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Electrochemistry - Theory and Practice

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Section 1 pH

1.1 Theory

pH in an aqueous solutions is a measure of hydrogen and hydroxide ions. Water molecules dissociate in hydrogen (H^+) and hydroxide (OH^-) ions,

$$H_2O \Leftrightarrow H^+ + OH^-$$

but the number of ions formed is very small. Water at 25°C contains 1×10^{-7} mol/L of hydrogen ions and the same concentration of hydroxide ions, where the concentration (mol/L) of hydrogen ions $[H^+]$ multiplied by the concentration (mol/L) of hydroxide ions $[OH^-]$ is constant:

$$K_w = [H^+]\,[OH^-]$$

K_w is the dissociation constant for water and it depends on temperature.

Temperature °C	K_w
10	$0{,}2920 \times 10^{-14}$
15	$0{,}4505 \times 10^{-14}$
20	$0{,}6809 \times 10^{-14}$
25	$1{,}008 \times 10^{-14}$
30	$1{,}469 \times 10^{-14}$

Acids in water increase the $[H^+]$ and because the product $[H^+]\,[OH^-]$ must be constant, acids decrease the $[OH^-]$. Bases increase $[OH^-]$ and decrease $[H^+]$. For example, suppose an acid is added to water at 25°C and the acid raises the $[H^+]$ to 1.0×10^{-3} mol/L. Because $[H^+]\,[OH^-]$ must always equal 1.0×10^{-14}, $[OH^-]$ will be 1.0×10^{-11} mol/L.

pH is the common way of expressing the hydrogen ion concentration $[H^+]$. Refer to Figure 1 for the definition of pH.

Figure 1 Definition of pH

$$pH = -\log [H^+]$$

In the example above, the hydrogen ion concentration is 1.0×10^{-3} mol/L and the pH is 3.00. Alternatively, adding base changes the $[H^+]$ to 1.0×10^{-11} then the pH is 11.0.

Figure 1 is valid for highly diluted solutions only. If concentrated solutions of acids or bases or salts are used, the hydrogen concentration must be replaced by the ion activity a_{H+} and the hydroxide concentration by a_{OH-}. Refer to Figure 2 for the relation between concentration and activity of an ion where f is the activity coefficient for that ion.

Figure 2 Activity of an ion

$$a_{ion} = f_{ion} * [ion]$$

The reason for the difference of activity and concentration is that in higher concentrated solutions the ions interact with each other and therefore show a different behaviour than in diluted solutions. That means in higher concentrated solutions the amount of "real" active ions is lower than expected. This leads to the common pH definition, refer to Figure 3.

Figure 3 General pH definition

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

1.1.1 pH measurement - a trace analysis

A pH value of 12.0 is equal to a H^+ ion concentration of 10^{-12} mol/L.

$$pH = 12.0 \quad \rightarrow \quad C_{H^+} = 10^{-12}\ mol/L$$

The concentration of 10^{-12} mol/L is equal to 0,000 000 000 001 mol/L or "pico mol/L"[1]. With the atomic mass of 1 g/mol there is only 1 pico g/L H^+ ions in the sample.

From micro gram per liter (µg/L) trace analysis starts and after nano gram (ng/L) follows the ultra-trace analysis area (pico- and femto gram). For getting the lowest concentrations, complicated and expensive analysis systems (e.g. MS, GC, ICP)[2] are necessary, for which extensive trainings are available to enable the handling and correct use of such high tech apparatus.

Based on this fact, pH measurement gets more important. With possibilities the pH glass sensor offers, will be more clear, if we consider the large measurement range of more than 10^{14} mol/L H^+ ions (1 mol/L H^+ down to 10^{-14} mol/L). Which other analysis method can cover such a measurement range without sample preparation and huge analytical and technical efforts?

A buffer solution of pH 7.0 contains µg/L H^+ ions (10^{-7}) and same amount of OH^- ions, the solution reacts "neutral". An alkaline solution of pH 14 contains only 10^{-14} H^+ ions in a superior number of 1 mol/L OH^- ions.

The pH glass electrode is an excellent, very specific sensor for hydrogen ions. The handling is very easy and without specific knowledge, even untrained staff can do pH measurements.

However, it is important to know that the "simple" pH electrode, which just measures in a water sample, is a high tech sensor.

Figure 4 pH electrode

1.1.2 How to measure pH

An electrochemical cell for pH measurement always consists of an indicating electrode, whose potential is directly proportional to pH, a reference electrode, whose potential is independent of pH, and the aqueous sample to be measured. If all three parts are in

[1] 10^{-3} milli (0,001)
10^{-6} micro (0,000 001)
10^{-9} nano (0,000 000 001)
10^{-12} pico (0,000 000 000 001)
10^{-15} femto (0,000 000 000 000 001)

[2] MS = mass spectroscopy
GC = gas chromatography
ICP = Inductively Coupled Plasma

contact with each other, a potential can be measured between the indicating electrode and the reference electrode, which depends on the pH of the sample and its temperature.

Because of the complexity of a pH measurement, the combination of indicating and reference electrode must be calibrated in advance, to compensate for slight changes over time. Refer to Calibration on page 6.

The relation between measured potential E (mV), pH and temperature (K) is the Figure 5.

Figure 5 Nernst equation

$$E(T) = E°(T) + 2.303\frac{RT}{nF}\log ai$$

Figure 6 Nernst equation (including pH definition)

$$E(T) = E°(T) - 2.303\frac{RT}{nF}pH$$

E(T) : Measured potential mV at temperature T (Kelvin)

E°(T) : Constant, standard potential mV at temperature T (Kelvin)

2.303 : Factor to convert ln to log

R : Molar gas constant (8.3144 J mol^{-1} K^{-1})

n : Charge of the ion

F : Faraday constant 96485 C mol^{-1}

T : Temperature K (Kelvin)

Therefore at a given (constant) temperature the potential of a solution depends on the pH only.

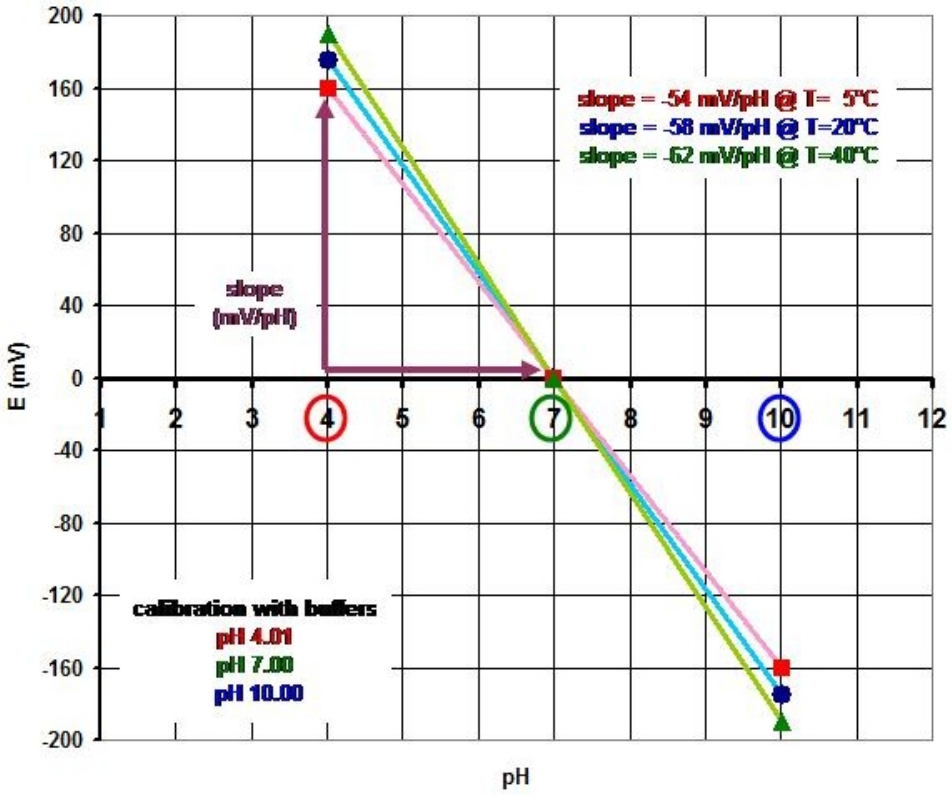
Figure 6 can be seen as the standard formula for straight lines Y = a + b X, where a is the offset and b is the slope of the line. In case of Figure 6 the offset is E°(T) and the slope is the temperature dependent factor:

$$-T * \frac{R}{M * F} = -T * 0.1984$$

at 25°C the slope gives

$$(273.15 + 25) * 0.1984 = -59.16\frac{mV}{pH}$$

Figure 7 Influence of temperature on the Nernst slope of a pH calibration



1.1.3 Calibration

The system of pH indicating electrode, reference electrode, pH-meter and lab conditions (stirring / no stirring, thermostated / not thermostated, ambient air humidity / pressure, and so on) is calibrated by placing the electrodes in solutions of known pH (buffers) and measuring the voltage of the cell. Because the cell potential is a linear function of pH (usually in the range of pH 2-11), two calibration points (2 pH buffers) are needed. A common calibration is for instance with IUPAC buffers pH 4.005 and pH 10.012 (@ 25°C).

If the pH measurements are done in extreme areas of pH < 2 or pH > 11 we recommend to calibrate specifically in the low pH range (buffer pH 1.09 + pH 4.01) or in the high pH range (buffer pH 10.012 + pH 12.45).

The calibration parameters are offset (or zero pH) and the slope. Many pH meters calculate the slope as a percentage of the theoretical value, which at 25°C is -59.16 mV/pH. For example, if the calibration slope is determined to be -58.78 at 25°C, it would equal 99.3% theoretical.

The following table lists theoretical slopes for different temperatures.

Temperature °C	Slope mV/pH
15.0	–57.18
20.0	–58.17
25.0	–59.16
30.0	–60.15
35.0	–61.14

1.1.3.1 pH buffers for calibrating pH electrodes

Figure 7 on page 6 shows the ideal pH measurement system, where the potential is zero when the pH is 7, and the slope is -0.1984 T over the entire pH range. A real pH system rarely has at pH 7 a potential of zero, but it is usually between –20 mV and +20 mV. The slope is also not –0.1984 T over the entire range of pH and normally changes at pH < 2 or pH > 11.

Because pH systems are not ideal, they must be calibrated before use with pH buffers. These pH buffers have a known pH at different temperatures and cover the whole pH scale. International cooperating institutes[3] provide the definition of the buffer solutions used for references for pH measurements. All pH measurements are referred to traceable buffer solutions so that those values can be compared worldwide.

How are the calibration parameters calculated during a pH calibration?

Usually two pH buffers are selected to check the pH probe performance, pH 4.01 and pH 7.00. The ratio of the measured potentials (E2 – E1) to the difference of pH (7.000 – 4.01), gives the slope of the straight line.

Figure 8 Definition of the slope

$$\text{Slope S} = \frac{E_2 - E_1}{pH_2 - pH_1} \left[\frac{mV}{pH}\right]$$

Figure 8 is valid at the specific temperature of the buffer solutions.

Example

pH buffer pH 4.01 and pH 7.00 are used for calibration. In buffer pH 4.01 the pH system measures a potential of 173 mV and in buffer pH 7.0 it measures a potential of -3.1 mV.

$$\text{Slope S} = \frac{173 - (-3.1)}{7.00 - 4.01} = \frac{176.1}{2.99} = 58.89 \left[\frac{mV}{pH}\right]$$

1.1.3.2 pH values of buffer solutions at different temperatures

Table 1 lists the coefficients describing the temperature dependency for several standard buffers. The coefficients A, B, C and D refer to the formula:

$$pH = \frac{A}{T} + B + C * T + D * T^2$$

where T is the temperature in Kelvin.

Table 1 pH buffer solutions and the parameters to calculate the pH value for different temperatures

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

	Phthalate	Acetate 0.1 M	Phosphate	Phosphate
pH, 25°C	**4.005**	**4.650**	**6.865**	**7.000**
A	0	0	3459.39	1722.78
B	6.6146	7.4245	–21.0574	–3.6787

[3] IUPAC = International Union of Pure and Applied Chemistry, NIST = National Institute of Standards and Technology, DIN = Deutsches Institut für Normung, JSI = Japan Standards Institute

	Phthalate	Acetate 0.1 M	Phosphate	Phosphate
10^2 * C	–1.8509	–1.8746	7.3301	1.6436
10^5 * D	3.2721	3.1665	–6.2266	0

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

1.1.3.3 Precautions using buffers

Because pH buffer solutions are always the reference of our pH measurements, the pH result can only be as good as the pH buffers used for calibration. If the buffers are contaminated or used improperly, the calibration will be false and all following measurements will be wrong. Therefore proper handling, storage and use of buffers is important.

- Always use pH buffers that enclose the pH of your sample. If the sample has a pH of 6 use buffers pH 4 and pH 7. If the sample has a pH of 7, use buffers with pH 4 and pH 10. If an alkaline sample is measured, calibrate with buffer pH 7 and pH 12.45.
- To shorten the stabilization time and to achieve an accurate calibration, make sure the sensor and the buffer are at the same temperature.
- For greatest accuracy measure samples at close to the same temperature as your calibration buffers.
- Buffers have limited shelf lives. Do not use a buffer if the expiration date has passed. Store buffers at controlled room temperature and if possible always at the same place.
- Never return used buffer to the buffer bottle. Discard it.
- Do not let the buffer bottle open for a longer time (exposure to air). The atmospheric carbon dioxide lowers the pH of alkaline buffers.
- If a calibration with alkaline buffer gives suspect results, first try changing the alkaline buffer. Alkaline buffers are susceptible to contamination by CO_2.
- Rinse the sensor with deionised water before placing it in the buffer. Remove excess water from the sensor by gently wiping it with a clean tissue.

1.1.3.4 Temperature compensation with pH buffers

All pH buffers are defined by international norms, including their individual change in pH as a function of the temperature (°C). pH meters have data tables stored of most common pH buffers to calculate the right pH based on temperature measurement. However, e.g. water samples from the nature, samples from production control etc. have not been analyzed to get their specific pH versus T function pH = F(°C).

Compared with pH buffer solutions, samples can NOT be temperature compensated.

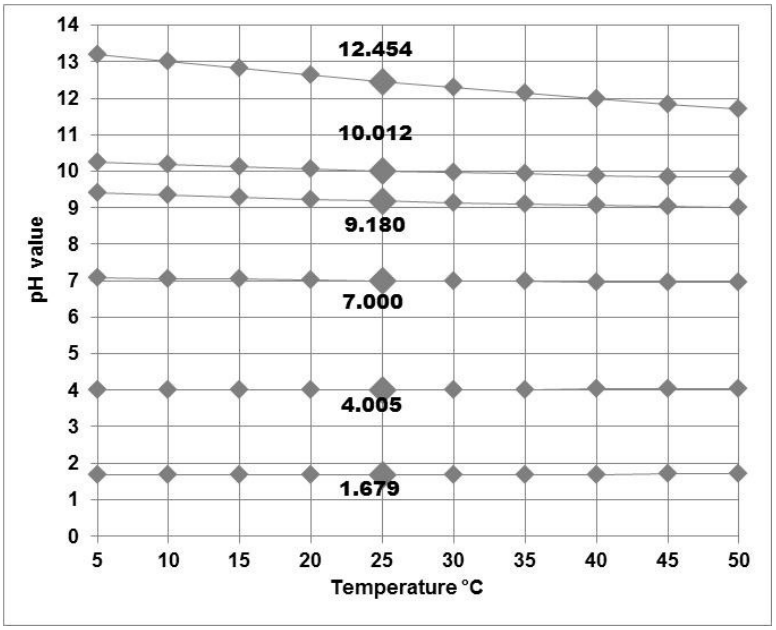
It is common practice that pH meters adjust the slope value from the calibration procedure to the temperature of the currently measured sample. This compromise, to do a temperature adjustment of the slope value, is at least more precise than using a slope value from a different / wrong temperature. It is essential for pH measurements to measure the temperature during calibration and sample measurement. Ideal is to have during the measurements the same temperature.

