

Basics of potentiometry



Theory, practical aspects, and trouble-shooting

1. Basics of potentiometry

1.1. Electrode construction

In potentiometry the measuring setup always consists of two electrodes: the measuring electrode, also known as the indicator electrode, and the reference electrode. Both electrodes are half-cells. When placed in a solution together they produce a certain potential. Depending on the construction of the half-cells, the potential produced is the sum of several individual potentials. Potential-determining transitions always occur at the phase boundaries, e.g. between the solution and the electrode surface.

pH electrode

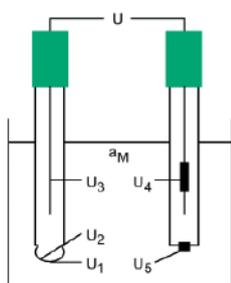


Figure 1: Schematic diagram of a pH electrode

Measuring electrode – glass electrode (left)

- U_1 = Galvani potential between measuring solution and glass membrane
- U_2 = Galvani potential between glass membrane and inner electrolyte
- U_3 = Galvani potential between inner electrolyte and inner reference electrode

Reference electrode – silver/silver chloride (right)

- U_4 = Galvani potential of reference electrode
- U_5 = Diaphragm potential (diffusion potential)
- a_M = Activity of measured ion in sample solution

The potentials U_2 , U_3 and U_4 can be kept constant by a suitable electrode construction. Constructive measures and the selection of a suitable reference electrolyte ensure that U_5 is also kept as constant as possible. Ideally the measured potential should depend only on the potential between the glass membrane and the solution. For practical reasons the half-cells of the measuring electrode and the reference electrode are normally contained in a single electrode; this is then known as a combined pH electrode.

Redox electrode

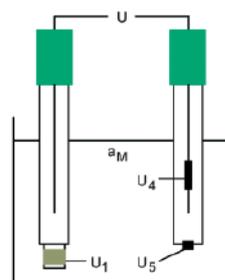


Figure 2: Schematic diagram of a redox electrode

Measuring electrode – metal electrode (left)

- U_1 = redox potential between measuring solution and metal surface

Reference electrode – silver/silver chloride (right)

- U_4 = Galvani potential of reference electrode
- U_5 = Diaphragm potential (diffusion potential)
- a_M = Activity of measured ion in sample solution

For metal electrodes the potential forming transitions U_2 and U_3 of the pH electrodes do not exist. Depending on the particular application, it may be possible to use a pH glass electrode as the reference electrode instead of the silver/silver chloride reference electrode. In the combined redox electrodes and Titrades from Metrohm the half-cells are also contained in a single electrode.

1.2. From the measured potential to the ion concentration

As each ion is surrounded by ions with the opposite charge, it is – to put it simply – no longer as effective as a free ion (see Debye-Hückel law). This affects both the reactivity and the size of the potentials at the measuring electrode. The activity of the measuring ion a_M , which is also used in the Nernst equation, is linked to the normally interesting analytical concentration c_M via the activity coefficient γ .

$$a_M = \gamma \cdot c_M$$

(1)

For dilute solutions with concentration $c_M \leq 0.001$ mol/L the activity coefficient γ tends towards 1 and the activity of the ion corresponds to its concentration as a first approximation. γ is a function of the ionic strength of the measuring solution.

The mathematical relationship between the activity a_M of a measuring ion in solution ions and the potential measured between the reference electrode and the measuring electrode is described by the Nernst equation. This applies only for the (ideal) case in which an electrode only responds to a single type of ion. Potentials U_2 to U_5 for pH electrodes and U_4 and U_5 for redox electrodes, which are normally constant, appear as potential U_0 in the Nernst equation.

$$U = U_0 + \frac{2.303 * R * T}{z * F} * \log a_M$$

(Nernst equation) (2)

U = measured potential

U_0 = temperature-dependent standard potential of electrode

R = general gas constant 8.315 J mol⁻¹ K⁻¹

T = temperature in Kelvin

z = ionic charge including sign

F = Faraday constant 96485.3 C mol⁻¹

The term in the Nernst equation in front of the logarithm is known as the Nernst potential U_N (also Nernst slope).

$$U_N = \frac{2.303 * R * T}{z * F}$$

(Nernst potential) (3)

Its value is 0.059 V at $T = 298.15$ K and $z = +1$. As a factor in the Nernst equation it represents the theoretical electrode slope. U_N corresponds exactly to the alteration in potential caused by increasing the activity a_M by a factor of ten. From the equation it can be seen that the electrode slope for electrodes that respond to ions with a double charge ($z = 2$) is only half the size of that for electrodes for ions with a single charge ($z = 1$). In addition, the sign for cation- and anion-sensitive measuring electrodes is different, as z also takes the charge on the ion into account. The Nernst potential is directly dependent on the temperature (see Equation 3). This is why it is absolutely necessary to take the temperature into account in all direct potentiometric measurements, as otherwise no correct results will be obtained.

pH value

In practice – particularly when measuring the acid/ base equilibrium – the term pH, introduced by Sørensen in 1909, is frequently used instead of the activity of the measuring ion a_M :

$$pH = -\log a_{H^+}$$

(Definition of the pH value) (4)

The pH value is the negative common logarithm of the hydrogen ion activity of a solution. The term p is frequently used for the simplified presentation of very large or small values. In a similar way pNa^+ can be used for the activity of sodium ion, or pK_A as acid constant or pK_B as base constant for reaction constants. In each of these cases what is meant is the negative common logarithm of the particular value. If this definition is inserted in the Nernst equation then we obtain for the measured potential U :

$$U = U_0 - \frac{2.303 * R * T}{z * F} * pH$$

(pH value and potential) (5)

Redox potentials (metal electrodes)

In a similar way to the Nernst equation (Equation 2) the equation for the activity-dependent potential is obtained as follows:

$$U = U_0 + \frac{2.303 * R * T}{z * F} * \log \frac{a_{ox} * a_{H^+}}{a_{red}}$$

(6)

Equation 6 usually allows the potential generated by a redox pair at the measuring electrode to be calculated. As protons are involved in most redox reactions, the measured potential depends on the pH. If proton reactions cannot be excluded then the pH should also be determined or adjusted to a defined value.

1.3. Measuring electrodes

1.3.1. pH glass electrodes

How does a pH glass electrode work?

