

Monograph



pH-measurement

Everything from A – Z
including best practices and examples

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Table of contents

1.	Foreword	7
2.	Terms and definitions – Everything from A – Z	8
	A – for adjustment	8
	A – for alkaline error	8
	B – for buildup of an electrode	9
	B – for buffers and buffer tables	10
	C – for calibration	11
	C – for cleaning	12
	C – for CO ₂ -absorption	12
	C – for crystals	13
	D – for diaphragm	14
	D – for dilution effect	15
	D – for diffusion potential	15
	D – for digital electrodes	15
	D – for double-junction	16
	D – for drift	17
	E – for electrode poisons	17
	E – for electrode test	17
	E – for electrode zero point	18
	E – for electrolyte	19
	E – for electrolyte outflow	19
	F – for filling opening	20
	F – for flow through cell	20
	G – for glass membrane	21
	H – for high-impedance measuring input	21
	H – for hydrated layer	21
	H – for hydrofluoric acid	22
	I – for immersion depth	22
	I – for indicator electrode	22
	I – for insulating resistance	22
	I – for ion-deficient matrixes	23
	L – for LL-reference system	23
	L – for low-maintenance	24
	M – for measuring device	24
	M – for mechanical stress	24
	M – for multi-point calibration	25

4	N – for Nernst equation	25
	N – for non-aqueous solution	26
	O – for offset potential	26
	P – for pH(0)	26
	P – for pH-electrodes	27
	P – for pH-measurement	27
	P – for pH-titration	28
	P – for pH-value	28
	P – for poisoning of the electrode	29
	R – for reference electrode	29
	R – for reference electrolyte	29
	R – for response time	30
	S – for sampling	30
	S – for steepness/slope	30
	S – for segmented calibration	31
	S – for solids	31
	S – for stirring	31
	S – for storage duration	32
	S – for storage	32
	T – for temperature compensation	33
	T – for temperature measurement	34
	T – for type of electrode	34
	T – for two-point calibration	34
	U – for USP<791>	34
	W – for wiping	35
3	pH-calibration and pH-measurement according to USP <791>	36
4	Example applications for the pH-measurement	37
4.1.	General tips for the pH-measurement	37
4.2.	pH-measurement in dyes	37
4.3.	pH-measurement in milk products	37
4.4.	pHe-measurement in bio ethanol according to ASTM D6423 and EN 15490	38
4.5.	pH-measurement in peppermint liquor	38
4.6.	pH-measurement in water according to EPA 150.1, ASTM D1293, ASTM D5464 and DIN EN ISO 10523	38
4.7.	pH-measurement of wet disinfection tissues (wipes)	39
4.8.	pH-measurement in molding sand	39

4.9.	pH-measurement in cheese	39
4.10.	pH-measurement of engine coolant and antirust related to ASTM D1287	39
4.11.	pH-measurements in soil according to ASTM D4972	40
4.12.	pH-measurement in soil according to ISO 10390 and EN 15933	40
4.13.	pH-measurement of wine according to OIV-MA-AS313-15	41
4.14.	pH-measurement in pasta	41
4.15.	pH-measurement in honey, sugar, and sweets	41
4.16.	pH-measurement in jams and fruit juices	41
4.17.	pH-measurement in beer according to AOAC 945.10	42
4.18.	pH-measurement in coffee powder	42
4.19.	pH-measurement in vinegar	42
4.20.	pH-measurement in paper according to ISO 6588-1 and ISO 6588-2	43
4.21.	Initial pH (ipH) of petroleum products according to ASTM D7946	43
4.22.	pH-measurement of washing detergents according to ASTM D1172-15	44
4.23.	pH-measurement in soaps according to ASTM D1172-15	44
4.24.	pH-measurement in leather according to ASTM D2810 and ISO 4045	44
4.25.	pH-measurement in gold electrolyte	45
4.26.	pH-value in ethanolic brews	45
4.27.	pH-measurement in water extract of halogenated organic solvents according to ASTM D2110	45
4.28.	Measuring apparent pH of electrocoat baths according to ASTM D4584	46
5	Tips & tricks for pH-measurement	47
5.1.	Before measurement	47
5.2.	pH-calibration	47
5.3.	Storage of the electrode	47
6	FAQ for pH-measurements	48
7	Literature	52
8	Appendix	54
8.1.	Buffer tables	54
8.2.	Overview of the most common electrodes	57

1 Foreword

pH measurement was established a long time ago and was founded in 1889 by the Nernst equation. This quintessential equation shows that the potential of monovalent ions between two electrodes are changed by 58.17 mV (at 20°C) if there's a 1:10 concentration quotient between inner and outer compartments. But how did this discovery lead to the pH-value scale of today?

This specific scale is defined for values between pH 1 – 14, where 1 is very acidic, 7 is neutral and 14 very alkaline. Who hasn't heard of this scale or of the pH-value before? The pH-value and its scale were discovered a long time ago. In 1909 the chemist Søren Sørensen discovered the advantages of plotting the pH value logarithmically and with that he had invented today's well-known pH-value scale. But why is the determination of the pH-value of such importance? The pH-value is crucial for many chemical reactions in various areas: determining whether or not a medicine is produced, if corrosion occurs, or if a biochemical process occurs in our bodies. Each change in pH-value may cause a disequilibrium or make a process less efficient. Thus, an accurate determination of the pH-value is important for many applications.

Therefore, the determination of the pH-value is one of the most conducted analytical methods worldwide. Normally people assume the determination of the pH-value is something easy, but there are some crucial points which must be considered. It is not only necessary to know the principle of this analytical method but also how to handle the measuring electrode and the corresponding devices. This monograph will give you an overview from A – Z and useful tips and tricks for the handling of electrodes as well as devices. Enjoy yourself reading this monograph and gaining some insights into the fabulous world of pH-measurement.

2 Terms and definitions – Everything from A – Z

8 In this chapter we will explain to you the most important terms and definitions from A to Z. This should serve as a reference book and to help you better understand the world of pH-measurement.

A – for adjustment

From time to time the measuring device must be adjusted (i.e., calibrated) with certified reference resistance. The adjustment is done by certified Metrohm service technicians. An annual service is recommended by Metrohm.

A – for alkaline error

Alkaline error occurs at very high pH-values where the H^+ -ion concentration is very low. It's possible that an excess of alkali ions acts like H^+ -ions. Hence a lower pH-value is measured. This effect can be seen most noticeably with lithium ions but may also occur with sodium and potassium ions.

This type of error can be minimized by choosing the appropriate membrane glass. In Metrohm's portfolio you will find electrodes which only show a very low cross-sensitivity towards alkaline ions. For example, the Unitrode easyClean offers excellent applicability towards alkaline samples as well as an extremely easy way to clean its diaphragm.

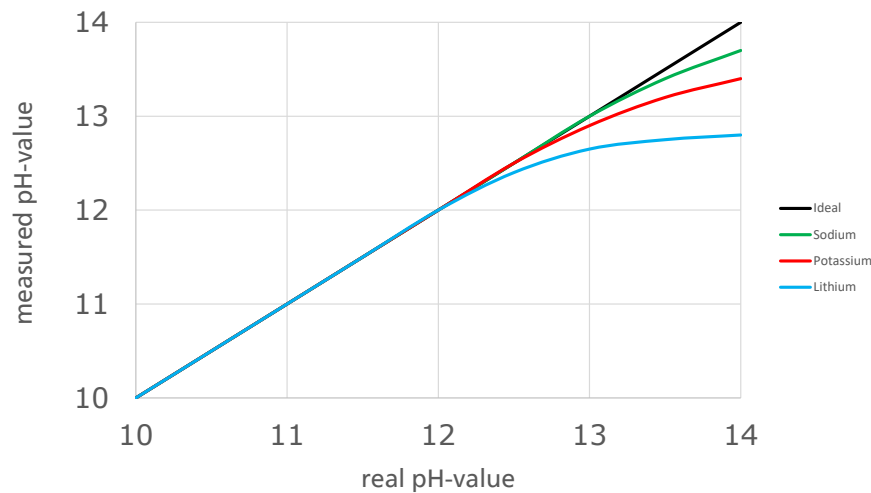


Figure 1: The alkaline error leads to a lower measured pH-value as theoretically existent.

B – for buildup of an electrode

To measure an electric potential, two half-cells are immersed into the same solution. In the case of a pH-electrode, these two half-cells are always a reference electrode which delivers a stable signal and the indicator electrode which changes its potential depending on the H^+ concentration in solution. Since the reference signal is always the same, the H^+ concentration can be calculated by the measured potential difference, and from the H^+ concentration the pH-value can be calculated.

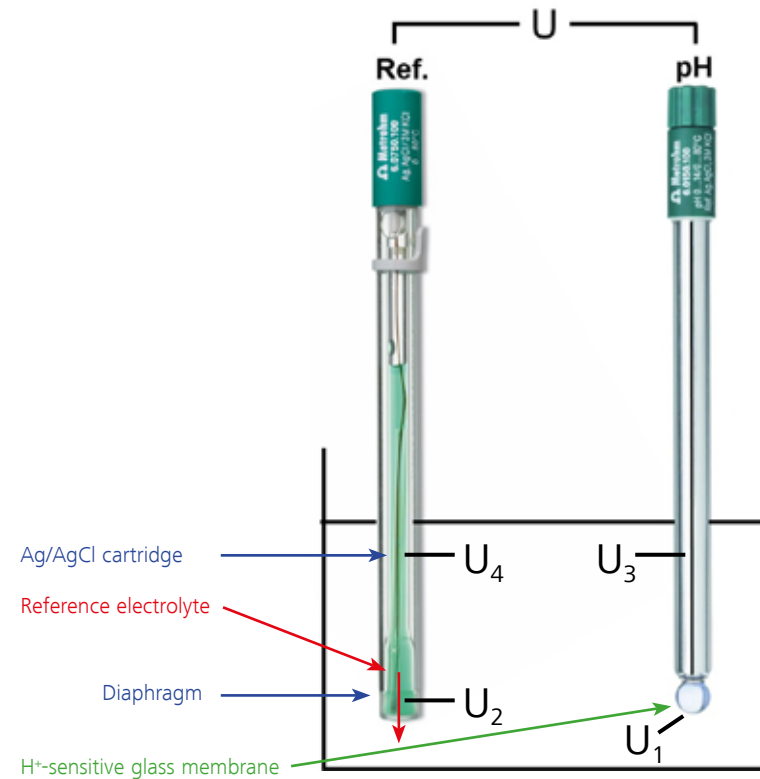


Figure 2: Two-electrode system consisting of an indicator and reference electrode

The pH-electrodes used today don't consist of two separate electrodes, but rather one electrode which combines the reference and indicator electrode in one sensor. This type of electrode is called a «combined pH-electrode.»

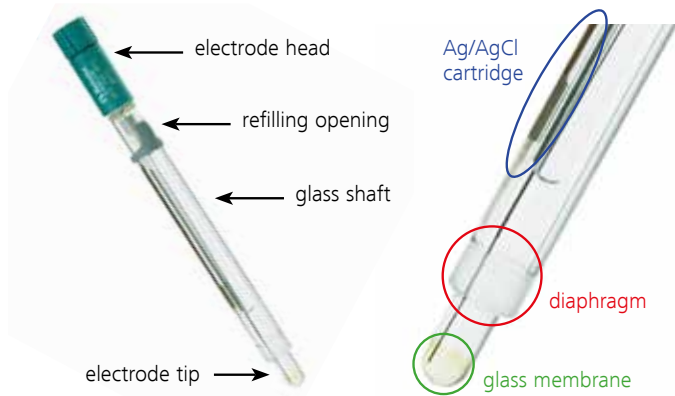


Figure 3: The combined pH-electrode contains all the important parts of a reference and an indicator electrode in one electrode.

This results in the advantage that only a single electrode is needed for measurement. As a result, less sample is required for measurements, which also allows for smaller vessel sizes.

B – for buffers and buffer tables

A buffer is a solution with a defined, consistent certified pH-value. Calibrations can be performed using these buffers. The value of the pH-buffer is temperature dependent, hence the current temperature must be recorded with a temperature sensor or be entered manually. During the calibration, the exact pH-value at the measured temperature is needed, so buffer tables are essential. These tables show the temperature dependence of the buffers and list the corresponding pH-values for nearly all temperatures. An example is given in Figure 4.

Many devices contain pre-programmed buffer tables from different manufacturers. Here, the user only chooses the type of the buffer being used. Assuming a temperature sensor is connected, and the temperature is measured correctly, the correct pH-value is automatically chosen for calibration.



Figure 4: Buffer sachet with on-print buffer table.

