



# Manual of Electrochemical Analysis

## Part 2

### Measuring the pH



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## What is pH?

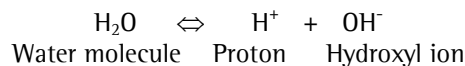
The pH is a unit of measure which describes the degree of acidity or alkalinity of an (aqueous) system. It is used to make quantitative statements about the nature of solutions, instead of subjective ones like "this solution is weakly acidic" or "orange juice is more sour than milk."

The concept of pH was originally defined in 1909 by the Danish chemist Søren Sørensen who used the formula:

$$\text{pH} \equiv -\log a_{\text{H}^+}$$

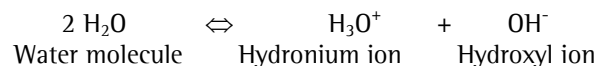
In other words, pH is the negative decadic logarithm of the hydrogen ion activity<sup>1</sup> of the proton  $a_{\text{H}^+}$  in moles per liter.

Water is an electrically neutral molecule made of two hydrogen atoms and one oxygen atom ( $\text{H}_2\text{O}$ ). In the molecule, the electrons are not distributed evenly among the atoms, but are located closer to the oxygen atom than to the two hydrogen atoms. That is the reason why a water molecule can give off electrically charged particles ( $\text{H}^+$  ions, protons). This process produces two ions.



The balance of this reaction is shifted greatly to the side of undissociated water. At 22 °C, only  $10^{-7}$  moles/L water are dissociated. One liter of water at 22 °C contains about 55 moles of water molecules<sup>2</sup>.

Since free protons cannot survive in aqueous systems and will immediately attach themselves to water molecules, the equation can also be written as:



In aqueous systems, the following relationship exists between the activity of protons and the activity of hydroxyl ions:

$$a_{\text{H}^+} \cdot a_{\text{OH}^-} = 10^{-14}$$

If the activity of one type of ion is known, the activity of the other can be calculated. In practice, we usually only look at the proton concentration. It does not make sense to directly state the ionic activity because of the low concentration of these ions in water. By using the negative decadic logarithm, numbers are obtained that are easier to work with. In other words, pH = 0 represents the activity of 1 mole/L of  $\text{H}^+$  ions (e.g. in a hydrochloric acid solution of 1 mole/L). By contrast, pH = 14 shows an activity of  $10^{-14}$  moles/L of  $\text{H}^+$  ions (which is equivalent to 1 mole/L of  $\text{OH}^-$  ions, e.g. to a sodium hydroxide solution of 1 mole/L). A pH of 7.0 defines a neutral aqueous solution. That means that the solution contains the same number of protons as hydroxyl ions.

**pH < 7    acidic**  
**pH = 7    neutral**  
**pH > 7    basic**

**Raising the pH by a factor of 1 produces a ten-fold increase in the  $\text{H}_3\text{O}^+$  ion activity.**

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<sup>1</sup> The activity defines the concentration of ions in a solution that are not affected by any other ions. In very diluted systems, the activity is equal to the concentration. When measuring the pH, it is always the activity that is determined, even when one uses the word "concentration" in simple language.

<sup>2</sup> The mole, abbreviated "mol" is the international unit defined as the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is "mol." One mole of a compound contains  $6.022 \times 10^{23}$  parts of that compound.

Some examples:

Sample	pH
Hydrochloric acid 1 mole/L	Approx. 0
Gastric acid	0.9 – 1.5
Lemon juice	2.0 – 2.5
Table vinegar	2.7 – 3.5
Sour milk	Approx. 4
Ion-free water	7.0
Hard spring water	8.0 – 8.7
Mild detergent (soap)	8.2 – 8.7
Borax solution 0.1 moles/L	9.1
Aqueous ammonia 0.1 moles/L	11.3
Lime water	12.3
Sodium hydroxide solution 0.1 moles/L	Approx. 13

The pH is temperature-dependent. For example, the pH of acidic buffers<sup>3</sup> increases as a function of temperature, in neutral and basic buffers it drops.

For ready-made buffer solutions, the pH is given at several different temperatures. Modern measuring devices have the pH as a function of the temperature of most conventional solutions stored in their memory and calculate on this basis, when an automatic calibration function is used. Even the neutral point of water can change; at 0 °C it has a pH = 7.74; at 50 °C its neutral point is around pH = 6.61 and, at 100 °C, the pH of pure water is 6.07.