The glass membrane of a pH glass electrode consists of a silicate framework containing lithium ions. When a glass surface is immersed in an aqueous solution then a thin solvated layer (gel layer) is formed on the glass surface in which the glass structure is softer. This applies to both the outside and inside of the glass membrane. As the proton concentration in the inner buffer of the electrode is constant (pH 7), a stationary condition is established on the inner surface of the glass membrane. In contrast, if the proton concentration in the measuring solution changes then ion exchange will occur in the outer solvated layer and cause an alteration in the potential at the glass membrane. Only when this ion exchange has achieved a stable condition will the potential of the glass electrode also be constant. This means that the response time of a glass electrode always depends on the thickness of the solvated layer. Continuous contact with aqueous solutions causes the thickness of the solvated layer to increase continuously – even if only very slowly – which results in longer response times. This is why conditioning the electrode in a suit-

able electrolyte is absolutely necessary to ensure an initial solvated layer condition that is as stationary as possible so that results can be obtained that are as reproducible as possible.

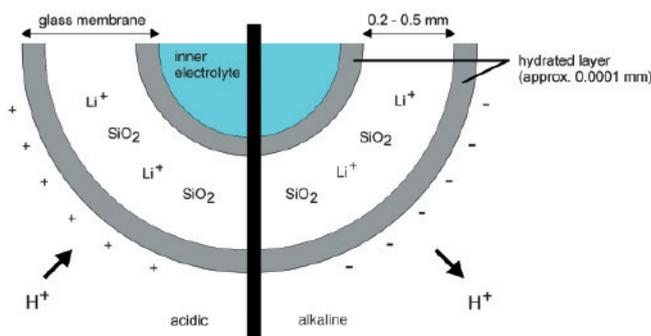


Figure 3: The silicate skeleton of the glass membrane contains lithium ions, among other things. During the formation of the solvated layer at the glass surface these are partly replaced by protons. If the concentration of the protons in the solution changes then a new stationary condition must again be achieved in the solvated layer; this results in a change in potential at the glass membrane.

Table 1: Overview of the different electrode membrane glasses used by Metrohm Ltd

Application	U glass (green)	T glass (blue)	M glass (colorless)	Aquatrode glass (yellow)	E glass (yellow)
pH range	0...14	0...14	0...14	0...13	0...13
Temperature range	0...80 °C	0...80 °C	0...60 °C	0...80 °C	0...80 °C
continuous	0...100 °C				
short-term					
Membrane surface	Electrodes with large membrane surface	Electrodes with medium to large membrane surface (mini-electrodes)	Electrodes with small membrane surface (micro-electrodes)	Large surfaces	Electrodes with medium to large membrane surface
Special features	For strongly alkaline solutions, long-term measurements and measurements at high temperatures	Measurements in non-aqueous sample solutions	Measurements in small-volume samples	Responds very quickly, so particularly suitable for measurements in ion-deficient or weakly buffered solutions	Quick response, excellent stability in continuous use
Membrane resistance (MΩ)	< 500	< 150	< 120	< 250	< 250
With reference to sphere membrane 10.5 mm diameter					

Why are there different types of glass for pH electrodes?

Different demands are placed on a pH glass electrode depending on the particular application. Various properties such as response time, thermal resistance, chemical stability, shape, size and electrical properties must all be taken into account in order to have an optimal electrode available to solve each problem. In order to be able to do justice to the numerous applications, different glasses are available with different properties (see table 1).

Why must a pH glass electrode be calibrated?

The potential of a measuring electrode can always only be given relative to that of a reference electrode. To be able to compare systems, the electrode zero point is defined as being 0 mV for pH 7 and 298.15 K or 25 °C. The electrode slope, i.e. the alteration in the measured value with the pH, is given by the Nernst equation and at 25 °C is 0.059 V per pH 1. These are ideal values from which MetroSensor pH electrodes only differ slightly. The electrode zero point is ± 0.015 V. The electrode zero point and the electrode slope may change as a result of the aging of the glass membrane or changes, (e.g. contamination) on the diaphragm. For this reason the pH meter must be adapted to the characteristics of the electrode, i.e. calibrated, at regular intervals by using buffer solutions.

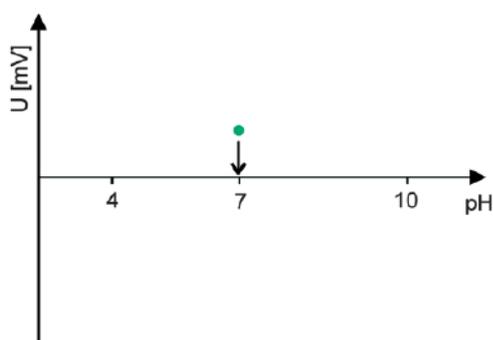


Figure 4: In the first calibration step with buffer pH = 7 the variation from the electrode zero point (= asymmetry potential) is determined and corrected.

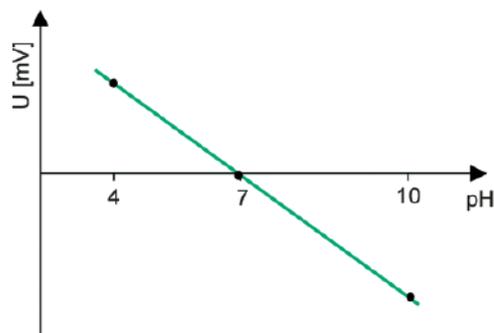


Figure 5: In the second calibration step with another buffer solution the electrode slope is determined and expressed as a percentage of the theoretical value of 0.059 V (at 25 °C).

The electrode zero point is set first (pH 7 corresponding to 0 mV for MetroSensor pH electrodes). The second and further buffer solutions are used to determine the slope of the pH electrode. This slope is expressed as a percentage of the theoretical value (100% = 0.059 V per $\Delta\text{pH} = 1$ at 25 °C). In order to minimize subsequent measuring errors, care should be taken that the expected measured value of the sample solution always lies within the pH range covered by the buffer solutions. Modern pH and ion meters such as the 780 pH Meter and the 781 and 867 pH/Ion Meter do not require any manual settings to be made. The buffer solutions are recognized automatically and can be presented in any sequence.

Calibration always includes a check of the measuring electrode. The calibration buffers have a medium acid-base concentration and their ionic strength is approximately that of the most common sample solutions. The dependency of the electrode slope on the temperature means that the calibration and measuring temperatures must be known. Information about the electrode condition is provided by the electrode slope, electrode zero point, response time of the signal and its streaming dependency. With the Metrohm 781 and 867 pH/Ion Meter and 780 pH Meter an automatic electrode test can be carried out; this provides an exact statement of the electrode condition and often allows a source of error to be localized.

pH and temperature – an inseparable couple!