C – for calibration

Frequent calibration of the electrode in use is always necessary. Depending on the usage, this can be done on a per-shift, daily, or weekly basis. We recommend a daily calibration to ensure that you obtain correct and precise results. But how is a calibration carried out? There are two different approaches. One option is a one-point calibration, and the other is a multiple-point calibration. The one-point calibration is recommended for estimates of the pH-value, rather than precise determination. Additionally, the electrode should show a fast response time and the slope should be near to the theoretical Nernst slope. A multi-point calibration is recommended when the precision of the result is crucial. The calibration is performed such that the measured value lies inside the calibration range. But how many calibration points are truly necessary? A two-point calibration can be used if the pH-range for the measurement is very narrow, e.g. all samples lie within two pH units. If the measuring range for your sample is wider, at least a three-point calibration is recommended.

The calibration is performed as follows: The pH-buffer with certified pH-values is measured sequentially while rinsing with deionized water in between measurements to avoid carryover error. The measured voltage for each buffer is noted and the theoretical pH-values at the given temperature are plotted against the voltages. A linear regression is obtained which is called the calibration curve. Modern measuring devices carry out the analysis automatically.

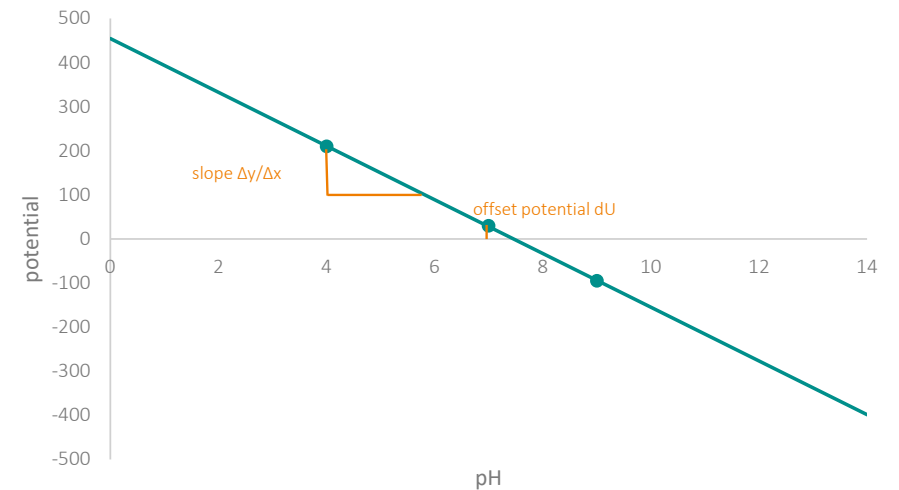


Figure 5: Example of a calibration including the offset potential and the slope.

The example curve of Figure 5 shows a calibration with pH 4, 7 and 9. The theoretical Nernst slope at 20°C is 58.17 mV, which is given by the Nernst-equation. The offset potential defines which potential is obtained for a buffer with pH 7.0. This can also be read out from the calibration curve. A high offset potential (>15 mV) suggests contamination of the reference electrolyte. Please have also a look at «R – for reference electrolyte».

C – for cleaning

Some substances appear to adhere to or react with the glass membrane, or to simply contaminate it. Additionally, a blockage of the diaphragm might appear. Therefore, the right cleaning procedure is essential. However, finding the right cleaning procedure may not be easy. The cause of the contamination must be found, whether it is caused by the sample reaction or by the matrix. Deposits on the glass membrane can be of organic origin or be caused by e.g. proteins.

Table 1 shows an overview of established cleaning agents for different kinds of contamination. Please make sure to open the filling port while cleaning the electrode as otherwise the cleaning agent might enter the reference system of the electrode. After cleaning the electrode make sure to rinse it two to three times with fresh electrolyte solution and allow the electrode to condition for at least a few hours, or ideally overnight in storage solution.

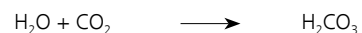
Table 1: Possible kinds of contamination and hints for the cleaning procedures.

Kind of contamination	Proposal for cleaning
Precautionary and frequent cleaning	pHit Kit*, cleaning solution Instructions for use are mentioned in the leaflet of the pHit Kit.
Blockage due to silver precipitation (black ceramic diaphragm)	Immerse the electrode in dilute ammonia solution or use 7% thiourea solution in $c(\text{HCl}) = 0.1 \text{ mol/L}$
Suspensions, solids, glue, resin, oils, fats	Cleaning is done with an appropriate solvent/solution.
Organic contaminations	Cleaning is done with an appropriate solvent.
Proteins	5% pepsin in $c(\text{HCl}) = 0.1 \text{ mol/L}$

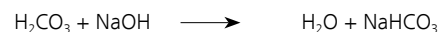
*The pHit kit contains cleaning solution, electrolyte solution $c(\text{KCl}) = 3 \text{ mol/L}$ and storage solution. A detailed instruction for use can be found inside the set.

C – for CO₂-absorption

The influence of carbon dioxide is mostly observed in alkaline solutions. The absorbed CO₂ reacts with water which leads to a lower pH-value as carbonic acid is formed in situ.



If a base (e.g. NaOH) is present in solution, the following reaction takes place:



In this example, the sodium in sodium hydroxide is needed for the formation of sodium bicarbonate. This means that the sodium hydroxide also now contains sodium bicarbonate as well, which lowers the pH.

Hence it is important to prevent alkaline solutions from CO₂-uptake. This can be done by choosing the optimal stirring rate (as fast as possible without forming a vortex) or using a nitrogen atmosphere or a closed vessel during the measurement. Finally, sparge nitrogen from the sample before measuring.

C – for crystals

If an electrode is not used for a long time and is not stored correctly, crystals can be formed in the reference electrolyte chamber. Crystals reduce the electrolyte outflow and therefore the contact of the reference system to your sample.



Figure 6: Electrode with completely crystallized reference electrolyte.

If an electrode with crystals is observed, rinse the reference chamber multiple times with reference electrolyte until all crystals have dissolved. If crystals persist, the electrode can be heated under warm running water. Afterwards, empty the reference electrolyte (e.g. using a bulb pipet) and rinse the chamber at least 3 times with reference electrolyte. In the last rinsing step, the electrolyte is filled up to the filling hole and the electrode is allowed to stand over night to so the diaphragm can recover.

D – for diaphragm

The diaphragm is a critical part of the electrode and is essential for a correct measurement. It establishes the contact between reference electrolyte and measuring solution. Therefore, it is important that the diaphragm is fully functional and clean. Table 2 shows an overview of the different types of diaphragm with their advantage and disadvantage.

Table 2: Overview of the different types of diaphragms which are used at Metrohm.

Type	Description	Advantage	Disadvantage
Ground-joint diaphragm	Two ground surfaces are in contact with one another. The roughness of the surfaces leads to an incomplete seal, so that electrolyte outflow is guaranteed. This creates the contact between reference electrolyte and measuring solution and hence a stable measuring signal. *Outflow approx. 0.1 – 0.8 mL/day, with flexible sleeves 2.4 mL/day	<ul style="list-style-type: none"> – Large surface area – Outflow around the electrode is stable and symmetric – Easy cleaning 	<ul style="list-style-type: none"> – The outflow is relatively high. Therefore, this might lead to contaminations of the sample if the electrode is immersed to long into the measuring solution.
Ceramic pin diaphragm	The diaphragm consists of a ceramic pin which is melted into the glass electrode shaft. This pin siphons the electrolyte and establishes the contact between reference electrolyte and measuring solution. Rinsing the electrode and diffusion of the electrolyte mean the ceramic pin is always «refilled» with new electrolyte from the reference chamber of the electrode. *Outflow approx. 0.1 – 0.4 mL/day	<ul style="list-style-type: none"> – Very low outflow 	<ul style="list-style-type: none"> – Fast clogging of the diaphragm with protein-containing samples or during precipitation titrations. – Diaphragm is porous and therefore offers a surface for chemical reactions.

Type	Description	Advantage	Disadvantage
Platinum thread diaphragm	With this kind of diaphragm, very thin platinum wires are bundled and melted into the glass shaft. The electrolyte transport is made by capillary forces along the thin wires. The platinum is soft and porous. Hence, a mechanical cleaning is not recommended. *Outflow: approx. 0.1 – 0.8 mL/day	<ul style="list-style-type: none"> – Can be used for electrodes with very small diameter. – Risk of contamination is lower as in the ceramic pin diaphragm – Can be used for biological samples 	<ul style="list-style-type: none"> – No mechanical cleaning possible – Cannot be used with highly redox-active solutions.
Capillary diaphragm	With the capillary diaphragm a tube is melted into the glass shaft of the electrode *Outflow: approx. 0.5 mL/day	<ul style="list-style-type: none"> – Constant and reproducible outflow – Short equilibration time 	<ul style="list-style-type: none"> – Only works with viscous electrolytes, otherwise the outflow is too high
Twin-Pore-diaphragm	This type of diaphragm is used with gel electrodes. *Outflow: nearly zero	<ul style="list-style-type: none"> – Nearly no outflow – Low maintenance reference system 	<ul style="list-style-type: none"> – Cannot be used for ion-deficient, low buffered solutions, otherwise the gel is leached out very fast.

*The outflow is always given for a water column of 10 cm at a temperature of 25°C. If the water column is higher, the outflow can be much higher.

D – for dilution effect

If water is added to the sample, the sample is diluted. This can lead to a shifting of the reaction equilibrium due to the fact that more salts are dissociating. This can then lead to a change of the pH-value.

D – for diffusion potential

The diffusion potential originates at the phase boundary between different electrolyte solutions, caused by an uneven distribution of the electrolyte. The diffusion potential can be understood as the difference of the electric potential between those phase boundaries. The potential is caused by different kinds of ions or different ion concentrations between the reference electrolyte and sample solution.

D – for digital electrodes

Digital electrodes have one big advantage over the analogue electrodes – they are not influenced by electrostatic disturbance. All components needed for signal detection are placed in the electrode head and are separated from the measuring device. The analog measuring signal

is converted to a digital one in the electrode head and can be transmitted undisturbed. Additionally, the chip in the electrode head can save all necessary data like last calibration, article number, serial number, etc. thereby giving a complete traceability.

D – for double-junction

A double-junction electrode is an electrode with two electrolyte chambers. The inner chamber is reserved for the reference electrolyte where the outer is used for the bridge electrolyte. The bridge electrolyte chamber can be filled with an arbitrary electrolyte for preventing chemical reactions of the reference system with the measuring solution. This type of electrode is often used for measuring solutions reacting with chloride or potassium ions, for example silver containing measuring solutions.

Additionally, this type of electrode can be used for measuring solutions containing electrode poisons like formaldehyde or hydrogen peroxide. Here, the additional electrolyte chamber prevents the electrode poison from directly entering the reference system of the electrode which prevents it from being damaged.

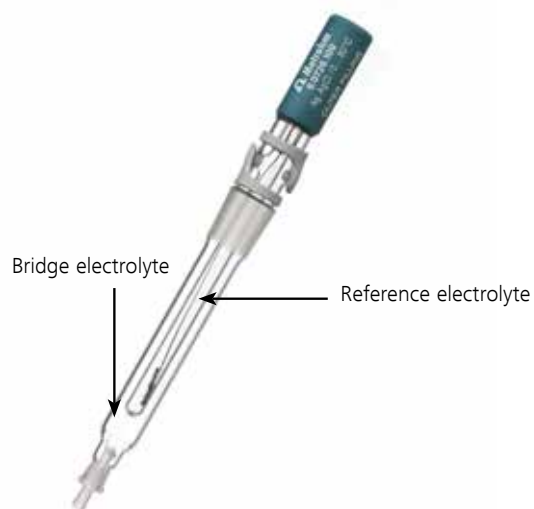


Figure 7: Example of a double-junction electrode.

D – for drift

The drift is a very important parameter for the performance of a measurement. It is indicated in mV/min and defines how strongly the signal may fluctuate. Moreover, the drift defines how strong the fluctuation can be before the measured value is accepted by the measuring device (undercut defined by the drift criteria). The drift therefore decides from which point on the measured value given is constant. The lower the chosen drift value the longer the measurement duration and the more precise the result. Normally the pH-value is measured with a drift between 0.1 and 2 mV/min. If a higher drift value is chosen, it is recommended to define a minimum measuring time. Otherwise, it's possible that no curve will be obtained as the measuring drift is already met when immersing the sensor and measuring the initial value.

E – for electrode poisons

Electrode poisons are substances which degrade the reference system of the electrode and might destroy it. Some examples of such poisons are chlorate-based solutions, formaldehyde, hydrogen peroxide and sulfides. For these types of samples an electrode with double junction system (see «D – for double-junction») must be used. Additionally, it is very important to exchange the bridge electrolyte on a regular basis to avoid the intrusion of these substances into the reference system of the electrode.