When stating the pH, you must always include the temperature the pH was measured at.

When working with highly concentrated solutions of strong acids or bases, the pH scale described above has to be extended: A hydrochloric acid solution with a concentration of 10 moles/L has a pH of approx. -1. A sodium hydroxide solution with a concentration of 10 moles/L has a pH of approx. 15. The pH of alcohols and other "water-like" polar solvents can also be measured. These kinds of solutions can have extremely high pH values (up to pH = 29, which is equivalent to an extremely low proton activity of  $10^{-29}$  moles/L). The neutral point of these (anhydrous) solvents is not around a pH of 7, but is at ranges much higher (with the exception of anhydrous acids like acetic acid). The neutral point is the pH at which the activity of the protons is the same as the activity of the particles that have given off the proton (hydroxyl ions in an aqueous system). Correspondingly, substances that cannot give off protons very easily have a neutral point at much lower concentrations (and consequently at higher pHs) than in aqueous systems. Figure 1 shows some examples of the pH ranges of non-aqueous systems.

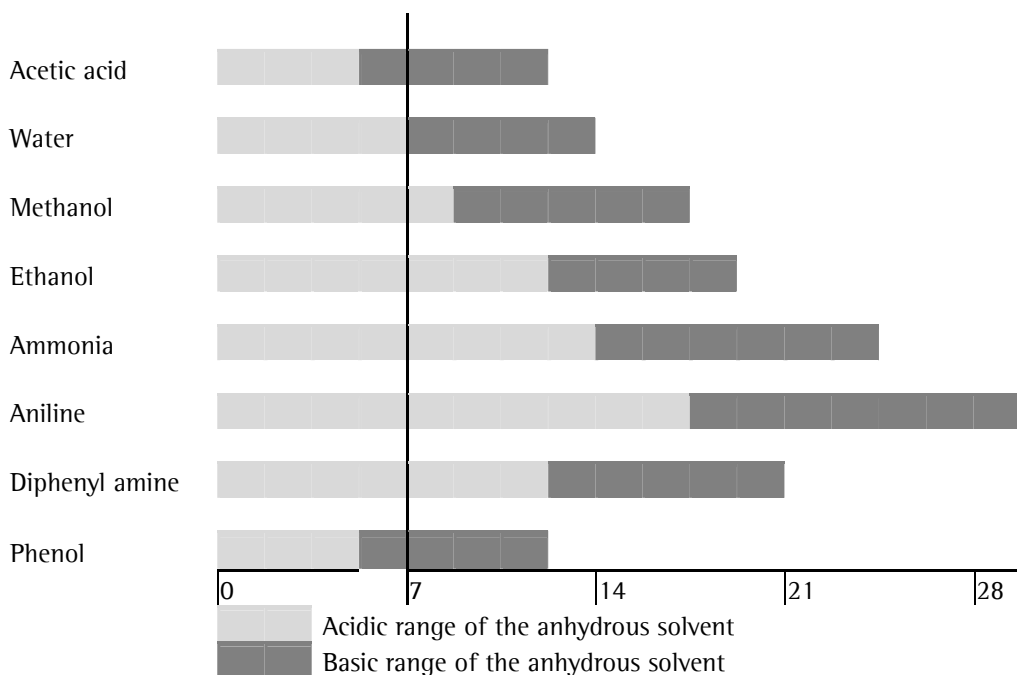


Figure 1: pH ranges of various solvents

The following section will deal with aqueous systems as they represent the main applications for pH measurements.

<sup>3</sup> Buffer: also called buffer solutions, aqueous solutions that are used to calibrate pH meters (see the chapter "Calibrating pH Meters")

## How Do You Measure the pH?

Two methods are commonly used for measuring the pH: Indicators and electrochemical measurements.

### Indicators

Indicators are dyes that change color as a function of pH. Surely the most well-known example is litmus, a plant pigment that turns red in the acidic range and blue in basic solutions. Liquid pH indicators can also be added to a solution; or a strip of paper or a test swab impregnated with the indicator is dipped into the liquid. The change in color of the indicator is compared with a given color scale which is usually shown on the packaging of the test strip or swab. There are universal indicator papers that cover the pH range from 0 to 14 and special indicator papers that cover a more narrow range and therefore have a higher accuracy. However, because the impression of color is subject to interpretation and influenced by the effects of the sample's intrinsic color or turbidity, indicator papers are only moderately accurate. On the other hand, they are appreciated as quick tests because of their easy handling. Liquid pH indicators are chiefly used to determine the endpoint of an acid-base titration<sup>4</sup>. Again, subjective perceptions of color can impact the measurement. That is why many titrations today are carried out with a potentiometric endpoint determination.