International norms (e.g. EN ISO 10523, DIN 19266) describe the temperature dependence of pH buffer solutions.

While pH buffer solutions are well known and the pH meters can automatically do temperature compensation (ATC), the temperature behavior of real samples is not known. ATC with samples is normally not possible.

T (°C)	pH buffer 1.679	pH buffer 4.008	pH buffer 7,000	pH buffer 9,180	pH buffer 10,012	pH buffer 12,454
5	1,668	3,998	7,087	9,395	10,245	13,207
10	1,670	3,997	7,059	9,332	10,179	13,003
15	1,672	3,998	7,036	9,276	10,118	12,810
20	1,675	4,001	7,016	9,226	10,062	12,627
25	**1,679**	**4,005**	**7,000**	**9,180**	**10,012**	**12,454**
30	1,683	4,011	6,987	9,139	9,966	12,289
35	1,688	4,018	6,977	9,102	9,925	12,133
40	1,694	4,027	6,970	9,068	9,889	11,984
45	1,700	4,038	6,966	9,038	9,856	11,841
50	1,707	4,050	6,964	9,010	9,828	11,705

As long as the temperature during calibration and sample measurement is the same or similar (±1°C), the sample pH measurement is reliable. Differences in temperature between calibration and sample can be "adjusted" by the pH meter. The calibration slope factor is recalculated to the sample temperature, to minimize the error.



Note: *For quick and reliable pH measurements it is recommended to store pH buffers outside of direct sunlight. Exposure to sunlight or placing them next to a heating can increase their temperature.*

1.1.3.5 Temperature correction or compensation of the sample

The pH of a solution is dependent of temperature (Nernst equation, refer to Figure 6 on page 5). Buffer solution "temperature correction" is not the same as sample "temperature compensation". Automatic temperature compensation (ATC) is the automatic calculation of pH from the measured potential and temperature, using an adjusted slope to the measured temperature.

The change in pH of a solution with temperature is called the solution temperature coefficient (unit is ΔpH/°C). Most standard pH buffers and some chemicals have known solution temperature coefficients, refer to Table 1 on page 7. The temperature variation of standard pH buffers is often printed on their bottles. As long as the solution temperature coefficient is not known for the sample solution, a solution temperature correction cannot be done. If necessary the temperature coefficient can be determined manually/empirically.

In any case it is recommended to do a calibration and a sample measurement at the same temperature.

The temperature coefficient of a sample is normally not known. Therefore no table exists correlating sample pH with temperature, as known from pH buffer solutions. That is why no exact temperature compensation can be made with sample measurements.

In order to correct a pH value of a sample to the calibration temperature, the following formula is commonly used in pH meter software.

$$S(T\ sample) = S(Tcal) * \frac{T_{(sample)} + 273.15}{T_{(cal)} + 273.15}$$

S = Slope

T = Temperature °C

cal = Calibration

With the new calculated slope S (T sample) from the mV signal, the pH of the sample can be calculated at sample temperature T(sample). A linear relation is assumed between sample pH and temperature.

Example
Calibration was done with pH buffers 4.01 and 7.00 at 24°C. The samples have been stored cool and now the measurement is done at 10°C.

The corrected pH value is calculated with slope (24°C) = –58,0 mV/pH and offset = 0.0 mV:

slope(10°C) = slope(24°C) * (10 + 273.15) / (24 + 273.15)

slope(10°C) = –58.0 * (283.15) / (297.15)

slope(10°C) = –55.28 mV/pH

pH value of the sample (measured potential +100 mV)

= 7 – (100 mV / –58.0 mV/pH) = pH 5.28 (not corrected),

= 7 – (100 mV / –55.28 mV/pH) = pH 5.19 (corrected)

The difference of 0.09 pH shows, how important it is to precisely measure and to correct for temperature.

1.2 Measurement

In nearly every industrial and scientific application, pH is determined by measuring the potential of an electrochemical cell. Figure 9 shows a simplified diagram of a combined pH glass electrode.

Figure 9 Combined pH glass electrode

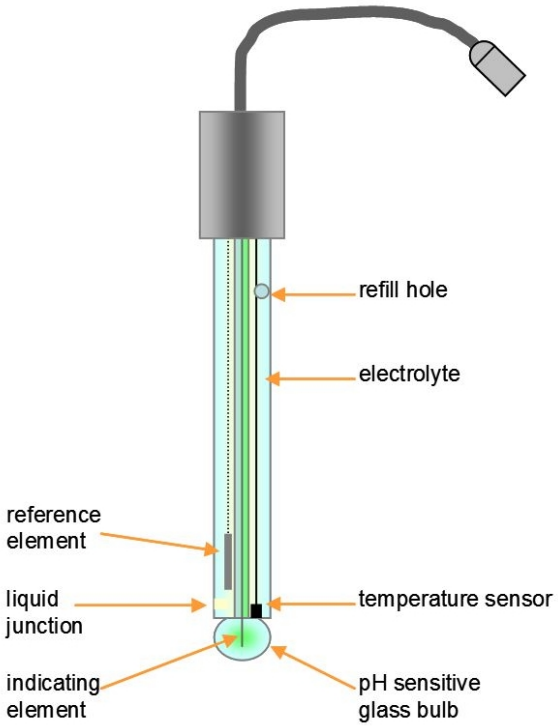
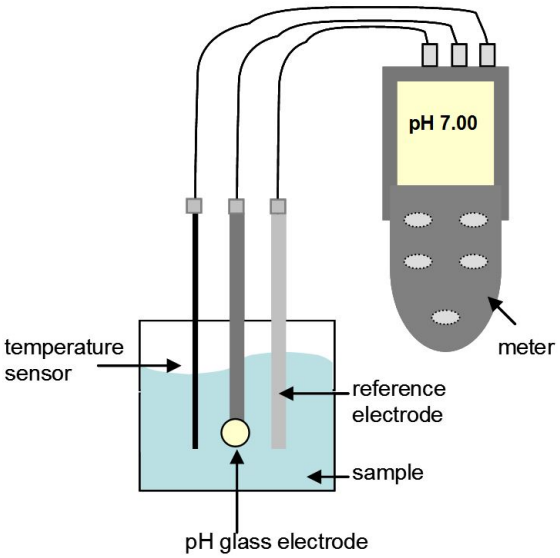
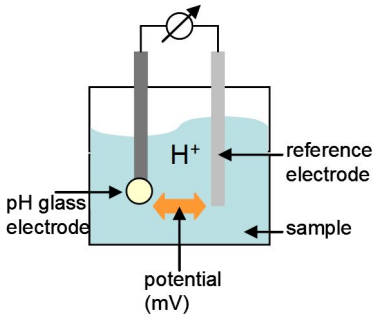


Figure 10 pH measurement system



A pH measurement system, shown in Figure 10 consists of a pH probe, reference probe, temperature sensor, pH meter and the sample to be measured. In most cases the three probes are combined in one electrode, refer to Figure 9. When the pH probe is in contact with a solution, a potential forms between the pH probe and the reference probe, refer to Figure 11. The meter measures the potential and converts it, using the calibration curve parameters, into a pH value.

Figure 11 Development of a potential (mV) between pH probe and reference probe: "pH cell"



The pH system (pH cell) has a high internal resistance; therefore the pH meter must have a very high input impedance. Never use a conventional volt meter to measure the potential of a pH electrode.

As long as the reference electrode is stable, the pH/potential measurement will vary only with temperature and sample. However, in certain samples the liquid junction plays a role. Based on the type and concentration of ions on both sides of the junction, the liquid junction can add some mV to the measurement potential.

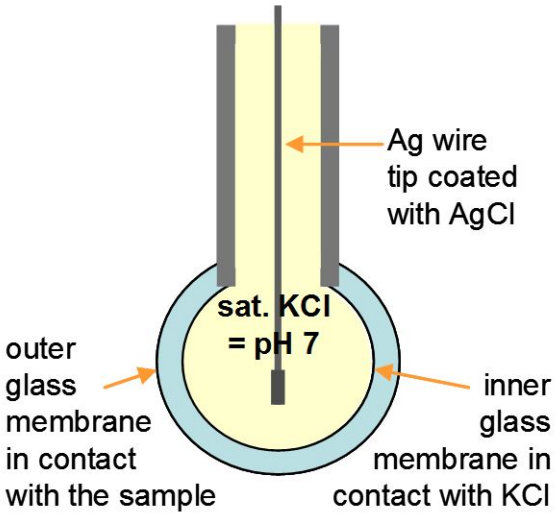
1.2.1 Combined pH electrode

Figure 9 on page 11 shows the internal components of the pH electrode. The heart of the electrode is a thin bulb of pH-sensitive glass, which is blown onto the end of a length of glass tubing. The pH-sensitive glass (glass membrane) is sealed to the electrode and contains a solution of potassium chloride at pH 7. A silver wire plated with silver chloride contacts the solution. The Ag/AgCl combination in contact with the filling solution sets an internal reference potential. This potential depends on the chloride concentration in the filling solution and as long as this electrolyte concentration is maintained, the electrode potential is constant.

Table 2 Common electrolyte filling solutions for combined pH glass and reference electrodes

Electrolyte	Concentration mol/L
KCl	saturated
KCl	3,5
KCl	3
KCl	3 saturated with AgCl
NH_4Cl	3

Figure 12 Working principle of a pH glass membrane



As Figure 12 shows, the outside surface of the glass membrane is in contact with the sample being measured, and the inside surface contacts the filling solution. A complex mechanism at each glass-liquid interface defines the potential of the pH glass electrode. While the inner pH glass / filling solution potential is constant, the outside potentials varies based on the $[H^+]$ in the sample. This equilibrium depends also on temperature.

1.2.2 Reference electrode

As Figure 12 on page 13 shows, the reference electrode is a silver wire coated with silver chloride in contact with a defined electrolyte solution, refer to Table 2 on page 12. In many reference electrodes a gel is used instead of a liquid as the internal filling. These gels also contain KCl to maintain the reference potential and add sufficient conductivity. As described in Combined pH electrode on page 12 the reference potential is constant as long as the internal electrolyte is constant. The reference potential also varies slightly with temperature.

The tube containing all the reference elements and solutions/gel is in contact with the sample to measure through a junction (diaphragm). It is essential to maintain a free flow of ions through the junction. Otherwise the reference electrode will not respond properly to pH changes in the sample.

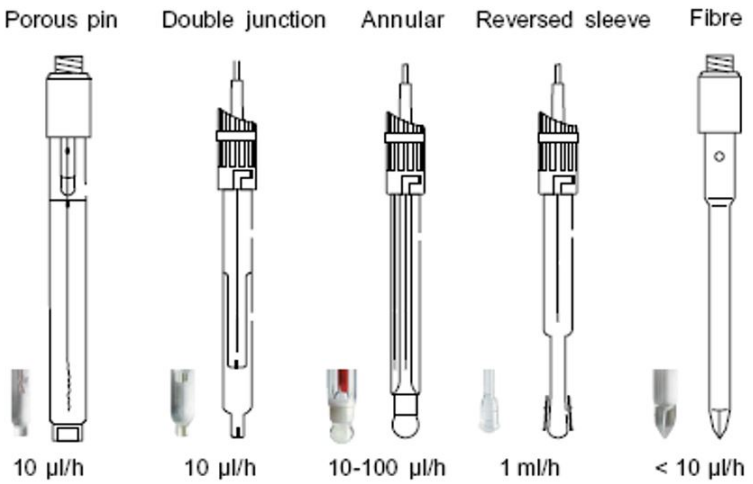
1.2.3 Electrolyte filling

Saturated KCl	A saturated solution of KCl, where additional KCl crystals are added, allows the reference system to work in a wide temperature range. At higher temperatures the additional crystals can dissolve and still maintain a saturated solution. At low temperatures more crystals form, but since the solution is already saturated, the KCl concentration is still saturated. In addition if the electrode has to measure over a longer period of time in an aqueous solution, sample liquid can go through the diaphragm inside the probe and dilute the electrolyte. A saturated solution has therefore a higher "buffer capacity" against dilution.
3 molar KCl	This is the most common electrode filling and available almost everywhere.
3 molar KCl saturated with AgCl	This is a way to longer maintain the Ag/AgCl reference electrode. The additional AgCl slows down the dissolution of the Ag/AgCl element.
Gel	The viscosity of the gel filling helps the probe to work under higher pressure conditions than with liquid fillings. In addition the gel usually does not require a refilling or other maintenance from the user. However, because the gel usually cannot be refilled, the lifetime of a gel-filled probe is much shorter than those with liquid filling, approx. 12 months only.

1.2.4 Liquid junction diaphragm

The salt bridge or diaphragm or liquid junction, refer to Figure 9 on page 11 and Figure 13 is an integral part of the reference electrode. It provides the electrical connection between the reference electrode and the sample being measured. Salt bridges have a variety of forms. Some are highly porous, where the pores are filled with ions from the filling solution and from the sample. Depending on the mechanical design of the diaphragms, the movement of material from inside the reference half-cell into the porous material, and from the sample into the porous material is different. For example using a gel-filled salt bridge, only ions are permitted to flow across the porous material and the liquid level of the reference compartment remains constant. Other materials allow liquid to flow out of the reference compartment, requiring periodic refilling. These types of diaphragms minimize contamination of the reference half-cell, since ions do not flow back from the sample.

Figure 13 Variety of diaphragms and there flow behaviour

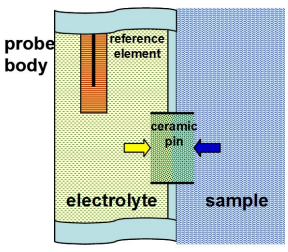


The liquid junction is the most problematic part of the probe. If it clogs due to sample particles going into the porous area or because crystals of the filling solution forming inside the junction, the final reading is false or takes much too long to stabilize.

If the electrolyte level inside the reference compartment is low, then another problem can arise where sample solution enters the reference compartment. This dilutes the electrolyte with sample solution and the reference potential is no longer constant.

In certain cases there is blockage due to precipitates forming inside the junction. This can occur if Ag^+ ions come together with S^{2-} ions to form Ag_2S precipitate. In samples with S^{2-} ion, or with biological or medical samples, it is recommended to use a reference probe with double junction, where the outer electrolyte is absolutely free of Ag^+ ions.

1.2.4.1 Function of a liquid junction



In order to maintain the reference element in a stable condition there must be a kind of "separator" between sample and electrolyte solution. This separator should work like a "valve": only a little liquid can pass (~10µL/h). This is called a liquid junction or diaphragm.

If the hydrostatic pressure of the electrolyte solution on the inner side of the diaphragm is higher than of the outer solution (sample), the electrolyte will flow out through the diaphragm. This makes the electrical contact where ions can transport the charge and develop a potential difference between reference and indicating element.