E – for electrode test

The electrode ages with time. This means the response time gets longer and the slope (slope of the calibration curve) will begin to decrease. Thus, the sensitivity for different pH-values decreases. To help determine when to exchange your electrode, Metrohm has developed an electrode test that is available on many devices. This test determines the slope of predefined pH-value couples (4/7, 4/9, 7/9), the offset potential, the response time, and the streaming potential after carrying out the test.

The below table gives you an overview over the different parameters which are evaluated as well as their limits regarding the electrode type.

Table 3: Evaluation of the electrode test for different types of electrodes.

Parameter	Excellent Electrode	Good Electrode	Usable Electrode
Electrode type: Standard			
Streaming potential dU [mV]	≤ 2.5	≤ 3.0	≤ 4.0
Total drift [mV]	≤ 2.0	≤ 2.5	≤ 3.0
Slope s [%]	96.5 ≤ s ≤ 101	96 ≤ s ≤ 102	95 ≤ s ≤ 103
Response time [s]	≤ 45	≤ 50	≤ 60
Offset potential U _{off} [mV]	-15 ≤ U _{off} ≤ 15		
Electrode type: Gel			
Streaming potential dU [mV]	≤ 3.0	≤ 3.5	≤ 4.5
Total drift [mV]	≤ 2.5	≤ 3.0	≤ 4.0
Slope s [%]	96.5 ≤ s ≤ 101	96 ≤ s ≤ 102	95 ≤ s ≤ 103
Response time [s]	≤ 60	≤ 75	≤ 90
Offset potential U _{off} [mV]	-15 ≤ U _{off} ≤ 15		
Electrode type: Non-aqueous			
Streaming potential dU [mV]	≤ 3.0	≤ 4.5	≤ 6.0
Total drift [mV]	≤ 5.0	≤ 7.0	≤ 9.0
Slope s [%]	88 ≤ s ≤ 120	80 ≤ s ≤ 130	70 ≤ s ≤ 140
Response time [s]	≤ 60	≤ 75	≤ 90
Offset potential U _{off} [mV]	-10 ≤ U _{off} ≤ 70		

More detailed information regarding the test procedure and the possible actions after the test can be found in our Application Bulletin «AB – 188: pH measurement technique».

E – for electrode zero point

The electrode zero point corresponds to the pH-value measured at 0 mV. It is frequently designated as pH(0) or pH_{assy} (asymmetry potential) and is determined by a calibration with buffers of known pH-values.

E – for electrolyte

Electrolytes are chemical compounds which are dissociated to ions in their solid, liquid and dissolved state. In the field of pH-measurement the term electrolyte is often used as abbreviation for reference electrolyte. Please have a look at «R – for reference electrolyte».

E – for electrolyte outflow

Please ensure that the electrode is always filled completely and with the right electrolyte up to the filling opening. This is important because the reference system of the electrode must always stay in contact with the measuring solution. This is ensured by the electrolyte. If no or a too low level of electrolyte is present in your electrode, the contact cannot be guaranteed any longer and it is possible that sample will diffuse into the electrode and «poison» it. Too low means in this case that the electrolyte level is below the level of your sample. If this happens then the electrode cannot be recovered by corresponding cleaning procedures anymore but must be replaced. Also sample solutions which do not contain electrode poisons might be problematic when they enter the reference system of the electrode as they can lead to possibly «unstable» measuring values which are difficult to explain. In worst case the electrolyte flow is completely disrupted, or the diaphragm is clogged. All these problems can be avoided by regular control of the filling level of the electrolyte.

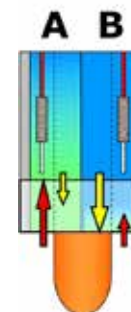


Figure 8: Outflow at low (A) and high electrolyte level (B), respectively.

On the left side (A) of Figure 8 you see the electrode in nearly empty state. In this state sample might diffuse into the electrode. On the right side (B) you see an electrode with filled electrolyte level. The diffusion of the electrolyte into the sample solution is guaranteed and therefore the diffusion of the sample into the electrode is prevented. At the same time the blocking of the diaphragm due to sample diffusion into the electrode is minimized or prevented.

F – for filling opening

Combined pH-glass electrodes contain a filling opening to refill the reference electrolyte. The electrolyte should be filled frequently up to the opening.



Figure 9: Shows an Unitrode which is refilled with electrolyte.

During the pH-measurement it is important that the filling opening is opened. Otherwise, the electrolyte cannot flow out constantly which might lead to an unstable reference signal, contamination of the electrode or clogging of the diaphragm. For cleaning purposes, the electrode filling must be opened as well.

During storage or if the electrode is not used for a longer time (e.g. over lunch time) the filling opening must be closed. This prevents an excessive outflow of the electrolyte or an evaporation of the electrolyte which might lead to crystal formation or even a drying out of the electrode.

F – for flow through cell

If the properties of the sample are highly changed by air (e.g. CO₂-absorption, degradation) it might be beneficial to measure the sample via a flow-through cell.



Figure 10 Flow through measuring vessel for 12 mm electrodes (list part number 6.1420.100)

G – for glass membrane

The glass membrane consists to 70% of glass-forming silica dioxide and variable amount of alkali and earth-alkali ions. For the specific functionality, three- and four-valent ions must be added. Depending on the ion these increase the mechanical robustness and/or decrease the cross-sensitivity of the corresponding electrode.

Due to the hydration layer on the glass membrane which is formed when the electrode is immersed into aqueous solutions a potential is formed. This hydration layer is approximately 0.1 µm thick. If this layer is not present anymore e.g. when the electrode is stored dry or the hydration layer is getting too thick because it was improperly stored (e.g. storage in reference electrolyte instead of storage solution) the electrode responds slower and shows unstable measuring signals. For more information about the hydration layer have a look at «H – for hydrated layer».

H – for high-impedance measuring input

The electrode has a very high insulating resistance. Hence it is important that also the measuring input is of high impedance. Normally the measuring devices show a resistance of approx. 1012 Ohm. Thereby it is ensured that the DC voltage signal is amplified unbiased, and the measurement is possible without problems. Therefore, it is important to connect the electrode always to the right measuring input on your device.

H – for hydrated layer

Each glass electrode develops during its storage in salt solutions or liquids, respectively, a very thin film on the glass which cannot be observed by eyes and therefore cannot be judged visually. This film is called hydration layer and is responsible that a change in potential can be detected. If acidic solutions are measured H₃O⁺ ions are incorporated into the hydration layer and the layer gets positively charged. A negative charge of the hydration layer takes place if the electrode is dipped into an alkaline solution. The OH⁻ ions are then incorporated which charges the hydration layer negatively. The thickness of the hydration layer is essential for a fast response time. Additionally, a shift in the zero potential can be observed if the layer is destroyed. Dry storage or storage in a wrong medium can lead to a thicker or destroyed hydration layer. Please also read the section «S – for storage».

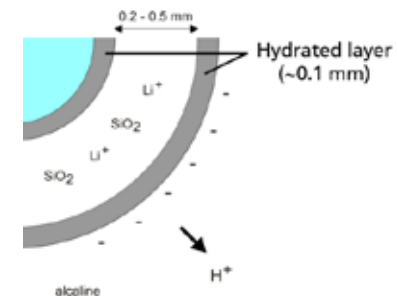


Figure 11: Cross section of a glass membrane. The hydrated layer is shown in grey

H – for hydrofluoric acid

Hydrofluoric acid attacks the glass and damages the pH-glass electrode. The hydration layer is destroyed, and the glass will get thinner and thinner with time until it breaks. Thereby the electrode becomes unusable. For solutions with a low content of HF we recommend the use of the Solitrode HF. If the amount of HF increases, frequent replacement of the electrode is inevitable. For acid-base titrations in solutions containing a high amount of HF, an antimony electrode is available. However, it is not made for pH measurements due to a different design.

I – for immersion depth

The electrode should be placed in such a way that the diaphragm is fully immersed into the sample solution. Otherwise, this might lead to measuring errors or to drifting measured values because the sample solution is not in contact with the measuring system. It should be observed that the level of the sample solution can change while stirring. Accordingly, the immersion depth should be checked with a running stirrer to ensure that not only the glass membrane but also the diaphragm is completely immersed into the sample solution.

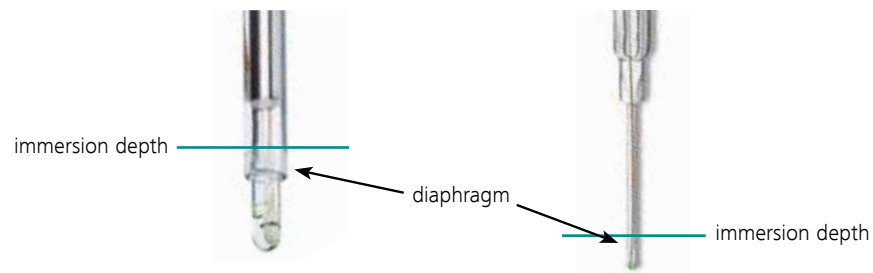


Figure 12: Minimal immersion depth for two pH-electrodes with different types of diaphragms.

I – for indicator electrode

To measure an (electric) potential two half cells, which are immersed into the sample solution are needed. These two half cells are called the indicator electrode and the reference electrode. The indicator electrode changes its potential depending on the concentration of the H^+ -ions in solution. When performing a pH-measurement, the glass membrane takes over the function of the indicator electrode. Nowadays pH-electrodes are normally sold as combined pH-electrodes. For a more detailed explanation of the design have a look at «B – for buildup of an electrode».

I – for insulating resistance

The insulating resistance is the ohmic part of the resistance between two conductors. When looking at the pH-measurement the whole measuring chain including the pH-electrode, the measuring device, and the cable for connecting the electrode is essential. Because the pH-electrode has a high inner resistance, the cables and measuring inputs must be high impedance.

I – for ion-deficient matrixes

Ion-deficient solutions e.g. deionized water have a low conductivity. The pH measurement in ion-deficient solutions is extremely challenging as the low conductivity leads to a higher resistance on the diaphragm. This contact resistance develops due to dilution of the electrolyte on the diaphragm. The outflow rate is thereby lowered, and the electrode becomes inactive. This effect can be avoided by using an electrode with the «right» diaphragm, in this case an electrode with ground-joint diaphragm.

L – for LL-reference system

The long-life reference system (LL-reference system) is typically built in into nearly all Metrohm electrodes. It is a cartridge which is filled with silver chloride particles and it allows an electrolyte exchange only. In normal electrodes, where the AgCl is freely available in the electrode, a relatively high amount of soluble aqueous silver chloride complexes is present: $[AgCl_2]^-$, $[AgCl_3]^{2-}$, $[AgCl_4]^{3-}$. The solubility of these AgCl-complexes depends on the chloride concentration of the solution. Measuring solutions normally contain a lower amount of chloride ions as the reference electrolyte. If we now assume that the reference electrolyte flows out into the measuring solution, a small amount of these complexes will precipitate as AgCl as the chloride concentration on the boundary decreases. This can lead to a blockage of the diaphragm.

The second reason for the LL reference system is the temperature dependence of the solubility of the AgCl. If the temperature is increased also the solubility increases. With normal electrodes this process takes place quite fast because a high surface area for the ion exchange is present. In contrast the AgCl in the cartridge cannot diffuse into the reference electrolyte of the reference chamber. Therefore, we do not have a risk that with a temperature gradient the AgCl precipitates in the diaphragm potentially causing a blockage

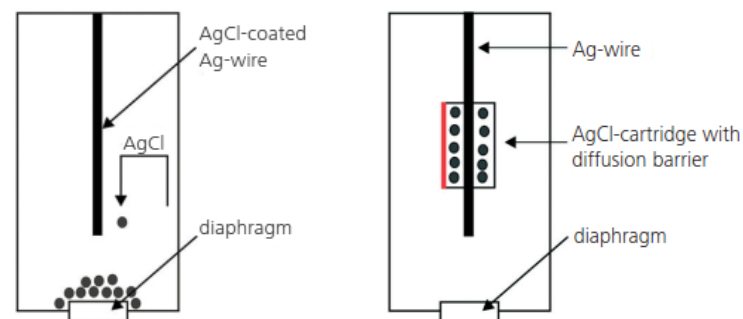


Figure 13: On the left: normal reference system with AgCl and an AgCl coated guide wire, on the right: the LL-reference system

L – for low-maintenance

Metrohm offers pH-electrodes which are filled with a gel reference electrolyte. This type of electrolyte shows nearly no outflow and therefore needs nearly no maintenance of the reference system. With this type of electrode, the electrolyte does not need to be refilled but it is consumed over time which is visualized by a higher transparency of the gel. If the gel is fully consumed which is visualized when the more transparent part of the gel reached the green line, the electrode should be replaced. This type of electrode should not be used in ion-deficient samples as the gel will leak out rapidly. Therefore, for ion-deficient samples, more suitable electrodes should be used. To find an appropriate electrode for your sample please visit our website www.metrohm.com under <https://www.metrohm.com/en/products/accessories/electrode-finder/>

M – for measuring device

The measuring device must have a high-impedance measuring input that can connect to a pH-electrode. There are different types of measuring devices, e.g. benchtop instruments for use in laboratories or handheld meters for mobile use. Handheld meters are built in such a way that only trace amounts of dirt and humidity can enter the device (protection class IP67). Many measuring devices are equipped with additional functions which offer more comfort and security regarding the accuracy of the measuring values. Examples are connection of a temperature sensor, calibration with automatic saving functions or miscellaneous monitoring functions.