The temperature has a considerable influence on the pH value and the pH measurement. If an electrode is calibrated at 25 °C then it should be capable of linear measurement throughout the whole pH range and provide correct results. However, if the electrode is then used at a different temperature the electrode slope will change – in accordance with the Nernst equation – and possibly the electrode zero point as well. The point at which the two calibration curves (without correction) for different temperatures intersect is known as the isothermal intersection point. Thanks to the optimized inner buffer and «Long Life» reference system precise measurements can be made with MetroSensor pH electrodes at different temperatures. This means that, although calibration is only carried out at a single temperature, measurements can then be made throughout the whole temperature range. The real behavior of MetroSensor pH electrodes varies from the ideal behavior by maximum ± 15 mV. Nevertheless it is still true that the accuracy of the measurement is increased when the electrode is calibrated at the temperature to be used for the subsequent measurements. At $T = 298.16$ K and $z = 1$, the Nernst potential U_N is equal to 59.16 mV. For other temperatures it can be corrected in the Nernst equation by using Table 2. Modern pH meters automatically take the temperature dependency of the Nernst potential into account if a temperature sensor is connected. In principle, within the context of GLP/ISO recording and documentation of the temperature is required for all measurements.

However, it must be remembered that a pH meter can only correct the temperature behavior of the electrode and never that of the solution to be measured. For correct pH measurements it is essential that the pH is measured at the temperature at which the sample was taken. For example, sodium hydroxide $c(\text{NaOH}) = 0.001$ mol/L at 0 °C has a pH of 11.94, at 50 °C it is pH = 10.26 and only at 25 °C is it pH = 11.00. This change in pH is caused by the dependency of the ionic product of water on the temperature.

In some conventional electrodes the temperature sensor is not located in the immediate vicinity of the membrane, i.e. in the electrode foot. This means that it cannot measure the temperature of the solution correctly and that the pH compensation will be incorrect as the temperature and pH are not measured at the same location. In modern pH electrodes the temperature sensor should be located within the electrode in the immediate vicinity of the glass membrane. This is the only way in which an accurate pH measurement is possible. If the sensor is located outside the membrane then problems when cleaning the electrode could easily occur.

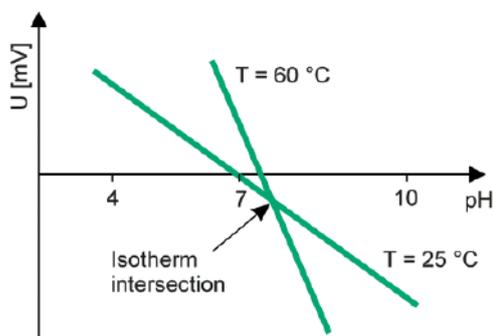


Figure 6: Isothermal intersection point

Table 2: Dependency of the Nernst potential U_N on the temperature

Temperature T (°C)	Slope U_N (mV)	Temperature T (°C)	Slope U_N (mV)
0	54.20	50	64.12
5	55.19	55	65.11
10	56.18	60	66.10
15	57.17	65	67.09
20	58.16	70	68.08
25	59.16	75	69.07
30	60.15	80	70.07
35	61.14	85	71.06
37	61.54	90	72.05
40	62.13	95	73.04
45	63.12	100	74.03

How to store a pH glass electrode?

The swelling of the glass surface is indispensable for the use of glass as membrane for pH glass electrodes; without this solvated layer, no pH measurement would be possible. Glasses for pH glass electrodes are optimized in such a way that only protons can penetrate into the glass membrane. However, because of the very slow but steady swelling of the glass, it is unavoidable that also other ions penetrate into the glass, e.g. sodium and potassium ions. At higher concentrations, these lead to the so-called alkali error of the glass electrode. This means that the measured value is falsified at comparatively low proton concentrations. If the glass electrode is stored for a very long time in a strong solution of potassium or sodium, this leads to prolonged response times of the glass membrane since the protons must expulse the «added ions» from the solvated layer.

One of the most used electrolytes for pH measurement is $c(\text{KCl}) = 3 \text{ mol/L}$, since the aequitransferent KCl causes only a very small diffusion potential at the diaphragm and is also economical. Normally a combined pH glass electrode is stored in $c(\text{KCl}) = 3 \text{ mol/L}$ only for this reason, as one wants to have it ready for immediate use without conditioning the diaphragm. However, on a long-term basis the storage in KCl affects the glass, since it leads to ever longer response times. For the membrane glass, storage in distilled water would be optimal, but then the diaphragm would have to be conditioned for several hours. The patented storage solution for combined pH glass electrodes (6.2323.000) solves exactly this problem. If a combined pH glass electrode is kept in this solution, the glass membrane remains unchanged regarding response time and alkali error. Moreover, if one uses $c(\text{KCl}) = 3 \text{ mol/L}$ as the reference electrolyte, the optimized composition of the storage solution keeps the pH glass electrode ready for measurement. Conditioning before the measurement is not necessary, no matter for how long the electrode has been stored.

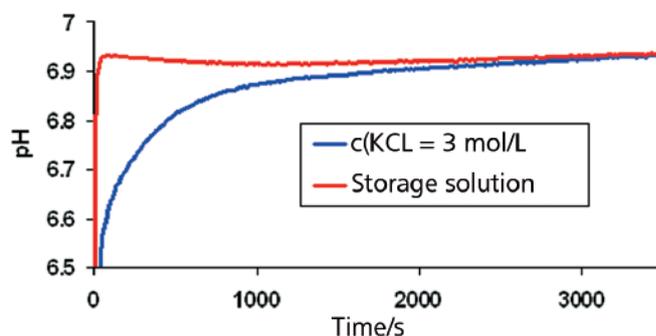


Figure 8: pH measurement in $c(\text{NaHCO}_3) = 0.05 \text{ mmol/L}$. A glass of the Aquatrode stored in the storage solution shows a substantially shorter response time than an electrode glass of the same type stored during the same period in KCl.

Table 3: The correct storage of pH glass electrodes

Electrode resp. reference electrolyte	Storage
Separate pH glass electrode	Distilled water
Combined pH glass electrode with $c(\text{KCl}) = 3 \text{ mol/L}$, Porolyte	6.2323.000 Storage solution
Combined pH glass electrode with another reference electrolyte (Idrolyte, non aqueous)	In the respective reference electrolyte
Gel (spearhead electrode), Ecotrode Gel	6.2308.000 Electrolyte solution $c(\text{KCl}) = \text{sat.}$

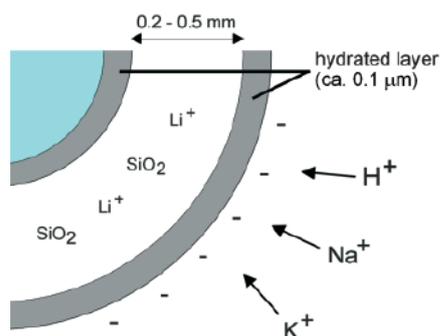


Figure 7: Cross-section of a pH glass membrane. If several kinds of cations are present in the measuring solution, these compete for the free spaces in the solvated layer. Especially potassium and sodium can penetrate into the glass membrane and prolong the response time.

