore based on this concept.

It should be mentioned in this connection that the Radiometer Analytical *buffers are defined using the hydrogen electrode measuring setup*. Radiometer Analytical buffers are directly traceable to the hydrogen electrode measuring setup at one of the few Primary Laboratories (including the National Institute of Standards and Technology, NIST and the Danish National Metrology Institute, DFM). For further information, please refer to the References at the end of the booklet).

The buffers used today have evolved over the years. However, it is interesting to note that it was actually S.P.L. Sørensen who proposed many of them. R.G. Bates (formerly employed at the National Bureau of Standards) has made research on a number of buffers and it is his work which forms the basis of the current series of IUPAC/NIST buffers. The series consists of 10 buffers which are listed in the Appendix, together with the temperature dependency of the pH values.

The temperature dependency of the buffers can be expressed using the formula: $pH = A/T + B + C \bullet T + D \bullet T^2$, where T is the temperature in Kelvin. The coefficients A, B, C and D are also listed for each buffer.

High precision buffers have only a limited stability. It is therefore recommended that they are used within a short period of time, depending though on how precise your measurements have to be. A solution in an opened (but, of course, capped) bottle will only last for a limited period of time. It is the alkaline buffers which pose most problems because they absorb carbon dioxide from the atmosphere. Therefore, even buffers in unopened, thin, plastic bottles have a relatively short shelf life. For the best protection and long shelf life, thick, plastic bottles placed in tins are the optimal solution.

Addition of small amounts of germicide is necessary in order to avoid microbiological growth as several of the buffers are excellent culture media. On the other hand, addition of other substances should be avoided as they could disturb the pH value or the stability of the solution. Some colour compounds may cause problems as they have an adverse effect on the liquid junction.

Calibration

Electrodes cannot be produced with exactly identical characteristics. Zero pH and sensitivity will vary with time and different manufacturers produce electrodes with different nominal values. The calibration matches the pH meter to the current characteristics of the electrodes. The calibration process is generally performed by measuring in two different buffer solutions. This enables both pH° (zero pH) and the slope (sensitivity) to be determined.

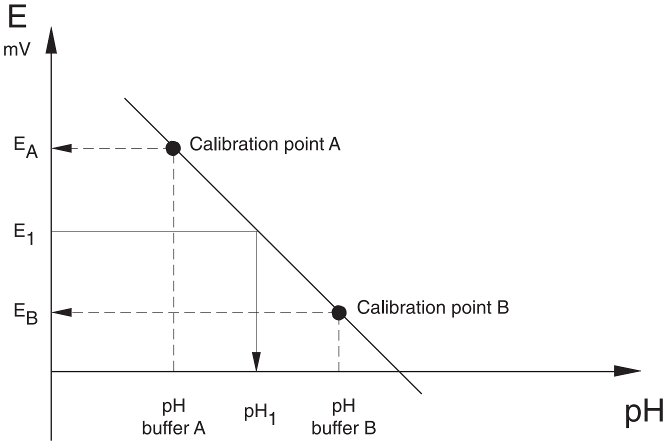


Fig. 11. Calibration curve

If the last calibration was performed recently or if you are in a hurry, a one-point calibration with measurement in only one buffer solution can be carried out. In this case, only pH° will be determined and the former sensitivity will be used.

The sensitivity is usually stated as a percentage of the theoretical value and should be independent of temperature. However, as mentioned before, the slope expressed as mV/pH is directly dependent on temperature. As an alternative to the sensitivity in %, a slope at 25°C is often used (100% = 59 mV/pH).

pH° is generally used to describe the electrode characteristics. However, the potential at pH 0 or pH 7 at 25 °C can also be given.

The calibration should be performed in a consistent manner, i.e. always with the same stirring and the same stability criteria or waiting time. The two buffers should also have the same temperature and this must be close to the temperature of the unknown samples. The two buffers should bracket the measuring interval, i.e. for sample measurements between pH 4.5 and 6.7, it would be appropriate to use buffers with pH 4.01 and pH 7.00. Still, the same buffers could also be used in the pH 3 - 8 sample range.

The buffer pH values can be entered from a keyboard or by means of adjusting dials. However, a number of microprocessor-controlled instruments allow autocalibration. This means that the instrument itself will select the right buffer value from a preprogrammed list. The temperature dependency will also be taken into account. It is obvious that the buffers used in autocalibration must have significantly different pH values. Using a buffer which is not included in the list, e.g. a pH 6.86 instead of a pH 7.00 buffer, will result in an incorrect calibration.