The color transition ranges of the main pH indicators

	Color at low pH	pH range of the Change in color	Color at high pH
Alizarine yellow	Yellow	10.1-12.0	Red brown
Phenolphthalein	Colorless	8.2-10.0	Red
Cresol red	Yellow	7.2-8.8	Red
Bromtymol blue	Yellow	6.0-7.6	Blue
Litmus	Red	5.0-8.0	Blue
Methyl red	Red	4.4-6.2	Yellow
Methyl orange	Red	3.1-4.4	Yellow
Thymol blue	Red	1.2-2.8	Yellow
	Yellow	8.0-9.6	Blue

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<sup>4</sup> Titration : A method of analysis by which a reagent solution with a concentration of known certainty is added to a sample of an unknown concentration. The reagent is added until the sample has undergone a complete reaction (as determined by the indicator changing color). The volume of the reagent consumed is used to calculate the content of compound sought in the sample.

## Potentiometric (Electrochemical) pH Measurements

The more accurate way to determine pH is by electrochemical measurement. The instrument used for this is a pH meter equipped with an electrode suitably designed to measure the pH. A pH electrode (measuring electrode) generates a potential as a function of the pH of the surrounding solution. This potential is measured against that of a reference electrode which provides a constant potential. The pH meter reads the potential difference of the two electrodes and converts it to pH units.

Accurate and reproducible measurements cannot be produced unless they are conducted under defined measuring conditions. In these cases, it is particularly important that the temperature of the medium to be tested is kept constant and that it is homogeneous. In some samples, the time between sample collection and measurement plays a key role. For example, a number of alkaline samples with a low buffer capacity rapidly change their pH when they absorb CO<sub>2</sub> from the air.

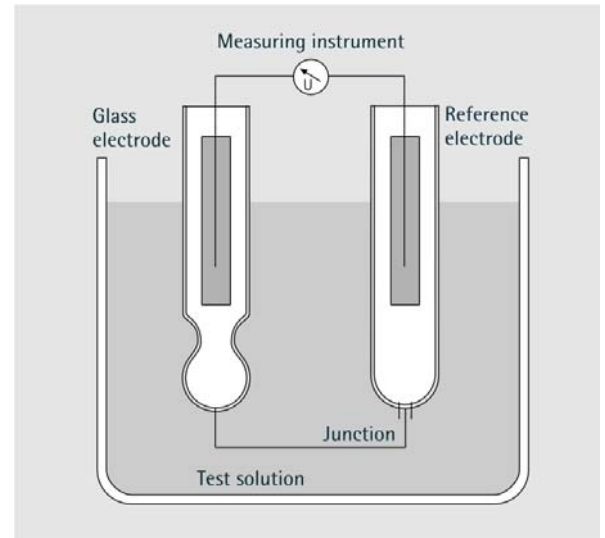
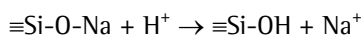


Figure 2: The closed circuit of a pH measurement

## Electrodes

The electrodes most commonly used to measure pH are glass membrane electrodes.

This type of electrode features a glass membrane. When it is immersed in an aqueous solution, a hydrated layer (also referred to as a gel layer) forms on its surface (see Figure 3). During this process, dissociation occurs at the junction site between glass and solution (in the older literature, this process is described as ion exchange). Alkali ions of the glass go into solution (dissociate) and are replaced by protons from the aqueous solution. This produces a thin layer containing abundant hydroxyl groups.



Since this process does not lead to a stable potential on the glass surface until after approx. 72 hours, new or dried out electrodes have to first be formatted or regenerated by soaking them in an electrolyte solution. By contrast, newly purchased electrodes that contain a sufficient amount of fill solution and electrodes that have enough electrolyte in the wetting cap can be used right away.