Troubleshooting

The cause of most problems is not to be found in the measuring electrode and its glass membrane, but rather in the reference electrode, as much more critical diaphragm problems can occur there. To avoid incorrect measurements and to increase the working life, attention must still be paid to the following possible sources of error:

Table 4: Possible sources of error and their remedies for pH glass electrodes

Source of error	Effects	Action	Alternatives
HF-containing solutions	Etching and dissolution of the glass membrane → corrosion potential during the measurement/short working life		Use of the Sb-electrode
High pH value and high alkali content	Increased alkali error → pH too low		Use of electrodes with U glass
High temperatures	Rapid rise in membrane resistance by aging → increased polarizability and drift		Use of electrodes with U glass
Measurements at low temperature	High membrane resistance → polarization effects		Use of electrodes with T glass and Idrolyte as reference electrolyte
Dry storage	Zero point drift	Store in water overnight	Store in storage solution 6.2323.000 or reference electrolyte
Reaction of a solution component with the glass	Slow response, zero point shift, slope reduction		Try other glass types
Non-aqueous media	Reduced sensitivity	Store in water	T glass/non-aqueous electrolyte solution
Deposition of solids on membrane surface	Slow response, zero point shift, slope reduction	Solvent or strong acids	
Electrostatic charging	Slow response	No dab-drying of the electrode	Grounding of measuring instrument
Deposition of proteins on membrane surface	Slow response, zero point shift, slope reduction	5% pepsin in 0.1 mol/L HCl	

Possible sources of error and care information for diaphragm problems are given in Section 1.4. for reference electrodes.

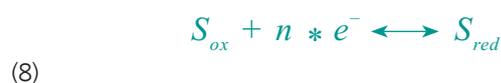
1.3.2. Metal electrodes

How does a metal electrode work?

Metal electrodes have an exposed metal surface. If ions of this metal are contained in the sample solution then an equilibrium is formed at the metal surface that depends on the concentration of the metal ions in the solution (see «Theory of the electrical double layer» in electrochemistry textbooks). Metal ions are accepted by the metal surface and simultaneously released into the solution.



This concentration-dependent equilibrium is characterized by a corresponding potential E^0 (Galvani potential), e.g. the Ag/Ag⁺ equilibrium at a silver surface has a value of $E^0 = 0.7999 \text{ V}$ (25°C). If the sample solution does not contain any ions of the corresponding metal then metal electrodes can still form a Galvani potential if a redox reaction occurs in the sample solution.



The electrode surface is inert to the redox reaction. No metal ions are released from the metal; in this case the metal surface only acts as a catalyst for the electrons. As gold and platinum electrodes are to a large extent chemically inert, they are used for the measurement of redox potentials. Silver electrodes are only used as indicator electrodes for titrations.

Calibrating a metal electrode

Redox-buffer solutions (6.2306.020) are used for quickly checking metal or redox electrodes. As the potential measured in a redox buffer solution is insensitive to the electrode's surface condition, contamination of the metal electrode is often not recognized. For this reason redox-buffer solutions are rather more suitable for checking the reference electrode. If the potential is displaced then the metal electrode is contaminated, the redox buffer partly oxidized or the functioning of the reference electrode is affected. Under no circumstances should the indicated potential be set to the theoretical value.

If measurements are made in weakly redox-buffered solutions then a suitable pretreatment of the metal electrode is recommended to adapt the surface condition as much as possible to the measurement conditions (abrasive pretreatment: carefully clean the electrode with abrasive paste). The reference electrode can either be checked against a second reference electrode that has already been checked in buffer solutions 4 and 7 (response behavior and reference potential) or by using the redox buffer.

In the literature the so-called standard redox potentials E^0 can usually be found.



The zero point of these systems is defined (arbitrarily) with the standard hydrogen electrode (SHE) which is assigned a standard potential of 0 mV. If electrons are released by a redox system to the SHE then this is reduced and the redox pair receives a negative sign; if electrons are accepted then the SHE is oxidized and the result is a redox potential with a positive sign. The standard hydrogen reference electrode is difficult to handle. The specifications of the SHE stipulate that a platinized platinum wire must be used; this is located in a stream of hydrogen gas at a partial hydrogen pressure of 1.0 bar, and that the activity of the hydrogen ions in the solution in which the platinized platinum wire is immersed is to be exactly 1.00 mol/L. The normal alternative is the Ag/AgCl/KCl reference electrode, which has a potential $E^0 = +207.6$ mV at $c(\text{KCl}) = 3$ mol/L and $T = 25$ °C. The Metrohm redox standard (6.2306.020) can be used for checking separate and combined metal electrodes. Platinum and gold electrodes together with the Ag/AgCl/KCl reference electrode ($c(\text{KCl}) = 3$ mol/L and $T = 20$ °C) produce a potential of $+250 \pm 5$ mV.

Table 5: Measuring data for 6.2306.020 redox standard as a function of the temperature

Temp. (°C)	10	20	25	30	40	50	60	70
mV ± 5	+ 265	+ 250	+ 243	+ 236	+ 221	+ 207	+ 183	+ 178
pH ± 0.05	7.06	7.02	7.00	6.99	6.98	6.97	6.97	6.98

If instead of an Ag/AgCl/KCl reference electrode $c(\text{KCl}) = 3$ mol/L an Ag/AgCl/KCl reference electrode $c(\text{KCl}) = \text{sat.}$ is used for the measurement then at 25 °C a correction of +10 mV must be applied; if the measurement is made using an Hg/Hg₂Cl₂/KCl calomel reference electrode, which for toxicological reasons is no longer available from Metrohm, the

correction to be applied is -37 mV. The Titrodes are checked by a standard titration as no suitable calibration or buffer solutions are available. For example, the certified ion standard $c(\text{NaCl}) = 0.1$ mol/L (6.2301.010) can be titrated with a silver nitrate standard solution.

Troubleshooting

Table 6: Problems encountered when measuring with metal electrodes

Electrode	Source of error	Effects	Cleaning	Alternatives
Ag	Electrode poisons such as S ²⁻ , I ⁻ , Br ⁻	Passivation of Ag layer → slow response	Cleaning with abrasives	
Pt/Au	Fats or oils	Isolating layer → slow response, incorrect potential	Cleaning with solvent	
	Weakly redox-buffered solution	Adsorbed ions on the surface (e.g. oxides) → slow response	Abrasive, oxidative (for oxidizing solutions) or reducing (for reducing solutions) pretreatment	Use of Au or Pt
	COD determination	Deactivation of Pt		Use of Au

1.3.3. Ion-selective electrodes

How does an ion-selective electrode work?