M – for mechanical stress

The mechanical stress of a pH-electrode is often underestimated. Severe damage of the sensitive glass membrane can happen, for instance when the electrode is misused as stirrer. Scratches and micro cracks can occur which make the electrode unusable and in rare cases can also cause short circuits in the electrode.

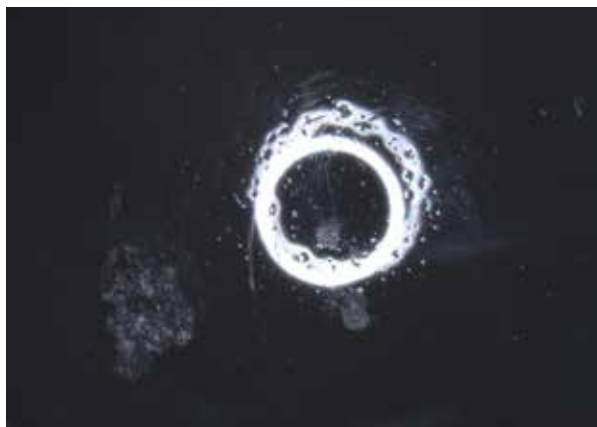


Figure 15: Microscopy recording of a glass membrane surface which show scratches after misusing the electrode as stirrer.

M – for multi-point calibration

If a calibration is done with three or more pH-buffers one talks about multi-point calibration. A special version of the multi-point calibration is the segmented calibration which is described in chapter «S – for segmented calibration».

A calibration with multiple pH-buffers is recommended if the pH range of the measurement is wider than 2 pH units.

Additionally, a multi-point calibration with three or more buffers allows for recognition of disturbances, e.g. contamination of the buffer solutions. The measured value of a contaminated buffer would strongly deviate from the linear regression of the calibration.

N – for Nernst equation

$$E = E^0 + \frac{R \cdot T \cdot 2.303}{F} \cdot \log a_{\text{H}_3\text{O}^+}$$

Where E and E₀ are the electrode and standard electrode potential, respectively, R is the universal gas constant (8.31447 J/mol x K), T is the absolute temperature in K, F is the faraday constant (96485.34 C/mol) and a_{H₃O⁺} is the activity of the hydronium ion.

The Nernst equation is one important keystone of the potentiometry. It predicates how much the voltage is changing when the activity of the hydronium ions is changed by one power of ten. In the region of low concentration, the activity is nearly proportional to the concentration of the ion in solution. Hence the equation pH = -log(c(H₃O⁺)) is valid. The Nernst equation also shows a temperature dependence between potential and concentration. Therefore, it is important to measure the temperature with each pH-measurement and to document it properly.

The following table should give you an overview of the temperature dependence of the Nernst slope.

Table 4: Temperature dependence of the Nernst slope.

temperature/°C	slope mV/pH unit
0	54.20
10	56.18
15	57.18
20	58.17
25	59.16
30	60.15
35	61.14
40	62.14

N – for non-aqueous solution

The pH-measurement in non-aqueous solutions is technically not possible because the pH-value is only defined for aqueous solutions. The activity of lysonium-ions is different than hydro-nium-ions. For example, when performing a pH-measurement of ethanol, we speak of a pHe-value and not of a pH-value.

Because pH-electrodes are calibrated with aqueous buffers pH-value measurements of non-aqueous media must be treated with care. You may also hear this referred to as the apparent pH-value.

O – for offset potential

The inner tubing of a pH-electrode is filled with buffer pH 7.



Figure 16: Filled inner glass tubing of a Unitrode which is marked in red.

Theoretically this means that if we measure a buffer with a pH of 7, the potential should be 0 mV, as the same solution is present both inside and outside the membrane. In practice, however, you normally observe a slight shift of the potential. Potentials between -15 and 15 mV are common and normal. This shift in potential is called offset potential. This occurs as the measuring chain (electrode and device) is never 100 % perfect, is liable to tolerances and the assembly parts might have small systematic errors.

The offset potential can be determined by performing a pH-calibration or by measuring a pH-buffer with a pH-value of 7.

P – for pH(0)

pH(0) is a common denomination for the electrode zero point. It corresponds to the pH-value which is measured at a potential of 0 mV. This value is determined during a calibration. The optimal value lies between a pH-value of 6.8 and 7.2.

P – for pH-electrodes

The pH-electrodes are the most important part of a pH-measurement. If the electrode is old, defective, or contaminated no precise measurement can be guaranteed. Information on how to test electrodes can be found in the chapter «E – for electrode test». When choosing an electrode, the pH-glass membrane and the type of diaphragm must be chosen according to their field of application. Metrohm AG offers for each requirement a suitable electrode. An overview can be seen in Table 5. If you don't find a suitable electrode in this table, please have a look at our electrode finder at www.metrohm.com.

Table 5: Variety of different electrodes.

**Unitrode easyClean**

- For routine application
- Ground-joint diaphragm for accurate measurements
- LL reference system
- pH-measurement in different sample matrices
- pH-range 0 – 14

Aquatrode plus

- For weakly buffered solutions
- Bridge electrolyte can be chosen freely
- Gellified reference electrolyte
- Ground-joint diaphragm for accurate measurements
- LL reference system

EtOH-Trode

- For pHe-measurements in ethanol or other non-aqueous media
- Ground-joint diaphragm for accurate measurements
- Double-junction system; bridge and reference electrolyte can be chosen freely
- LL reference system

P – for pH-measurement

For performing a pH-measurement, a suitable pH-electrode as well as a high-impedence measuring device is needed. If you go to «P – for pH-electrodes» you will get some help to find the right electrode and under «L – for low-maintenance».

Metrohm offers pH-electrodes which are filled with a gel reference electrolyte. This type of electrolyte shows nearly no outflow and therefore needs nearly no maintenance of the reference system. With this type of electrode, the electrolyte does not need to be refilled but it is

consumed over time which is visualized by a higher transparency of the gel. If the gel is fully consumed which is visualized when the more transparent part of the gel reached the green line, the electrode should be replaced. This type of electrode should not be used in ion-deficient samples as the gel will leak out rapidly. Therefore, for ion-deficient samples, more suitable electrodes should be used. To find an appropriate electrode for your sample please visit our website www.metrohm.com under <https://www.metrohm.com/en/products/accessories/electrode-finder/>

«M – for measuring device» you will find some tips regarding the measuring device. Practical tips & tricks for the pH-measurement can be found in chapters 3 to 5.

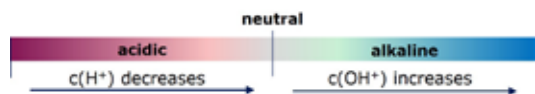
P – for pH-titration

While performing pH-titrations the change of the pH-value after addition of titrant is detected. For evaluation and calculation, the equivalence point is used. Hence the exact determination of the pH-value can be neglected for most kinds of titrations. Therefore, also a calibration is not necessary in most cases. However, from time to time it is recommended to calibrate the pH-electrode as a quality control. The only exception is the end point titration where we titrate up to a defined pH-value. Here, a calibration is mandatory.

More information about titration in general can be found in the monograph «practical aspects of modern titration» of Metrohm. Practical examples for the pH-titration you can find in our Application finder under <https://www.metrohm.com/en/applications>.

P – for pH-value

The pH-value determines if a sample is acidic, neutral, or alkaline.



It is defined as the negative logarithm of the hydronium ions concentration in solution:

$$\text{pH} = -\log(c(\text{H}_3\text{O}^+))$$

The concentration of hydronium ions ($c(\text{H}_3\text{O}^+)$) is considered logarithmically for the pH-value determination / pH-value calculation. The determination of the pH-value is extremely important for biological processes and a very important control parameter for industrial processes as well as a quality parameter for convenience products. Examples for different products and biological liquids are mentioned in Table 6.

Table 6: Examples of different pH-values of different substances.

pH-value	substance	pH value	substance
1	Hydrochlorid acid	7.5	Blood
1.5	Gastric acid	9.5	Soap
3	Coke	10	Detergent
5	Mineral water, coffee	12	Chalk
6	Urine	14	Sodium hydroxide
7	Ultrapure water		

P – for poisoning of the electrode

Different chemicals can act as electrode poisons if they enter the reference electrode system. These chemicals can irreversibly change the properties of your reference system or even destroy it.

For example, these poisons can be disinfectant containing chlorate, sulfide, formaldehyde, and hydrogen peroxide. If such chemicals are present in your sample, we recommend using an electrode with a double-junction system. Please keep in mind that the bridge and reference electrolyte must be exchanged on a frequent basis.

R – for reference electrode

To measure an (electric) potential, two half-cells must be immersed into the same solution. These two half-cells are called the indicator and reference electrode. The reference electrode delivers a stable potential independent of the concentration of the measuring ion. The stable potential is caused by the outflow of a reference electrolyte as a connection between the diaphragm and the sample solution is established.

20 years ago, reference electrodes were still produced with mercurial calomel. Nowadays a new reference system consisting of Ag/AgCl is used. When having a look at the Metrohm pH-electrodes the LL reference system takes over the part of the reference electrode. Today pH-electrodes are offered as combined pH-electrodes. Please have also a look at «B – for buildup of an electrode»

R – for reference electrolyte

The reference electrolyte establishes the connection of the reference electrode with the sample. Thus, it is important that the electrolyte can flow out from the diaphragm continuously to ensure a proper contact. Please have also here a look at «E – for electrolyte outflow».

In most cases KCl is used as reference electrolyte. If potassium or chloride ions are disturbing the measurement an electrode with a double junction system can be used. Here the bridge

electrolyte can be chosen freely, e.g. $c(\text{KNO}_3) = 1 \text{ mol/L}$. By default, Metrohm electrodes mention the corresponding electrolyte which is filled into the electrode on the electrode head. Please make sure to refill the electrode also with the mentioned electrolyte. Low maintenance pH-electrodes normally use a jellified reference electrolyte. Have also a look at «L – for low-maintenance».

R – for response time

The response time of the electrode corresponds to the time between starting the measurement and reaching the end measured value $\pm 1 \text{ mV}$. This means if the end measured value corresponds to 120 mV, the time is evaluated from immersing the electrode until the point of 119 or 121 mV is reached, respectively. The response time is dependent on the electrode type as well as its state. In general, the following is applicable:

Table 7: Response time for different types of electrodes.

Type of electrode	Excellent electrode	Good electrode	Usable electrode
Standard	$\leq 45 \text{ s}$	$\leq 50 \text{ s}$	$\leq 60 \text{ s}$
Gel	$\leq 60 \text{ s}$	$\leq 75 \text{ s}$	$\leq 90 \text{ s}$
Non-aqueous	$\leq 60 \text{ s}$	$\leq 75 \text{ s}$	$\leq 90 \text{ s}$

The response time can easily be determined using an electrode test.

S – for sampling

Representative sampling is a very important point of every analysis. For sampling regarding pH-measurements a few things must be considered. If the sample should be collected and then analyzed in the laboratory, it must be ensured that the sample is not contaminated onto its way to the laboratory. The sampling bottle must be clean and the temperature during transportation must be kept constant. Otherwise, what might happen is that with high temperatures the substances degrade, and with low temperature the substances are inactivated. Additionally, each beaker or bottle, respectively, should be cleaned once with the sample before the real sampling is done. Carbon dioxide may also change the pH-value of the sample. Here, it is necessary to take note of the amount of air in the bottle after sampling. If the volume is too large, CO_2 might be incorporated into the sample. This is especially valid for ion-deficient matrixes. For such matrixes it is recommended to measure the pH-value direct on-site.

