

Monograph



Electrodes in Potentiometry

Dr. Christian Haider

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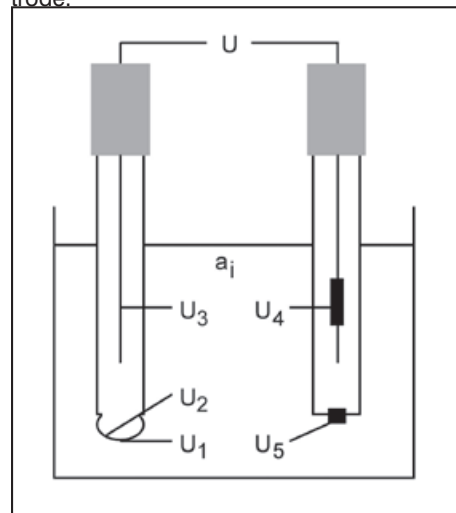
Table of contents

1	Basics of potentiometric measurements	5
2	Ion-sensitive electrodes	7
2.1	Basics and overview	7
2.2	pH glass electrodes	10
	Problems with glass electrodes?	12
	Care of pH glass electrodes	13
2.3	Surfactant electrodes	14
	Characterization of various surfactant electrodes	14
3	Redox electrodes	14
	Selecting redox electrodes	1
	Care of redox electrodes	16
	Problems with redox electrodes?	16
4	Ag metal electrodes	17
	Care of Ag metal electrodes	17
5	Reference electrodes	18
	Diaphragm (Liquid junction)	18
	Problems with the diaphragm?	19
	Electrode with bridge electrolyte (Double junction)	20
	Diffusion potential	21
	Reference systems	21
6	Which electrode for which application?	23
7	Literature	23
8	Index	24

1 – Basics of potentiometric measurements

Potentiometry is an extremely versatile analytical method which allows rapid and simple analyses.

The setup for potentiometric measurements consists of an indicator and a reference electrode. The indicator electrode provides a potential that depends on the composition of the sample solution. The task of the reference electrode is to supply a potential which is as independent as possible of the sample solution. The measured potential U is composed of individual potentials produced by indicator and reference electrode. Fig. 1 shows a schematic representation of the situation using a pH glass electrode with a separate reference electrode.



Indicator electrode (left) and reference electrode (right).

The potentiometric measurement is carried out practically currentless with a voltmeter with a high impedance measuring input (pH Meter).

U_1 : Galvani potential of the indicator electrode relative to the sample solution

U_2 : Galvani potential of the reference electrolyte relative to the glass membrane

U_3 : Galvani potential of the internal reference electrode relative to the reference electrolyte

U_4 : Galvani potential of the reference electrode

U_5 : Diffusion potential at the diaphragm

Fig. 1: Setup for potentiometric measurements

The individual potentials U_2 , U_3 , and U_4 are given by the electrode assembly and thus constant for a specific electrode pair. The diffusion potential at the diaphragm U_5 can be kept more or less constant and small through use of suitable measures (see page 21), so that the potential measured between the two electrodes depends only on U_1 , the potential between the indicator electrode and the sample solution. On the other hand, this potential depends on the activity a_i of the measuring ion. This relationship is described by the Nernst equation:

$$U = U_0 + \frac{2.303 \cdot RT}{z_i \cdot F} \cdot \log a_i = U_0 + U_N \cdot \log a_i \quad (1)$$

U : Measured potential between indicator and reference electrode

U_0 : Standard potential of the measuring assembly, depends on its construction

R : Gas constant (8.31441 J K⁻¹ mol⁻¹)

T : absolute temperature in K (T in °C + 273.15 K)

z_i : Charge of measuring ion i (including sign)

F : Faraday constant (96'484.56 C mol⁻¹)

a_i : Activity of measuring ion

U_N : Nernst slope

2.303 is the conversion factor for the natural logarithm to base ten.

The Nernst slope U_N specifies the theoretical electrode slope. U_N corresponds to the potential change caused by the change in a_i by the factor of ten. It depends on the temperature and the charge z of the measuring ion. It is 59.16 mV at 25 °C for univalent, positively charged ions ($z = +1$).

Fig. 2 shows the potentials for different measuring ions as a function of $\text{p}a_i = -\log a_i$ at 25 °C. Table 1 lists Nernst slopes at different temperatures for $z = 1$.

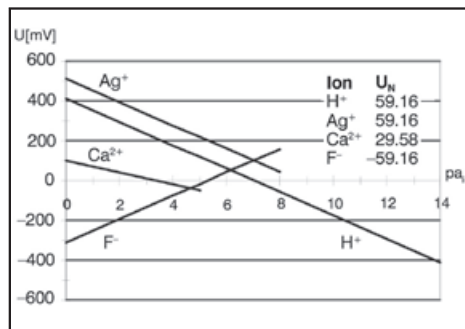


Fig. 2: Nernst slope for different measuring ions (25 °C)

Temperature [°C]	Nernst slope [mV]
0	54.20
10	56.18
20	58.17
25	59.16
30	60.15
38	61.74
40	62.14
50	64.12
60	66.10
70	68.09
80	70.07
90	72.06

Table 1: Temperature dependence of Nernst slope for univalent positive ions ($z = 1$)

Instead of two separate electrodes – an indicator and a reference electrode – combined electrodes are frequently used in practice. Combined electrodes contain an indicator and a reference electrode in the same shaft. Such electrodes are more convenient to handle than two separate electrodes.

However, a separate reference electrode is used

- if no combined electrodes are available for the task, e. g. in the case of surfactant electrodes or ion-sensitive electrodes (for measuring ions $\neq \text{H}^+$).

2 – Ion-sensitive electrodes

2.1 Basics and overview

Ion-sensitive electrodes (ISE) have a sensor element which can detect a specific ion in a mixture of ions as selectively as possible. The following sensor elements are frequently used in practice:

- Glass membranes for H^+ , Na^+
- Crystal membranes for F^- , Cl^- , Br^- , I^- , CN^- , SCN^- , S^{2-} , Ag^+ , Cu^{2+} , Cd^{2+} , Pb^{2+}
- Polymer membranes for Na^+ , K^+ , Ca^{2+} , NO_3^- , BF_4^-

The pH glass electrode is a very selective electrode. It is also the most important of all the ion-sensitive electrodes and therefore described separately in chapter 2.2.