An ion-selective electrode (ISE) can selectively recognize an ion in a mixture of ions in a solution. There are various types of ion-selective electrodes, the most commonly used ones are:

Glass membrane	framework of silicate glass with interstitial sites for H ⁺ and Na ⁺
Crystal membrane	crystal lattice containing defined gaps for the ion to be measured
Polymer membrane	polymer membrane containing a molecule (= ionophore) that only binds the ion to be measured

In contrast to metal electrodes, an ISE does not measure a redox potential. If the ion to be measured is contained in the sample solution then this ion can penetrate the membrane. This alters the electrochemical properties of the membrane and causes a change in potential. One hundred percent selectivity for exactly one type of ion is only possible on rare occasions. Most ion-selective electrodes have «only» a particular sensitivity for a special type of ion, but also often react with ions with similar chemical properties or a similar structure (see Table 7). This is why the cross-sensitivity to other ions that may be contained in the sample solution must always be taken into consideration when selecting an ISE. One of the

best-known examples of such a cross-sensitivity is the so-called alkali error of pH glass electrodes. With some types of glass the linear range does not extend throughout the whole pH range from 0 to 14 and at high pH values a departure from linear behavior can be observed. The reason for this is that at very low H⁺-concentrations any alkali ions present in the solution (possibly released from the walls of the vessel) will falsify the measured value. Unfortunately there are only a very few ion-selective electrodes that have a linear range similar to that of pH glass electrodes. The use of an ISE is normally restricted to a concentration range of 6 to 8 powers of ten. If an ISE is used for a measurement right at the limit of the linear range then the Nernst equation (Eq. (5), Section 1.2.) must be extended by the contribution made by the particular interfering ion for the evaluation of the measured potential:

$$U = U_0 + \frac{2.303 * R * T}{z * F} * \log (a_M + K_S * a_S)$$

(Nikolsky equation) (9)

K_S is the so-called selectivity coefficient of the ion-selective electrode for interfering ion S. This is a factor that describes the influence of the interfering ion in relationship to the ion to be measured. These selectivity coefficients are known for the most important interfering ions for an ISE and therefore a simple estimation can be made as to whether an interfering ion contained in the sample solution will influence the measured value or not.

Direct measurement or standard addition?

The question often arises as to which determination method is most suitable for a particular sample. In principle there are three different ways of carrying out an ion measurement with ion-selective electrodes:

Direct measurement

Direct measurement is chiefly of benefit with high sample throughputs or with a known sample solution of a simple composition. The ion-selective electrode is calibrated with special standard solutions of the ion to be measured before the measurement itself in a similar way to the calibration of a pH glass electrode and can then be used for several determinations in series.

Standard addition

Standard addition is recommended whenever a determination only needs to be carried out occasionally or when the composition of the sample is unknown. Defined volumes of a standard solution of the ion to be measured are added to the sample solution in several steps. The concentration in the original solution can then be calculated from the initial potential and the individual potential steps after the addition of the standard. The advantage of standard addition is that the ISE is calibrated directly in the sample solution, which eliminates all matrix effects.

Sample addition

Similar to standard addition, with the difference that defined volumes of the sample solution are added to a defined amount of an ion standard.

Modern ion meters such as the 781 and the 867 pH/Ion Meter from Metrohm can carry out these addition methods automatically. The addition of the standard or sample solution is automatically controlled from the ion meter – by pressing a single key – and evaluated by using the Nikolsky equation.

ISA and TISAB – when and why?

The activity coefficient of an ion (Section 1.2.) is a function of the ionic strength. For this reason care must be taken that ion-selective measurements are always carried out in solutions with approximately the same ionic strength. In order to achieve this, the so-called ISA solutions (**I**onic **S**trength **A**djustor) or TISAB solutions (**T**otal **I**onic **S**trength **A**djustment **B**uffer) should be added to the sample solution (see Table 7). These are chemically inert and have such a high ionic strength that the ionic strength of the sample solution can be neglected after their addition.

Table 7: Interfering ions and recommended ISA and TISAB solutions for ion-selective electrodes

Ion	Membrane material	pH range ¹	ISA or TISAB ²	Most important interfering ions ³	Remarks
Ag ⁺	Crystal	2...8	c(KNO ₃) = 1 mol/L	Hg ²⁺ , Proteins	1) The given pH range only applies to ion-selective electrodes from Metrohm Ltd.
Br ⁻	Crystal	0...14	c(KNO ₃) = 1 mol/L	Hg ²⁺ , Cl ⁻ , I ⁻ , S ²⁻ , CN ⁻	
Ca ²⁺	Polymer	2...12	c(KCl) = 1 mol/L	Pb ²⁺ , Fe ²⁺ , Zn ²⁺ , Cu ²⁺ , Mg ²⁺	
Cd ²⁺	Crystal	2...12	c(KNO ₃) = 1 mol/L	Ag ⁺ , Hg ²⁺ , Cu ²⁺	2) Alternatives or more detailed compositions can be found in the manual «Ion Selective Electrodes (ISE)», order number 8.109.1476
Cl ⁻	Crystal	0...14	c(KNO ₃) = 1 mol/L	Hg ²⁺ , Br ⁻ , I ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻	
CN ⁻	Crystal	10...14	c(NaOH) = 0.1 mol/L	Cl ⁻ , Br ⁻ , I ⁻ ,	
Cu ²⁺	Crystal	2...12	c(KNO ₃) = 1 mol/L	Ag ⁺ , Hg ²⁺ , S ²⁻	
F ⁻	Crystal	5...7	NaCl/glacial acetic acid/CDTA	OH ⁻	
I ⁻	Crystal	0...14	c(KNO ₃) = 1 mol/L	Hg ²⁺ , S ²⁻ , S ₂ O ₃ ²⁻ ,	
K ⁺	Polymer	2.5...11	c(NaCl) = 0.1...1 mol/L	TRIS ⁺ , NH ⁴⁺ , Cs ⁺ , H ⁺	
Na ⁺	Polymer	3...12	c(CaCl ₂) = 1 mol/L	SCN ⁻ , K ⁺ , lipophilic ions	
NH ₄ ⁺	Gas membrane	11	–	–	
NO ₃ ⁻	Polymer	2.5...11	c((NH ₄) ₂ SO ₄) = 1 mol/L	Cl ⁻ , Br ⁻ , NO ₂ ⁻ , OAc ⁻	
Pb ²⁺	Crystal	4...7	c(NaClO ₄ ·H ₂ O) = 1 mol/L	Ag ⁺ , Hg ²⁺ , Cu ²⁺	
S ²⁻	Crystal	2...12	c(NaOH) = 2 mol/L	Hg ²⁺ , Proteins	3) More detailed information about interfering ions and other interferences can be found in the manual «Ion Selective Electrodes (ISE)», order number 8.109.1476
SCN ⁻	Crystal	2...10	c(KNO ₃) = 1 mol/L	Cl ⁻ , Br ⁻ , I ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻	