1.2.4.2 Types of diaphragms

There are many different materials and mechanical designs of liquid junctions. Here is an overview of most common types:

Open / hole diaphragm
The contact between electrolyte and sample is realized by a gel filled electrode. The gel does not flow out and can directly get in contact with the sample.

Advantage: low maintenance.

Disadvantage: the gel can be contaminated with sample or can dry out when not correct stored in electrolyte.

Sleeve diaphragm
For samples of very low conductivity or where the diaphragm may be blocked from viscose samples, a sleeve is the best option.

Outflow approx. 1 mL/h.

Advantage: high electrolyte outflow, easy to clean.

Disadvantage: outflow has to be adjusted manually and may be not reproducible. Electrolyte level can be very low after short time.

Porous pin diaphragm
One or up to 3 ceramic pins separate the (mainly liquid) electrolyte from the sample. Based on its structure the ceramic pin allows an outflow of approx. 10 µL/h.

Advantage: can be used at high temperatures, strong acid or base.

Disadvantage: small particles from the sample can block the way through the ceramic.

Fibre and metal bundle diaphragm
A bundle of fibre or platinum wires have many little channels which allow a liquid contact between electrolyte and sample.

Outflow <10 µL/h.

Advantage: metal wires withstand high temperatures and are durable in most samples.

Disadvantage: strong oxidizing acids damage the metal bundle.

Ring diaphragm
A ring of PTFE or porous glass around the lower end of the tube provides a continuous flow of liquid electrolyte solution into the sample.

Outflow approx. 10-100 µL/h.

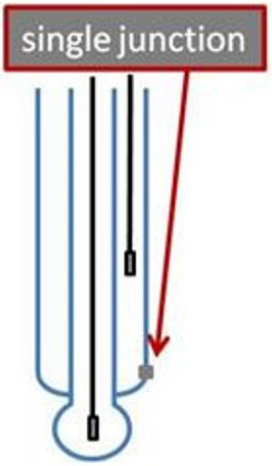
Advantage: The porous glass is suitable for high temperatures and can even be used in organic solvents.

Disadvantage: almost no.

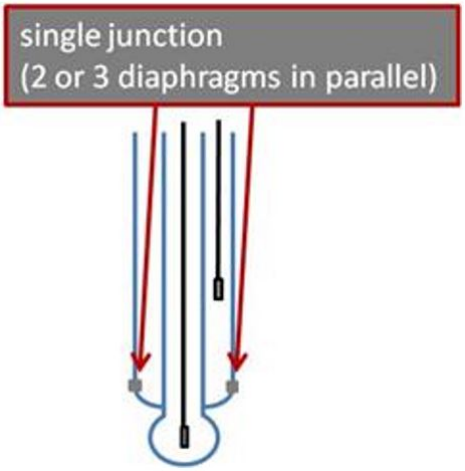
1.2.4.3 Double junction

Electrodes with liquid electrolyte solution (pH, ORP, ISE or reference electrode) can have one or several diaphragms. These diaphragms make the electrical contact between reference electrode and sample solution. Beside the various types of diaphragms (ceramic, sleeve, ring, etc.) the orientation and position in the electrode defines its application range. There are electrodes with single diaphragm, with two or three equal diaphragms or with a double junction. What is the difference between these variations?

Single diaphragm (one electrolyte solution)
The electrolyte solution is in contact with sample solution through one diaphragm. With one diaphragm (e.g. ceramic) only a little volume of electrolyte can pass into the sample. With samples containing particles, the diaphragm can easily be blocked, what is indicated by increasing stabilization times up to no probe reaction.



Two or three diaphragms (one electrolyte solution)
The problem of a single diaphragm can be solved by using two or three equal diaphragms in "parallel", positioned in one level at the lower probe end. All diaphragms have the same function. This increases the electrolyte outflow and decreases the problem that a single diaphragm can be blocked by sample particles or precipitations. Mainly 2 or 3 ceramic pins are built in an electrode. Similar effects have ring diaphragms (PTFE, glass frites or sleeves).

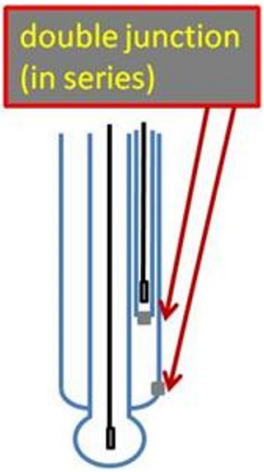


Two diaphragms as "double junction" (two different electrolyte solutions)
There are two diaphragms built in, but not in parallel as described above, and in series. One diaphragm is inside the electrode and protects the reference electrode from outer electrolyte. A second diaphragm provides a liquid junction to the sample solution. Therefore such electrodes need two electrolyte fillings.

The advantage of this type is indeed the filling with two electrolytes. The reference electrode remains stable in a defined electrolyte, while the second electrolyte can be exchanged to almost any solution. The inner electrolyte can be 3 M KCl, so the outer electrolyte solution can be 3 M KCl, as well, but can also have different composition. For samples sensitive to chloride ions, potassium nitrate KNO3 can be used. With reference electrodes for ISE measurements potassium sulphate or sodium acetate is recommended. This double junction type can even be used in organic solvents, where the

second electrolyte is replaced by Lithium chloride (LiCl) in Ethanol. Therefore the reference system can specifically be adopted for individual samples.

In addition this double junction concept helps maintaining a stabile reference electrode over a longer period of time and acts also a silver ion barrier.

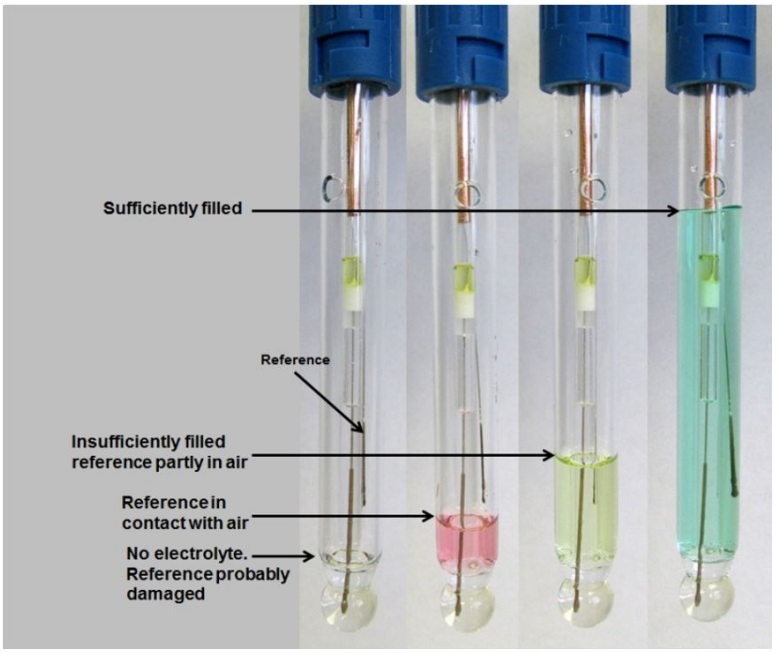


1.2.5 Electrode filling solution

Depending on the measuring conditions and on the type of diaphragm, more or less electrolyte can flow through the diaphragm, lowering the electrolyte level.

The reference element must be covered with electrolyte solution, otherwise it can be damaged. The level of electrolyte provides a certain hydrostatic pressure on the inner side of the diaphragm to keep sample solution out. If the electrolyte level decreases, the pressure decreases as well. Depending on the depth of immersion of the pH probe, sample solution may have a higher hydrostatic pressure than the inner electrolyte. Sample solution can flow through the diaphragm inside the probe. The contamination with sample solution dilutes the electrolyte. It introduces ions, which may react with the reference electrode material or form particles or precipitates - last can block the diaphragm. All above is the reason for unreliable pH measurements.

The following photos explain the different steps of fill level and the possible risk of contaminated reference element.



1.2.5.1 Function of the electrolyte filling level

Electrolyte filling level should be 5 mm below the refill hole. If the level is 2 cm lower or more, refill the electrode. Never let the reference element become dry and in contact with air. This will damage the reference element.

As long as the fill level is high enough, no sample can pass the diaphragm inside the probe to contaminate the inner filling solution.

Figure 14 shows the electrolyte outflow through the junction and the development of the ion cloud in the sample (red/orange). The hydrostatic pressure of the inner electrolyte is high enough to ensure an outflow.

Figure 14 Correct filling level

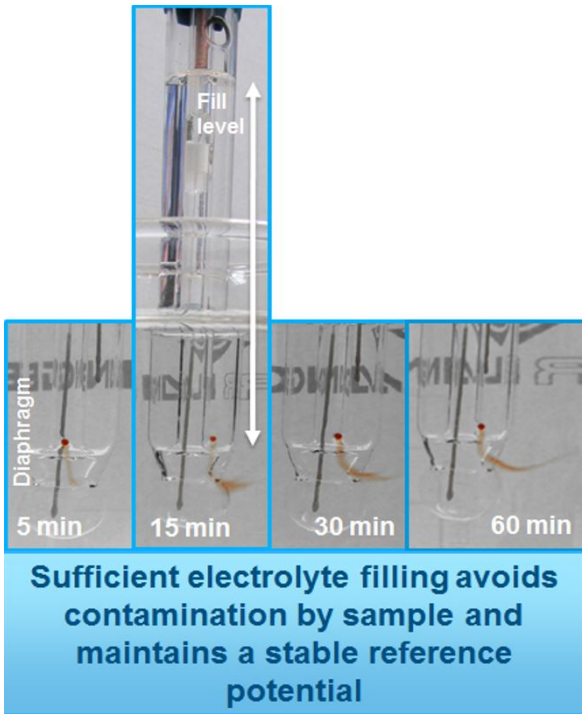
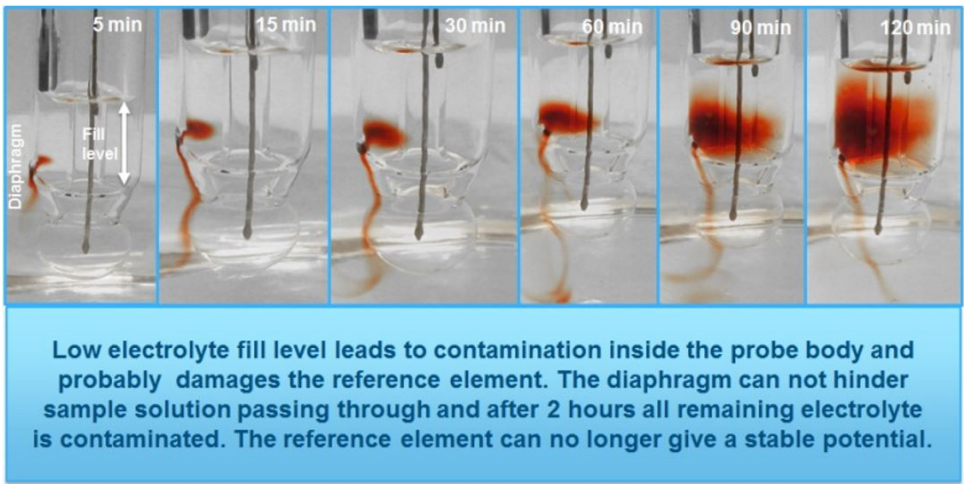


Figure 15 shows the opposite, where a very low electrolyte level inside the probe cannot prevent sample passing the junction and forming the red/orange contamination.

Within short time the inner electrolyte is contaminated and then the reference element can be damaged. This can lead to unstable readings and even wrong measurements.
Note: *To avoid this scenario it is important to regularly check the electrolyte fill level.*

Figure 15 Filling level too low



1.3 Digital and analogue measurement technique

With classic technique the analogue signal from the sensor is transferred through the cable and connectors into the meter. There an electrical circuit board which "translates" the signal from analogue to digital (A/D converter) and the display shows the value, e.g. pH 4.01. This display may be a classic analogue indicator (needle) or the digital display (e.g. LED, LCD).

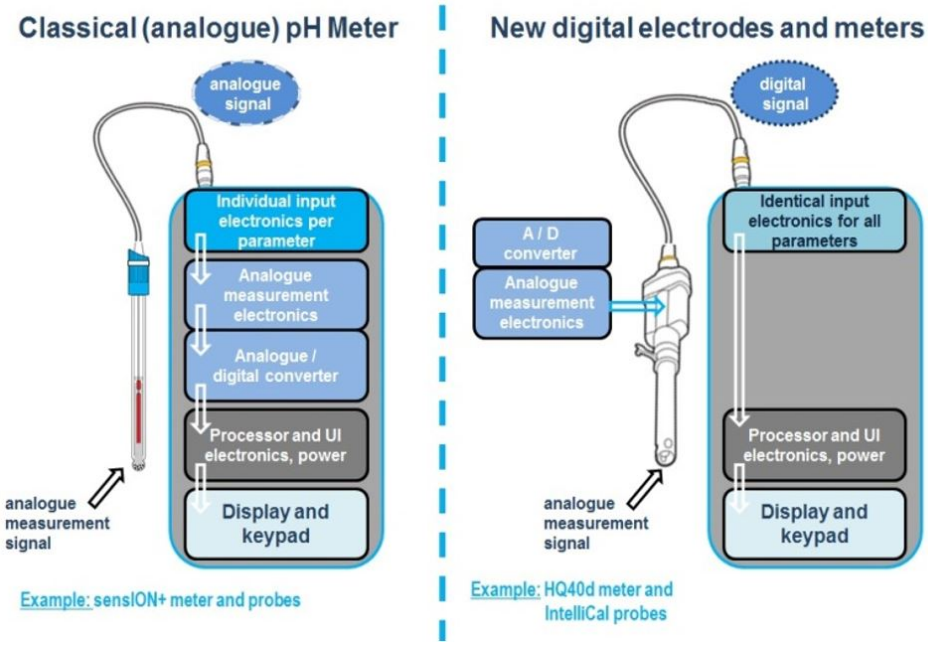
With the digital technology the analogue signal from the sensor is converted directly inside the electrode from analogue to digital. This new digital signal is send through cable and connectors into the meter, where only the memory and digital display is handled. There is no more an electrical circuit board inside, which manipulates the original signal.

If a probe has to be calibrated, the procedure is the same for analogue and digital. The preparation and pH buffers and calibration procedure are also the same. However, when changing pH probes or taking calibrated pH probes to another meter, the differences are huge.

While any analogue pH probe needs to be "recalibrated" every time before use with different meters, the digital probes have their electronics inside their probe head. The signal from the sensing element (pH glass vs. Ag/AgCl-reference) is quickly converted into a digital information, which passes thru the cable into the "display" electronics in the meter.

Analogue pH probe mV signals have to pass the electrode cable. There is a risk, that the mV potential is "modified" by electromagnetic forces (like pumps, generators, etc.). The interferences must be neglected, because they may change the pH reading up to 1 pH.

Figure 16 Analogue vs digital electrode and meter



A digital data transmission through a cable cannot be changed due to magnetic fields etc. In addition much longer cables can be used. With the digital probe head the calibration information is stored with each electrode. When connected to a digital meter, the probe can transmit the calibration data and is quickly ready to use.

	classic / analogue	digital
Sensor tip signal	analogue	analogue
Signal from sensor to meter	analogue	digital
Cable length	max. 3 m (pH)	up to 30 m

	classic / analogue	digital
Plug/connector	individual per parameter	for all parameters the same connection type
Signal/noise ratio	analogue signal interfered by electrical / magnetic parts	digital signal inert against electrical / magnetic interference
Sensor specific data	stored as manual input in meter	stored in electrode head, automatically send to meter
pH/conductivity/dissolved oxygen measurement in parallel	pH is influences by measurment of other parameters, e.g. COND	signal is converted inside the probe, no influence of other parameters

1.4 Frequently asked questions

1.4.1 FAQ—pH measurement in samples

QUESTION: What factors need to be taken into account when measuring low ionic strength samples and deionised water?