The construction of ion-sensitive electrodes resembles that of pH glass electrodes:

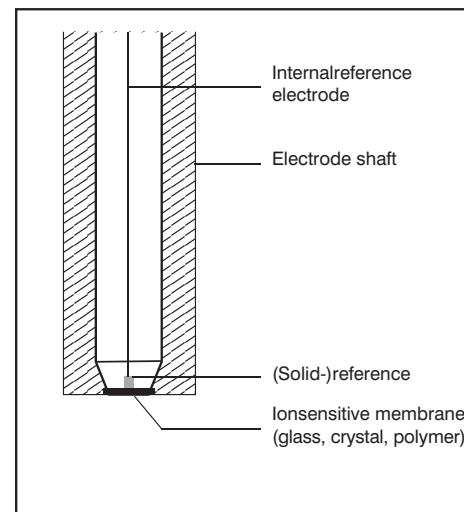


Fig. 3: Construction of ion-sensitive electrodes

At the interface ion-sensitive membrane / sample solution, a potential is developed which depends on the activity of the measuring ion in the sample solution.

A liquid reference can be used instead of a solid one. This is the case for the F^- -sensitive electrode, for all polymer membrane electrodes, and for the glass electrodes.

Gas-sensitive electrodes for NH_3 , CO_2 etc. are in principle pH electrodes which are immersed in a solution. This internal solution and the sample solution are separated by a gas permeable membrane. The gas diffusing through the membrane alters the pH value of the internal solution and thus allows measurement of the gas concentration.

Unfortunately, only a few ion-sensitive electrodes are that selective (except the pH glass electrode) that the Nernst equation tells exactly the connection between the measured potential and the activity of the measuring

ion. Often, not only the measuring ion contributes to the potential. Other ions, interfering ions, contribute too. The influence of these interfering ions on the potential of the measuring assembly is described by the Nikolskij equation. This equation is an expanded Nernst equation which takes the selectivity of the ion-sensitive electrode into account:

$$U = U_0 + 2.303 \cdot \frac{RT}{z_i \cdot F} \cdot \log \left(a_i + \sum_{j \neq i} K_{ij} \cdot a_j^{z_i/z_j} \right) \quad (2)$$

a_i : Activity of measuring ion
 a_j : Activity of interfering ion
 K_{ij} : Selectivity constant

z_i : Charge of measuring ion i
 z_j : Charge of interfering ion j

K_{ij} is in the range of $10^{-1} \dots 10^{-5}$ for most ion-sensitive electrodes. For an ideal electrode, K_{ij} should be $= 0$ for all interfering ions; it would then respond only to the measuring ion.

The pH glass electrode is the most selective electrode. The selectivity constant K_{H^+/Na^+} is app. 10^{-13} (see also alkali error, page 10). If, for example, the sample has a sodium activity of 1 mol/L at $a(H^+) = 10^{-12}$ mol/L (pH = 12) this gives

$$pH = -\log(10^{-12} + 1 \cdot 10^{-13}) = 11.96 \quad (3)$$

In other words, if conclusions are drawn from the measured potential regarding the activity of H^+ , an error of only 10 % is incurred for the example above: $a(H^+) = 1.1 \cdot 10^{-12}$ mol/L instead of $1.0 \cdot 10^{-12}$.

Table 2 lists a few ion-sensitive electrodes together with their measuring range and interfering ions. Interfering ions which poison the electrode (they can destroy it!) are printed in bold. Such ions must therefore be absent. Ions which do not cause interference until their concentration exceeds that of the measuring ion are shown in brackets.

According to the Nikolskij equation, a potential measurement provides information about the activity of an ion. In practice, however, it is the concentration that is of interest. The activity a_i is related to the concentration c_i by the following equation:

$$a_i = y_i \cdot c_i \quad (4)$$

y_i is the molar activity coefficient. It is a function of the total ionic strength of the solution and therefore not easily accessible. For very dilute solutions y_i is equal to 1, i. e. the activity of the measuring ion is equal to its concentration. To make the desired ionic concentration accessible to the analyst through a simple potential measurement, special analysis techniques have been developed that make exact knowledge of the activity coefficient unnecessary: The ionic strength of the sample solution is kept constant by addition of a solution of an inert electrolyte. This solution has a much higher ionic strength than the sample, the contribution of the sample to the ionic strength can therefore be neglected. Often, the pH is kept constant at the same time and the influence of interfering ions is eliminated. These solutions are called TISAB (Total Ionic Strength Adjustment Buffer).