S – for steepness/slope

The steepness or slope of the electrode is determined when performing a calibration. Frequently the result is given as percentage of the ideal Nernst slope. A good electrode has a slope between 98 and 103%.

If you need more information regarding the Nernst slope and Nernst equation, please have a look at «N – for Nernst equation».

S – for segmented calibration

The segmented calibration is a special variety of the multi-point calibration. In contrast to the normal calibration the linear regression is not made over the whole range of measuring points but always between to neighboring points. The advantage of this method is the consideration of the alkali error at higher pH-values, and the disadvantage is that the linear regression cannot be checked as only sequential linear regressions with 2 point are evaluated.

S – for solids

pH-values are normally measured in liquids, but the pH-measurement of surfaces or solids is also possible. This can be done either by the using the flat membrane electrode for surfaces, or with the spearhead electrode for semi-solids like cheese.

The flat membrane electrode has a very low immersion depth of only 1 mm. For the measurement it is important that the surface is wetted, and the electrode is pressed onto the water drop. Only then can the contact between the measuring solution and reference system be granted.

The spearhead electrode has a peaked formed-glass membrane which can be used to pierce the sample. Here it is advantageous if the sample is pre-pierced to prevent a break or splinter of the electrode in the sample. Additionally, the electrode should be turned when removing it from the sample as otherwise a vacuum could be formed which lead to break of the gel. Not doing this can lead to instable measuring signals.



Figure 17: On the left the spearhead electrode and on the right the flat membrane electrode is shown. These electrodes are used for special applications in half-hard solid samples and on surfaces, respectively.

S – for stirring

The sample must be homogeneous during measurement. To ensure this, the sample is stirred with a magnetic or a rod stirrer. It is important that the stirring speed is chosen in such a way that no vortex occurs. Otherwise, CO_2 from the air might be incorporated into the solution or

the solution might be spilled. Nevertheless, the stirring rate should be chosen as fast as possible to be able to mix the sample thoroughly. During calibration and measurement, the same stirring speed should be applied.

S – for storage duration

pH-electrodes age during their storage which leads to longer response times. Hence it is important to not keep too many electrodes on hand. We recommend using the pH-electrode with gel or Idrolyte as reference electrolyte at latest 18 months after production date. All other electrodes should be used at latest 24 months after production date.

S – for storage

The storage of the electrode is mostly neglected. The glass membrane of the electrode has a hydration layer which is destroyed when the electrode is stored dry. Here the electrode gets slower until it is unusable. If we look at the electrode and its needs, there are different parts of the electrode which have different needs. For the glass membrane, deionized water would be the best storage solution because the hydration layer is best formed in water. However, the diaphragm would best be stored in reference or bridge electrolyte as the concentration of the electrolyte in and outside the diaphragm would be the same.

If one stores the pH-electrode of electrode type standard with $c(\text{KCl}) = 3 \text{ mol/L}$ as reference electrolyte in KCl solution, then it can be observed that the response time of the electrode is elongated.

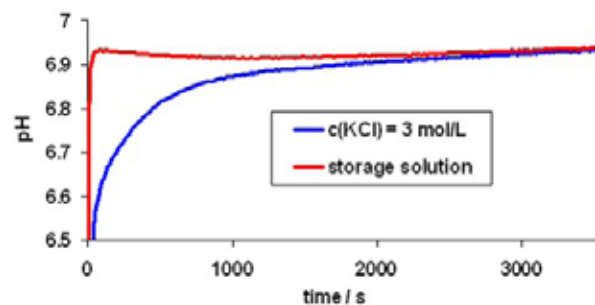


Figure 18: Two electrodes (same type) stored in two different solution: blue in reference electrolyte, red in a special storage solution

This effect is observed due to the migration of potassium ions into the hydration layer which thereby gets thicker. To avoid this, Metrohm has developed a potassium free storage solution. By using this solution, the response time after storage is not affected and at the same time the diaphragm is kept in the best possible condition.

For all pH-electrodes which are not filled with $c(\text{KCl}) = 3 \text{ mol/L}$ as reference electrolyte or bridge electrolyte, we recommend storing the electrode in the corresponding electrolyte. For pH-elec-

trodes which have a jellied electrolyte we recommend storing the electrode in saturated KCl solution to avoid a leach out of the gel and therefore to prevent the electrode of an early aging.

T – for temperature compensation

Based on the Nernst-equation the slope of the calibration line can be corrected depending on the measured temperature. The temperature dependence of the pH-value of the sample however cannot be corrected. As mentioned before under «B – for buffers and buffer tables», the buffer as well as the sample change their pH-value depending on the temperature. If one wants to compare the pH-value of the sample, all samples must be measured at the same temperature. But how does the correction of the steepness of the calibration curve work?

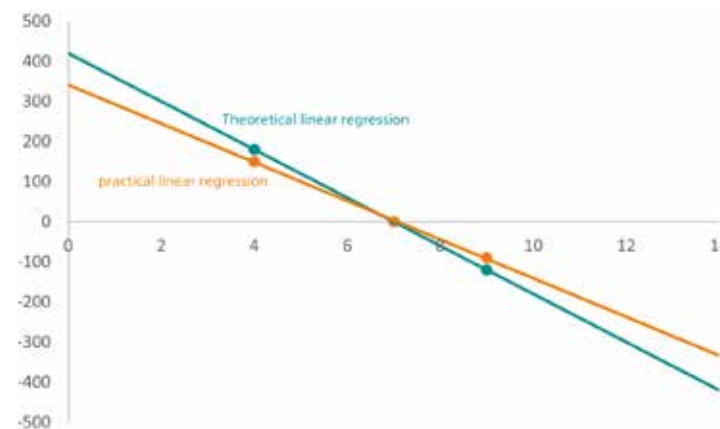


Figure 19: An effective measured pH calibration in comparison to an ideal calibration curve.

To explain this temperature compensation, which is done by the device itself, we will have a look at a practical example: Figure 19 shows two different linear regressions: orange shows the effective calibration curve, recorded at 25°C and the turquoise one the ideal, theoretical linear regression given by the Nernst-equation. The measuring device does not evaluate the slope as mV/pH, but gives the slope in %, means the measured slope is divided by the theoretical slope. According to the chapter «N – for Nernst equation» the theoretical slope at 25°C is 59.16 mV per pH-unit. At this example a slope of 49.17 mV per pH-unit was obtained which in other words mean 83.11 % of the theoretical slope. If now the sample is measured at another temperature as 25°C (e.g. 30°C), the theoretical slope will be calculated for 30°C (60.15 mV/pH) and multiplied by the percentage value of the calibration. In case of 30°C and 83.11% the slope would be 49.99 mV/pH. The measured potential of the sample will be calculated into the corresponding pH-value.

However, not only the slope of the electrode is temperature dependent, but also the offset potential is temperature dependent and cannot be compensated. Therefore, it is recommended whenever possible to perform the calibration and to measure the sample at nearly the same temperature.

T – for temperature measurement

As seen on the Nernst equation the pH-value measurement is temperature dependent. The higher the temperature the higher also the theoretical Nernst equation is. For this we would like to refer to «N – for Nernst equation». The influence of the temperature can be compensated up to a certain point.

As not only the slope of the electrode is temperature dependent, but the temperature can also have an influence on the offset potential and the pH-value as well, which cannot be compensated, the calibration and the sample measurement should be performed in the same temperature range. For comparisons the sample must be measured always at the same temperature.

T – for type of electrode

Metrohm differs between three different types of electrodes: standard, non-aqueous and gel. The non-aqueous electrodes are filled either with TEABr in ethylenglycol or with LiCl in ethanol. Every electrode filled with porolyte, idrolyte or with any kind of gel will be counted to the gel electrodes. Standard electrodes are normally filled with aqueous KCl solution. Due to this differentiation the criteria for the response time, slope and drift are defined for each type separately (see «E – for electrode test»).

T – for two-point calibration

The two-point calibration is the easiest kind of a multipoint calibration. For more information have a look at «C – for calibration».

U – for USP<791>

The general chapter <791> of the US Pharmacopoeia describes the pH-measurement how it is in general performed. For more information please have look at chapter 3.

W – for wiping

Often the electrode is wiped off with a paper cloth before immersing it again into the new solution. Therewith it should be ensured that no cleaning solution, which is often deionized water, is transferred to the next sample. But what does wipe off make with your electrode? Caused by friction or by drying the electrode with the cloth, respectively, the electrode is electrostatically charged, which causes that the electrode is reacting much slower towards changes in potential. In such cases the measuring time is significantly increased. In 99% of the cases a drop of deionized water on the membrane is uncritical and might not lead to any falsification of your pH-value. Hence, we do not recommend wiping off your electrode.

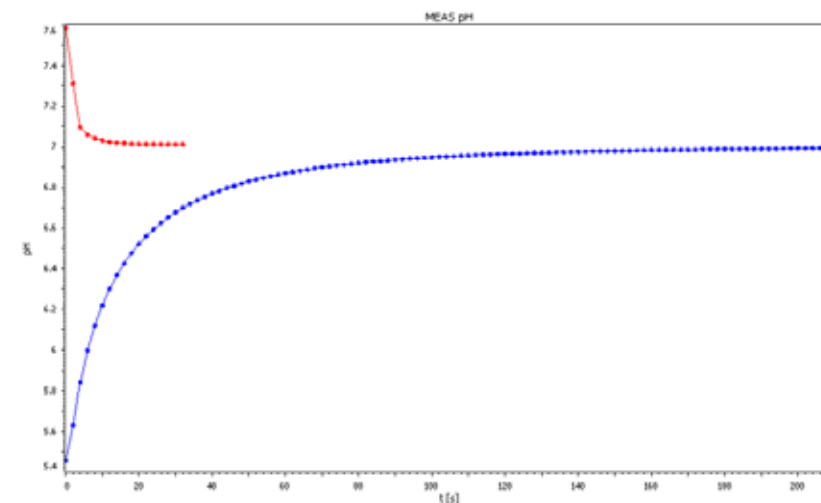


Figure 20: Example of a pH-measurement without (red) and after wiping off the electrode (blue).

3 pH-calibration and pH-measurement according to USP <791>

36

The USP describes a standard operating procedure for the pH-measurement in the general chapter <791>. The procedure for the calibration as well as for the measurement is described in this chapter.

Before the calibration can be started, the electrode must be inspected. Especially the filling level of the electrolyte is controlled (up to the filling hole of the electrode), and the cleanness of the diaphragm is inspected. Afterwards three buffers are chosen, which cover the whole measuring range. Two buffers are used for calibration and the third is needed for the control measurement. Though the pH of the control buffer must lie between the calibration range of the other two buffers. As example it is allowed to calibrate with buffer pH 4 and pH 9 and afterwards to control with buffer pH 7 but it is not allowed to calibrate with pH 4 and pH 7 and afterwards to check with pH 9. For the calibration the procedure is as following:

- A two-point calibration is chosen on the device.
- The electrode is rinsed with deionized water and afterwards with the first buffer.
- The electrode is immersed into the first buffer solution.
- Measurement is started; if no temperature sensor is connected, the measuring temperature is entered manually to perform a temperature compensation.
- Waiting until the measuring signal is stable. The measured value is noted or automatically overtaken by the device.
- Electrode is rinsed with deionized water and afterwards with the second buffer.
- Immersion of the electrode into the second buffer.
- Measurement is started; if no temperature sensor is connected, the measuring temperature is entered manually to perform a temperature compensation.
- Waiting until the measuring signal is stable. The measured value is noted or automatically overtaken by the device.
- Evaluation of the calibration. Check if the slope is between 90...105% and the offset between ± 30 mV (between pH 6.5 and 7.5 at 25°C). If this is not the case the electrode needs to be cleaned or replaced and the calibration must be re-performed.
- If the slope and the offset are inside the boundary values, the electrode is rinsed with deionized water and afterwards with the control buffer.
- The electrode is immersed into the control buffer.
- Measurement is started and the measuring temperature is entered where necessary.
- The pH of the control buffer must not exceed ± 0.05 units of the theoretical value. Otherwise, the calibration must be re-performed.

For a multi-point calibration with more than two buffers the procedure for an additional buffer is repeated. Between two subsequent buffers a control buffer must be measured, respectively.

The sample solutions, where not specified otherwise, should be prepared with deionized water. All measurements must be performed with a manual or automatic temperature compensation.

4 Example applications for the pH-measurement

37

This section gives an overview of different applications / application fields. The suitable electrodes are also mentioned and described in more detail in the appendix.

4.1. General tips for the pH-measurement

The Application Bulletin AB-188 gives an overview of the theoretical fundamentals, explains the electrode test in more detail and shows how the electrode can be checked by yourself. In addition it contains continuing tips & tricks for the pH-measurement.