ANSWER: As a general rule, standard pH probes contain a 3 or 3.5 molar KCl electrolyte solution or a gel. As low ionic strength samples and deionised water contain little or no salt, they try to get ions (salt) out of the electrolyte solution. When conventional pH probes are used (e.g. with gel filling), this phenomenon may lead to poor response and unstable readings.

For applications such as these, HACH offer pH probes specifically designed for low ionic strength samples. These probes have high reference electrolyte flow rates to insure a free flowing reference junction.

When KCl crystals are added, the ionic strength can be increased and the response time improved. It is important to use high purity KCl to avoid influencing the pH.

Closed sample containers (flasks) present the advantage of avoiding CO_2 contamination. Use of scrupulously clean equipment and glassware and thorough rinsing before measurement are essential to avoid contamination from previous samples.

Prior to sample measurement, the probe must be calibrated by using high-precision pH buffer solutions.

QUESTION: What is the best way to measure pH in soil?

ANSWER: It is advisable to use a specific pH probe with a strong glass tip and high electrolyte outflow. Mix a 5 g soil sample with 25 g deionised water while stirring carefully. Then let the mixture stand without stirring for 10 minutes to separate the particles from the liquid. Insert the pH probe in such a way that the glass bulb is totally covered by particles, but the diaphragm is not. Wait for a stable reading.

QUESTION: What is the best way to measure pH in high temperature samples?

ANSWER: Before measuring samples over 80°C, check whether the probe is designed to stand such high temperatures. Gel-filled pH probes can be used up to 80°C but not higher. HACH pH probes have an Ag/AgCl reference system which is ideal for higher temperatures. We recommend pH probes with saturated KCl filling solution. As KCl crystals are soluble at higher temperatures, it is a good idea to ensure excess crystals so that the solution remains saturated. If at all possible lower the temperature of the sample to the temperature of the buffers at calibration.

QUESTION: What is the best way to measure pH in high alkaline samples and samples with high salt content?

ANSWER: We recommend pH probes with saturated KCl filling solution. As KCl crystals are soluble at higher temperatures, it is a good idea to ensure excess crystals so that the solution remains saturated. Samples with high salt content and pH>12 may be subject to "sodium error". HACH offer high alkalinity electrodes that minimize "sodium error".

QUESTION: What is the best way to measure pH in emulsions or fatty solutions?

ANSWER: When measuring fats and emulsions, it is important to choose an electrode with the right diaphragm, reference electrolyte and a junction that is easy to clean. We therefore recommend open liquid junctions or sleeve junctions. After the measurement, the probe should be cleaned thoroughly, i.e. any remaining fat or oil must be removed with soap or surface-active agent.

1.4.2 FAQ—Maintenance and storage

QUESTION: How should pH probes be stored best?

ANSWER: All HACH pH probes are delivered with a plastic protection cap that can also be used for storage. Pour a few drops of saturated KCl solution into the cap to ensure that the glass membrane is kept hydrated and ready to use.

For short-term storage, the pH probe can be placed in a solution of 3.5 molar KCl or pH 4.0 or pH 7.0 pH buffer. Always rinse before use.

As a general rule, pH probes (especially reference probes) should never be stored in deionised water.

Overnight, the probe should be stored in the corresponding electrolyte solution, usually saturated KCl.

For long-term storage (2 weeks or more), the pH probe should be stored with its protection cap filled with storage solution and sealed with Parafilm Ô .

QUESTION: What is the best way to remove air bubbles from inside a pH probe?

ANSWER: Air bubbles can get trapped in the electrolyte solution of the reference system. This results in unreliable and unstable readings and may make it impossible to achieve a reading. In order to remove air bubbles, hold the probe firmly by the cable and swing around so that the air bubbles move to the upper end of the probe. If air bubbles are trapped inside the solid KCl crystals, heat the electrode tip in warm water (max. 60°C). This will dissolve the crystals and release the air. Afterwards, swing the probe around once more as described above and leave it to cool down. Air bubbles inside the pH glass stem are normal and cannot be removed. They will not cause problems if they are at the upper end of the probe.

QUESTION: Can a pH probe be used straight out of the box?

ANSWER: Although HACH pH probes come with a protective cap which is wet inside, the glass membrane can dry out. For best results, we recommend rinsing with deionised water then conditioning the probe in pH 4.0 buffer for at least 2 hours. After further rinsing, it is ready to be calibrated. The normal (quick) response time will be achieved after 24 hours hydration. If measurements are needed before this time, calibrations should be repeated often due to drifting potentials.

QUESTION: Do dirty and wet cables have an influence on the pH reading?

ANSWER: Due to the extremely small currents which pass through the pH electrode, the cable, plug and connector must be kept clean and dry if reliable measurements are to be obtained.

QUESTION: How much electrolyte should the pH probe contain?

ANSWER: The level of electrolyte solution should be 1 cm below the filling hole. This is the only way to ensure that the hydrostatic pressure applied to the diaphragm will be high enough to prevent sample passing through the diaphragm into the probe.

QUESTION: What causes a diaphragm to get blocked and how can this be remedied?

ANSWER: Liquid junctions with fibre or ceramic diaphragms can occasionally get blocked due to KCl crystallisation. Try soaking the electrode in warm tap water to dissolve the KCl crystals that cover the diaphragm. Other types of blockage can occur in the form of a precipitate, for example, silver chloride or silver sulphide. Gentle polishing with abrasive paper and soaking in saturated KCl can help. Alternatively, the probe can be cleaned with HACH RENOVO solutions or immersed in KS410 Thiourea solution for several hours.

1.4.3 FAQ—Measurement technique

QUESTION: What is the maximum cable length between the pH meter and pH probe?

ANSWER: All pH electrodes have a high impedance and the mV signal is amplified by the electronics in the pH meter or, with Hach digital electrodes, in the probe head. With analogue electrodes, cable lengths of 3 m can normally be used. Digital probes work with cable lengths of up to 30 m or more, because the digital signal is not impaired by the magnetic fields of motors, e.g. pumps.

QUESTION: How does the temperature influence the impedance of the pH glass membrane?

ANSWER: The lower the temperature, the higher the impedance of pH glass. For every 10°C decrease in temperature, the glass impedance will increase about 2.5 times, resulting in slow response. For example, if the pH glass impedance is 100 MOhm at 25°C it will increase to 250 MOhm at 15°C.

QUESTION: What is the lifetime of a pH probe?

ANSWER: The lifetime of a pH electrode depends on several factors including storage conditions, correct maintenance and the type of sample measured. Under normal laboratory conditions, for aqueous samples, the average lifetime is between 12 and 18 months, supposing of course that the electrode is kept clean and kept hydrated during storage.

If the probe is used with dirty samples (e.g. stirred solutions with particles), is subjected to mechanical abrasion or used at high temperature or high pressure, the lifetime may be only a few weeks. In hot alkaline solutions, pH probes can be damaged after only a few hours.

Regular maintenance helps pH probes keep working efficiently for several years.

QUESTION: What is the difference between pH probes with glass body and an epoxy body?

ANSWER: Both electrodes have a glass membrane, a diaphragm, a reference system and offer the same measuring quality. However, epoxy electrodes have a limited temperature range of maximum +80°C, while glass bodies can withstand temperatures of 100-110°C (with an Ag/AgCl reference system). If you are working in the field or in tough conditions, epoxy bodies have the advantage of being more robust and less liable to crack. Electrodes with glass bodies tend to be used in the lab, because they can be cleaned more easily and, unlike epoxy bodies, can withstand organic solvents. pH probes with epoxy bodies are usually less expensive and therefore represent a cost-effective alternative.

QUESTION: What is the point of automatic temperature compensation (ATC)?

ANSWER: Automatic temperature compensation (ATC) has to do with correcting the pH calibration slope to account for the actual temperature of the sample so the pH electrode gives an accurate reading of the pH of the sample. The pH calibration equation is linear and has a slope value at 25ºC. Any deviation of the actual temperature from 25ºC is compensated in the slope according to the Nernst equation. The pH of the internal solution of the pH bulb is called the isopotential pH. If the pH of the sample is the same as the isopotential pH there is essentially zero potential across the pH membrane. The isopotential pH of most pH electrodes is around pH 7. Temperature has little effect on sample measurement around the isopotential pH and becomes more important as the sample becomes more acidic or basic. ATC becomes important the further the sample pH is away from pH 7.

QUESTION: Is it always necessary to perform a 2-point calibration or is a 1-point calibration sufficient?

ANSWER: If the last calibration was performed on the same day, a control calibration with one buffer is sufficient. Then only the zero potential is adjusted, the old slope will remain as it was.

Otherwise, a 2-point calibration is recommended, because only then an actual probe status can be determined and taken into account for the measurements to come.

QUESTION: What is the recipe of IUPAC pH buffers?

ANSWER:

HCl (pH1.094): 0.1 M HCl,

Oxalate (pH 1.679): 0.05 mol/kg $KH_3C_4O_8$,

Phthalate (pH 4.005): 0.05 mol/kg $KHC_8H_4O_4$,

Acetate (pH 4.650): 0.1/0.1 mol/kg $C_2H_4O_2/C_2H_30_2Na$,

Phosphate (pH 6.865): 0.025/0.025 mol/kg KH_2PO_4/Na_2HPO_4,

Phosphate (pH 7.000): approx. 0.020/0.0275 mol/kg KH_2PO_4/Na_2HPO_4,

Phosphate (pH 7.413): 0.008695/0.03043 m KH_2PO_4/Na_2HPO_4,

Borate (pH 9.180): 0.01 m $Na_2B_4O_7$,

Carbonate (10.012): 0.025/0.025 mol/kg $NaHCO_3/Na_2CO_3$,

$Ca(OH)_2$ (pH 12.45): saturated (at 25°C) and filtered

1.4.4 FAQ—Troubleshooting

PROBLEM: The pH probe response is slow, tends to drift and results are not reproducible

SOLUTION: This may be caused by one of the following:

- the glass membrane or the diaphragm is dirty, e.g. oil, fat, paint, dirt.

- the pH probe is reaching the end of its lifetime.

- a sample of low ionic strength (< 100 µS/cm) is being measured with a conventional rather than a specially designed pH probe.

PROBLEM: The pH measurement system can no longer be calibrated by auto-buffer-recognition

SOLUTION: Check all parts of the system. First eliminate possible mechanical defects such as loose plugs, damaged cable or probe, electrolyte level too low, etc.

Ensure that fresh pH buffers were used. Buffers are only detected automatically if the mV signal is within a certain range. Old buffers or buffers not meeting DIN/IUPAC specifications cannot be detected by the meter software (AUTOCAL). For instance, pH 6.86 and pH 7.00 buffers are too close together and cannot be distinguished. In order for auto buffer recognition to work properly, the correct type of buffers has first to be selected. Typical combinations of pH buffers are pH 4, 7, 10 or pH 4.01, 6.86, 9.18. Finally, the pH electrode must be cleaned using special cleaning and conditioning solutions which can be found in the GK Annex Electrode Maintenance Kit from Hach/Radiometer Analytical.

If the pH probe still does not react normally and a slope of 95% to 102% cannot be achieved during calibration, it should be replaced.

PROBLEM: The response time of the pH probe keeps increasing.

SOLUTION: If the response time is gradually becoming longer, the diaphragm may be blocked or dirty, or the surface of the pH glass membrane may have fat, oil or paint deposits. In order to clean the diaphragm, use the special RENOVO.N and RENOVO.X cleaning solutions found in the Electrode Maintenance Kit. Fat deposits can be cleaned off glass membranes by using surfactant solutions. If the glass membrane does still not react properly, it can gently be etched.

Procedure for etching glass membranes:

The glass bulb is lowered for 1 minute into a 20% ammonium fluoride solution and then for 15 seconds into a 6 molar HCl. It should then be rinsed thoroughly with deionised water and stored for 24 hours in a slightly acidic buffer such as pH 4.01.

QUESTION: What is the usual stabilisation time for a pH probe in pH buffers?

ANSWER: At room temperature (20-25°C) and with fresh pH buffer solutions, the stabilisation time should not exceed 1 minute; normally a stable reading should be achieved after 30 seconds. Otherwise the pH electrode should be cleaned and conditioned again.

QUESTION: Is it possible to use a pH probe in alcoholic solutions?

ANSWER: Yes, but short-term only. Longer exposure to high percentage alcoholic solutions leads to dehydration of the glass membrane which then has to be conditioned again.

Section 2 ORP (oxidation reduction potential)

2.1 Theory

The Oxidation Reduction Potential (ORP or Redox-Potential) is a measure of an aqueous system's capacity to either release or gain electrons from chemical reactions. The oxidation process involves losing electrons while reduction involves gaining electrons.

From a water treatment perspective ORP is often used to control water disinfection with chlorine and chlorine dioxide e.g. in cooling towers, swimming pools, potable water supplies, and other water applications. Studies have shown that the life span of bacteria in water is strongly dependent on the ORP value.

2.1.1 The ORP sensor

The operation of the ORP sensor is very similar to that of the pH sensor except that it uses an inert metal (usually platinum) half cell instead of a pH sensitive glass membrane half cell. A two-electrode system is used to make a potentiometric measurement. The platinum electrode serves as an electron donor or electron acceptor depending upon the test solution. A reference electrode is used to supply a constant stable output for comparison. Electrical contact from the reference half cell is made with an electrolyte solution (e.g. saturated potassium chloride KCl solution) through a restrictive diaphragm. The electrode behaviour is described by the **Nernst equation**:

$$E = E_0 - \frac{R * T}{n * F} \ln \frac{C_{ox}}{C_{red}}$$

where

E = Measured potential (mV) between the platinum and the reference electrode

E_o = Measured potential (mV) between the platinum and the reference electrode at a concentration of $C_{ox} = C_{red}$

R = Universal gas constant (R = 8.314 J mol^{-1} K^{-1})

T = Temperature in K (Kelvin), where T (K) = 273.15 + t °C and t is the temperature of the measured solution

F = Faraday constant (96485 C mol^{-1})

n = Electrical charge of the ion

C_{ox} = Oxidant concentration in moles/L

C_{red} = Reductant concentration in moles/L.

Platinum is normally used as indicating sensor and the potential is measured against a reference electrode, usually Ag/AgCl. Other noble metals can also be used, such as Gold or Silver.

The ORP potential is temperature dependent and so the temperature must be recorded with every measurement in order to be able to compare two ORP values.
Note: *Typically there is no temperature correction factor available in ORP meters.*

ORP measurements are often pH dependent, e.g. chlorine exists in solutions as hypochlorous acid (HOCl) and depending on the pH this HOCl can provide more or less free chlorine. At lower pH values more chlorine is formed.

ORP measurements are slow compared to pH measurements. While a pH value can be obtained within seconds, a stable ORP value can take up to several minutes if not hours to reach the final equilibrium. The ORP behaviour is strongly influenced by the platinum surface condition. A new unconditioned ORP electrode will show different values than ORP probes "in use".