Measuring ion	Measuring range [mol/L]	Most important interfering ions	Application examples
Ag^+	$1 \cdot 10^{-7} \dots 1$	Hg²⁺ , proteins should be absent.	Fixing baths, ores; titrations with Ag^+
BF_4^-	$7 \cdot 10^{-6} \dots 1$	Halogenides , NO_3^- , SO_4^{2-} , ClO_4^- , F^- , acetate	Surfactants, electroplating, determination of boron
Br^-	$5 \cdot 10^{-6} \dots 1$	Hg²⁺ , I^- , S^{2-} , CN^- , $(NH_3, S_2O_3^{2-})$	Baths, crude oil, plastics, clinical analytics
Ca^{2+}	$5 \cdot 10^{-7} \dots 1$	Na^+ , Pb^{2+} , Fe^{2+} , Zn^{2+} , Cu^{2+} , Mg^{2+}	Beer, soil, foodstuff, water, wine
Cd^{2+}	$1 \cdot 10^{-7} \dots 10^{-1}$	Ag⁺ , Hg²⁺ , Cu²⁺ , (Fe^{3+}, Pb^{2+})	Electroplating, lubricating oils, water, mud, soil
Cl^-	$5 \cdot 10^{-5} \dots 1$	Hg²⁺ , Br^- , I^- , S^{2-} , CN^- , NH_3 , $S_2O_3^{2-}$	Water, foodstuff, beverages, plastics, pharmaceuticals, pesticides, glass, paper
CN^-	$8 \cdot 10^{-6} \dots 10^{-2}$	S²⁻ , Ag⁺ complexing substances , I^- , (Cl^-, Br^-)	Ore dressing, electroplating, crude oil, water
Cu^{2+}	$1 \cdot 10^{-8} \dots 10^{-1}$	Ag⁺ , Hg²⁺ , S²⁻ , $(Cl^-, Br^-, I^-, Fe^{3+}, Cd^{2+})$	Ores, electroplating, water
F^-	$1 \cdot 10^{-6} \dots \text{sat.}$	OH^-	Electroplating, etching baths, fertilizers, pesticides, foodstuff, pharmaceuticals, cosmetics, plastics
H^+	$1 \cdot 10^{-14} \dots 1$		pH measurements and pH titrations
I^-	$5 \cdot 10^{-8} \dots 1$	Hg²⁺ , S^{2-} , CN^- $(Cl^-, Br^-, S_2O_3^{2-})$	Pharmaceuticals, agricultural products, clinical analytics
K^+	$1 \cdot 10^{-6} \dots 1$	Na^+ , NH_4^+ , Cs^+ , H^+	Soil, fertilizers, wine, biological liquids
Na^+ glass	$1 \cdot 10^{-5} \dots 1$	$pH > (pNa+4)$, Li^+ , K^+ , Ag^+	Water, biological liquids
Na^+ polymer	$1 \cdot 10^{-6} \dots 1$	SCN^- , acetate	Water, biological liquids
NO_3^-	$7 \cdot 10^{-6} \dots 1$	Br^- , NO_2^- , Cl^- , acetate	Scouring baths, soil, meat, plant material, water
Pb^{2+}	$1 \cdot 10^{-6} \dots 10^{-1}$	Ag⁺ , Hg²⁺ , Cu²⁺ , (Fe^{3+}, Cd^{2+})	Electroplating, water
S^{2-}	$1 \cdot 10^{-7} \dots 1$	Hg²⁺ , proteins	Paper, foodstuff, beverages, water
SCN^-	$5 \cdot 10^{-6} \dots 1$	Br^- , I^- , S^{2-} , CN^- , $S_2O_3^{2-}$, (Cl^-)	Water, electroplating

Table 2: Measuring range and interfering ions of ion-sensitive electrodes

Ion-sensitive electrodes are used in practice as follows:

- For the indication of titrations. Ion strength is not important and a calibration is unnecessary.
- Measurements with standard addition. The first potential is measured in the sample. Then a known amount of measuring ion (standard solution) is added and the potential is measured again. The concentration of the measuring ion is calculated from the potential difference. Usually, multiple standard additions are carried out.
- Single measurements and determination of the concentration by means of a calibration curve.

2.2 pH glass electrodes

pH glass electrodes respond to hydrogen ions, i. e. they are ion-sensitive electrodes for H^+ . The ion-sensitive measuring element is a glass membrane of special composition. This glass membrane has to be soaked in water in order to prepare the electrode for measurements. It then forms a thin (app. $1000 \text{ \AA} = 10^{-4} \text{ mm}$) gel-like hydrated layer. If the glass electrode is immersed in water at room temperature, the swelling of the membrane is completed within 24 – 48 h. The formation of this hydrated layer is accelerated at higher temperatures for some pH glass membranes. In corrosive media, organic solvents and F^- containing solutions, this layer can be damaged.

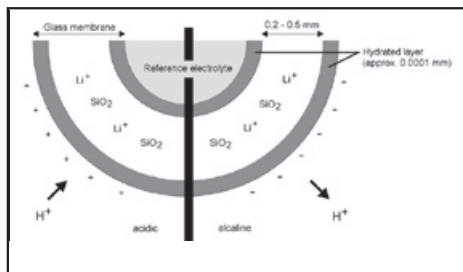


Fig. 4: Schematic drawing of the hydrated layer of a glass electrode

Several important terms in connection with pH measurements will be explained. They are alphabetically arranged.

Alkali error

In strongly alkaline solutions measurement errors may appear due to the potential contribution of alkali ions (e. g. Na^+). They contribute in addition to the hydrogen ions, see Nikolskij equation, page 7. The pH value appears to be lower.

The alkali error depends on the pH value, the temperature, as well as on the type and concentration of the alkali ions present. Modern pH glasses show only extremely small alkali errors.

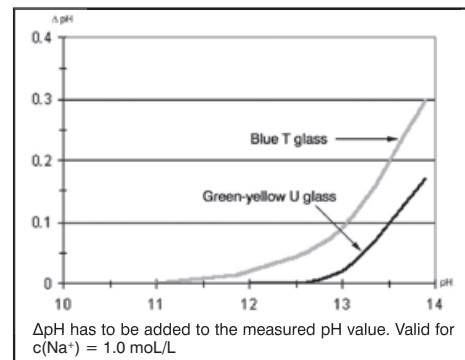
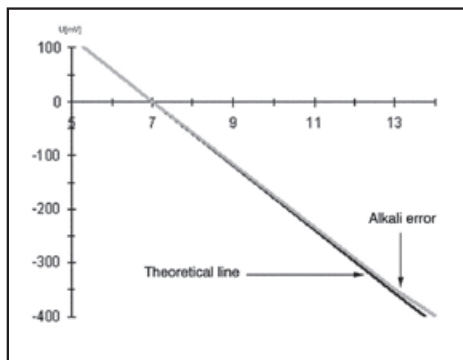


Fig. 5: Alkali error and typical correction curves for different pH glasses

Asymmetry potential

If a glass electrode is immersed in a sample solution which is identical to the reference electrolyte, the galvanic potential should be zero. The deviation of a few mV is called asymmetry potential.

Usually, the reference electrolyte has a pH value of 7, i. e. at $pH = 7$ the measured potential should be 0 mV for a symmetrical measuring assembly (a measuring assembly with identical internal and external reference electrode).

Formerly, “asymmetry potential, U_{as} ” and “asymmetry pH, pH_{as} ” were also used for the zero point of the measuring assembly, see Fig. 6.

pH_0 , zero point

See pH calibration.

pH calibration

The condition of the pH measuring assembly is subject to fluctuations over the course of time. Depending on the accuracy demands, a pH calibration should therefore be performed periodically, e. g. once a day.

In the pH calibration, the current characteristic line of the electrode (i. e. pH_0 and Nernst slope) is overlaid on the characteristic line of the pH Meter ($pH_0 = 7.0$ and $s_{rel} = 1.000$). Remember that the slope depends on the temperature, see page 6.