4.2. pH-measurement in dyes

With this kind of samples, it is assumed that ingredients of the dyes react or precipitate with high concentrated potassium chloride solution. This was observed by addition of $c(\text{KCl}) = 3$ mol/L for test purposes. Thus, an electrode with a double-junction system, like the Profitrode, must be used. The reference electrolyte (inner filling) is filled up with $c(\text{KCl}) = 3$ mol/L and the bridge electrolyte (outer filling) with a diluted potassium chloride solution of $c(\text{KCl}) = 0.1$ mol/L.

Due to the high streaming potential, which is caused by the highly diluted electrolyte solution, we do not recommend calibration in the alkaline region. Hence for this application a two-point calibration with pH 4 and pH 7 is recommended. Between the measurement of the sample the electrode is rinsed with deionized water. The reference and bridge electrolyte must be replaced every two days.

4.3. pH-measurement in milk products

Due to the high protein concentration in milk, a special electrode for the pH-measurement must be used with a diaphragm which will not tend to block with proteins. Metrohm has developed a special electrode with a capillary diaphragm, the Porotrode. The used electrolyte Porolyte is more viscous than the normal electrolyte $c(\text{KCl}) = 3$ mol/L as otherwise the outflow would be too high.

For the measurement the electrode is first calibrated with buffer pH 4 and buffer pH 7. Afterwards the electrode is immersed into the sample until a stable pH-value is obtained. This value is documented together with the temperature. Between the measurements the electrode is rinsed with deionized water.

More information can be gathered in Application Bulletin AB-086.

4.4. pHe-measurement in bio ethanol according to ASTM D6423 and EN 15490

The EtOH-Trode, a double-junction electrode was especially developed for the pHe-measurement in bio ethanol. Two different standards are available for this kind of measurement.

According to ASTM D6423 the EtOH-Trode is calibrated with buffers pH 7 and pH 4. Afterwards the electrode is immersed into the sample and exactly after 30 s the pH-value is recorded. All calibration buffers and sample solutions must be adjusted to $22 \pm 2^\circ\text{C}$. As reference and bridge electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$ is used. More information on this procedure can be found in Application Note AN-T-173.

For the pHe-measurement according to EN 15490 $c(\text{KCl}) = 3 \text{ mol/L}$ is used as reference electrolyte and $c(\text{LiCl}) = 1 \text{ mol/L}$ in ethanol is used as bridge electrolyte. The electrode is calibrated with buffer pH 4 and buffer pH 10 and then checked with buffer pH 7. Afterwards the sample is measured until a stable value is obtained. All calibration and sample solutions are adjusted to $22 \pm 2^\circ\text{C}$. More information to this application can be found in Application Note AN T-183.

4.5. pH-measurement in peppermint liquor

Peppermint liquor must show a pH-value between 6.9 and 7.0 before filling. To ensure this the pH-value must be determined exactly. For this kind of sample matrix (water, 15 – 25% alcohol, sugar, essential oils, colorants) the Unitrode is the most suitable electrode.

The Unitrode is calibrated by a three-point calibration with buffer pH 4, pH 7 and pH 9. Afterwards 40 mL sample is poured into a beaker and the electrode is immersed into the solution. When reaching a stable pH-value the value is noted together with the temperature. Between two samples the electrode is rinsed with deionized water.

4.6. pH-measurement in water according to EPA 150.1, ASTM D1293, ASTM D5464 and DIN EN ISO 10523

Water is an ion-deficient matrix with low conductance. Therefore, a special electrode is needed which can measure accurately and precisely in ion-deficient matrixes. Metrohm offers for this purpose the Aquatrode plus.

Before measurement the electrode is calibrated with buffer pH 4, pH 7 and pH 9. After performing the calibration, the measurement can be started. The electrode is immersed into the sample until a stable pH-value (drift $< 0.1 \text{ pH/min}$) is reached. A twofold determination is performed for each sample and the pH-values of both analyses must not vary more than 0.1 pH unit from each other. The temperature is also documented besides the pH-value.

More information regarding the water analysis can be found in Application Bulletins AB-178 and AB-221.

4.7. pH-measurement of wet disinfection tissues (wipes)

The pH-value of disinfection tissues can either be determined directly on the tissues or in solution after wringing the solution out of the tissue. As the amount of liquid is very small, a flat membrane electrode is used for this purpose. This kind of electrode has a very low immersion depth of only 1 mm and can be used for pH-measurement on surfaces.

The electrode is calibrated with pH 4, pH 7 and pH 9. Afterwards the electrode is pressed directly onto the tissue or the solution is wrung out onto a watch glass and the electrode is immersed into the solution. Both type of analyses shows comparable results. The temperature is always documented with the measured value.

4.8. pH-measurement in molding sand

The pH-value of molding sand can be determined using the Unitrode as this kind of electrode has a little sensitivity towards solid particles.

25 g of the sample is weighed into a beaker, 50 mL deionized water is added, and the mixture is stirred to get a homogeneous suspension. The suspension is stirred for 5 min and afterwards the electrode is immersed until a stable pH-value is obtained. This value is documented along with the temperature of the sample.

4.9. pH-measurement in cheese

To measure the pH-value of cheese the Spear-head electrode can be used. With this type of electrode, you can pierce soft solid samples and the pH-value can be determined without sample preparation. If the pH-value in semi-hard samples is determined it is mandatory to predrill a hole for the electrode as otherwise the electrode might break.

The electrode is calibrated with buffer pH 4, pH 7 and pH 9. Afterwards the electrode is pierced into the cheese. The pH-value as well as the temperature are documented as soon as a stable pH-value with a drift lower than $\leq 2 \text{ mV/min}$ is reached. When removing the electrode please make sure to turn the electrode as otherwise vacuum might occur which break the gel. Additionally, care must be taken that the glass membrane does not touch the bark of the cheese as otherwise unreproducible results would be obtained.

4.10. pH-measurement of engine coolant and antirust related to ASTM D1287

For both samples either the Profitrode or the Ecotrode Gel can be used. Both electrodes do not exactly fulfill the specifications according to ASTM D1287, but they show results which are in the accuracy and reproducibility range mentioned by the standard.

The electrode is calibrated with buffer pH 4, pH 7 and pH 9. Afterwards 10 mL sample is pipetted into a beaker and approx. 90 mL deionized water is added. After a stirring duration of about one minute the pH-value including the temperature is noted as soon as the drift goes below of 2 mV/min.

More information can be found in Application Note AN-T-201.

4.11. pH-measurements in soil according to ASTM D4972

For the pH-measurement in soil the Flat membrane electrode is used because the amount or the level of the supernatant solution, respectively, is very small. Additionally, the glass membrane is less prone to damage from scratching particles.

The electrode is calibrated with pH 4, pH 7 and pH 9. Afterwards buffer pH 7 is used to check the calibration. The obtained pH value must lie between pH 6.9 and 7.1. After each 10th sample the calibration is rechecked with pH 7. If the obtained pH lies outside the range of pH 6.9 – 7.1 all samples measured before must be re-analyzed.

10 g samples are weighed into a 100 mL beaker and 50 mL of deionized water is added. The suspension is stirred for one hour. Afterwards the stirrer is switched off and the pH-value of the supernatant solution (on the top) and in suspension (on the bottom) is measured. The same analysis is performed with 50 mL $c(\text{CaCl}_2) = 0.01 \text{ mol/L}$ instead of deionized water. All measured values are noted down including the temperature.

More information regarding the soil analysis can be found in Application Bulletin AB-071.

4.12. pH-measurement in soil according to ISO 10390 and EN 15933

For the pH-measurement in soil the Flat membrane electrode is used because the amount or the level of the supernatant solution, respectively, is very small. Additionally, the glass membrane is less prone to damage from scratching particles.

The electrode is calibrated with pH 4, pH 7 and pH 9.

5 g of air-dried soil is weighed into a 50 mL beaker and filled up with the appropriate amount of deionized water. The suspension is stirred for three hours. It is important that the suspension does not get into contact with the air. Afterwards the pH-value is determined while stirring slowly. No vortex should be formed which will incorporate air into the suspension. The same analysis is performed with the same appropriate amount of $c(\text{CaCl}_2) = 0.01 \text{ mol/L}$ instead of deionized water. All measured values are noted, including the temperature.

More information regarding the soil analysis can be found in Application Bulletin AB-071.

4.13. pH-measurement of wine according to OIV-MA-AS313-15

For this type of measurement, the Profitrode is used as wine may contain ingredients which could poison the electrode.

The electrode is calibrated with buffers between pH 2 and pH 7 because the pH of wine normally lies between 3.4 and 4.0. The electrode is immersed into solution until the diaphragm is completely covered by solution. As soon as the pH-value is stable it is noted down with the temperature. Afterwards the electrode is rinsed with deionized water and if not in use stored in storage solution.

More information regarding the wine analysis can be found in Application Bulletin AB-225 or in Application Note AN-T-211.

4.14. pH-measurement in pasta

For the pH-measurement in pasta the Flat membrane electrode is used to prevent scratching the glass membrane.

The electrode is calibrated by a three-point calibration with buffer pH 4, pH 7 and pH 9. Afterwards 90 mL deionized water are poured into a 250 mL beaker and 10 g crushed sample is added. The suspension is stirred. Next, the electrode is immersed into the suspension, keeping the diaphragm submerged, and as soon as a stable pH-value is reached, it is noted down along with corresponding temperature.

4.15. pH-measurement in honey, sugar, and sweets

Due to the different compositions of these types of samples the Unitrode is used for the pH-measurement.

The electrode is calibrated by a three-point calibration with pH 4, pH 7 and pH 9 buffers. Afterwards 10 g sample are weighed into a 150 mL beaker and 75 mL deionized water is added. The electrode is immersed fully covering the diaphragm and as soon as a stable pH-value is obtained it is recorded along with the corresponding temperature of the sample.

4.16. pH-measurement in jams and fruit juices

Due to the different compositions of these types of samples, the Unitrode is used for the pH-measurement.

The electrode is calibrated by a three-point calibration with pH 4, pH 7 and pH 9 buffers. Afterwards, the electrode is immersed into the sample, covering the whole diaphragm. When

measuring the fruit juices the sample is stirred, where with the jams the stirring is omitted. After reaching a stable pH-value, it is recorded, along with the temperature.

More information regarding the analysis of jams and fruit juices can be found in Application Bulletin AB-085.

4.17. pH-measurement in beer according to AOAC 945.10

Due to the different composition of these samples the Unitrode is used for pH-measurement. The electrode is calibrated by a three-point calibration with buffers pH 4, pH 7 and pH 9. Afterwards the sample is degassed by placing the sample into an ultrasonic bath or by applying vacuum. All carbon dioxide must be removed before starting the measurement or the pH will read falsely low or be unstable. After removing all the CO₂, the electrode is immersed completely, covering the diaphragm and as soon as a stable pH-value is obtained it is recorded, along with the corresponding temperature.

4.18. pH-measurement in coffee powder

Due to the different composition of these samples the Unitrode is used for pH-measurement. The electrode is calibrated by a three-point calibration with buffers pH 4, pH 7 and pH 9. Afterwards 10 g sample is added to a 250 mL Erlenmeyer flask, along with 200 mL of deionized water. The suspension is heated up and boiled for 5 min. After reaching room temperature again the suspension is filtered into a 250 mL volumetric flask and filled up to the mark with deionized water. The electrode is fully immersed, covering the diaphragm, into an aliquot of the sample and the measured value, as well as the temperature, are recorded as soon as a stable pH-value is reached.

Instant coffee is directly dissolved in deionized water. No filtration is necessary.

4.19. pH-measurement in vinegar

For this measurement the Profitrode is used as vinegar may contain ingredients which can poison the electrode.

The electrode is calibrated by a two-point calibration with pH 4 and pH 7. Afterwards the electrode is immersed completely, covering the diaphragm, into the undiluted vinegar and as soon as the pH-value is stable it is recorded, along with the temperature of the sample.

More information regarding the vinegar analysis can be found in Application Bulletin AB-084.

4.20. pH-measurement in paper according to ISO 6588-1 and ISO 6588-2

The pH-measurement of paper can be performed in three different ways, after cold extraction, after warm extraction, or on the surface of the paper itself. For the pH-measurement of the extract, the Unitrode easyClean is proposed while for the pH-measurement on the surface the Flat membrane electrode is the most suitable electrode.

The electrodes are calibrated with a two-point calibration with buffer pH 4 and buffer pH 7. The sample preparation of the paper is done in the following manner:

Cold extraction: 5 g sample is weighed into a 250 mL beaker and 50 mL deionized water is added. The mixture is suspended. Afterwards another 50 mL deionized water is added and the beaker is closed with a watch glass. After 1 h the pH-value of the supernatant solution is measured, and the temperature is recorded.