Note: *Most natural waters contain many species that are involved in the redox process so that it is not possible to calculate the ORP using the Nernst equation. All redox species do however reach equilibrium. A Standard solution of known redox potential for a particular ORP electrode is used to calibrate the ORP sensor. The ORP sensor then gives a calibrated response in mV when placed in a sample.*

The result of the redox measurement can be given as ORP or as E_h. E_h refers to the SHE (Standard Hydrogen Electrode) in order to document comparable values between different ORP probe types. Normally only the raw ORP value is recorded to see relative changes over time, so that E_h is not necessary to calculate.

Example
If using a Ag/AgCl reference electrode with 3 M electrolyte solution, a measured redox potential of +150 mV changes to E_h = +360 mV, just by adding 210 mV for the potential shift from Ag/AgCl to SHE (@ 25°C). Refer to Table 4 on page 28.

2.2 Calibration / Check standards

There are several redox standard solutions available, most common are

- Zobell's solution
- Light's solution
- Quinhydrone solutions.

Note: *The following mV readings at 20°C are given for a Ag/AgCl reference electrode with 3 M KCl filling solution.*

Prepare a Zobell's solution
Soluble 2.64 g $K_4[Fe(CN)_6]$ * 3 H_2O and 2.06 g $K_3[Fe(CN)_6]$ * H_2O under stirring in 500 ml buffer pH 7.00 at 25°C. After approx. 15 min stirring the solution is ready to use.

Potential @ 20°C = +228.5 mV ± 5 mV

Prepare a Light's solution
Soluble 1.861 g $Fe(NH_4)_2$ $(SO_4)_2$ * 6 H_2O and 2.411 g Fe NH_4 $(SO_4)_2$ * 12 H_2O under stirring in 500 ml 1 M H_2SO_4 at 25°C. After approx. 15 min stirring the solution is ready to use.

Potential @ 20°C = + 462.4 mV ± 5 mV

Prepare Quinhydrone solutions
Solution A : Add 3 g Quinhydrone to 500 ml buffer pH 4.01 and stir for 15 minutes. un-dissolved Quinhydrone powder must be present. If necessary add Quinhydrone powder.

Potential @ 20°C = + 265.1 mV ± 5 mV

Solution B : Add 3 g Quinhydrone to 500 ml buffer pH 7.00 and stir for 15 minutes. There must be access of Quinhydrone powder un-dissolved. If necessary add Quinhydrone powder.

Potential @ 20°C = + 87.4 mV ± 5 mV

2.2.1 ORP probe calibration

Select in the meter the ORP standard with the correct value versus temperature. After rinsing the probe with DI water dip the probe into the selected ORP standard solution and wait until the signal is stable. Take a reading. There can be a deviation from the theoretical ORP value for that standard at the temperature. This "Offset" (refer to Acceptance criteria for calibration / offset data on page 27) has to be stored for further sample readings.

Table 3 shows typical mV readings in ORP standard solutions at different temperatures (Reference Ag/AgCl 3M KCl).

Table 3 Typical mV readings

Temperature °C	Zobell's Solution		Temperature °C	Chinhydron in pH 7.00
10	243.5		10	95.4
15	236.0		15	92.9
20	228.5		20	87.4
25	221.1		25	81.5

Table 3 Typical mV readings (continued)

Temperature °C	Light's Solution		Temperature °C	Chinhydron in pH 4.01
10	447.4		10	268.4
15	453.2		15	267.6
20	462.4		20	265.1
25	469.3		25	261.3

2.2.2 Acceptance criteria for calibration / offset data

There are different ± mV ranges stated in the literature of probe and standard manufacturers from ± 5 up to ± 20 mV. As long as the reference electrode is working properly, the ORP standards should be found at a defined temperature (e.g. 20 °C) within a range of ± 5 mV up to maximum ± 10 mV for ORP probes in routine use.

Over the time of use and depending on the type of sample the platinum disk / ring may become coated with chemical and/or biological layers, which may cause a shift in potential (30-50 mV). Then a cleaning procedure is necessary, refer to Cleaning on page 27.

For an accurate sample measurement it is recommended to first check the ORP probe performance against an ORP standard solution. The difference between the set standard mV and the mV measured is called the **Offset**. This offset has to be subtracted from the sample mV readings. This offset values are typically in the range of ± 10 mV for ORP probes in routine use.

2.3 Cleaning

In case of shifting potential over time, decreasing stabilization times or instable readings, a cleaning of the ORP probes is recommended. In the order of lowest effect on the platinum surface start with "standard cleaning" and if this does not help try the "aggressive cleaning". It is recommended to be as careful as possible to not destroy the platinum surface by too aggressive and too often chemical cleaning. Over-aggressive cleaning can lead to ORP probe replacement.

Standard cleaning procedures:

1. Soak the probe for 10-15 minutes in fresh tap water containing a few drops of a commercial detergent like for dishwashing. Additionally wipe the Pt surface with a cotton cloth, but take care to not break any part of the probe. Afterwards rinse with fresh tap water.
2. Soak the probe for 20-25 Minutes in 1 M hydrochloric acid (HCl). While following the acid safety instructions wipe the Pt surface on a cotton cloth or swab. Afterwards rinse with fresh tap water.

Aggressive cleaning procedures:

1. Soak the probe for 1-2 hours in a 50:50 dilution of commercial chlorine bleach.
   Note: *Make sure that the diaphragm (ceramic pin or open junction etc.) is NOT in the chlorine bleach.*

   Afterwards rinse with fresh tap water and soak the probe for 1-2 hours in tap water to remove the remaining bleach. It might be necessary to repeat the rinsing to remove all bleach from the probe, otherwise the results of calibration and sample measurement can be false due to chlorine bleach.
2. Polishing the platinum surface with an abrasive paper of 600 grid or higher, or use a extra fine grinding paste and polish with a cotton cloth. Soak the probe afterwards for 10 minutes in 1 M hydrochloric acid (HCl) and rinse thoroughly with fresh tap water.

To achieve best and reproducible results it is recommended to let the probe condition for a certain time. After cleaning procedures soak the ORP probe in the reference electrolyte solution over night, then rinse with DI water and do a calibration.

The offset in an ORP standard should be of max. ± 10 mV.

If the calibration is not satisfactory replace the ORP probe.

2.4 Measurement

Before measuring a sample the probe must be calibrated to check its performance. Use one of the ORP standard described above and do a calibration as defined by the meter to get the actual mV offset value for correction. Take several readings in that same ORP standard to verify the final result.

Calculate the offset by: $E_{offset} = E_{standard} – E_{measured}$ [mV]

Add that mV offset to all sample results to adjust for the actual ORP probe performance. If necessary also add on the mV value for the reference system used to get the mV value referred to SHE (standard hydrogen electrode).

$E_{SHE} = E_{offset} + E_{reference} + E_{measured}$ [mV]

Table 4 Ag/AgCl reference potentials [mV]

Filling solution [M]	Temperature [°C]			
mol/L	**15**	**20**	**25**	**30**
0.1	286	287	289	290
1	236	236	236	237
3	211	210	210	210
3.5	207	207	206	206
4	203	203	203	203
sat.	188	188	187	187

Note: *In contrast to conductivity (and similar to pH) there is no automatic temperature compensation for ORP measurements of samples. For ORP measurements the temperature of the sample must always be recorded for further reference. For some samples it might be necessary to also record the actual pH value, because some RedOx couples are pH dependent.*

HACH's HQd meter series allows the offset from a ORP standard measurement (ORP calibration) to be calculated and stored. This offset is then subtracted from each sample mV reading automatically.

2.4.1 Measurements in drinking water

Drinking water (DW) can be of very low ionic strength (e.g. 80 to 200 µS) and that can cause problems regarding stabilization time and final reading. After calibration of the ORP probe rinse the probe with the drinking water sample and then transfer the probe into a new beaker with the DW sample to be measured. Wait at least 15 minutes for a first reading and then check every 5 minutes for stability. Depending on the temperature (low takes longer) and on the conductivity (low takes longer) it might take several hours to get a final reading.

The reading is finished if the mV change per minute is less than 1 mV. Most pH/ORP meters offer a stability function with adjustable or pre-defined stability criteria. Refer to the user's manual of the meter for specific information about stability criteria used.

2.4.2 Measurements in Surface Water

Surface water (SW) has usually a conductivity of more than 600 µS/cm. The ORP measurement can be done right after calibration. Because rivers, reservoirs and wells contain sufficient ORP active species the measurement should be stable within 6 minutes.

Rinse the probe after each measurement with tap water to remove any biological layer from the Pt surface. This will help keeping the Pt surface always ready to measure.

2.4.3 Measurements in Waste Water

Waste water (WW) is of sufficient ionic strength for fast ORP measurement. Its temperature is usually below 20°C and consists of a mixture of chemical and biological (human) residuals. Depending on the location in the WWTP (waste water treatment plant) the influent, aeration basin, nitrification / denitrification, and effluent can show different ORP values.

While the influent often comes with ORP readings of around -200 mV the WW stream changes the ORP to positive values of around +50 mV due to oxidation of the reducing species. The table shows typical ORP values of waste water in a WWTP.

ORP [mV]	**Process**
–280 to –150	Development of Methane
–200 to +100	Reduction of Sulphate
+180 to +400	Reduction of Iron
+220 to +500	Reduction of Manganese
+300 to +600	Reduction of Nitrate

The reading can be disturbed by air bubbles (aeration), floating particles, biological layers and so on. Therefore it is essential for a continuous ORP control to measure always at the same location and depth and under reproducible ORP probe conditions. It can be faster to grab a sample and measure outside instead of waiting on a stable reading inside the basin or stream.

After each WW measurement the probe has to be cleaned with DI water, soap solution, and again rising with DI water. Wipe the surface dry with a soft cloth and store the probe in the recommended storage solution between the measurements. This procedure will guarantee a long lifetime and reproducible and accurate results.

Section 3 ISE (ion selective electrodes)

3.1 Theory

Ion selective electrodes (ISE) consist of an ion-specific half-cell and a reference half-cell. The ion-specific part gives a potential against the reference part depending on the specific ion concentration. When the specific ion concentration (the sample or an ion standard) changes, the potential changes too. The mathematical relationship between the potential measured with the ISE and the ion concentration in the measured solution is expressed using the **Nernst equation**:

Figure 17 Nernst equation

$$E = E_0 - 2.303 * \frac{R * T}{n * F} \log (C + C_0)$$

E = Measured potential (mV) between the ion selective and the reference electrode

E_o = Measured potential (mV) between the ion selective and the reference electrode at a C = 1 concentration

R = Universal gas constant (R = 8.314 J mol^{-1} K^{-1})

T = Temperature in K (Kelvin), with T (K) = 273.15 + t °C if t is the temperature of the measured solution (°C)

F = Faraday constant (96485 C mol^{-1})

n = Electrical charge of the ion

C = Concentration of ion to be measured C_0 = detection limit

R and F are constants. The electrical charge and measured potential at C = 1 of the ion to be measured is also known. As the sample or standard temperature is a variable of the Nernst equation, it is essential to thoroughly record the temperature while measuring.

Therefore Figure 17 can be simplified to:

Figure 18 Simplified Nernst equation

$$E = E_0 - S * \log (C + C_0)$$

where S = is called the slope of the ISE[4].

Example of ion	n (electrical charge of the ion)	S (T=25°C)
Copper (Cu^{2+})	+2	+29.58
Sodium (Na^{+}), Potassium (K^{+})	+1	+59.16
Fluoride (F^{-}), Chloride (Cl^{-})	–1	–59.16
Sulphide (S^{2-})	–2	–29.58

As known from pH measurement and calibration, the slope S is an indicator of ISE performance. If the slope decreases over time, it will be necessary to implement a maintenance cycle to clean the ion selective part, refill inner fill solution, replace the membrane or, in the worst case, replace the entire ISE.

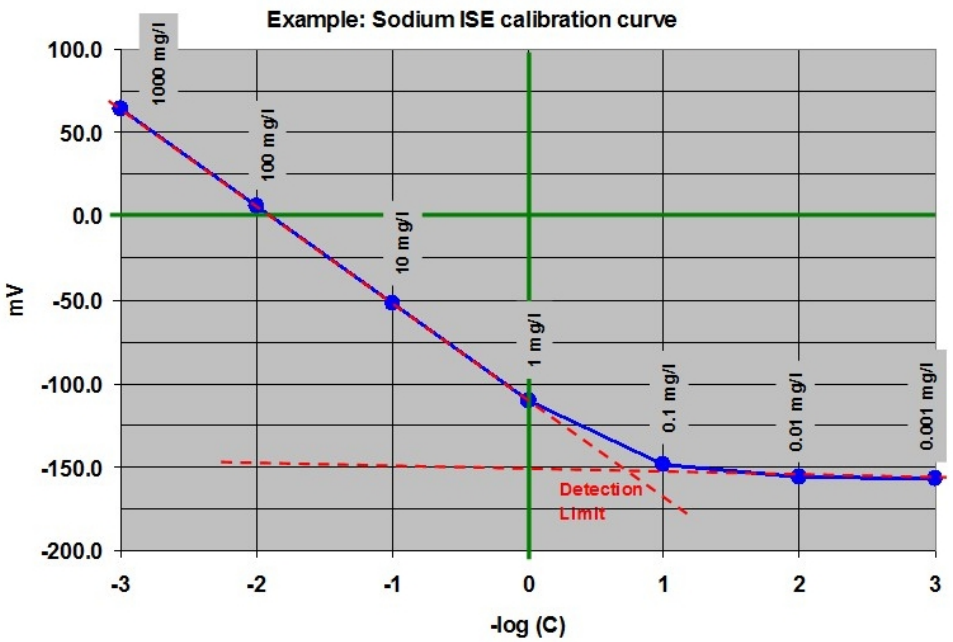
In order to characterize ISE behaviour, it is customary to prepare standard solutions of the specific ion in concentration steps of 10 (e.g. 0.001 / 0.01 / 0.1 / 1.0 / 10 / 100 / 1000 mg/L). When all standard solutions are measured, the ISE characteristic can be displayed by plotting concentration vs. potential. However, it is useful to either plot the concentrations on a logarithmic axis or easier to calculate the log (C), which using the above example becomes (–3, –2, –1, 0, +1, +2, +3).

[4] Anions have a negative slope, cations have a positive slope

The table shows the real measured mV values of a Sodium ISE for 7 Na^+ standard solutions (mg/L).

–log C	mV	mg/L Na^+
3	–156.5	0.001
2	–156.4	0.01
1	–148.2	0.1
0	–110.0	1
–1	–51.8	10
–2	6.4	100
–3	64.5	1000

Figure 19 Example of sodium ISE calibration curve (blue) and detection limit (red)



The slope of the curve decreases with decreasing Na^+ concentrations. While the linear section (1mg/L up to 1000 mg/L) shows a slope of -58.2 mV/pC at 20°C, the lower concentrations, shown in the flat (left) part of the curve, show a slope of almost zero. That means the ISE calibration curve has a non-linear part. When measuring low Na^+ concentrations it must be taken into account that the differentiation of small Na^+ concentrations is more and more difficult to detect. A slope difference from one standard to another of less than 30 mV/pC (for a monovalent ion) leads to less reliable and reproducible measurements.

3.1.1 Design of ion selective electrodes

Solid state electrodes: Here the ion selective part is a solid substance that is in direct contact with the solution to be measured. The main characteristic of a solid state electrode is that the sensing material is insoluble in water. For example, the most commonly used solid crystal is Lanthanium fluoride (LaF_3) and is used to detect fluoride ions. The equilibrium in aqueous solutions is:

$$LaF_3 \Leftrightarrow La^{3+} + 3F^-$$

The solid crystal is in contact with the aqueous solution where few La^{3+} ions and F^- are formed and produce a certain potential. If there are F^- ions present in the sample

solution, then the equilibrium changes giving a different potential and making it possible to detect specific F^- concentrations.