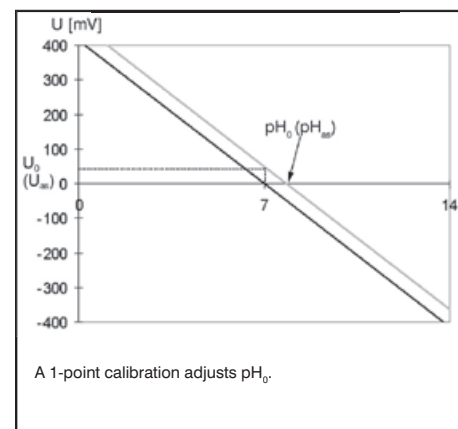
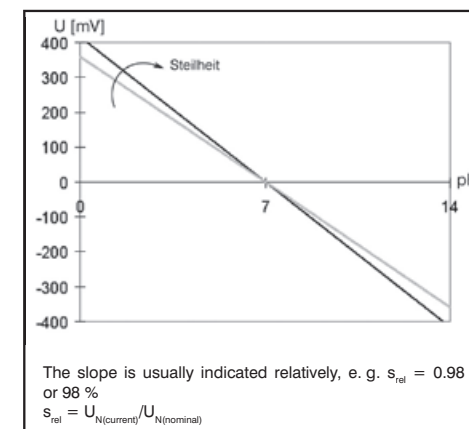


Fig. 6: pH calibration



For pH calibration, buffer solutions of known pH values are used. Please note, that the pH value of these buffer solutions depends on the temperature, see Table 3. The calibration temperature and the measuring temperature should be the same for very accurate measurements.

T [°C]	Buffer		
	pH 4.00 ± 0.02	pH 7.00 ± 0.02	pH 9.00 ± 0.02
10	3.99	7.06	9.13
20	3.99	7.02	9.04
25	4.00	7.00	9.00
30	4.00	6.99	8.96
38	4.02	6.98	8.91
40	4.02	6.98	8.90
50	4.04	6.97	8.84
60	4.07	6.97	8.79
70	4.11	6.98	8.74
80	4.15	7.00	8.71
90	4.20	7.01	8.68

Table 3: Temperature dependence of pH values of Metrohm buffers

Problems with glass electrodes?

Problem	Possible cause	Remedy
Display of pH meter drifts	No constant diffusion potential at the reference electrode	Select the correct bridge or reference electrolyte, see page 20 or page 21
	Loose contact	Repair damage
	Electrode not plugged in or faulty cable	Repair damage
Display of pH meter is sensitive to ambient influences	Reference electrode is not correctly filled	Fill with electrolyte solution without air bubbles
	Reference electrode filled with water	Empty electrode and refill with reference electrolyte
	Blocked diaphragm	Clean diaphragm, see below
	Measurement in poorly conducting solution	Use suitable electrode, see page 23, add indifferent salt
Slow adjustment of measured value	Adsorption at glass membrane	Clean glass membrane, see below
	Dirty diaphragm	Clean diaphragm, see below
Slope too small	Dirty diaphragm	Clean diaphragm, see below
	Adsorption at glass membrane	Clean glass membrane, see below
	Glass membrane deswollen after measurement in non-aqueous solution	Immerse electrode in water between measurements
	Old electrode	Replace electrode
	Poor buffer solutions	Replace buffers
Same measured value in buffer pH 4 and 7	Crack in glass membrane	Replace electrode
	Electrical connectors damp or dirty	Dry or clean connectors

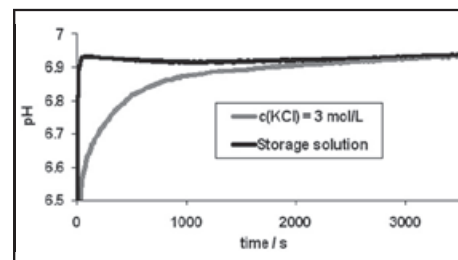
Table 4: Troubleshooting for measurements with pH glass electrodes

Care of pH glass electrodes

Storage

- Combined glass electrodes:

Electrodes with reference electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$: The long-term storage in $c(\text{KCl}) = 3 \text{ mol/L}$ can lead to ever-increasing response times because of the inclusion of potassium in the glass membrane. If a combined electrode is stored in water, AgCl can precipitate in the diaphragm! That's why Metrohm recommends the Storage solution 6.2323.000. Thanks to the optimized composition the performance of the glass membrane does not change with respect to the response time. The electrode can be used immediately without conditioning even after a longer storage period.

Fig. 7: pH measurement in $c(\text{NaHCO}_3) = 0.05 \text{ mmol/L}$

Electrodes with other reference electrolytes: The electrode should be stored in that reference electrolyte in order to ensure that the electrode is ready for immediate use.

- Separate glass electrodes:

The electrode should be stored in distilled water.

Cleaning the diaphragm

- After measurements in solutions with low chloride concentration (precipitated AgCl in the diaphragm \rightarrow dark diaphragm): Immerse electrode at least for 1 h in reference electrolyte ($c(\text{KCl}) = 3 \text{ mol/L}$) at $50 - 60^\circ\text{C}$ or put it overnight in concentrated NH_3 , rinse it with water and replace the reference electrolyte.
- After measurements in sulphide-containing solutions (Ag_2S in diaphragm \rightarrow dark diaphragm): Immerse electrode in freshly prepared, slightly acidic 7 % thiourea solution. Then rinse it with water and replace the reference electrolyte.
- Organic contaminations: Empty electrode and rinse / immerse with / in suitable solvent. Then rinse thoroughly and replace the reference electrolyte.

Care of the glass membrane

- After measurements in non-aqueous solutions: Immerse electrode in water between measurements.
- After measurements in protein-containing solutions: Immerse electrode in a solution of pepsin and hydrochloric acid (5 % pepsin in $c(\text{HCl}) = 0.1 \text{ mol/L}$) for several hours. Then rinse and immerse electrode in water.

2.3 Surfactant electrodes

Surfactant electrodes have a ionophore i. e. a sensor element responding to surfactants. For measurements with these electrodes, the Nernst equation is not always exactly valid. Surfactant electrodes are therefore not suitable for direct measurements of surfactant concentrations. In potentiometric titration, however, they can be used successfully.