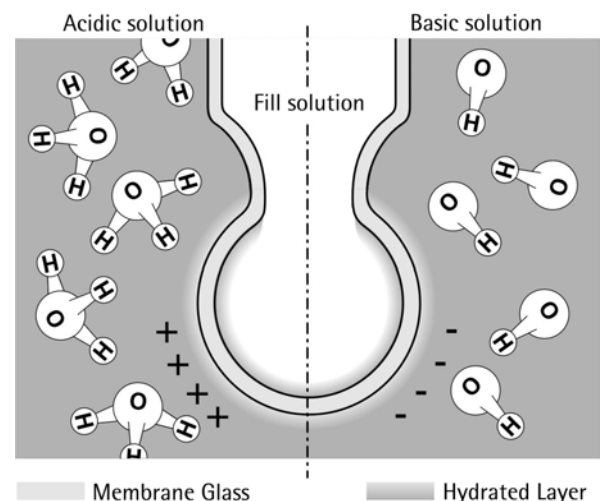
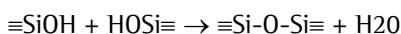
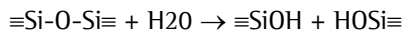


Figure 3: Hydrated layer of a glass membrane electrode

In acidic to neutral solutions, a residue rich in silicic acid forms on the electrode surface over time; such corrosion products have to be constantly rinsed off and new hydrated layers are reproduced.



In basic solutions, by contrast, the silicic acid dissolves gradually. The dissolution rate of the outer layer is at a minimum when with a pH range = 3 ... 5.



Depending on the pH of the sample, protons diffuse into the hydrated layer or out of it. This creates an electrochemical potential. The number of protons that can diffuse into this hydrated layer is limited by the number of solidly anchored hydroxyl and oxonium groups. On the inside of the membrane, the interior buffer ensures a constant potential. The potential at the glass membrane is measured against a reference electrode.

The reference electrode has a constant potential that is independent of the sample. It is comprised of a reference element that is immersed in a solution with a known, constant composition. The most well-established and widespread system uses silver/silver chloride (Ag/AgCl) that is immersed in a KCl solution. Although they are very accurate, mercury/mercury chloride electrodes (calomel electrodes) are hardly used anymore because they are harmful to the environment. Electrodes with "gel electrolyte" are extremely maintenance-free and suitable for many standard types of measurements. In this electrode, the KCl solution is thickened by adding viscosifiers to form a gel that is so thick that it cannot escape through the junction and therefore does not have to be refilled.

The electrical contact between the reference electrode and sample is generated at the junction site. This is an opening with a very small diameter which allows direct contact between the fluids but prevents them from becoming mixed together rapidly. In order to prevent the test solution from penetrating into the reference electrode, a slight overpressure in the reference electrode must be maintained to keep out the test solution. The escaping electrolyte solution forces back any test solution that is trying to diffuse into the opening. This is accomplished by filling the electrode in such a way that the level of electrolytes is approx. 2-3 cm higher than that of the fluid level of the sample. A highly concentrated KCl solution is used to avoid disturbances due to a diffusion potential at the junction site. In general, concentrations of 3 moles/L, 4 moles/L are common or a saturated KCl solution is used. The type of electrode filling is usually labeled on the body of the electrodes, thereby ensuring that the electrode filling is refilled to the right concentration.

Today, mostly electrodes are used in which the test and reference electrode are housed in one body (combination electrodes, see Figure 4). A number of combination electrodes additionally have a built-in temperature sensor, making it possible to capture all relevant parameters with just a single sensor.

Combination electrode

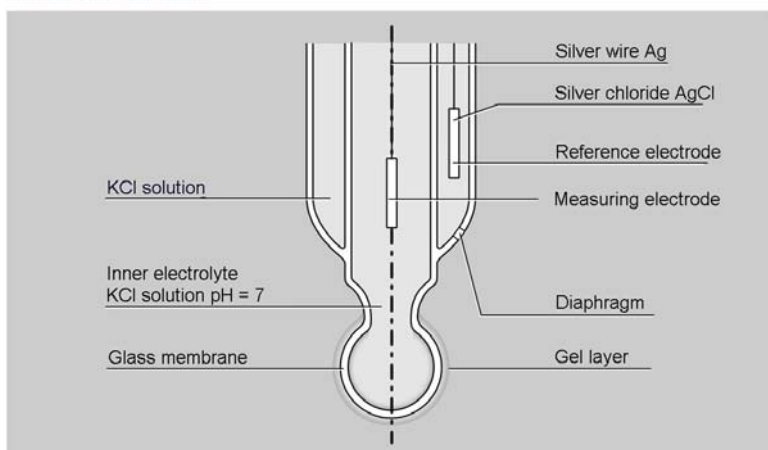


Figure 4: The combination electrode

pH electrodes need to be kept moist at all times, if stored dry a complicated regeneration procedure is required before the next measurement can be performed. For storage, a plastic "wetting cap" is placed over the electrode. This cap contains a few milliliters of storage solution (usually KCl solution). pH electrodes can also be stored in a diluted buffer solution with a pH = 7.00 during work breaks.