Troubleshooting

Table 8: Possible sources of interference and remedies for ion-selective electrodes

Electrode	Source of interference	Effects	Action
Ion-selective crystal membrane	Dissolution processes, oxidation processes	Rough surface → slow response, poor detection limits	Polish with polishing cloth
	Electrode poisons	Formation of more sparingly soluble salts on the electrode surface than with the ion to be measured → zero point shift, reduced linearity range	Polish with polishing cloth, mask interfering ion
Ion-selective polymer membrane	Dissolution processes	Diffusion into the membrane or dissolution of membrane component	Elimination of interfering components
NH ₃ sensor	Volatile bases (amines)	Electrolyte becomes contaminated → displacement of calibration line, limited linearity	Change electrolyte
	Surfactants	Membrane becomes wetted → slow response	Replace membrane

1.4. Reference electrodes

Reference electrodes are usually electrodes of the second kind. In this type of electrode a metal electrode is in contact with a sparingly soluble salt of the same metal. The potential depends only on the solubility of the salt. As a first approximation, electrodes of the second kind do not themselves react with the solution and therefore supply a constant potential.

The most frequently used reference electrode is the silver/silver chloride electrode (Ag/AgCl/ KCl). The calomel electrode (Hg/Hg₂Cl₂/KCl), which was formerly widely used, is hardly used at all today as mercury and its salts are extremely toxic and all the applications can also be carried out with the silver/silver chloride reference electrode. The standard hydrogen electrode SHE is also an electrode of the second kind. It is only

used for calibration purposes. Some titrations offer the possibility of using pH glass electrodes as reference electrodes. Even if protons are transferred during the titration it is usually still possible to make an accurate determination of the end-point.

1.4.1. Silver/silver chloride reference electrode

The reference element of the silver/silver chloride reference electrode is the silver/silver chloride/potassium chloride solution system: Ag/AgCl/KCl. The reference electrode is usually filled with c(KCl) = 3 mol/L or saturated KCl solution. Tables 9 and 10 show the potentials of the reference electrode as a function of the reference electrolyte and temperature. Each of these values has been measured against the standard hydrogen electrode under isothermal conditions.

Table 9: Standard redox potentials of the silver/silver chloride reference electrode as a function of the temperature and concentration

Temp. (°C)	0	+10	+20	+25	+30	+40	+50	+60	+70	+80	+90	+95
E° (mV) with c(KCl) = 3 mol/L	+224.2	+217.4	+210.5	+207.0	+203.4	+196.1	+188.4	+180.3	+172.1	+163.1	+153.3	+148.1
E° (mV) with c(KCl) = sat.	+220.5	+211.5	+201.9	+197.0	+191.9	+181.4	+170.7	+159.8	+148.8	+137.8	+126.9	+121.5

Table 10: Standard redox potentials of the silver/silver chloride reference electrode as a function of the concentration

c(KCl) / mol/L (25 °C)	0.1	1.0	3.0	3.5	sat.
E° (mV)	+291.6	+236.3	+207.0	+203.7	+197.0

1.4.2. The MetroSensor «Long Life» reference system

Most electrodes are equipped with the silver/silver chloride reference system. The solubility product of silver chloride in water is very small ($10^{-10} \text{ mol}^2/\text{L}^2$). In the concentrated, chloride-containing solution of the reference electrolyte soluble complexes of the series $(\text{AgCl}_2)^-$, $(\text{AgCl}_3)^{2-}$, $(\text{AgCl}_4)^{3-}$ are formed. This means that the reference system poses several problems. Outside the electrode the chloride concentration is frequently lower and the complexed silver chloride precipitates in the region surrounding the diaphragm («liquid junction»). The result: precipitated silver chloride blocks the diaphragm, and the response time of the pH electrode increases. A further problem is presented by the dependency of the solubility product of AgCl on the temperature. If the electrode is used at a different temperature then the equilibrium that determines the potential of the reference electrode must be reestablished. The larger the surface with solid AgCl in relationship to the electrolyte volume, the shorter the time required. The «Long Life» reference system prevents high concentrations of complexed AgCl from occurring in the outer electrolyte, as the silver chloride reservoir is connected with the outer electrolyte by a highly effective diffusion barrier. The concentration of the silver complex in the reference electrolyte remains low. Even after one year the concentration of complexed silver ions in the outer electrolyte has only reached 5% of the saturation value.

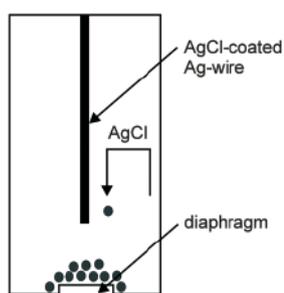


Figure 9: Conventional Ag/AgCl/KCl system. The chloride concentration outside the electrode is usually lower than in the electrolyte chamber. The soluble silver chloride complexes precipitate out in the region surrounding the diaphragm and may block it.

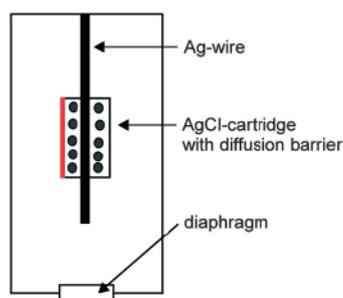


Figure 10: The Metrohm «Long Life» reference system. The dissolved AgCl is retained in the AgCl cartridge and can no longer block the diaphragm.

The advantages of the «Long Life» reference systems at a glance:

- Long working life of the electrode
- Rapid response to changes in pH
- Rapid response to temperature changes
- Less sensitive to electrode poisons, e.g. S^{2-}

Blocking the diaphragm by crystallized AgCl also affects the electrolyte flow. If the «Long Life» reference system is used then the flow of the KCl solution through the diaphragm into deionized water only decreases slightly.

As in the «Long Life» reference system the silver chloride is present in a smaller volume of potassium chloride solution, the thermodynamic equilibrium between silver, silver chloride (solid) and silver chloride (dissolved) is established very quickly and the potential of the reference electrode becomes stable after a very short time.

1.4.3. Diaphragms

Faulty measurements, unstable measured values and very long response times usually have their source in the «liquid junction» between the sample solution and the reference electrode. The diffusion, streaming and Donnan potentials that occur there – which are normally known together as the diaphragm potential – have various causes and can result in a very incorrect measured value.

The measuring error may assume vast proportions if measurements are made under the following conditions:

- with a blocked, virtually impermeable diaphragm,
- in ion-deficient solutions with an unsuitable diaphragm,
- in strong acids and bases with an unsuitable diaphragm,
- in colloidal solutions.