Characterization of various surfactant electrodes

Surfactant electrodes are stored in a dry condition. They are prepared by carrying out 1 – 3 pretitrations. Surfactrodes are immediately ready for use.

The following table gives an overview of various surfactant electrodes.

Surfactant electrode	Application	Incompatibilities	Regeneration
Ionic Surfactant Cationic Surfactant Polymer membrane electrode	Aqueous titration of ionic surfactants	<ul style="list-style-type: none"> Chlorinated hydrocarbons (e. g. CHCl_3) Hydrocarbons (e. g. benzene, toluene) Oils Solvents swelling or dissolving PVC 	30 min in sodium dodecylsulfate solution (0.004 mol/L)
NIO electrode Polymer membrane electrode	Aqueous titration of non-ionic surfactants Use separate electrode for each type of non-ionic surfactant!	<ul style="list-style-type: none"> Chlorinated hydrocarbons e. g. CHCl_3) Hydrocarbons (e. g. benzene, toluene) Oils Solvents swelling or dissolving PVC 	30 min in sodium tetraphenylborate solution (0.01 mol/L)
Surfactrode Refill Ionophore in refill paste	2 phase titration without CHCl_3	<ul style="list-style-type: none"> CHCl_3; chloroform can be replaced by e. g. methyl isobutyl ketone or n-hexane 	Refill sensor material
Surfactrode Resistant Ionophore in graphite	2 phase titration also with CHCl_3	<ul style="list-style-type: none"> Samples with high salt concentrations and low surfactant concentrations (e. g. electroplating baths), pH has to be lower than 10 	<ul style="list-style-type: none"> Roughen sensor surface (e. g. with sandpaper) In oven for 1 h at 60 °C 1 % solution of polyethylene glycol 1000

Table 5: Overview of surfactant electrodes

3 – Redox electrodes

In redox measurements the electrode shows the potential which corresponds to the electrochemical potential of the redox system by exchanging electrons with this system. The electrode exchange can only be unrestricted with reversible redox systems.

The measured redox potential isn't a direct measure of the activity of ions. It is rather a measure of the equilibrium position of the conjugate redox couple and is described by the Peters equation:

$$U = U_0 + U_N \cdot \log \frac{a_{\text{ox}}}{a_{\text{red}}} \quad (5)$$

U_0, U_N : Standard potential of the redox couple and Nernst slope, respectively

$a_{\text{ox}}, a_{\text{red}}$: Activities of the oxidized and reduced form of the redox couple

Redox electrodes are mostly used for the indication of titrations. If hydrogen ions participate in the redox reaction, the potential depends also on the pH value, e. g.



The corresponding Peters equation is:

$$U = U_0 + U_N \cdot \log \frac{a_{\text{MnO}_4^-}}{a_{\text{Mn}^{2+}}} - U_N \cdot 8 \cdot \text{pH} \quad (7)$$

with a Nernst slope $U_N = 1/5 \cdot 59.16 \text{ mV} = 11.83 \text{ mV}$ at 25 °C.

Redox electrodes used in practice are electronic conductors, e. g. noble metals such as Pt or Au, or carbon electrodes. However, these electrodes are not completely neutral to influences of ions. Au electrodes also respond to cyanide or chloride ions (formation of stable complexes with Au^+).

The behavior of redox electrodes depends frequently on their history. They tend to form thin oxide coatings which lead to passivation of the electrode. Such electrodes can be regenerated with a solution of quinhydrone, see page 16.

Redox standards are used to check pure Pt or Au electrodes. The potentials and pH values of the Metrohm redox standard are given in Table 6. They apply to combined Metrohm electrodes with $\text{Ag/AgCl/c(KCl)} = 3 \text{ mol/L}$ as reference system.

	10 °C	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C
U [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

Table 6: Measured data for Metrohm redox standard

If redox potentials should be referred to the standard hydrogen electrode, the measured values can be converted according to the equation

$$U_{\text{absolute}} = U_{\text{measured}} + U_{\text{reference system}} \quad (8)$$

The potential of the reference system used for measurement (see table 9, page 22) is added to the measured value including its sign.

Selecting redox electrodes

Experience plays a large part in the selection of the best redox electrode. It is virtually impossible to give general rules. Despite this, we try to provide a few tips for the selection of redox electrodes:

- Pt electrodes are by far the most frequently used.
- Au electrodes can be better than Pt electrodes in some special cases. This is true e. g. for diazotizations, for oxidations of cyanides or generally for redox reactions which run in alkaline solutions.
- The shape of the electrode can also be important. Metal ring electrodes have a greater surface than wires. They should be used in heterogeneous samples (precipitations) or if the electrode surface is subject to passivation or corrosion during the analysis.
- Plug-in electrode rods of solid metal have a virtually unlimited lifetime. They can be cleaned in a flame. Such electrodes are selected for measurements in highly contaminated or corrosive solutions.

Care of redox electrodes

Storage

- Pt- and Au Titrode: In distilled water
- Combined Pt and Au electrodes: In the reference electrolyte, $c(\text{KCl}) = 3 \text{ mol/L}$
- Separate electrodes: In dry condition

Problems with redox electrodes?

- If the electrode tends to "run-in", its metal surface may be passivated. Place the electrode in a solution of 0.5 g quinhidrone in 50 mL buffer $\text{pH} = 4$. Then rinse with water.

Or:

Connect the degreased electrode to the minus pole of a direct current source (e. g. battery). Connect the plus pole to an inert counter electrode and electrolyze during approximately 3 min in diluted H_2SO_4 at 10 mA.

- If the metal surface is contaminated it can be cleaned with scouring agent. Rinse the electrode afterwards with water. Plug-in electrode rods of solid metal can be heated to redness in a flame.
- Check the diaphragm in the case of combined electrodes, see page 13.

4 – Ag metal electrodes

Ag metal electrodes are primarily used in precipitation titrations with Ag^+ (e. g. titration of Cl^- with Ag^+). The corresponding Nernst equation is:

$$U = U_0 + U_N \cdot \log a_{\text{Ag}^+} \quad (9)$$

U_0 :	Standard potential of the measuring assembly
U_N :	Nernst slope
a_{Ag^+} :	Activity of silver ions

Remove the silver salt precipitate from time to time from the electrode surface. However, it is easier to prevent such undesired coating of the electrode by adding polyvinyl alcohol to the sample solution. The electrode can then be cleaned by simply rinsing it. Polyvinyl alcohols can be purchased from leading chemical producers.