Temperature influence

Temperature plays an important role as regards sample and buffer pH and an electrode's characteristics. The temperature dependency of the buffers is fully known and is shown on the rear of the buffer bottles from Radiometer Analytical. The pH variation due to temperature is minimal for inorganic acid buffers, whereas it is significant for alkaline buffers and some organic buffers (please see the buffer tables in the Appendix). As regards the electrodes, compensation can be made for the influence of temperature on the slope. On the other hand, no compensation can been made for the pH shifts caused by altered reference potentials or a change of pH in the inner solution in the glass bulb. Finally, almost nothing is known about the influence of temperature on a sample's pH. It is therefore essential that the temperature is registered together with the pH value.

To sum up, samples, buffers and electrodes should all have the same temperature. Some compensation can be performed but it is not possible to calculate the pH of a sample measured at one temperature back to the sample pH at another (reference) temperature.

Theoretically speaking, the sample measurements and calibration should be performed at the same temperature. However, a temperature difference of 2 to 5°C will be acceptable in most cases.

Plotting the pH versus mV at a number of different temperatures will, for most electrodes, reveal that the lines intersect at almost the same point (see Figure 12). This point is called the iso potential point or iso-pH. If, by electrical circuitry or calculation, the pH° and iso-pH are made to coincide, compensation is made for the electrode's temperature dependence and measurements in a fairly large temperature range will be possible. The errors can be controlled if sample measurement and calibration are performed at two distinct temperatures. If the glass and reference electrode comprise the same electrochemical system like, for example, the Radiometer Analytical pHC2xxx series of electrodes, the temperature range allowed is larger than it would be with an unequal electrode construction.

The iso-pH is usually determined after a normal two-point calibration by making a third calibration. The third buffer should be the same as one of the first two buffers but the calibration temperature must differ by at least 20°C.

When pH°, sensitivity and iso-pH have all been determined, the pH can be calculated using the following formula:

$$pH_T = pH^\circ \bullet \frac{T_{cal}}{T} - \frac{E}{R' \bullet S \bullet T} + pH_{iso}\,(1 - T_{cal} / T)$$

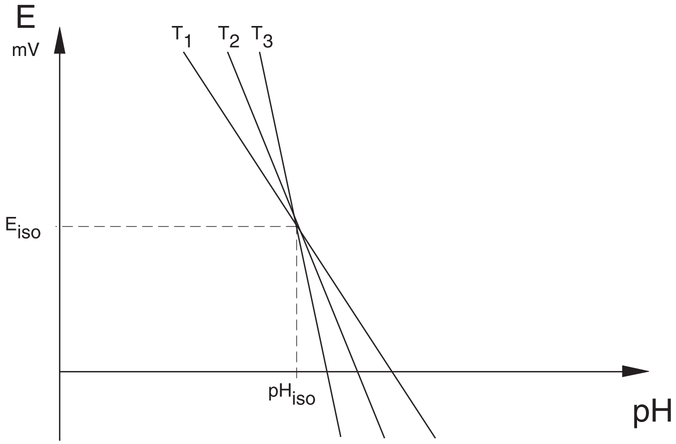


Fig. 12. Definition of iso-pH.
The intersection points do not coincide for isotherms at great variations in temperature

Measuring precautions

The obtainment of reliable measurement results depends on:

- the use of high quality equipment
- the maintenance of electrodes
- a meter in good condition
- proper procedures being followed.

This means that the calibrations should be performed regularly and that the results should be documented. It is of the utmost importance that the same procedure is used for measurements of the same type. For example, the stirring conditions should be the same during both calibration and sample measurement. Similarly, the electrode signal's stability criteria should not vary within the same measuring situation. This is most easily achieved using modern microprocessor pH meters as the electrode signal's stability is monitored automatically.

Odd results are sometimes obtained in suspensions and colloids. In fact, three different pH values may be measured. If the solution is stirred thoroughly, one value is obtained. On the other hand, in a sample which has not been stirred and in which the sediment is precipitated, two other values may be measured: one when the electrode(s) is dipped into the layer of sediment, and another if the electrode(s) is only in contact with the liquid above the sediment.

The electrodes should be held firmly in place and the sample beaker should be in a secure position. Use of an electrode stand specifically constructed to fulfill these requirements is therefore recommended.

Temperature should be controlled and, for accurate research measurements, a thermostatting bath should be used.

For measurements in solutions with a very low conductivity (these are usually non-aqueous), metal screening of the measuring beaker may be necessary. The alternative, adding a conductive (soluble) salt, is only allowed in special cases as the pH may change. These cases also require special reference electrodes which are compatible with the non-aqueous solutions, or which have a large outflow of salt-bridge solution.