An electrode is selected that is appropriate for the targeted application. However, most common laboratory measurements can be performed suitably with standard electrodes like the PY-P10 or PY-P11 from Sartorius. Many compounds in the test solution will produce slightly soluble precipitates when they come into contact with the KCl electrode filling and will clog the junction:  $\text{Hg}_2^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{ClO}_4^-$ . Such precipitates have to be removed by placing the electrode in a thiourea solution for several hours. Afterwards, the electrode filling has to be replaced and the electrode regenerated. If samples that produce these kinds of precipitates have to be measured frequently, it is better to use an electrode with a sleeve junction diaphragm. In this case, the escaping electrode filling practically rinses out the diaphragm and it is easier to clean the electrode occasionally. The sample then has to be discarded.

#### Overview of glass membrane electrodes supplied by Sartorius AG

Electrode	Junction	Escape rate of electrode filling	Working properties of the diaphragm	Areas of application
PY-P10 PY-P20	Fiber	<< 1 ml/day (PY-P10)  n.a. (PY-P20)	+ Quick adjustment, easy handling - Sample can enter reference system, not possible to clean reference system	Routine measurements General wastewater, swimming pools, electroplating waste  Temperature range: -5...80 °C pH: 0...14
PY-P11 PY-P21 PY-P22	Platinum	≈ 1 ml/day	+ Universal in use, quick adjustment, constant readings, contamination resistant, defined outflow channels, low liquid junction potential - can only be chemically cleaned, no mechanical cleaning	Complicated measurements, PY-P22 for small sample size  Water, beverages, milk, tenside-containing solutions, titrations  Temperature range: -5...100 °C pH: 0...14
PY-P23	Annular gap junction	n.a.	+ Annular gap symmetrical, easy handling, contamination resistant - Sample can penetrate into reference system, not possible to clean reference systems	Surface measurements e.g. Paper, leather, skin, culture media  Temperature range: -5...100 °C pH: 2...13
PY-P24	sleeve junction	≈ 3 ml/day	+ Easy to clean, variable outflow - Fragile construction	Precision measurements, Emulsions and suspensions, extreme pH values, low-ionic strength water  Temperature range: -5...100 °C pH: 0...14

## The pH meter

At the core of a pH meter is a high-precision voltmeter which determines the potential difference between test and reference electrode. The input impedance of a pH meter is approx. 100,000 times that of the voltmeters commonly used in electrotechnology. If this kind of voltmeter were connected to a pH electrode would cause a short that would destroy the electrode. A processor housed in the instrument uses the potential difference to calculate the pH according to the Nernst equation.

The Nernst equation describes the relationship between activity  $a_x$  of a compound in a solution and the electrical potential created on the electrode immersed in the solution:

$$U = U_0 + \frac{RT}{nF} \cdot \ln a_x$$

At a constant temperature, the following formula can be derived:

$$U = U_0 + U_N \cdot \frac{\lg a_x}{n}$$

$U_N$ : "Nernst voltage" or "Nernst factor"; at 25 °C is  $U_N=59,16$  mV

$U_0$ : Zero point potential at pH = 7.00

$n$ : Ionic valence

$a_x$ : Ionic activity of ion X

$T$ : Temperature / K

$R$ : General gas constant (8.314 J/molK = 8.314 VAs/molK)

$F$ : Faraday constant ( $9.648 \cdot 10^4$  C/mol =  $9.648 \cdot 10^4$  As/mol)

## Calibrating pH Meters

In pH measurements, the term calibration is often used differently than commonly used otherwise. In general, calibration is understood to mean that the reading in the display on a measuring instrument is checked against a standard; any deviation that exists between the true value and the value displayed in the reading is determined. The term adjustment is used to describe the process by which reading in the display is corrected to fit the true measurement. In the stricter sense, a calibration performed on a pH meter is really an adjustment. But since the term calibration is more common in the field of electrochemical analysis, we will stick to this terminology here as well.