In all such cases errors may occur that cannot be tolerated. This is why the following questions must be in the foreground whenever an electrode and therefore the optimal type of diaphragm are to be selected:

- Does the reference electrolyte react with the sample solution to form a precipitate in the diaphragm?
- Does the electrolyte flow alter the composition of the sample solution in an unacceptable way?
- Is there a risk of depositing sample solution components on the diaphragm?
- Is the chemical resistance assured?
- Can physical parameters such as flow, pressure or temperature cause measuring errors?
- Does the process allow cleaning/maintenance of the electrode at certain intervals?
- Is a short response time and/or high reproducibility necessary?

The time required for cleaning and maintenance can usually be considerably reduced if the correct choice of electrode is made. The most frequent cause of measuring problems is contamination of the diaphragm. This is why with pH electrodes the chief attention is paid to the diaphragm during maintenance with the pH membrane being of secondary importance. If existing means cannot be used to determine whether the indicator electrode or the reference electrode requires cleaning/regeneration, then it is usually best to treat the reference electrode. Various types of diaphragm are available to satisfy the diverse requirements. These requirements have already been taken into consideration for the electrode recommendations in the application lists on pages 6 and 7.

Ceramic pin diaphragms

Ceramic pin diaphragms are frequently used diaphragms. They are primarily suitable for clear, aqueous sample solutions. They normally have pore diameters of up to 1 μm with a length and diameter each of about 1 mm. This results in an electrolyte flow rate of up to 25 $\mu\text{L/h}$, depending on the condition of the diaphragm. This means that the reference electrolyte only requires refilling at long intervals; this is why electrodes with ceramic pin diaphragms are particularly suitable for long-term measurements. On the other hand, because of their small pores and large polar surface ($\gg 500 \text{ mm}^2$), ceramic diaphragms tend to become blocked and therefore should not be used in solutions containing precipitates. An important advance with regard to the prevention of diaphragm blockages by silver chloride and silver sulfide has been achieved by the introduction of the «Long Life» reference system (see Section «The Metrosensor «Long Life» reference system»).

Ground-joint diaphragms with fixed or separable ground-joint

Ground-joint diaphragms with fixed or separable ground-joint are used in ion-deficient media, among others, as they produce a steady signal that is almost independent of sample flow conditions. The risk of blockage by silver chloride or by precipitates formed in the sample solution is relatively low because of the large surface area. Streaming potentials, which may occur in measurements in flowing or stirred solutions, remain negligibly small. These properties are particularly important for a SET titration to a defined pH or potential value. For example: the determination of the carbonate alkalinity by a SET titration to $\text{pH} = 5.4$ according to ISO 9963-2 is a widely used method in the routine analysis of drinking water. During a titration it is not possible to dispense with stirring, i.e. with an incorrectly measured pH or potential at the start of the titration an incorrect endpoint is the inevitable result. Figures 11 and 12 clearly show the difference between the Aquatrode Plus (6.0253.100), which was specially developed for this application, and a conventional pH glass electrode with ceramic pin diaphragm.

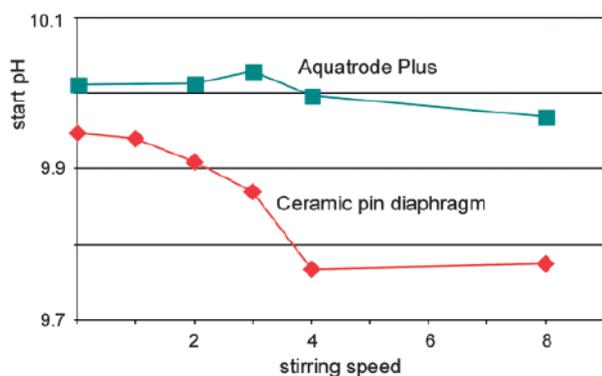


Figure 11: Measured pH of a solution with $c(\text{Na}_2\text{CO}_3) = 0.14 \text{ mmol/L}$. Even under vigorous stirring the Aquatrode Plus deviates by only approx. 0.05 pH units (corresponding to approx. 3 mV) from the unstirred value, in contrast the pH glass electrode with ceramic pin diaphragm deviates by approx. 0.2 pH units.

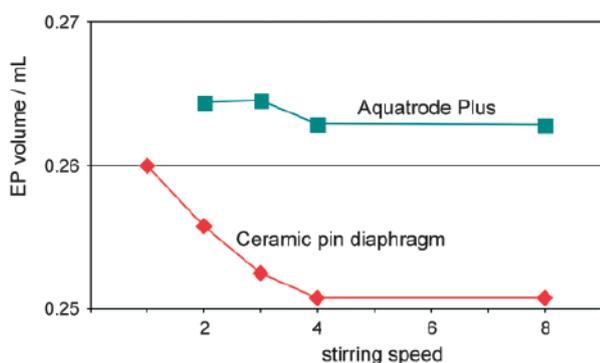


Figure 12: Endpoint volumes of a SET titration of a solution with $c(\text{Na}_2\text{CO}_3) = 0.14 \text{ mmol/L}$ with the titrant $c(\text{H}_2\text{SO}_4) = 0.035 \text{ mol/L}$ to pH 5.4. The endpoints of the Aquatrode Plus are virtually independent of the stirring speed. At higher stirring speeds the deviation from the theoretical value of the pH electrode with ceramic diaphragm amounts to approx. 5%.

Fixed ground-joint diaphragms have a uniform and reproducible electrolyte flow and are therefore particularly suitable for use with sample changers.

Separable ground-joint diaphragms are easy to clean and therefore particularly suitable for applications where contamination of the diaphragm cannot be prevented. The electrolyte flow may reach up to $100 \mu\text{L/h}$ and is normally considerably higher than the amount of electrolyte flowing from a ceramic or fixed ground-joint diaphragm. The ring-shaped geometry and the small polar surface of the ground-joint diaphragm have a favorable effect on the measurement. The increased electrolyte flow influences the sample solution more than if a ceramic pin diaphragm was to be used, the reference electrolyte normally needs refilling on a daily basis during long-term measurements.

An alternative is the easyClean diaphragm. It allows easy, contact-free cleaning just by pressing once on the electrode head. The spring in the electrode head returns to the defined starting position thereby ensuring greater accuracy and reproducibility of the electrolyte outflow.