Hot extraction: 5 g sample is weighed into a 250 mL round-bottomed flask and 100 mL deionized water is added. The round-bottomed flask is equipped with a reflux condenser. The extraction is done for 1 h at 95°C. Afterwards the suspension is allowed to cool down to room temperature and the pH-value and temperature of the supernatant solution are measured.

For the pH-measurement on the paper surface, 5 x 5 cm pieces are cut and one drop (approx. 0.1 mL) deionized water is added to the surface. The flat membrane electrode is pressed onto the wet section of the paper. After about 30 s the measuring value should be stable and the pH as well as the temperature are noted down.

More information can be found in Application Bulletin AB-040.

4.21. Initial pH (ipH) of petroleum products according to ASTM D7946

For this measurement the Solvotrode is used. Initially this electrode was developed for non-aqueous titrations, but it also fulfills the conditions for the electrode according to ASTM D7946.

To check the functionality of the electrode the potential difference of pH 4 and pH 7 is measured. The Solvotrode is first immersed into buffer pH 4 and after one minute the potential is recorded. The same is done with buffer pH 7. The potential difference should be >162 mV.

The calibration is done with aqueous buffers pH 4 and pH 7.

The sample is heated in its original container up to 60°C ± 5°C. After suspending all the particles, the oil is filtered over a 100 mesh filter.

For the measurement, 2.5 ± 0.3 g sample is weighed into a 100 mL beaker and 70 mL solvent mixture (composition of the solvent mixture: 5 mL deionized water, 495 mL isopropanol, 500 mL toluene) is added. The solution is stirred without forming a vortex. After one minute the electrode is immersed and the ipH-value is measured until the potential is not changing by more than 2 mV over 20 seconds. The determination duration must not exceed 2 minutes after immersing the electrode.

4.22. pH-measurement of washing detergents according to ASTM D1172-15

For this measurement the Profitrode is used as washing detergents may contain ingredients which could poison the electrode.

The pH-electrode is calibrated with a three-point calibration with buffers pH 4, pH 7 and pH 9. Afterwards 1 g sample is added to a 1 L measuring flask and dissolved in deionized water, and then filled to the mark with deionized water. The electrode is immersed completely, covering the whole diaphragm, and the measured value and temperature are recorded when stable.

4.23. pH-measurement in soaps according to ASTM D1172-15

For this type of measurement, the Unitrode is used.

The pH-electrode is calibrated with a two-point calibration with buffer pH 9 and buffer pH 11. The sample is prepared by weighing 0.3 g into a 250 mL Erlenmeyer flask and adding 100 mL of boiling deionized water. The temperature in the Erlenmeyer flask is observed using a thermometer. The solution is swirled until everything is dissolved. Afterwards the solution is cooled down immediately up to 43°C with the aid of cold water. The measurement of the pH-value is done at 40°C with the electrode submerged completely, covering the diaphragm. The pH-value is noted as soon as the measured value is stable.

4.24. pH-measurement in leather according to ASTM D2810 and ISO 4045

For this analysis the Unitrode is used.

The pH-electrode is calibrated with a three-point calibration with buffers pH 4, pH 7 and pH 9. Afterwards two samples each are prepared for a two-fold determination. The sample is weighed into the Erlenmeyer flask to a precision of 0.1 g and a twenty-fold amount of deionized water is added. The Erlenmeyer flask is closed with a stopper and swirled from time to time. After 4 to 18 hours, the solution is transferred into a beaker and the pH-value is mea-

sured. The electrode must be immersed completely into solution, covering the whole diaphragm. The measured value and temperature are recorded when stable.

4.25. pH-measurement in gold electrolyte

Basic materials can be plated galvanically with gold to make them more stable against corrosion and to improve their appearance. To obtain the best as possible plating results, monitoring the pH-value is essential.

For this application, the Unitrode easyClean is used. The electrode is calibrated by a three-point calibration with pH 4, pH 7 and pH 9 buffers. A representative bath solution is transferred into a beaker and the electrode is immersed into a stirred solution, covering the whole diaphragm. The pH-value is recorded, along with the temperature as soon as the measuring value is stable.

4.26. pH-value in ethanolic brews

For these semi-aqueous samples, the Unitrode easyClean with integrated temperature sensor is the most suitable electrode.

The electrode is calibrated with buffers pH 4, 7 and 9. Before each measurement, the electrode is rinsed with ethanol before immersing it completely, covering the diaphragm, into the sample solution. After 30 s the measurement is started. Once stability is reached, the pH value is noted, along with the temperature. The electrode is cleaned with ethanol and then with deionized water.

4.27. pH-measurement in water extract of halogenated organic solvents according to ASTM D2110

Depending on the stabilizers used in the solvents, the pH-value of the water extract will vary. Solvents with alkaline stabilizers (types of amine) show a pH-value between 7 and 11 where solvents with a neutral stabilizer (types of epoxide) show a pH between pH 5 and 7.

Before measurement, the water for extraction must be prepared. For this purpose, 1 L deionized water is boiled for 5 min in a container made of borosilicate glass and stainless steel and then cooled down to room temperature. 50 mL of the water which has reached room temperature, is adjusted to a pH between 7.0 and 7.3 either with $c(\text{HCl}) = 0.01$ mol/L or $c(\text{NaOH}) = 0.01$ mol/L by titration. The amount of titrant used is multiplied by 19 and added to the left over 950 mL deionized water. The pH-value of another 50 mL adjusted water is checked again.

50 mL halogenated solvent is given into a separating funnel and 50 mL prepared water is added as well. The separating funnel is shaken for 2 min and then the phases are allowed to separate. The organic phase is discarded. The aqueous phase is given into a 100 mL beaker and the pH of the solution is measured using a calibrated Unitrode easyClean. The measured value and temperature are recorded when stable.

4.28. Measuring apparent pH of electrocoat baths according to ASTM D4584

For this sample the Unitrode easyClean is used because of its robustness. Depending on the bath, the electrode is either calibrated with buffers pH 4 and pH 7 (cationic system) or with buffers pH 7 and pH 10 (anionic system).

A representative sample is taken from a homogeneous bath and added to a beaker containing a magnetic stirrer. The sample is stirred as fast as possible without forming a vortex. The electrode is completely immersed into the sample solution, covering the whole diaphragm. After a stable pH-value is reached, it is recorded, along with the corresponding temperature. A second measurement is carried out and both results must not deviate more than 0.1 pH units from each other. Otherwise, the measurement has to be repeated.

5 Tips & tricks for pH-measurement

5.1. Before measurement

The electrode must be examined before each measurement:

- Is the electrode filled with clean, crystal-free electrolyte up to the filling opening?
- Are the diaphragm and the glass membrane clean?
- Is the glass membrane free from scratches?

5.2. pH-calibration

pH-calibration is essential for an accurate and precise pH-measurement. The pH-measurement can only be as good as the calibration. Ideally, more than two buffers should be used for the calibration. Additionally, the buffers must be fresh. The more alkaline the buffer, the faster it must be used or discarded, respectively. A pH-calibration should always be performed from the highest to the lowest buffer value as the H⁺-ion concentration is lower at higher pH-values.

Between each measurement, the electrode is rinsed with deionized water and the electrode is not wiped off!

5.3. Storage of the electrode

After use, the electrode should be stored in its storage vessel. The storage solution depends on the pH-electrode and the corresponding electrolyte. When $c(\text{KCl}) = 3 \text{ mol/L}$ is used as electrolyte, the storage vessel should be filled with approx. 1 – 2 mL storage solution. With all other electrodes and different electrolytes, the storage vessel is filled with approx. 1 – 2 mL of the corresponding electrolyte. If a low-maintenance gel electrode is used, then the storage vessel is filled with approx. 0.5 – 1 mL of saturated KCl-solution. Optimal storage conditions for the electrode help to keep it in the best as possible condition for the next measurement.

6 FAQ for pH-measurements

48

Why is the measuring signal unstable?

An unstable measuring signal can have multiple causes. First, check to see if the electrode is plugged into the correct measuring input. Second, check if the membrane and the diaphragm are immersed in solution and fully covered by solution while the sample is being stirred. This is essential for a stable and reproducible measurement. Next, ensure that the connection is secure. For this, hold the electrode cable with your hand and move it slightly back and forth. At this point a little change in potential or measuring value, respectively, is normal. If the measuring value or potential, respectively, is changing significantly, the cable must be replaced.

Also, the electrode itself can be the cause for unstable measuring signals. Check the electrode first visually. You should be able to see if the diaphragm is dirty or clogged. Ceramic pin diaphragms clog most frequently. When a ceramic pin diaphragm is dirty or clogged, the diaphragm will appear gray or black instead of white. The glass membrane could also be the reason for unstable measuring signals. The hydration layer could have been destroyed by reaction of the glass with the sample or by improper storage or handling of the electrode. The electrode could be tested with the electrode test, which is implemented in many Metrohm devices. If the electrode shows the same behavior after cleaning and storage in corresponding electrolyte overnight, the electrode must be replaced.

The glass membrane of my electrode is so dirty that I cannot measure correctly anymore. What can I do?

The electrode contamination will be related to the types of samples being analyzed. Through testing different solvents and cleaning agents, a suitable one can be found to clean the membrane. Examples of a few cleaning solutions can be found under «C – for cleaning». Additionally, we recommend allowing the electrode to stand overnight in the cleaning solution if the contamination is really significant. For better cleaning, the solution can also be stirred. Please make sure that the filling opening of the electrode is opened to allow for electrolyte outflow. This will ensure that the cleaning solution does not poison the electrode. We recommend exchanging the reference electrolyte after the cleaning procedure.

During calibration, my electrode measures 0 mV or the same potential for all buffers. What can I do?

In this case, the electrode may have a short circuit. The electrode cannot be repaired and must be replaced. Before ordering a new electrode, ensure that the electrode is plugged in properly. This could also be the source of the error.

How should I clean the electrode between two measurements?

Between two measurements the electrode should be rinsed with deionized water or a suitable solvent. After using solvents, the electrode should be rinsed with deionized water again. Do not wipe off the electrode because it might get electronically charged.

My measuring device has two identical measuring inputs. One is indicated with Ind the other with Pol. Where do I need to plug in my electrode?

Ind and Pol stand for indicator and polarizable input. For pH-measurements, the electrodes are always connected to the Ind connection on your device. Pol is only used for bi-voltametric measurements.

I accidentally connected my electrode to the Pol connection of my device. Do I need to exchange my electrode now?

If the electrode is connected to the Pol connection a current is conducted through the electrode. The electrode will get electrically charged and longer response times or unstable measuring values will be observed. If this is the case, you need to wait until the electrode is completely discharged. This is best done if a long-time measurement is carried out until a constant pH-value is obtained. As soon as this is the case, your electrode is ready-for-use again.

There is no pH reading on my meter. What am I doing wrong?

Some measuring devices offer the possibility to measure different parameters with the same device, or even in parallel. This means, for example, that you can measure conductivity in addition to the pH value. Make sure that you are on the appropriate channel for the desired measurement type so that you can read the measured value. You should also check whether the appropriate electrode cable is plugged in properly.

I don't have a magnetic stirrer on hand at the moment. Can I stir with the electrode?

This is not a good idea. If you use the electrode as a stirring rod, you may get scratches or even micro-cracks on the membrane surface. As time progresses, these can lead to a long response time or even to a short circuit. Therefore, please refrain from stirring with the electrode. Instead, you can swivel the sample cup with the sample without the electrode touching the cup.

Can I connect a Metrohm electrode to devices from other manufacturers?

Most of the time this works with the correct cable without any problems. However, depending on the electrode plug head or device socket, the temperature sensor may not be able to be used because a corresponding adapter does not exist. For further information, please contact your Metrohm representative.

My device has an intelligent and an analog connection. Can I use them for two parallel measurements?

This depends on your device. If both connections are on the same measuring input, the two electrodes cannot be used in parallel because the measuring input is already reserved. However, you can connect two electrodes and measure sequentially. It is important in this case, that both electrodes are not immersed into the same solution because the electrodes can influence each other. For example, if you are a producer of foodstuff and you need to determine the pH-value in juices and water, for the water you would need the Aquatrode and for the juices you would need a Unitrode. You can connect both electrodes to one device and, depending on the sample, you can choose either the Aquatrode or the Unitrode for measurement.

49

I accidentally filled my electrode with the wrong electrolyte. Can I somehow rescue my electrode?

The electrode can be «rescued» by removing the wrong electrolyte with a pipette and rinsing it 2 to 3 times with fresh, correct electrolyte solution. Afterwards the electrode is stored in storage solution overnight so that the diaphragm can be filled with the correct electrolyte solution.