Very often, Ag electrodes are coated with AgCl , AgBr , AgI or Ag_2S for titrations with Ag^+ . The response of such electrodes is faster and more stable. We recommend Ag_2S coated Ag electrodes for the following applications:

- Titration of sulphides and mercaptans
- Titration of cyanides
- Titration of chlorides in solutions with high ionic strength
- For low concentrations

Care of Ag metal electrodes

Storage

- Ag Titrode: In distilled water
- Combined electrodes: **In the reference electrolyte, $c(\text{KNO}_3) = \text{sat.}$**
- Separate electrodes: In dry condition

Cleaning

- Clean the electrode with scouring agent. Rinse the electrode afterwards with water.
Only for electrodes without Ag salt coating!

Refilling the reference electrolyte in combined electrodes

- Refill only with KNO_3 solution, see printing on electrode head, never refill with KCl !
- If there are KNO_3 crystals in the reference system, rinse with dist. water and refill with fresh reference electrolyte.

Check the diaphragm in the case of combined electrodes, see page 13.

5 – Reference electrodes

A good reference electrode provides a constant potential which is independent from the composition of the sample solution. This is usually achieved by electrodes of the 2nd kind: A metallic conductor contacts a sparingly soluble salt of its metal and a solution of constant composition, the reference electrolyte. The reference system consists of the metallic conductor, the sparingly soluble salt and the reference electrolyte. A Ag/AgCl reference system consists therefore of a Ag wire, sparingly soluble AgCl and a chloride containing electrolyte solution, e. g. $c(\text{KCl}) = 3 \text{ mol/L}$. Fig. 8 shows the Ag/AgCl/c(KCl) = 3 mol/L reference system.

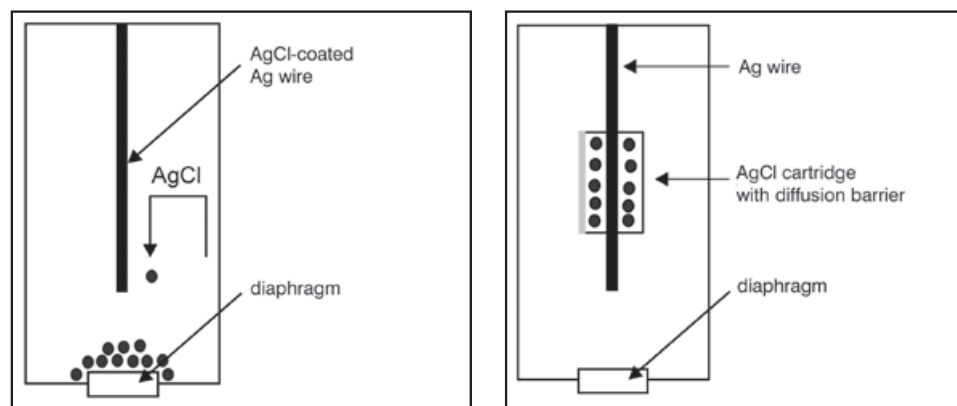


Fig. 8: Ag/AgCl reference system, conventional (left) and Long Life LL system (right)

LL electrodes do have less problems with sparingly soluble precipitations of silver salts in the diaphragm than conventional reference electrodes because the silver chloride is retained in the cartridge with diffusion barrier.

The reference electrolyte solution is connected with the sample solution in such a manner that no free mixing of the solutions occurs. This liquid junction can be effected with a diaphragm.

Diaphragm (Liquid junction)

The diaphragm allows a slow constant flow of reference electrolyte solution into the sample. A porous ceramic pin is often used as diaphragm. According to the application other diaphragms (such as ground joint diaphragms, capillaries or pinholes) can be advantageous. The most important types of diaphragm including application examples are listed in Table 7.

Diaphragm	Flow rate for $c(\text{KCl}) = 3 \text{ mol/L}$ at 25°C	Application
Ceramic pin: Rare refilling of reference electrolyte.	3 ... 25 $\mu\text{L/h}$	For general measurements in clear, aqueous solutions with conductivity $> 10 \mu\text{S/cm}$ Specially suitable for long-term measurements if the solutions are not strongly alkaline
Ground joint: Small and constant diffusion potential. Easy cleaning, practically no blocking danger.	20 ... 100 $\mu\text{L/h}$ according to contact pressure	For non-aqueous and virtually salt-free media (conductivity $< 10 \mu\text{S/cm}$) For concentrated or highly contaminating solutions as well (easy cleaning)
Fixed ground joint: Small and constant diffusion potential.	5 ... 20 $\mu\text{L/h}$	For pH measurements in poorly conducting, virtually salt-free measurements (e. g. Aquatrode), as well as for highly contaminating solutions such as suspensions, emulsions (e. g. Unitrode)
Capillary: The contact layer is renewed constantly by electrolyte flow.	15 ... 25 $\mu\text{L/h}$ thickened Porolyte as electrolyte	For pH measurements in difficult media, e. g. protein containing or concentrated and highly contaminating solutions (e. g. Porotrode)
Pinhole: No refilling of reference electrolyte.	--- solid polymer electrolyte	For pH measurements in semi-solid, difficult media (e. g. cheese, meat, fruit)

Table 7: Diaphragms and their applications

Problems with the diaphragm?

Contaminated diaphragms are the most frequent problem with potentiometric measurements. Diaphragms can be blocked by sparingly soluble Ag salts from the Ag/AgCl reference system:

- AgCl is better soluble in the presence of chloride ions because of the formation of soluble chloro complexes AgCl_3^{2-} und AgCl_4^{3-} . In media with low chloride content, AgCl may precipitate in the diaphragm and block it.
- Ag^+ forms sparingly soluble salts with bromide, iodide, cyanide and particularly with sulphide. Sulphide exists in many organic compounds (e. g. in proteins).

Troubles may also arise if ions of the reference electrolyte react with the sample solution. Precipitations from these reactions may block the diaphragm. The following ions in the sample cause problems if you use aqueous KCl solutions as reference electrolyte:

- ClO_4^- : KClO_4 is sparingly soluble
- Hg_2^{2+} , Ag^+ , Pb^{2+} , Cu^+ : form sparingly soluble chloride salts.