A pH meter is calibrated in order to correct for any deviation of real electrodes from their ideal behavior. For this purpose, standard solutions with defined pH values are used. In general, a pH of 7.00 is the zero point for today's electrodes. The slope of the electrode in question is usually determined using two additional buffer solutions (e.g. pH = 4.00 and pH = 10.00) and stored in the meter for the subsequent test run. The single-point calibration (zero point calibration with buffer pH = 7.00) is a suitable method when the electrode slope is known with certainty. The two-point calibration (pinch-clamp method) is the most frequently used method of calibration. Ideally, the pH values of both buffer solutions will be slightly above and below the expected pH of the sample. For practical reasons, the use of buffers with a greater differential in pH values has become the convention (e.g. pH = 4.00 and pH = 7.00 or pH = 7.00 and pH = 10.00). The multi-point calibration is a commonly used method and is usually carried out as a three-point calibration (typically pH = 4.00, pH = 7.00 and pH = 10.00). The measuring accuracy of the system can be determined if a multi-point calibration is used with at least five buffers and a suitable mathematical evaluation of the calibration curve carried out.

During the calibration, the pH electrode is placed in a buffer. Either the meter recognizes the buffer automatically or the pH of the buffer solution has to be entered manually. The instrument uses the measured voltages to calculate the zero point voltage ( $U_0$ ) at pH = 7.00 and the practical Nernst factor ( $U_N$ , the electrode slope). Electrodes with a slope that is 90-105% of the theoretical slope (59.16 mV/pH) can be used for normal measuring applications. The pH meters by Sartorius not only show whether an electrode is working properly, but they also indicate the last measuring slope during calibration in the "SETUP" menu (PB-20) or under "Cal Data" (Professional Meter).

## Buffer Solutions

Standard solutions (reference solutions) should maintain a constant pH even in the presence of contamination by acids or bases. This is a property common to buffer solutions.

	pH	After adding 10 ml of HCl 1 mol/L to one liter	Difference $\Delta$ pH
Pure water	7.00	2.01	4.99
Acetic acid 0.1 mole/L	2.47	2.00	0.47
Acetic acid – acetate buffer	4.75	4.71	0.04

Typical buffer solutions are mixtures of a weak acid with a salt that forms this acid together with a strong base or a mixture of a weak base with a salt that forms the base in combination with a strong acid. The most commonly used varieties are mixtures of acetic acid and sodium acetate (the sodium salt of acetic acid) or citric acid and sodium citrate (the sodium salt of citric acid).

When a buffer is diluted with pure water, the ratio of acid to salt does not change. The only thing that changes is the concentration and the activity coefficient. That means that only minor changes in pH occur. Because the dissociation of water is temperature-dependent, the pH of buffer solutions is also dependent on the temperature. In commercial buffer solutions, the pH values are listed in a table as a function of temperature. These tables are usually printed on the packaging or enclosed as a package insert. When working with modern pH meters with automatic buffer recognition, it is imperative to make sure to use a buffer that has its temperature coefficient stored in the instrument.

Buffers are pH standard solutions used for calibration (or adjustment) of the electrode and the instrument. Buffer solutions for calibration are selected in accordance with the accuracy required for the specific measurement. According to IUPAC<sup>5</sup> recommendations, a primary standard is not necessary for most measurements if appropriate secondary standards are available. So-called technical buffers (uncertainty  $\pm 0.02$ ) are less sensitive to impurities, but have a lower accuracy than standard buffer solutions (uncertainty  $\pm 0.005$ ). For medical applications, special buffers are available that are adapted to the specific measuring conditions e.g. blood.

The conventional buffer solutions used in the laboratory are technical buffers to calibrate the pH to two decimal places. They are supplied in a variety of packages (glass vials or sealed 25-ml plastic bags, capsules with powder to be dissolved in water, variously sized bottles). Whichever type of packaging you select depends on how often you have to calibrate because buffer solutions only have a limited shelf-life. In particular, strongly alkaline solutions will change their pH noticeably when they come into contact with CO<sub>2</sub> in the air. If stored in sealed bottles, buffers will keep for several months to two years, especially if they have a fungicidal additive. Once the bottle has been opened, the solutions should be used within a few weeks as well. Buffer solutions prepared from capsules will remain stable at room temperature for approx. 10 - 14 days. Therefore, it makes more sense to prepare 100 ml of solution regularly rather than larger amounts like 500 ml all at once. To avoid any migration of fluids into the buffer, calibrations should NEVER be carried out in the storage container. You should NEVER pour used buffer back into the storage container. Buffer solutions will remain stable in a glass beaker for a maximum of 2 hours. Alkaline buffers in particular should never be reused.