PVC membrane electrodes: There are many different types of membrane electrodes. Usually the PVC material is mixed with an organic solvent and a specific organic substance reactive to the ions being detected. This specific organic substance (ionophore) creates a potential on the surface of the membrane proportional to the concentration of the specific ion. Such membranes have to be maintained regularly and may have a shorter useful life than solid state ISEs, depending on the usage. Common examples of PVC membrane ISEs are Calcium Ca^{2+} and Nitrate NO_3^-.

Gas-sensing electrodes : These ISEs use a gas permeable membrane to separate the gaseous form of a species from the rest of the sample. The gaseous species diffuses through the membrane and is captured inside the electrode and measured by detecting changes in the capturing solution. For example, ammonium can be measured by detecting the ammonia in solution, because there is an equilibrium:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

By making the solution basic, the reaction is driven to the left creating NH_3. The NH_3 diffuses through the membrane and collects in the capture solution where it changes the pH. A pH sensor then measures the change in pH and correlates it to the ammonium concentration of the sample.

3.2 Calibration

3.2.1 Prepare sodium standard solutions

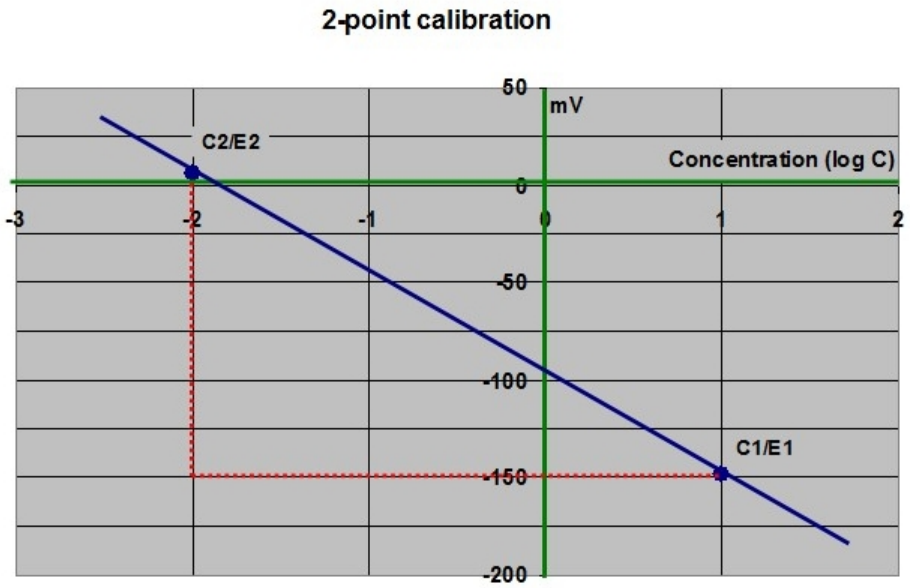
1. Weigh exactly 2.542 g NaCl and transfer it into a 1000 mL glass flask and fill with DI water up to the mark (**solution A: 1000 mg/L Na^+**).
2. Pipette 10 mL of solution A into a 100 mL glass flask and fill with DI water up to the mark (**solution B: 100 mg/L Na^+**) and shake a to mix the solutions.
3. Pipette 10 mL of solution B into a 100 mL glass flask and fill with DI water up to the mark (**solution C: 10 mg/L Na^+**).
4. Pipette 10 mL of solution C into a 100 mL glass flask and fill with DI water up to the mark (**solution D: 1 mg/L Na^+**).
5. Pipette 10 mL of solution D into a 100 mL glass flask and fill with DI water up to the mark (**solution E: 0.1 mg/L Na^+**).
6. Pipette 10 mL of solution E into a 100 mL glass flask and fill with DI water up to the mark (**solution F: 0.01 mg/L Na^+**).
7. Pipette 10 mL of solution F into a 100 mL glass flask and fill with DI water up to the mark (**solution G: 0.001 mg/L Na^+**).

3.2.2 2-point calibration

Out of such a calibration with 2 standards the slope is calculated for a specific concentration / potential area. As long as the ion concentration of the sample is within this concentration range, a 2-point calibration is sufficient.

However, the difference of the concentrations of the standards used should be at least a factor of 10. For instance if the sample is expected to have 30–50 mg/L sodium, then a calibration with 2 standards of 10 mg/L and 100 mg/L is sufficient. Because of the temperature effect on the Nernst equation, a 2-point calibration and a sample measurement must be done at the same temperature. A maximum deviation of 2°C is acceptable, although it affects the accuracy of the final result.

Figure 20 Linear curve of two standard solutions (C_1 and C_2) and their resulting potential measured as E_1 and E_2

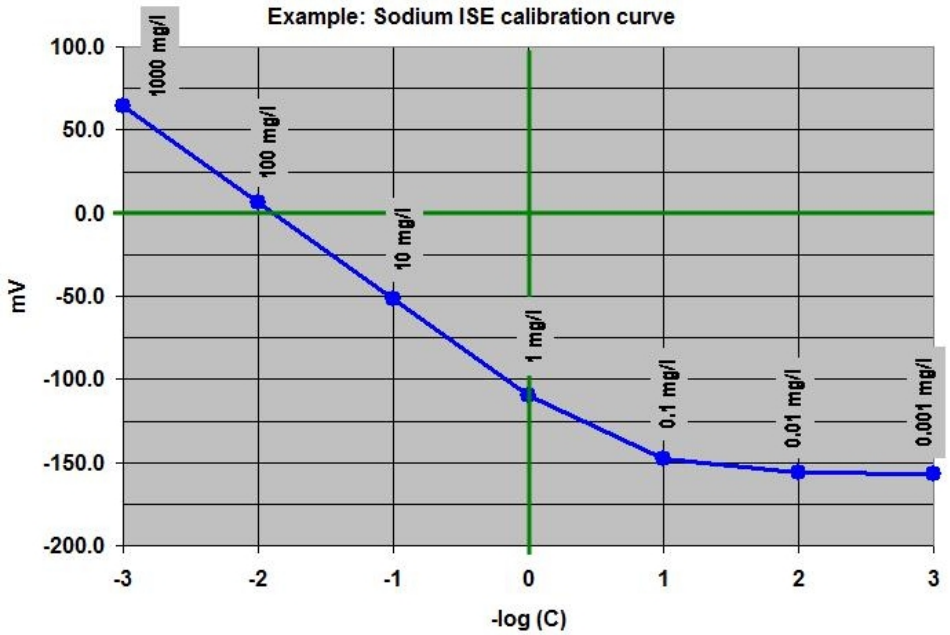


3.2.3 Multi-point calibration

Lastly, the multi-point calibration is used to determine where the ISE leaves the linear area and where the detection of small concentrations is limited. Especially for low concentrations, it is mandatory to use several standards to cover the full non-linear range.

By using the non-linear calibration curve technique, the reliability and accuracy of the result is much higher, especially if samples are examined with a broad range of ions, like sodium.

Figure 21 Non-linear curve of 7 standard solutions (C_i) and their resulting potential measured as E_i



3.2.4 Detection limit

After recording the calibration curve it is recommended to extract the detection limit of that ISE. This can be done graphically by adding one tangent (red line) to the upper linear

part of the curve and one tangent to the lower linear part (almost parallel to the X-axis). The detection limit of the ISE is the point at which both tangents cross, refer to Figure 20 on page 34.

However, this detection limit applies to a concentration of a specific ion detected with a specific ISE. It depends on the characteristic of the sample and of course on the behaviour of the ISE. The older the ISE, the less reliable is the measurements of low concentrations. In addition the temperature plays an important role. ISEs in samples at cold, hot or room temperature have different slopes.

3.3 Measurement

When performing ISE measurements for the first time with a new electrode it is normal for the stabilization time to be longer and the signal may be noisier than the user is accustomed to from previous measurements. If this is the case, the new ISE electrode should be conditioned in diluted standards for several hours before a fast and stable reading may be achieved.

It is recommended to always use a stirrer to mix the solution of the sample and of the standards. This helps to transport ions to the ion selective surface of the electrode. Especially for low concentrations stirring may shorten the stabilization time.

When using a magnetic stir plate, it can be necessary to insulate the sample beaker from the plate to avoid heating the sample. As mentioned above, changes in temperature can lead to result variations. The easiest way to insulate the beaker from the stirrer is to place a piece of cardboard on the plate.

3.3.1 Selectivity of the specific ion measurement

At the beginning of the ISE introduction, we assumed that an ISE electrode has a sensitive part specific to just one ion to be detected among other ions in the solution. This is not the case for most of the ISEs. Since the ion selective part is sensitive to a few ions which are similar in ion radius, charge and mobility, this must be taken into account in the measurement of samples. So it is possible that an excess of an interfering ion can lead to higher or lower concentrations of the ion of interest.

The sodium ISE electrode is selective for Na^+, but also responds to potassium K^+ and lithium Li^+. *The selectivity constant for* ***K^+ is 0.001*** *and for* ***Li^+ is 0.01***. What does that mean? For example, a small selectivity constant of 0.001 means that the interfering ion is contributing 0.001 of its concentration toward the potential of the electrode. With sodium and potassium in the same solution at the same concentration, the potassium will cause a small change in the potential.

But, if potassium is 1000 times more concentrated than sodium, the potential measured is almost 50/50 resulting from both ions, Na^+ and K^+. This of course leads to false results, where Na^+ is assumed to be of a higher concentration than it is in reality.

In order to calculate the influence of interfering ion regarding the final potential, an extended Nernst equation can be used. Nikolsky developed a specific equation, where all interfering ions can be considered.

Figure 22 Nikolsky equation

$$E = E_0 - 2.303 * \frac{R * T}{n * F} \log \left(a + \sum_{a_j \neq a_i} K_{is} * a_j^{\frac{n_i}{n_s}}\right)$$

n_i = Electrical charge of the ion to be measured

n_s = Electrical charge of the interfering ion

a_i = Activity of ion to be measured

a_j = Activity of interfering ion

K_{is} = Selectivity constant (ion to be measured // interfering ion)

3.3.2 Ionic strength

All ions in a solution add to the total ionic strength. Ions are the only species to transport charge through the solution. If there are sufficient ions present, the ion transport to the ion selective surface is continuous. In case of low ionic strength samples, like drinking water, boiler water etc. the charge transport through the solution is covered by only a few ions and the transport of the ions is impeded.

Figure 23 Ionic strength

$$I = 0.5 * \sum c_i * z_i^2$$

I = Ionic strength

C_i = Concentration of the ion i

Z_i = Charge of the ion i

To avoid such a random situation, where diffusion potentials contribute to the concentration potential, an ionic strength adjustment (ISA) normalizes the ionic strength between standards and samples without interfering with the ion searched for. In the case of the sodium ISE the ISA is an ammonium salt like NH_4Cl. It creates a constant ionic strength in all standards and samples and does not interfere with the sodium ISE. In addition, some ISAs also contain a pH adjusting chemistry to create the best pH environment for the specific ion to be measured.

3.4 Measurement mode

The most common ISE measuring technique is *Direct Measurement*. The Direct Measurement mode creates a calibration curve that is based on two or multiple-points from known standards. Once the calibration has been performed and saved, the sample can be measured directly and the ion concentration is calculated by the ion meter.

The *Incremental Measurement* mode should be used instead of *Direct Measurement* whenever the matrix of a sample changes the analytical sensitivity of the method. For example, the slope and/or offset of the working curve for standards made with distilled water could be different from the same working curve made up in a matrix that is close to your sample. In this case several methods can be used, such as

- Standard addition on page 36
- Double standard addition
- Standard subtraction
- Sample addition on page 37
- Sample subtraction

3.4.1 Standard addition

This is the most common method. The ISE is placed in the sample and the potential is recorded. Then a standard solution is added and again the potential is recorded. After entering the sample volume, standard volume, standard concentration into the ion meter, it calculates the sample concentration. This can also easily be done by a spreadsheet programm like Microsoft Excel by using the following equation:

Figure 24 Equation for standard addition

$$C_p = \frac{\frac{V_S * C_S}{V_p}}{\left(1 + \frac{V_S}{V_p}\right) * 10^{\frac{E_2 - E_1}{S}} - 1}$$

C_p = Concentration of the sample

C_s = Concentration of the standard

V_p = Volume of the sample

V_s = Volume of the standard

E_1 = Potential of the sample before addition

E_2 = Potential of the sample after standard addition

S = Slope at the sample and standard temperature

The optimal addition is to double the sample concentration, or a ratio (sample: standard addition) of maximum 1:10 is possible. Therefore it is recommended to work with high concentrated standard solutions, where the standard volume added is rather small compared to the sample volume.

3.4.2 Sample addition

This method is as easy to perform as the Standard Addition method. You first take a standard solution and measure the potential. Then you add a defined volume of your sample and measure the potential again. It is recommended to add the sample volume so that the standard concentration is increased by 2 to 10 times. The ion meter can then calculate the concentration.

Figure 25 Equation for sample addition

$$C_p = \frac{C_S * \left(1 + \frac{V_p}{V_S}\right) * 10^{\frac{E_2 - E_1}{S}} - 1}{\frac{V_p}{V_S}}$$

C_p = Concentration of the sample

C_s = Concentration of the standard

V_p = Volume of the sample

V_s = Volume of the standard

E_1 = Potential of the standard before addition

E_2 = Potential of the standard after sample addition

S = Slope at the sample and standard temperature

3.5 Maintenance

Since the sodium ISE has a glass sensing element, there is low risk of contamination inside the layer by other ions. However, the H^+ and Li^+ ions are small enough to enter the glass "net" material and to exchange with Na^+. Therefore, it is recommended to store the Na^+ ISE always in the special storage solution, usually delivered with the electrode. For first-time use the Sodium ISE must be conditioned in a 0.1 mol/L Na^+ standard for several hours; refer to the manufacturer's recommendations.

Since the glass bulb of the Sodium ISE can be treated like a pH probe, the cleaning procedure is very similar. However, any abrasive polishing or scratches must be avoided, because this irreversibly damages the sensing surface.

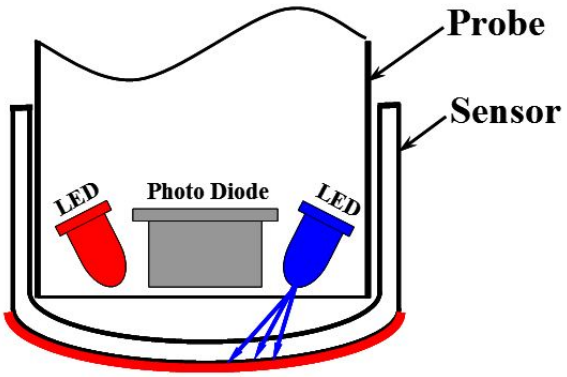
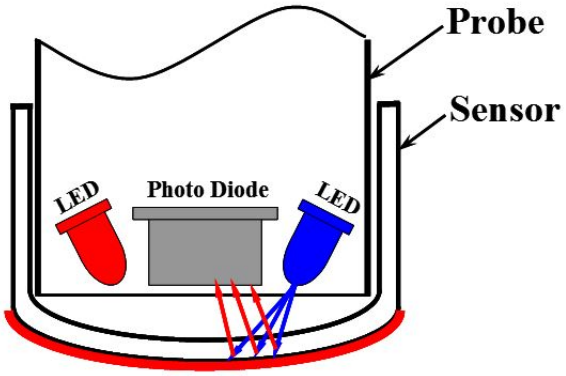
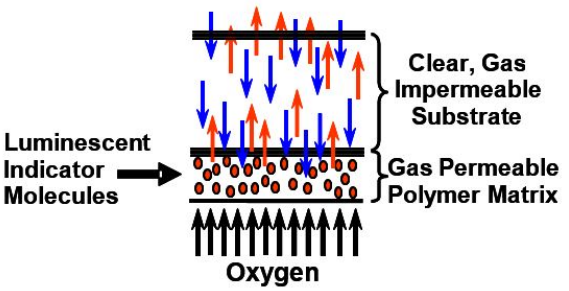
For oil / fat deposits on the glass bulb soaking in a solution with mild detergent will help. Afterwards the probe must be rinsed with DI water and again a conditioning step should be added. In any case, use only soft tissues to wipe the probe or sensing element. Never store the ISE probe dry. This will make it necessary to condition before measurement or may even damage the probe .