Capillary diaphragms

In pH measurements in critical samples the very small pores of conventional ceramic diaphragms are easily blocked. The concept that has been realized in the Porotrode (6.0235.100), with two capillaries and a flow rate of $15\text{--}25 \mu\text{L/h}$ ensures unhindered contact between the reference electrolyte and the sample solution (liquid/liquid phase boundary), while the two capillaries of the Porotrode are practically insensitive to contamination. The reference electrode is filled with Porolyte, which has been specially developed for this electrode. The constant flow of Porolyte ensures that the potential is established quickly and reproducibly. The flow rate and therefore the refilling intervals are comparable to those of conventional electrodes. Extra maintenance work is not necessary. Measurements in problematic samples can be carried out easily and reproducibly thanks to the concept that has been realized in the Porotrode. The pH of samples containing protein, such as milk and beer, can now be determined without any diaphragm problems. In contrast to traditional pH electrodes the Porotrode measures correctly even at high surfactant concentrations.

Twin pore

Measuring the pH in semi-solid samples such as cheese, meat and fruit places special demands on an electrode. Proteins, fats and carbohydrates and other semi-solid substances in foodstuffs tend to block the fine pores of the ceramic diaphragms used in most pH electrodes, as such substances adhere extremely well to the fine-pore ceramic surface. With the development of the spearhead electrode (6.0226.100) and the polymer electrolytes this problem has been elegantly eliminated: two pinhole diaphragms take over the function of the «liquid junction» between the sample and the reference electrode. The polymer electrolyte adjacent to the openings, which is spiked with potassium chloride and thickened, is to a large extent insensitive to contamination by media containing proteins and fats. This insensitivity to contamination, the efficient protection of the reference electrode against the penetration of electrode poisons and the optimized inner buffer of the measuring electrode ensure that the new spearhead elec-

trode has an outstanding long-term behavior: even when used in difficult media the electrode zero point retains its long-term stability. The use of polymer electrolytes means that refilling a liquid reference electrolyte is no longer necessary.

The new Ecotrode Gel electrodes (6.0221.x00) are equipped with this diaphragm which keeps maintenance effort low.

Plied platinum wire

In combination with the reference electrolyte Idrolyte, which contains glycerol, the plied-platinum-wire diaphragm is outstandingly suitable for applications in biological media. The precipitation of proteins is suppressed by using an electrolyte with a low KCl content. The multi-capillary system (channels between the platinum wires) reduces contamination effects and the electrically conductive platinum reduces the response time and the diaphragm resistance. However, cross-sensitivity may occur in strongly redox-buffered solutions.

Cleaning and care of diaphragms

Table 11: Recommended ways of cleaning diaphragms

Type of diaphragm	Type of contamination	Cleaning
General	Preventiv and regular care	pHit kit (6.2325.000) according to instructions
	Precipitates of silver halides and silver sulfides	Immerse diaphragm for several hours in a solution of 7% thiourea in 0.1 mol/L HCl.
	Proteins, polypeptides	Immerse diaphragm for several hours in a solution of 5% pepsin in 0.1 mol/L HCl.
	Suspensions, solids, resins, glues, oils, fats	Clean electrode with suitable solvent
Fixed ground-joint	All types of contamination	Aspirate off reference electrolyte and immerse electrode in the corresponding cleaning solution.
Separable ground-joint	All types of contamination	Loosen the ground-joint sleeve (using hot water if necessary) and clean according to the type of contamination.
Capillary	Electrolyte flow interrupted	Apply slight counterpressure to electrolyte refilling opening

1.4.4. Reference electrolytes and bridge electrolytes

The reference or bridge electrolyte is in electrical contact with the sample solution via the diaphragm. The sample solution and electrolyte form a phase boundary with different ion concentrations on each side. This difference in concentration causes diffusion of the ions to the other side and, because of the different ion mobilities, a so-called diffusion potential occurs. In order to achieve a high degree of measuring accuracy the electrolyte composition must be selected so that any diffusion potentials formed are as negligible as possible; this is to

a large extent achieved by the use of $c(\text{KCl}) = 3 \text{ mol/L}$. On the one hand the ionic mobilities of K^+ and Cl^- are practically the same, on the other hand the ionic concentration in the sample solution is normally negligibly low in comparison to $c(\text{KCl}) = 3 \text{ mol/L}$. This is why the equal-transference KCl electrolyte is used as standard in all combined Metrohm electrodes and reference electrodes. However, certain media require the use of other electrolyte compositions in order to suppress effects that occur in addition to the diffusion potential.

Table 12: Alternatives to the standard reference electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$

Medium	Problems with standard electrolytes $c(\text{KCl}) = 3 \text{ mol/L}$	Alternative electrolyte
Silver ions	Reaction with Cl^- with precipitation of $\text{AgCl} \rightarrow$ slow response	$c(\text{KNO}_3) = 1 \text{ mol/L}$ (or Titrode for more or less constant pH value)
Non-aqueous	Precipitation of KCl, solutions and electrolyte immiscible \rightarrow unsteady signal	$c(\text{LiCl}) = 2 \text{ mol/L}$ in ethanol or LiCl saturated in ethanol
Ion-deficient water	Contamination of the medium by salt \rightarrow drift	KCl solution of lower concentration
Proteins/polypeptides	Precipitation of the proteins with KCl and $\text{AgCl} \rightarrow$ zero point shift/reduced slope	Idrolyte ¹
Semi-solid substances	Contamination of diaphragm \rightarrow zero point shift/slow response	Solid electrolyte in combination with pinhole diaphragm
Surfactants (proteins)	Adsorption on diaphragm \rightarrow zero point shift/reduced slope	Porolyte ²

¹ Idrolyte is a glycerol-based electrolyte whose chloride ion activity corresponds to that of a KCl solution with $c(\text{KCl}) = 3 \text{ mol/L}$. This means that the latter can also be readily replaced by Idrolyte. Idrolyte is excellent for use with solutions containing proteins and aqueous solutions with an organic fraction.

² Porolyte is a KCl solution that has been gelled by polymerization and is used in electrodes with a capillary diaphragm (Porotrode).

Table 13: Electrolyte flow rates and viscosities

Electrolyte	Viscosity (25 °C) (mPas)	Flow rate $\mu\text{L/h}$ (10 cm water column)				
		Ceramic pin	Flexible ground-joint	Fixed ground-joint	Ceramic capillary	Plied Pt wire
$c(\text{KCl}) = 3 \text{ mol/L}$	~1	Standard electrode 5...25 Microelectrode 5...15	$\varnothing 10 \text{ mm}$: 20...100 $\varnothing 5 \text{ mm}$: 5...30	5...30	–	–
$c(\text{KNO}_3) = 1 \text{ mol/L}$	~1	10...25	$\varnothing 10 \text{ mm}$: 20...100 $\varnothing 5 \text{ mm}$: 5...30	–	–	–
Idrolyte	8...10	–	–	–	–	3...25
Porolyte	1200...1500	–	–	–	5...30	–