If the diaphragm is blocked by sparingly soluble salts, the problem may be solved by selecting a suitable diaphragm type (see above) and/or a suitable reference system with a bridge electrolyte.

Note that the solubility of salts decreases generally with decreasing temperature. Salts of concentrated solutions may therefore crystallize at low temperatures. For low temperature measurements, electrolyte solutions of lower concentrations are used, e. g. $c(\text{KCl}) = 1.5 \text{ mol/L}$ instead of $c(\text{KCl}) = \text{sat.}$ or 3 mol/L .

Electrode with bridge electrolyte (Double junction)

If the sample solution contains ions which are incompatible with the reference electrolyte, a double junction electrode may be used. Double junction electrodes provide another electrolyte (a bridge electrolyte), a liquid junction between the sample solution and the reference electrolyte, see Fig. 9. The bridge electrolyte can be adapted rather freely to the needs of the sample solution with the limitation of compatibility with the reference electrolyte (no reaction e. g. precipitations).

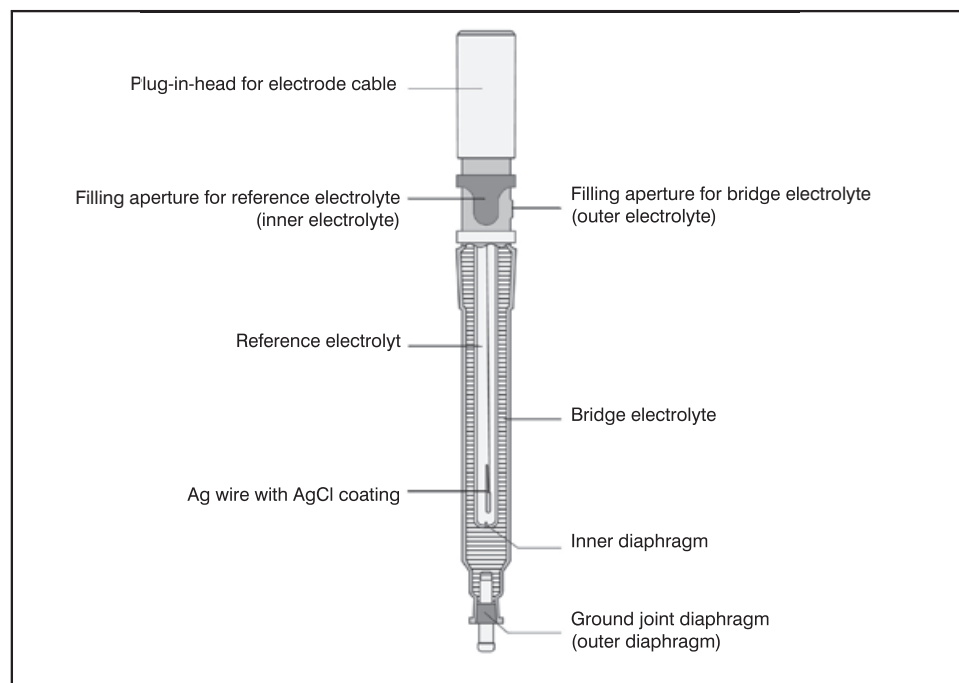


Abb. 9: Double junction reference electrode with Ag/AgCl reference system and ground joint diaphragm

For measurements in non-aqueous solutions reference and bridge electrolyte should be non-aqueous. Thus the system has no boundaries aqueous/non-aqueous where salts can crystallize which are only soluble in aqueous media. LiCl in ethanol can be used as a reference electrolyte for these systems.

Diffusion potential

A diffusion potential appears where the reference electrolyte and the sample solution meet. The reason for this potential is the difference in mobility of anions and cations. If anions and cations with strongly different mobility are present in the electrolyte solution, they diffuse through the diaphragm at different rates. This results in a local charge separation at the diaphragm and therefore a potential difference arises, the diffusion potential. This difference depends on the type and concentration of the ions as well as on the temperature.

The contribution of the diffusion potential should be as small and constant as possible. This can be achieved by the following measures:

- Use reference electrolytes which are as concentrated as possible. Their anions and cations should have comparable mobilities, e. g. KCl, KNO_3 . Table 8 shows the mobility of some ions.
- Keep the stirring speed constant during measurements.
- The diaphragm is clean and the optimal type for the task.

Cation	$I^+ [\text{cm}^2 \Omega^{-1} \text{mol}^{-1}]$	Anion	$I^- [\text{cm}^2 \Omega^{-1} \text{mol}^{-1}]$
H^+	349.8	OH^-	199.1
Li^+	38.6	F^-	55.4
Na^+	50.1	Cl^-	76.35
K^+	73.5	NO_3^-	71.46
NH_4^+	73.5	ClO_4^-	67.3
NMe_4^+	44.9	CH_3COO^-	40.9

Table 8: Limits of ion mobilities I in aqueous solution (25 °C)

Reference systems

Since every measuring assembly consists of an indicator and a reference electrode, the potential of the reference system contributes to the measured potential U . When changing the reference system, the new measuring assembly potential U_{new} is calculated as follows:

$$U_{\text{new}} = U_{\text{old}} + U_{\text{Ref,old}} + U_{\text{Ref,new}} \quad (10)$$

The most frequently used reference system is the Ag/AgCl reference system. Formerly used calomel reference systems are not advisable any more because of their mercury content.

Table 9 shows some reference systems and their potentials vs. the standard hydrogen electrode.

Reference system	U [mV]					
	15 °C	20 °C	25 °C	40 °C	60 °C	80 °C
Silver chloride:						
Ag/AgCl/c(KCl) = sat.	+207	+202	+197	+181	+160	+138
Ag/AgCl/c(KCl) = 3 mol/L	+214	+211	+207	+195	+178	+160
Ag/AgCl/c(LiCl) = sat. in Ethanol	+164	+170	+143			
Ag/AgCl/c(LiCl) = 2 mol/L in Ethanol			+157			
Ag/AgCl/c(KNO ₃) = sat			+467			

Table 9: Various reference systems and their potential compared to the standard hydrogen electrode

In addition to the already mentioned reference systems, any electrode can be used which supplies a potential that is independent from the composition of the sample solution. This is used with Ag Titrodes for precipitation titrations with Ag⁺; with Pt or Au Titrodes for redox titrations. The pH glass electrode is used as reference electrode. Pre-requisite for using a pH electrode as reference is a constant pH value of the sample solution during measurements (precipitation titrations with Ag⁺ are usually carried out in very acidic solutions; redox titrations either in very acidic or very alkaline solutions). The advantage of this measuring assembly is that it has no diaphragm (no troubles with contaminated or blocked diaphragms, no refilling of reference electrolyte!).