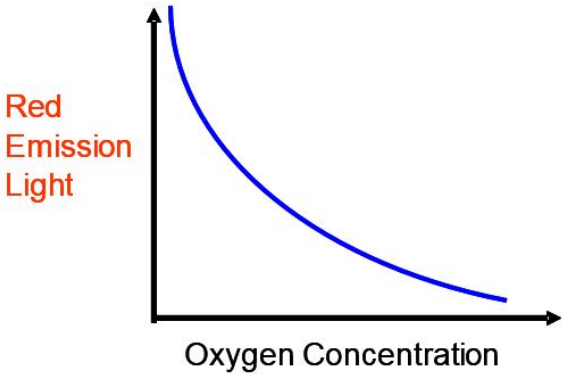
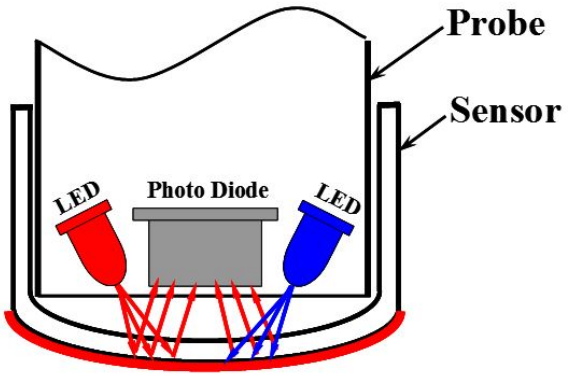
Section 4 LDO (dissolved oxygen) photometric method

4.1 Theory

Back in 2003 HACH launched the new photometric technology to measure dissolved oxygen in aqueous samples, such as drinking water, surface water, waste water and so on. The common DO measurement method was the electrochemical DO electrode, using a certain current flow through noble metal electrodes which are in contact with a electrolyte solution, which is separated from the sample by a specific oxygen permeable membrane - the so called CLARK electrode.

Although this CLARK technique conforms to international norms and standards, the setup, preparation, conditioning and maintenance is enormous. Often linked to these steps are errors and malfunctions of the DO measurement system.

Description	Picture
• A sensor is coated with a luminescent material. • Blue light from an LED strikes the luminescent chemical on the sensor. • The luminescent chemical instantly becomes excited.	
• As the excited chemical relaxes, it releases red light. • The red light is detected by a photo diode. • The time is taken for the chemical to return to a retaxed state is measured.	
• When oxygen contacts the luminescent chemical, the intensity of the red light decreases. • The amount of time is takes for the material to relax is reduced.	

Description	Picture
• The higher the oxygen concentration, the less red light is emitted by the sensor. • The instrument detects / measures the time it takes after excitation for the red light to be emitted, the lifetime of the luminescence, but not its intensity.	
• A red LED is also present in the probe. • Between flashes of the blue LED, a red LED of known intensity, is flashed on the sensor. • The red LED acts as an internal standard (or reference) for a comparison to the red light given off by the luminescent chemical.	
• By using common DO standards (e.g. water saturated air = 100% in a BOD bottle) the LDO probe can be checked and calibrated.	

Advantages of LDO technology

- No start up time
- No polarization time
- No refilling of the electrode
- No polishing of the inner electrodes
- No poisoning of the inner electrodes
- Ready to measure right after "power on"
- Stable reading within short time
- Reliable readings
- Simple calibration with 100% or 0% DO standards
- No specific conditioning

Figure 26 The Hach LDO method (360.3) is approved by USEPA

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 26 2006

OFFICE OF WATER

MEMORANDUM

SUBJECT: Recommendation for Use of Hach Method 10360 [Revision 1.1, January 2006] (ATP Case No. N04-0013)

FROM: Robin K. Oshiro, Ph.D.
ATP Coordinator
Engineering and Analytical Support Branch (4303 T)

TO: USEPA Regional Administrators (all Regions)

We have reviewed the Hach Method 10360 (Revision 1.1, January 2006, *Luminescence Measurement of Dissolved Oxygen in Water and Wastewater*), and the supporting validation data in ATP Case No. N04-0013. We have determined that this method meets all requirements for measurements of dissolved oxygen in water and wastewater. That is, the performance of this method is substantially similar to part 136 methods for measurement of dissolved oxygen (DO) in wastewater. We believe that this method also may be used to measure DO when a Part 136 method requires measurement of DO in determining biochemical oxygen demand in wastewater.

We will recommend that this method be included in future regulatory actions in which we periodically update the methods approved at 40 CFR Part 136.3. Meanwhile, Regions may wish to exercise their authority under 40 CFR part 136.5 to allow use of this method.

If I can be of any additional assistance on this matter or others, please contact me at oshiro.robin@epa.gov.

cc: Quality Assurance Managers (all Regions)
Water Management Division Directors (all Regions)
ATP Coordinators (all Regions)
Carey Jackson, Ph. D., Hach Company
Kevin Roberts, CSC, SCC

4.1.1 LDO probe design

The LDO probe consists of a probe body containing the electronics and optical parts, and a membrane cap with the luminescent chemical to react on dissolved oxygen.

The sensor cap is made of plexiglas and withstands many chemicals and some organic solvents. However, the black coating to protect the luminescent layer is sensitive to organic solvents and can easily be scratched and damaged.

Figure 27 LDO probe design

The sensor cap is screwed onto the probe body where a sealing (o-ring) avoids sample entering the cap. If for some reason a liquid passed that o-ring, it is easy to unscrew the cap and dry it with a soft cloth.

The lower end of the probe contains the optical parts of the LDO probe. This little window is also sensitive to organic solvents and must be protected against such solvents. For cleaning only use water and / or neutral detergents to remove any dirt or fat/oil or finger tips.

Before use check whether the sensor cap is screwed tightly to the probe body, but do not over tighten because this can damage the cap. Also check the black coating protecting the luminescent layer for scratches or other damages. Up to a certain level of damage the LDO probe can compensate for such changes in the chemical layer, but it is recommended to replace the cap if 10% layer is damaged.

The compensation is done by using a reference LED light source to give a 100% signal to the receiver what is compared with the 100% DO standard signal. So internally any deviations can be calculated and compensated.

The electronics inside the LDO probe are immediately calculating the DO content in mg/l and, with regard to the ambient air pressure, the DO content in percent. This information is sent to the HQd meter, where it is stored and displayed.

4.2 Calibration

100% DO standard
The common method to calibrate any DO electrode is to use a 100% DO and/or a 0% DO standard. For practical use we recommend to use a standard BOD bottle with approximately 1 cm filled with tap water. Close the bottle with a stopper and shake it for a minute, then open and close the stopper to remove any drops at the stopper in the bottle neck. Wait for a minute while the bottle remains still.

Then open the bottle and quickly insert the LDO probe, but make sure that the sensor cap does NOT touch the water inside. The LDO probe must be located in water saturated air, which is the 100% DO standard.

Then press "cal" on your HQd meter to start the calibration process.

0% DO standard
There are some DO standards using a sulphite to remove any oxygen in a solution. Since this chemical is hazardous we recommend to use a mixture of ascorbic acid with sodium hydroxide in DI water.

While stirring dissolve 500 mg ascorbic acid in 50 mL distilled water, then add 4 mL 1 N NaOH (pH 11,08). After 10 minutes switch off the stirrer and start with the 0% calibration (the remaining dissolved oxygen in this solution is below 0.05mg/L).

How often a calibration is necessary
Depending on the frequency of sample measurements the LDO probe should be first checked using a DO check standard, which can be defined in the HQd meter. If the LDO probe is used less than once per week, we recommend to use the 100% check standard. If the DO reading is within +/- 3%, the LDO probe can be used with the current calibration data. If the reading is off by more than 3% we recommend to re-calibrate with a 100% standard, before the new sample measurement series starts. If the check standard is not found within 10% we recommend to perform a 2-point 0% and 100% calibration.

The condition of the LDO probe, mainly the sensor cap, depends also on the way of storage. If the probe is stored dry under ambient air conditions, the sensor cap may need some minutes longer to stabilize, when measuring first time. In order to have a quick response time the LDO probe should be stored in a humid environment, such as the BOD bottle with a few ml of water (like the 100% calibration).

If the LDO probe was not used for more than 4 weeks, we always recommend doing a 100% calibration, just to be on the safe side.

If the calibration data is not acceptable then replace the sensor cap.

The HACH LDO probe provides the measurement of ambient air pressure automatically with a built-in pressure sensor.

4.3 Measurement

The usual oxygen content in drinking water (DW) is around 8-9 mg/l, what corresponds to 100% DO. Depending on the temperature of the water sample and the ambient pressure of the environment it is necessary to adjust for the solubility of O_2 in water in mg/l. In addition for water samples of higher salt content it is necessary to correct for the salinity.

Table 5 Oxygen solubility vs. Temperature vs. Pressure

Oxygen concentration (ppm) for varying pressures (mmHg) and temperatures (degrees Celsius) at 100% relative humidity										
Pressure (mmHg) ---------- Temperature (Celsius)	790	775	760	745	730	715	700	685	670	665
0.0	15.20	14.90	14.60	14.30	14.00	13.70	13.40	13.20	12.90	12.60
1.0	14.80	14.50	14.20	13.90	13.60	13.30	13.10	12.80	12.50	12.20
2.0	14.40	14.10	13.80	13.50	13.30	13.00	12.70	12.40	12.20	11.90
3.0	14.00	13.70	13.40	13.20	12.90	12.60	12.40	12.10	11.80	11.60
4.0	13.60	13.40	13.10	12.80	12.60	12.30	12.10	11.80	11.50	11.30
5.0	13.30	13.00	12.80	12.50	12.20	12.00	11.70	11.50	11.20	11.00
6.0	12.90	12.70	12.40	12.20	11.90	11.70	11.40	11.20	10.90	10.70
7.0	12.60	12.40	12.10	11.90	11.60	11.40	11.20	10.90	10.70	10.40
8.0	12.30	12.10	11.80	11.60	11.40	11.10	10.90	10.70	10.40	10.20
9.0	12.00	11.80	11.60	11.30	11.10	10.90	10.60	10.40	10.20	9.94
10.0	11.70	11.50	11.30	11.00	10.80	10.60	10.40	10.10	9.92	9.69
11.0	11.50	11.20	11.00	10.80	10.60	10.40	10.10	9.91	9.69	9.47
12.0	11.20	11.00	10.80	10.50	10.30	10.10	9.90	9.68	9.47	9.25
13.0	10.90	10.70	10.50	10.30	10.10	9.89	9.68	9.47	9.26	9.04
14.0	10.70	10.50	10.30	10.10	9.88	9.67	9.46	9.26	9.05	8.85
15.0	10.50	10.30	10.10	9.87	9.67	9.46	9.26	9.06	8.86	8.65
16.0	10.30	10.10	9.85	9.65	9.45	9.26	9.06	8.86	8.66	8.46
17.0	10.00	9.84	9.65	9.46	9.26	9.07	8.87	8.68	8.48	8.29
18.0	9.83	9.64	9.45	9.26	9.07	8.88	8.69	8.50	8.31	8.12
19.0	9.63	9.45	9.26	9.07	8.89	8.70	8.51	8.33	8.14	7.95
20.0	9.44	9.25	9.07	8.89	8.70	8.52	8.34	8.15	7.97	7.79
21.0	9.26	9.08	8.90	8.72	8.54	8.36	8.18	8.00	7.82	7.64
22.0	9.07	8.90	8.72	8.54	8.37	8.19	8.01	7.84	7.66	7.48
23.0	8.91	8.73	8.56	8.39	8.21	8.04	7.86	7.69	7.52	7.34
24.0	8.74	8.57	8.40	8.23	8.06	7.89	7.72	7.55	7.38	7.20
25.0	8.58	8.41	8.24	8.07	7.90	7.74	7.57	7.40	7.23	7.06
26.0	8.42	8.26	8.09	7.92	7.76	7.59	7.43	7.26	7.10	6.93
27.0	8.28	8.11	7.95	7.79	7.62	7.46	7.30	7.14	6.97	6.81
28.0	8.13	7.97	7.81	7.65	7.49	7.33	7.17	7.01	6.85	6.69
29.0	7.99	7.83	7.67	7.51	7.35	7.20	7.04	6.88	6.72	6.57
30.0	7.85	7.70	7.54	7.38	7.23	7.07	6.92	6.76	6.61	6.45
31.0	7.72	7.56	7.41	7.26	7.10	6.95	6.80	6.64	6.49	6.34
32.0	7.58	7.43	7.28	7.13	6.98	6.83	6.68	6.53	6.38	6.22
33.0	7.46	7.31	7.16	7.01	6.86	6.71	6.57	6.42	6.27	6.12
34.0	7.34	7.20	7.05	6.90	6.76	6.61	6.46	6.32	6.17	6.02
35.0	7.22	7.07	6.93	6.79	6.64	6.50	6.35	6.21	6.06	5.92
36.0	7.11	6.96	6.82	6.68	6.53	6.39	6.25	6.11	5.96	5.82
37.0	6.99	6.85	6.71	6.57	6.43	6.29	6.15	6.00	5.86	5.72
38.0	6.89	6.75	6.61	6.47	6.33	6.19	6.05	5.91	5.77	5.63
39.0	6.79	6.65	6.51	6.37	6.23	6.10	5.96	5.82	5.68	5.54
40.0	6.68	6.55	6.41	6.27	6.14	6.00	5.86	5.73	5.59	5.45
41.0	6.58	6.44	6.31	6.18	6.04	5.91	5.77	5.64	5.50	5.37
42.0	6.49	6.35	6.22	6.09	5.95	5.82	5.69	5.55	5.42	5.28
43.0	6.39	6.26	6.13	6.00	5.87	5.73	5.60	5.47	5.34	5.20
44.0	6.30	6.17	6.04	5.91	5.78	5.65	5.52	5.39	5.25	5.12
45.0	6.21	6.08	5.95	5.82	5.69	5.56	5.43	5.30	5.17	5.04
46.0	6.12	5.99	5.86	5.73	5.60	5.47	5.35	5.22	5.09	4.96
47.0	6.03	5.91	5.78	5.65	5.53	5.40	5.27	5.14	5.02	4.89
48.0	5.95	5.83	5.70	5.57	5.45	5.32	5.19	5.07	4.94	4.82
49.0	5.87	5.75	5.62	5.49	5.37	5.24	5.12	4.99	4.87	4.74
50.0	5.79	5.66	5.54	5.42	5.29	5.17	5.04	4.92	4.79	4.67

The solubility of oxygen in water decreases with increasing salt content. Therefore the salinity of the sample must be measured to enter the actual value into the DO meter for correction.