How long can I use a buffer if it is opened?

The more alkaline a buffer the faster it must be used. In general, the following applies at optimal storage: buffer pH 4 and 7 can be stored up to 3 months after opening and buffer pH 9 max. 1 month after opening as the pH-value of alkaline buffer is changed due to the CO₂-uptake. In general, we can say: the pH-measurement can only be as good as the performed pH-calibration.

The slope of my electrode is getting flat quite fast! What is the reason for this?

If the slope of your electrode is flattened quite fast, this can be caused by contamination of the glass membrane by the sample. More often this can be related to the alkaline buffer which has taken up CO₂. Thereby the pH-value of the alkaline buffer is reduced, and the measured potential is changed accordingly. When calculating the slope this can lead to too low values. In such a case please redo the calibration with new buffers.

See example below:

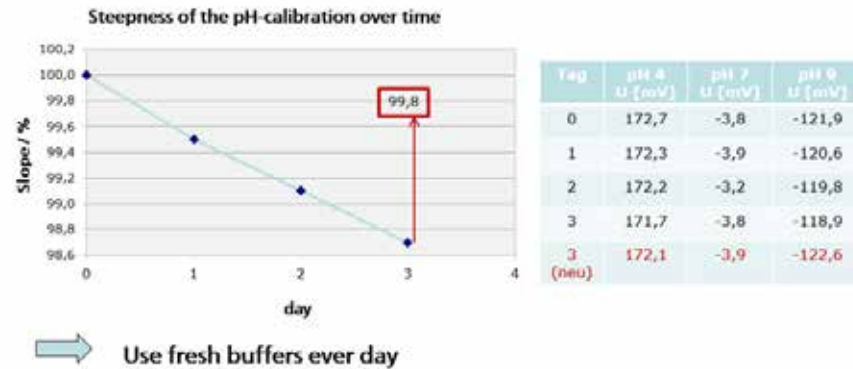


Figure 21: Decline of the slope of an electrode over time. If a new buffer is used the slope gets recovered again.

Why is the electrode delivered with such a small amount of storage solution in the storage vessel? The membrane is not even covered.

The electrode is tightly pressed into the storage vessel. In the storage vessel a humid atmosphere is formed which is enough to ensure a proper hydration layer of the glass membrane. Since the electrode must withstand different pressures and temperatures during transportation, more storage solution is not added to the storage vessel.

Why does the pH-value decrease with each measurement?

The reason for this in weakly buffered, slightly alkaline samples is the sample absorbing CO₂. Only after reaching a CO₂-equilibrium will the pH value become stable. This equilibrium lies in the slightly acidic region.

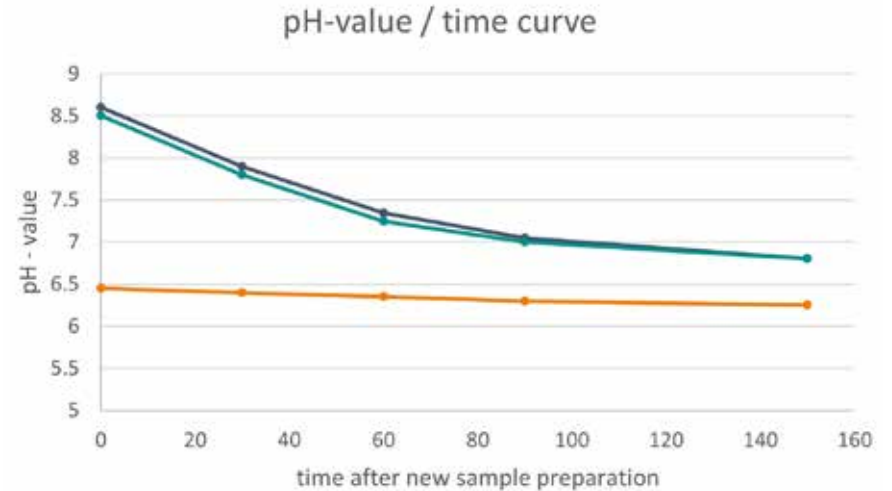


Figure 22: Decrease of the pH-value by absorption of CO₂. The pH-value stabilizes when the CO₂-equilibrium is reached.

7 Literature

52

All Metrohm Application Bulletins and Application Notes can be downloaded from the Metrohm Homepage without charge. The documents can be easily found by entering the Number e.g. AB-xyz in the search field.

Metrohm Application Note AN-T-173 – Determination of the pHe value of denatured ethanol fuel in accordance with ASTM D6423

Metrohm Application Note AN-T-183 – Ethanol as blending component for petrol – Determination of pHe according to EN 15490

Metrohm Application Note AN-T-201 – Determination of pH of engine coolants and anti-rusts according to ASTM D1287

Metrohm Application Note AN-T-211 – Fully automated wine analysis – Determination of free and total sulfurous acid, reductants, total acidity and pH value according to OIV

Metrohm Application Bulletin AB-040 – Determining the pH value of paper

Metrohm Application Bulletin AB-071 – pH value and oxidation reduction potential in soil samples

Metrohm Application Bulletin AB-084 – Titrimetric analysis of vinegar

Metrohm Application Bulletin AB-085 – Titrimetric analysis of jams, fruit and vegetable juices and their concentrates

Metrohm Application Bulletin AB-086 – Measuring the pH value of dairy products

Metrohm Application Bulletin AB-178 – Fully automated water analysis

Metrohm Application Bulletin AB-188 – pH measurement technique

Metrohm Application Bulletin AB-221 – Standard methods in water analysis

Metrohm Application Bulletin AB-225 – Simple wine analysis

Metrohm Monograph: Electrodes in Potentiometry

Metrohm Monograph: Practical aspects of modern titration

ASTM D6423 Standard Test Method for Determination of pHe, Ethanol, Denaturated Fuel Ethanol and Fuel Ethanol Blends

EN 15490	Ethanol as a blending component for petrol – Determination of pHe
EPA 150.1	pH in Water by Electrometric Method
ASTM D1293	Standard Test Methods for pH of Water
ASTM D1287	Standard Test Method for pH of Engine Coolants and Anti-rusts
ASTM D4972	Standard Test Methods for pH of Soils
ISO 10390	Soil quality – Determination of pH
EN 15933	Sludge, treated biowaste and soil - Determination of pH
OIV-MA-AS313-15	pH value
AOAC 945.10	pH of Beer
ISO 6588-1	Paper, board and pulps – Determination of pH of aqueous extracts – Part 1: Cold extraction
ISO 6588-2	Paper, board and pulps – Determination of pH of aqueous extracts – Part 2: Hot extraction
ASTM D7946	Standard Test Method for Initial pH (i-pH)-Value of Petroleum Products
ASTM D1172	Standard Guide for pH of Aqueous Solutions of Soaps and Detergents
ASTM D2810	Standard Test Method for pH in Leather
ASTM D5464	Standard Test Method for pH Measurement of Water of Low Conductivity
EN ISO 10523	Water quality – Determination of pH
ASTM D2110	Standard Test Method for pH of Water Extractions of Halogenated Organic Solvents and Their Admixtures
ASTM D4584	Standard Test Method for Measuring Apparent pH of Electrocoat Baths
ISO 4045	Leather – Chemical tests – Determination of pH and difference figure

53

8 Appendix

8.1. Buffer tables

The following chapter should give you an overview of the temperature dependence of pH-buffers. The mentioned data are from April 2020 and can change anytime. The current values can be found either in the manual of the device, on the packaging of your buffer or in the help of your software – if implemented.

Metrohm AG

Temperature (°C)	Buffer pH 4	Buffer pH 7	Buffer pH 9
0	3.99	7.11	9.27
5	3.99	7.08	9.18
10	3.99	7.06	9.13
15	3.99	7.04	9.08
20	3.99	7.02	9.04
25	4.00	7.00	9.00
30	4.00	6.99	8.96
35	4.01	6.98	8.93
40	4.02	6.98	8.90
45	4.03	6.97	8.87
50	4.04	6.97	8.84
55	4.06	6.97	8.81
60	4.07	6.97	8.79
65	4.09	6.98	8.76
70	4.11	6.98	8.74
75	4.13	6.99	8.73
80	4.15	7.00	8.71
85	4.18	7.00	8.70
90	4.20	7.01	8.68
95	4.23	7.02	8.67

NIST

Temperature (°C)	Buffer pH 1	Buffer pH 4	Buffer pH 7	Buffer pH 9	Buffer pH 13
0	-	4.010	6.984	9.464	13.423
5	1.668	4.004	6.950	9.392	13.207
10	1.670	4.001	6.922	9.331	13.003
15	1.672	4.001	6.900	9.277	12.810
20	1.676	4.003	6.880	9.228	12.627
25	1.680	4.008	6.865	9.184	12.454
30	1.685	4.015	6.853	9.144	12.289
35	1.691	4.025	6.843	9.107	12.133
40	1.697	4.036	6.837	9.076	11.984
45	1.704	4.049	6.834	9.046	11.841
50	1.712	4.064	6.833	9.018	11.705
55	1.715	4.075	6.834	8.985	11.574
60	1.723	4.091	6.836	8.962	11.449
65	1.732	4.108	6.840	8.941	-
70	1.743	4.126	6.845	8.921	-
75	1.754	4.145	6.852	8.902	-
80	1.766	4.164	6.859	8.885	-
85	1.778	4.185	6.867	8.867	-
90	1.792	4.205	6.877	8.850	-
95	1.806	4.227	6.886	8.833	-

DIN

Temperature (°C)	Buffer pH 1	Buffer pH 3	Buffer pH 4	Buffer pH 7	Buffer pH 9	Buffer pH 12
0	1.08	-	4.67	6.89	9.48	-
5	1.08	-	4.66	6.86	9.43	-
10	1.09	3.10	4.66	6.84	9.37	13.37
15	1.09	3.08	4.65	6.82	9.32	13.15
20	1.09	3.07	4.65	6.80	9.27	12.96
25	1.09	3.06	4.65	6.79	9.23	12.75
30	1.10	3.05	4.65	6.78	9.18	12.61
35	1.10	3.05	4.66	6.77	9.13	12.44
40	1.10	3.04	4.66	6.76	9.09	12.29
45	1.10	3.04	4.67	6.76	9.04	12.13
50	1.11	3.04	4.68	6.76	9.00	11.98
55	1.11	3.04	4.69	6.76	8.97	11.84
60	1.11	3.04	4.70	6.76	8.92	11.69
65	1.11	3.04	4.71	6.76	8.90	11.56
70	1.11	3.04	4.72	6.76	8.88	11.43
75	1.12	3.04	4.74	6.77	8.86	11.30
80	1.12	3.05	4.75	6.78	8.85	11.19
85	1.12	3.06	4.77	6.79	8.83	11.08
90	1.13	3.07	4.79	6.80	8.82	10.99
95	-	-	-	-	-	-

8.2. Overview of the most common electrodes

**Unitrode easyClean**

- For routine measurements in the laboratory
- Ground-joint diaphragm for reliable measurements
- LL reference system
- pH-measurement in different sample matrixes
- usable range pH 0 ... 14

**Aquatrode plus**

- For weak-buffered sample solution
- Bridge electrolyte can be chosen freely
- Gel reference electrolyte
- Ground-joint diaphragm for reliable measurements
- LL reference system

**EtOH-Trode**

- Especially designed for pH_E-measurements in ethanol
- Ground-joint diaphragm for reliable measurements
- Double-junction system; Bridge and reference electrolyte can be chosen freely
- LL reference system

**Profitrode**

- Specially designed for difficult matrixes
- Ground-joint diaphragm for reliable measurements
- Available in different lengths
- LL reference system



Porotrode

- For measurement in very contaminated, protein-containing, and viscous samples
- Low-maintenance capillary diaphragm
- Electrolyte on polymer-base for a uniform outflow
- LL reference system



Flat membrane electrode

- For pH-measurements on surfaces
- For pH-measurements in small volumes of sample
- Made completely of glass with finely sanded surface
- LL-reference system



Ecotrode Gel

- Ideal for routine measurement in the same type of samples
- Ideal for polymer dispersions
- Maintenance-free
- Has an age indicator
- LL-reference system



Spearhead Electrode

- For measurements in semi-solid samples e.g. cheese, fruits...
- Maintenance-free
- Diaphragm can be cleaned easily
- Has an age indicator
- LL-reference system

Metrohm AG has over 200 electrodes in its portfolio. Do you need something specific or are you not sure if a specific electrode is the right choice for your application? Then have a look at our electrode finder at www.metrohm.com or contact your sales representative.

www.metrohm.com