Owing to its high impedance (of several 100 MΩ!), the reference glass electrode has to be connected to the high impedance measuring input of the measuring instrument. Normally, the indicator electrode is connected to this input. The indicator electrode (e. g. the Ag electrode) is then connected to the low impedance input. The resulting titration curve runs therefore in the opposite order, see Fig. 11.

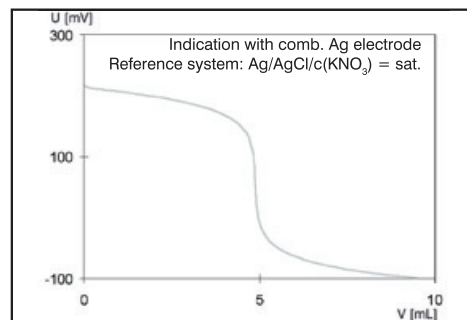
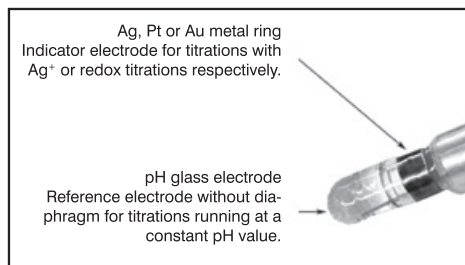
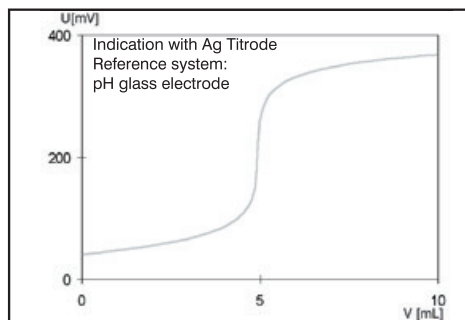
Fig. 11: Titration of Cl⁻ with Ag⁺

Fig. 10: Titrode with metal ring as indicator electrode and pH glass electrode as reference electrode (In special cases, the Titrode can also be used as pH indicator electrode.)



6 – Which electrode for which application?

The following table gives an overview about measuring tasks and suitable electrodes.

Measurement	Description	Electrode
pH measurements and titrations	General measurements in clear, aqueous solutions with a conductivity > 10 μS/cm	Comb. LL Solitrode
	Virtually salt free media, e. g. rainwater, boiler feedwater	Aquatrode Plus
	Highly contaminating media e. g. suspensions, emulsions	Comb. LL Unitrode
	Difficult media, e. g. protein-containing samples, suspensions, emulsions	Comb. LL Viscotrode Comb. LL Porotrode
	Solutions containing HF and/or strongly hygroscopic media	Comb. LL antimony electrode (pH 2 ... 11)
	Non-aqueous media (titration)	Comb. LL Solvotrode
	Non-aqueous, very poorly conducting media	Glass electrode + separate double junction reference electrode with shielding + auxiliary electrode; with differential amplifier
Titrations with Ag ⁺		Ag Titrode (poss. with silver salt coating), see page 17
Redox	Potential measurements	Comb. LL Pt or Au electrode, see page 16
	Titration	Pt or Au Titrode, see page 16
ISE	Direct measurements and complexometric titrations	Corresponding ion-sensitive electrode + separate double junction «LL ISE Reference»
Surfactants	Titration of surfactants	Surfactant electrode, see page 14

Table 10: Electrode selection

7 – Literature

- Metrohm “**Electrode catalog**”
Catalog with theoretical introduction about electrodes
- H. Galster, pH measurement: fundamentals, methods, applications, instrumentation, VCH Verlagsgesellschaft, Weinheim, 1991
Good introduction for pH measurements
- K. Cammann, Working with ion-selective electrodes, Springer-Verlag, Berlin, 1979
Standard work about handling ion-sensitive electrodes
- P.L. Bailey, Analysis with ion-selective electrodes, Heyden, London, 2nd Edition, 1980
Overview of ion-sensitive electrodes
- Metrohm monograph
“**Ion Analysis from A to Z**”
List of Metrohm Application Bulletins (substances and methods in alphabetical order)
- www.metrohm.com, Applications: Application Notes
- U. Tinner, Metrohm monograph
“**Practical aspects of modern titration**”
Short introduction into titrations

8 – Index

A

Activity	5
Ag metal electrodes	17
Care	17
Ag precipitation titration	17
Ag/AgCl reference electrode	19
Ag/AgCl-Reference electrode	23
Alkali error	8
Antimony electrode	25
Aquatrode Plus	25
Argentometric titration	17
Asymmetry pH	8
Asymmetry potential	8

B

Bridge electrolyte	21
--------------------------	----

C

Care	
Ag metal electrode	17
pH glass electrode	11
Redox electrode	15

D

Diaphragm	20
Cleaning	11
Diaphragm free assembly	24
Diffusion potential	2, 22
Double junction electrode	21

E

Electrode selection	25
Electrode slope	3, 8

H

Hydrated layer	7
----------------------	---

I

Indicator electrode	2
Ion-sensitive electrodes	4

L

Liquid junction	20
Long Life reference system	19

N

Nernst equation	2
Nernst slope	3
Nikolskij equation	5

P

Peters equation	14
pH calibration	8
pH glass electrode	7
Care	11
Problems	10
pH ₀	8
Porotrode	25

R

Redox electrode	14
Care	15
Passivation	14
Problems	16
Reference electrode	2, 19

S

Solitrode	25
Solvotrode	25
Surfactant electrodes	12
Cationic Surfactant electrode	12
Ionic Surfactant electrode	12
NIO electrode	12

T

TISAB	6
Titrode	25

U

Unitrode	25
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V

Viscotrode	25
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