Checking the meter

If problems occur, e.g. during calibration, it is recommended that you check the meter without electrodes in order to separate the two possible problem areas. Electrode simulators exist but are not readily available and are often rather expensive. A less expensive yet still effective check can be made using only simple items and is described below.

1. First of all, check the pH meter in the mV range. Connect the high impedance input (for the glass electrode) to the low input (for the reference electrode). For Radiometer Analytical pH meters supplied with both a black and red banana bushing, use the black one.
2. The pH meter should now display only a few mV, ideally 0.0 mV. Now connect a normal 1.5 V dry cell to the same electrode inputs. The meter should, depending on the state of the dry cell, display a reading in the vicinity of 1.5 V.
3. Switch the pH meter to pH mode and connect the high and low impedance inputs to each other again. The red banana bushing must be used for Radiometer Analytical pH meters.
4. Adjust the temperature to 25°C and (if adjustable) the sensitivity to 100% (59 mV/pH). Most meters will now display a value between pH 5.5 and 8.0. If the meter has a buffer adjustment (standardising) dial, turning this dial should alter the display value.
5. Connect the 1.5 V dry cell again. The display should go off range. As 60 mV is approximately 1 pH, the 1.5 V correspond to pH 25.

The above checks indicate that the pH meter is operating correctly and that the display and microprocessor, if any, are working. However, any misalignment and need for internal calibration will not be revealed. The input circuitry of the input amplifier may also be faulty, i.e. low input impedance and high terminal current. This can be checked if a high ohmic resistor is available. Perform the check in the following way:

1. Short-circuit the high and low impedance inputs as above (mV range). Note the reading on the display.
2. Now repeat this action but use a resistance of 1GΩ (1000 MΩ). Note the reading on the display. The difference should not be more than approx. 1 mV.
3. Connect the 1.5 V dry cell again and note the reading on the display.
4. Connect the dry cell through the 1 GΩ resistor and note the display reading. The difference should not be more than a few mV.

Appendix

pH values of buffer solutions at different temperatures

The tables below list the coefficients describing the temperature dependency for the buffers: pH 1.094, 1.679, 3.557, 3.776, 4.005, 4.650, 6.865, 7.000, 7.413, 7.699, 9.180, 10.012 and 12.454 at 25°C. The pH values at different temperatures are listed on the following pages.

The coefficients A, B, C and D refer to the formula:

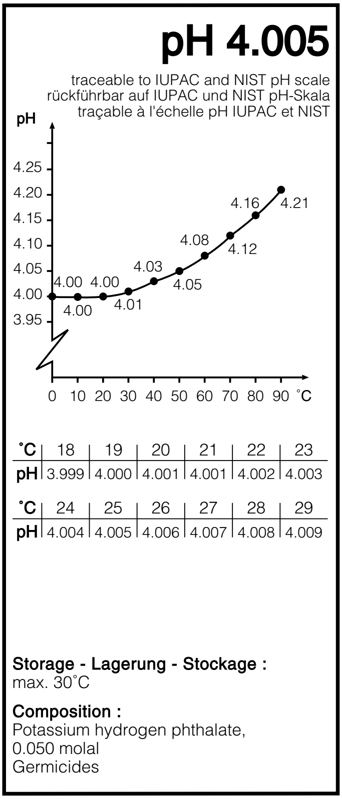
$$pH = A/T + B + C \bullet T + D \bullet T^2$$

where T is the temperature in Kelvin.

	BUFFER			
	HCl 0.1 M	**Oxalate**	**Saturated Tartrate**	**Citrate 0.05 m**
pH, 25°C	**1.094**	**1.679**	**3.557**	**3.776**
A	0	-362.76	-1727.96	1280.40
B	1.0148	6.1765	23.7406	-4.1650
$10^2 \bullet C$	0.0062	-1.8710	-7.5947	1.2230
$10^5 \bullet D$	0.0678	2.5847	9.2873	0

	BUFFER			
	Phthalate	**Acetate 0.1 M**	**Phosphate**	**Phosphate**
pH, 25°C	**4.005**	**4.650**	**6.865**	**7.000**
A	0	0	3459.39	1722.78
B	6.6146	7.4245	-21.0574	-3.6787
$10^2 \bullet C$	-1.8509	-1.8746	7.3301	1.6436
$10^5 \bullet D$	3.2721	3.1665	-6.2266	0