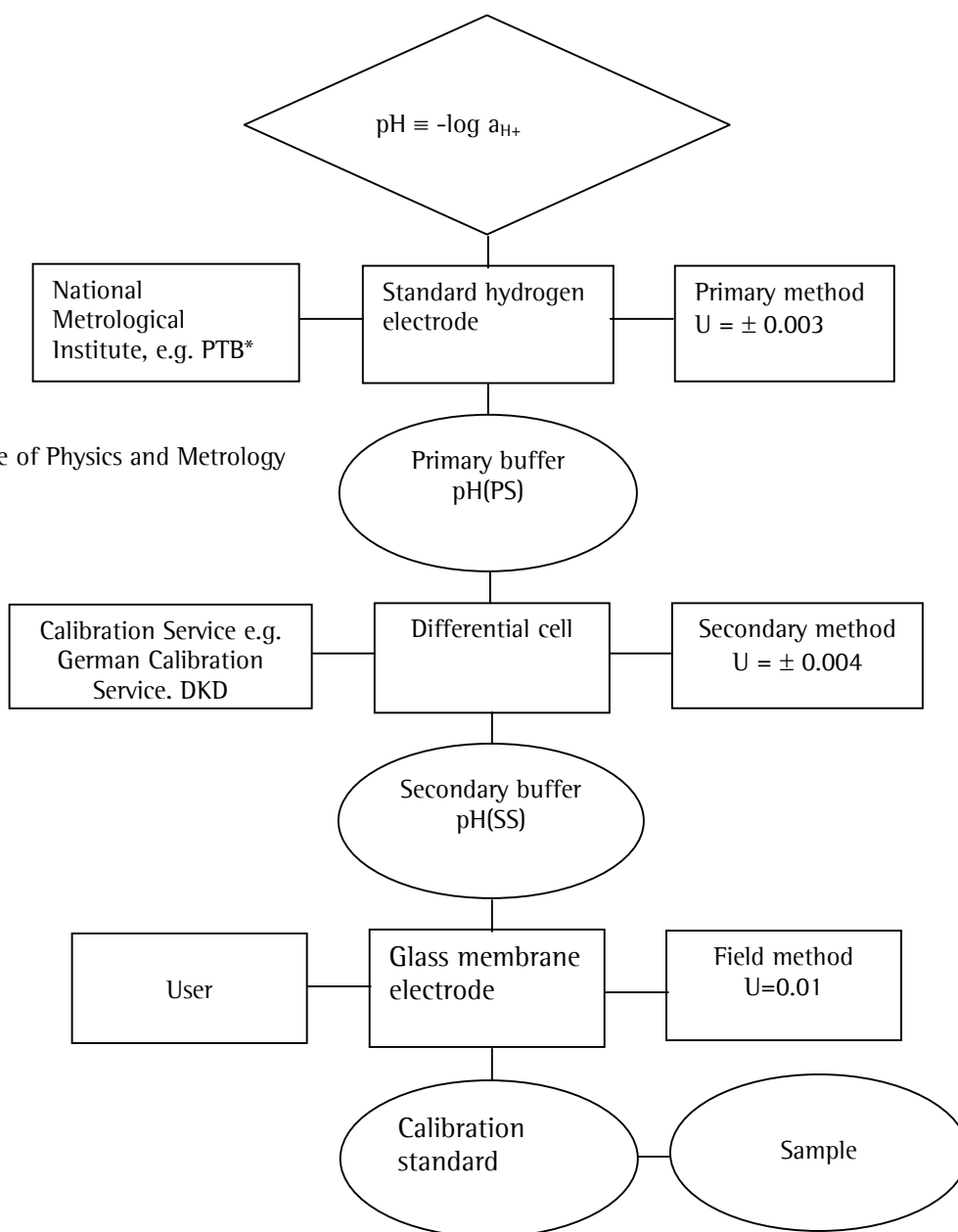
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<sup>5</sup> IUPAC: International Union of Pure and Applied Chemistry

## The Traceability of Buffer Solutions to International Standards

Just like with all calibration and adjustment instruments that work on the principle of standards, pH buffer solutions can also be assigned to international norms. Traceability is defined as the “property of an unknown sample X whereby its pH value can be related to primary standards through an unbroken chain of comparison” and where the uncertainty of the measurement which ultimately yields the tolerance of the commercial standard is known for each reference measurement.