	BUFFER				
	Phosphate	**Tris 0.01/0.05**	**Borate**	**Carbonate**	**$Ca(OH)_2$**
pH, 25°C	**7.413**	**7.699**	**9.180**	**10.012**	**12.454**
A	5706.61	3879.39	5259.02	2557.10	7613.65
B	-43.9428	-12.9846	-33.1064	-4.2846	-38.5892
$10^2 \bullet C$	15.4785	3.5539	11.4826	1.9185	11.9217
$10^5 \bullet D$	-15.6745	-3.2893	-10.7860	0	-11.2918



pH 4.005

traceable to IUPAC and NIST pH scale
rückführbar auf IUPAC und NIST pH-Skala
traçable à l'échelle pH IUPAC et NIST

˚C	18	19	20	21	22	23
pH	3.999	4.000	4.001	4.001	4.002	4.003

˚C	24	25	26	27	28	29
pH	4.004	4.005	4.006	4.007	4.008	4.009

Storage - Lagerung - Stockage :
max. 30˚C

Composition :
Potassium hydrogen phthalate,
0.050 molal
Germicides

Fig. 13. The pH at different temperatures is clearly shown on the buffer bottles from Radiometer Analytical

	BUFFER / pH			
Temp.	**HCl**	**Oxalate**	**Tartrate**	**Citrate**
0°C	1.082	1.666		3.863
5°C	1.085	1.668		3.840
10°C	1.087	1.670		3.820
15°C	1.089	1.672		3.803
18°C	1.090	1.674		3.793
19°C	1.091	1.675		3.791
20°C	1.091	1.675		3.788
21°C	1.092	1.676		3.785
22°C	1.092	1.677		3.783
23°C	1.093	1.678		3.780
24°C	1.093	1.678		3.778
25°C	**1.094**	**1.679**	**3.557**	**3.776**
26°C	1.094	1.680	3.556	3.774
27°C	1.094	1.681	3.555	3.772
28°C	1.095	1.681	3.554	3.770
29°C	1.095	1.682	3.553	3.768
30°C	1.096	1.683	3.552	3.766
35°C	1.098	1.688	3.549	3.759
37°C	1.099	1.690	3.548	3.756
40°C	1.101	1.694	3.547	3.754
45°C	1.103	1.700	3.547	3.750
50°C	1.106	1.707	3.549	3.749
55°C	1.108	1.715	3.554	
60°C	1.111	1.723	3.560	
65°C	1.113	1.732	3.569	
70°C	1.116	1.743	3.580	
75°C	1.119	1.754	3.593	
80°C	1.121	1.765	3.610	
85°C	1.124	1.778	3.628	
90°C	1.127	1.792	3.650	
95°C	1.130	1.806	3.675	

	BUFFER / pH			
Temp.	**Phthalate**	**Acetate**	**Phosphate**	**Phosphate**
0°C	4.000	4.667	6.984	7.118
5°C	3.998	4.660	6.951	7.087
10°C	3.997	4.655	6.923	7.059
15°C	3.998	4.652	6.900	7.036
18°C	3.999	4.651	6.888	7.024
19°C	4.000	4.651	6.884	7.020
20°C	4.001	4.650	6.881	7.016
21°C	4.001	4.650	6.877	7.013
22°C	4.002	4.650	6.874	7.009
23°C	4.003	4.650	6.871	7.006
24°C	4.004	4.650	6.868	7.003
25°C	**4.005**	**4.650**	**6.865**	**7.000**
26°C	4.006	4.650	6.862	6.997
27°C	4.007	4.651	6.860	6.994
28°C	4.008	4.651	6.857	6.992
29°C	4.009	4.651	6.855	6.989
30°C	4.011	4.652	6.853	6.987
35°C	4.018	4.655	6.844	6.977
37°C	4.022	4.656	6.841	6.974
40°C	4.027	4.659	6.838	6.970
45°C	4.038	4.666	6.834	6.965
50°C	4.050	4.673	6.833	6.964
55°C	4.064	4.683	6.833	6.965
60°C	4.080	4.694	6.836	6.968
65°C	4.097	4.706	6.840	6.974
70°C	4.116	4.720	6.845	6.982
75°C	4.137	4.736	6.852	6.992
80°C	4.159	4.753	6.859	7.004
85°C	4.183	4.772	6.867	7.018
90°C	4.208	4.793	6.876	7.034
95°C	4.235	4.815	6.886	7.052

	BUFFER / pH				
Temp.	**Phosphate**	**Tris**	**Borate**	**Carbonate**	**$Ca(OH)_2$**
0°C	7.534	8.471	9.464	10.317	13.424
5°C	7.500	8.303	9.395	10.245	13.207
10°C	7.472	8.142	9.332	10.179	13.003
15°C	7.448	7.988	9.276	10.118	12.810
18°C	7.436	7.899	9.245	10.084	12.699
19°C	7.432	7.869	9.235	10.073	12.663
20°C	7.429	7.840	9.225	10.062	12.627
21°C	7.425	7.812	9.216	10.052	12.592
22°C	7.422	7.783	9.207	10.042	12.557
23°C	7.419	7.755	9.197	10.032	12.522
24°C	7.416	7.727	9.189	10.022	12.488
25°C	**7.413**	**7.699**	**9.180**	**10.012**	**12.454**
26°C	7.410	7.671	9.171	10.002	12.420
27°C	7.407	7.644	9.163	9.993	12.387
28°C	7.405	7.617	9.155	9.984	12.354
29°C	7.402	7.590	9.147	9.975	12.322
30°C	7.400	7.563	9.139	9.966	12.289
35°C	7.389	7.433	9.102	9.925	12.133
37°C	7.386	7.382	9.088	9.910	12.072
40°C	7.380	7.307	9.068	9.889	11.984
45°C	7.373	7.186	9.038	9.857	11.841
50°C	7.367	7.070	9.010	9.828	11.705
55°C			8.985		11.574
60°C			8.962		11.449
65°C			8.941		
70°C			8.921		
75°C			8.902		
80°C			8.884		
85°C			8.867		
90°C			8.850		
95°C			8.833		

The composition of the buffers is as follows:

Available from Radiometer Analytical:

HCl **(pH1.094)**: 0.1 M HCl, part no. S11M009.

Oxalate (**pH 1.679**): 0.05 mol/kg $KH_3C_4O_8$, part no. S11M001.

Phthalate (**pH 4.005**): 0.05 mol/kg $KHC_8H_4O_4$, part no. S11M002.

Acetate (**pH 4.650**): 0.1/0.1 mol/kg $C_2H_4O_2/C_2H_30_2Na$, part no. S11M010.

Phosphate (**pH 6.865**): 0.025/0.025 mol/kg KH_2PO_4/Na_2HPO_4, part no. S11M003.

Phosphate (**pH 7.000**): approx. 0.020/0.0275 mol/kg KH_2PO_4/Na_2HPO_4, part no. S11M004.

Phosphate (**pH 7.413**): 0.008695/0.03043 m KH_2PO_4/Na_2HPO_4, part no. S11M005.

Borate (**pH 9.180**): 0.01 m $Na_2B_4O_7$, part no. S11M006.

Carbonate (**10.012**): 0.025/0.025 0.025/0.025 mol/kg $NaHCO_3/Na_2CO_3$, part no. S11M007.

$Ca(OH)_2$ (**pH 12.45**): saturated (at 25°C) and filtered, part no. S11M008.

The second phosphate buffer is Radiometer Analytical's own recipe. The other buffers are specified by IUPAC/NIST or DIN 19266/19267.

Not available from Radiometer Analytical:

Tartrate (**pH 3.557**): saturated (at 25°C) $KHC_4H_4O_6$.

Citrate (**pH 3.776**): 0.05 mol/kg $KH_2C_6H_5O_7$.

Tris (**pH 7.699**): 0.01667/0.05 0.025/0.025 mol/kg Tris/Tris-HCl.

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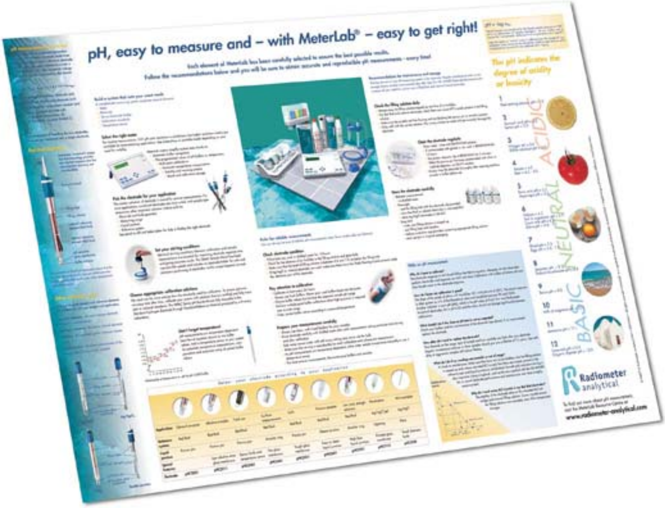

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The pH indicates the degree of acidity or basicity

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Radiometer analytical

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- behind the scenes at Radiometer Analytical

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Electrodes are manufactured at Radiometer Analytical's premises in Villeurbanne, France using a combination of traditional know-how and state-of-the-art technology. It takes between 2 and 11 days and many skilful operations to transform a simple crystal tube into the high-precision combined pH electrode you use every day.

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