Primary standards are standards that comply with the guidelines of the IUPAC which are known or generally accepted to satisfy the highest metrological requirements and whose value is accepted without comparison with other standards of the same nominal composition. Primary pH standards are aqueous solutions of selected buffers whose pH [pH(PS)] is measured over a temperature range of 0 - 50 °C that have been measured with a cell without transference, called the Harned Cell. Secondary standards are derived by secondary methods, which allow the assignment of pH values by comparison with primary standards of the same nominal composition.



\* German Federal Institute of Physics and Metrology

## The Actual pH Measurement

In the following, we will look at pH measurements under typical laboratory conditions. The pH range is between  $\text{pH} = 2$  and  $\text{pH} = 12$ , the temperature between  $10\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$ . The system is buffered, aqueous and homogeneous, with a NaCl salinity of approx. 0.5 - 4 moles/L. This is the range in which virtually all standard electrodes can be used and if the pH meter is calibrated, samples can be measured. Immerse the electrode in the sample solution and provide moderate stirring (approx. 1 - 5 minutes) until a stable reading is displayed. Modern pH meters like the Sartorius measuring devices have a symbol in the display that signals when the reading has stabilized.

After each measurement, the electrode must be rinsed off with deionized water and carefully patted with a soft absorbent paper and without directly touching the glass membrane (never rub the electrode).

## Optimizing pH Measurements

The electrode's properties (slope, clogged diaphragm etc.) have the greatest impact on the results of a pH measurement. Thus, the best way to prevent malfunctions is to calibrate the instrument at regular intervals. The pH meters in the Professional series are equipped with a feature that allows you to define the calibration interval. The instrument then reminds the user automatically whenever a calibration is due.

Meticulous laboratory procedures can minimize a number of other effects that can disturb the measurement, for example, different levels of the electrode filling. Measurements that must be very accurate are also affected by how intensively the sample is stirred, particularly if an exchange of carbon dioxide takes place with the air, the reading can be subject to drift. The reading can also drift when the electrode is taken from a strongly acidic solution (e.g.  $\text{pH} = 1$ ) and transferred directly to a strongly basic solution or vice versa (memory effect).

## Quick Guide for Measuring the pH with Glass Membrane Electrodes

1. Select an electrode that is suitable for the current pH and temperature range and the material to be measured (liquid, gel, suspension, ...). If the pH meter is not equipped with a temperature sensor, use a separate temperature sensor.
2. Preparing the electrode  
When using electrodes with liquid fill solution, open the fill hole (remove the rubber stopper or open the slide cover), and fill up with electrolyte if necessary.  
The fill hole must ALWAYS remain open during the calibration and the measurement.  
Remove the wetting cap from the electrode.  
Rinse the electrode with deionized water and pat dry.
3. Connect the electrode (and, if appropriate, the temperature sensor) to the pH meter according to instructions.
4. Standardize the pH meter  
Select a buffer suitable for the expected pH range (e.g. technical buffers with pH = 4.0, pH = 7.0 and pH = 10.0).  
The pH values of the buffer solutions should be bracketed by at least two units to be recognized automatically.  
Always standardize within the temperature range in which the measurements are to be performed.  
Select a buffer set from the pH meter menu.  
Select the "pH" mode on the pH meter.  
Prepare buffer solution in suitable vessel.  
Immerse the electrode (and, if appropriate, the temperature sensor) in the buffer solution (e.g. pH = 7.0), provide moderate stirring and wait for a stable reading (equilibrium).  
Enter the reading by pressing "Standardize".  
Remove the electrode from the buffer solution, rinse it with deionized water and pat dry.  
Proceed in exactly the same way for the second and any additional buffers.  
On the Basic Meter PB-20, the message "good electrode" appears in the display when the characteristic slope of the electrode is okay (90 ... 105% of the theoretical value). The display on pH meters of the PP series will give an error reading if the characteristic slope of the electrode is not okay.
5. Measuring the sample  
Add the prepared sample to a suitable vessel.  
Rinse the electrode with deionized water and pat dry.  
Immerse the electrode (and, if appropriate, the temperature sensor) in the sample, stir carefully and wait for a stable reading.  
Remove the electrode from the sample, with rinse it with deionized water and pat dry.
6. Storing the Electrode  
In-between two measurements, store the electrode in an aqueous medium (e.g. diluted buffer pH = 7), not in deionized water with the fill hole closed.  
If the electrode is not to be used for longer periods, disconnect it from the meter, rinse with deionized water and replace the wetting cap filled with KCl solution and then close the fill hole.