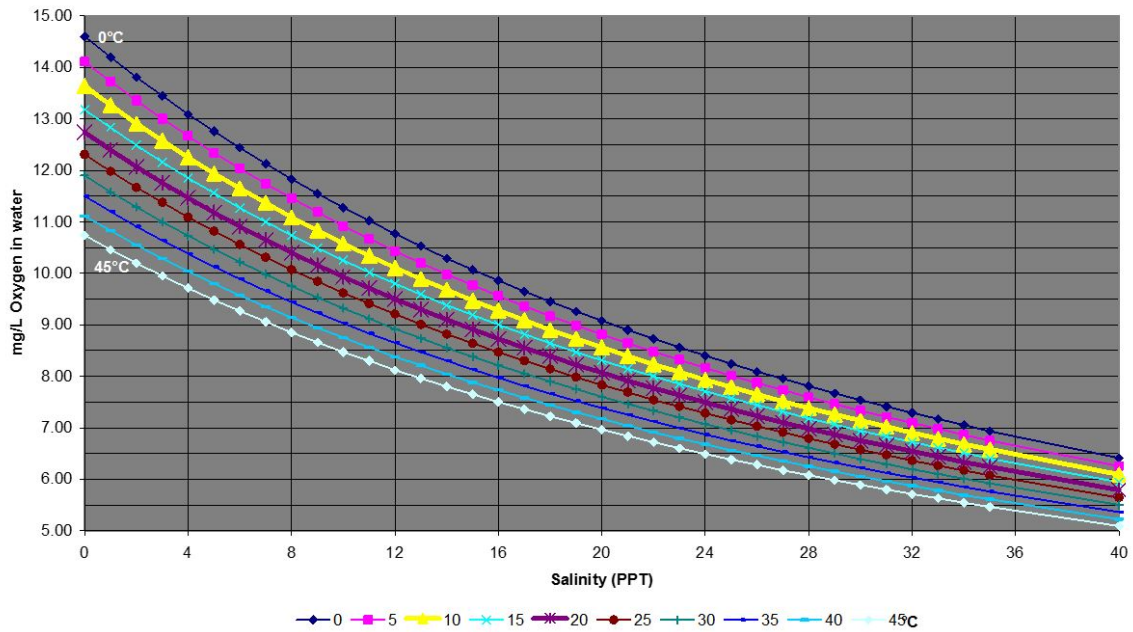
Table 5 shows the influence of temperature and pressure and Table 6 illustrates the influence of salinity and temperature. Most DO meter have a function to enter the Salinity value (PPT or °/$_{oo}$) for further correction of the DO reading.

Table 6 Oxygen solubility vs. Temperature vs. Salinity (@ 760 mmHg)

760 mm Hg	Salinity (°/oo)									
Temp. °C	0	5	10	15	20	25	30	35	40	45
0	14.60	14.11	13.64	13.18	12.74	12.31	11.90	11.50	11.11	10.74
5	12.76	12.34	11.94	11.56	11.18	10.82	10.47	10.13	9.80	9.48
10	11.28	10.92	10.58	10.25	9.93	9.62	9.32	9.03	8.75	8.47
15	10.07	9.77	9.47	9.19	8.91	8.64	8.38	8.13	7.88	7.65
20	9.08	8.81	8.56	8.31	8.07	7.83	7.60	7.38	7.17	6.96
25	8.24	8.01	7.79	7.57	7.36	7.15	6.95	6.75	6.56	6.38
30	7.54	7.33	7.14	6.94	6.75	6.57	6.39	6.22	6.05	5.89
35	6.93	6.75	6.58	6.40	6.24	6.07	5.92	5.76	5.61	5.46
40	6.41	6.25	6.09	5.94	5.79	5.64	5.50	5.36	5.22	5.09

Most sample are checked on several parameters and one of them is conductivity, which can be calculated as salinity. The salinity value has to be taken into account when measuring dissolved oxygen. This is also valid for optical DO measurement techniques.

Figure 28 Solubility of oxygen in water (mg/L) vs. Temperature (°C) vs. Salinity (PPT)



When using the HACH HQ30d or HQ40d meter a conductivity probe can be connected to measure the actual salinity of the sample. This salinity can be entered manually in the LDO measurement section for automatic correction, when measuring DO.

Optical dissolved oxygen measurement technique (LDO) now available as DIN and ISO norm:

Water quality - Determination of dissolved oxygen -
Optical sensor method (ISO 17289:2014)

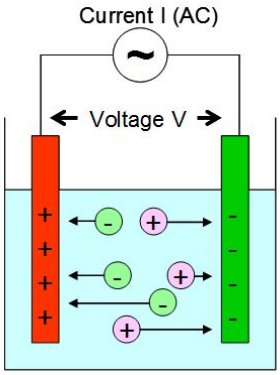
Section 5 Conductivity

5.1 Theory

Conductivity is the ability of a solution, a metal or a gas - in brief all materials - to pass an electric current. In solutions the current is carried by cations and anions whereas in metals it is carried by electrons. How well a solution conducts electricity depends on a number of factors:

- Concentration
- Mobility of ions
- Valence of ions
- Temperature

All substances possess some degree of conductivity. In aqueous solutions the level of ionic strength varies from the low conductivity of ultra pure water to the high conductivity of concentrated chemical samples.



How is conductivity measured?
Conductivity is measured by applying a constant, alternating electrical current (I) to two electrodes immersed in a solution and measuring the resulting voltage (V). During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor.

What is a conductive solution?
Conductivity is typically measured in aqueous solutions of electrolytes. Electrolytes are substances containing ions, i.e. solutions of ionic salts or of compounds that form ions in solution. The ions in solution are responsible for carrying the electric current. Electrolytes include acids, bases and salts and can be either strong or weak. Most conductive solutions measured are aqueous solutions, as water has the capability of stabilising the ions formed by a process called solvation.

Typical conductivity values at 25°C

- Pure water 0.055 µS/cm
- Deionised water 1 µS/cm
- Rainwater 50 µS/cm
- Drinking water 500 µS/cm
- Industrial wastewater 5 mS/cm
- Seawater 50 mS/cm
- 1 mol/L NaCl 85 mS/cm
- 1 mol/L HCl 332 mS/cm

5.1.1 Definition of terms

Resistance	The resistance of the solution (R) can be calculated using Ohm's law $V = R * I$ or $R = V / I$ where: V = voltage (volts) I = current (amperes) R = resistance of the solution (ohms)
Conductance	Conductance (G) is defined as the reciprocal of the electrical resistance (R) of a solution between two electrodes. $G = 1/R$ (S) [S = Siemens] The conductivity meter in fact measures the conductance and displays the reading converted into conductivity.
Cell constant	This is the ratio of the distance (d) between the electrodes to the area (a) of the electrodes. $K = d/a$ K = cell constant (cm^{-1}) a = effective area of the electrodes (cm^2) d = distance between the electrodes (cm)
Conductivity	Electricity is the flow of electrons. This indicates that ions in solution will conduct electricity. Conductivity is the ability of a solution to pass current. The conductivity reading of a sample will change with temperature. $\kappa = G * K$ κ = conductivity (S/cm) G = conductance (S), where G = 1/R K = cell constant (cm^{-1})
Resistivity	This is the reciprocal of the conductivity value and is measured in ohm•cm. It is generally limited to the measurement of ultrapure water, the conductivity of which is very low.
Reference temperature	Conductivity readings are often referenced to a specific temperature, typically 20°C or 25°C, for comparative purposes.
Automatic temperature correction	Algorithms for automatic conversion of sample conductivity to a reference temperature.
Total Dissolved Solids (TDS)	This is the measure of the total concentration of ionic species of a sample. Its magnitude is relative to the standard solution used to calibrate the meter.
TDS factor	Conductivity readings are converted to TDS readings by multiplication with a known mathematical factor. The factor depends on the reference material used to prepare the standard.
Salinity	Salinity is a measurement without unit corresponding to the weight of dissolved salts in seawater.

5.1.2 Platinised cells

Covering the cell poles (plates or rings) with a layer of platinum black is another way to minimise polarisation effects and avoid error on the measurement. The surface of the pole is increased, the current density is decreased, and therefore the polarisation effect is less. Consequently, the cell constant is linear over 2–3 decades towards the higher conductivity range. The platinum black must not be damaged or scratched, as this will modify the surface of the poles and therefore the cell constant. However, one minor disadvantage of platinised cells is that the cell constant tends to drift faster than the constant of non-platinised cells. It is advisable to use platinised cells only in non-viscous samples, without suspensions and to perform frequent calibrations.

Flow-through cell
Flow-through type conductivity cells are designed for flow measurements and measurements in small sample volumes. These measurements can be performed in a

closed liquid system protected from air. If a measurement is to be performed in pure water, it is necessary to use a flow cell. Contact with air must be avoided. The reason for this is that the carbon dioxide in the air forms hydrogen carbonate ions in water and leads to a change of conductivity.

A circulation/flow thru cell can be used in two ways:

- Circulation: the solution flows non-stop during the measurement.
- Pipette: a quantity of solution is drawn into the cell. This technique is ideal for small sample volumes

5.2 Conductivity measurement

Determination of the cell constant

Calibration is important, because it delivers the actual/correct value of the cell constant under your working conditions. The cell constant is a factor that is used to convert the measured conductance to conductivity (refer to Definition of terms on page 46).

Conductivity (S × cm^{-1}) = Cell constant (cm^{-1}) * Conductance (S)

It is determined by the geometry of the cell, but in practical terms can only be measured using a standard of known conductivity, for example KCl 0.01 D solution, refer to Demal solution on page 51. The cell constant changes with time. Some modifications can occur due to contamination or due to physical-chemical modification in case of platinised cells. It is therefore recommended to calibrate the cell at least once a week. However, if you use a platinised cell, it is advisable to perform a daily conductivity measurement in a standard. If the result obtained is in accordance with the theoretical value, continue your measurements. If not, your cell needs to be cleaned (if non-platinised) or replatinised (if platinised).

For high-precision measurements, it is necessary to determine the cell constant by performing a calibration measurement on a standard maintained at the desired temperature.

Note: *For 2-pole cells, the standard used for the calibration must have a conductivity value as close as possible to the conductivity of the sample to measure.*

When using a 2-pole cell, the choice of the cell constant value varies with the linear measurement range of the cell selected. Typically, a cell with K = 0.1 cm^{-1} is chosen for pure water measurements while, for environmental water and industrial solutions a cell with K of 0.4 to 1 cm^{-1} is used. Cells with up to K = 10 cm^{-1} are best for very high conductivity samples.

In the case of a 4-pole cell, the cell constant value is generally included in the range 0.5 to 1.5 cm^{-1}.

Low conductivity measurements (pure water)

Note: *Conductivity measurements can only be performed after calibration, as the actual cell constant value is used to calculate the conductivity.*

One of the main applications of low conductivity measurements is checking the quality of pure water. Pharmaceutical laboratories are obliged to respect regulations laid down by national pharmacopoeias, for example the 5th supplement of the United States Pharmacopoeia (USP) lays down rules for checking the quality of pure water or fully deionised water used for the production of injection products.

Principle of pure water measurements

According to USP	The conductivity partly depends on the pH, the temperature and the amount of atmospheric carbon dioxide, which has been dissolved in the water to form ions (intrinsic conductivity). The conductivity also depends on the chloride, sodium and ammonium ions considered as water impurities (extraneous conductivity). The conductivity (intrinsic and extraneous) of the water is measured and compared to values listed in a table to evaluate whether the studied water is suitable or not for use in pharmaceutical applications. If the sample fails stage 1, additional tests have to be performed (stages 2 and 3) in order to determine whether the excessive conductivity value is due to intrinsic factors or extraneous ions. The main requirement is that the cell constant be known with an uncertainty better than ±2%.
According to the European Pharmacopoeia	The cell consists of two parallel platinum plates at a defined distance. It is confined within a glass jacket with two pipe connectors enabling measurement in flow mode. This cell is calibrated using a conductivity standard of 26.6 µS/cm at 20°C, which is traceable to NIST. All measurements are made with a precision conductivity meter using AC current at a low frequency.

5.2.1 Temperature effect

Conductivity measurements are temperature dependent, if the temperature increases, conductivity increases. For example the conductivity measured in a 0.01 D KCl solution at 20°C is 1.273 mS/cm whereas, at 25°C, it is 1.409 mS/cm.

The concept of reference temperature was introduced to allow the comparison of conductivity results obtained at different temperature. The reference temperature is usually 20°C or 25°C. The conductivity meter measures the actual conductivity and temperature and then converts conductivity to the reference temperature using a temperature correction function. It is mandatory to always associate the temperature together with a conductivity result. If no temperature correction is applied, the conductivity is the value taken at measurement temperature.

For temperature correction different options can be selected:

- Linear function
- Non-linear function for natural waters according to ISO/DIN7888.
- No correction

To perform correct conductivity measurements, it is recommended to use a temperature sensor or a conductivity cell with built-in temperature sensor. For high accuracy measurement, it is necessary to thermostat samples, so that the same temperature is used for the calibration and measurement.

Linear temperature correction

In moderate and high conductive solutions, temperature correction can be based on a linear equation involving a temperature coefficient (θ). The coefficient is usually expressed as a conductivity variation in %/°C. Linear temperature correction is used, e.g. for saline solutions, acids and leaching solutions.

$$K_{Tref} = \frac{100}{100 + \theta * (T - T_{ref})} * K_T$$

where:

K_{Tref} = Conductivity at T_{ref}

K_T = Conductivity at T

T_{ref} = Reference temperature

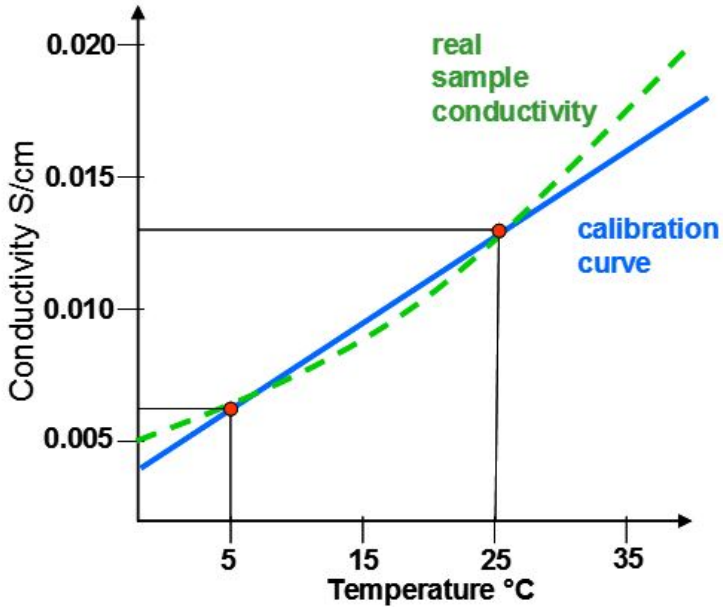
T = Sample temperature

θ = Temperature coefficient

Note: *Note that the correction is accurate only within a limited temperature range around T_1 and T_2.*

Figure 29 shows : T_1 = 26°C, T_2 = 14°C and T_{ref} = 25°C. The greater the difference between T and T_{ref}, the higher the risk of error.

Figure 29 Conductivity versus temperature



Determination of the temperature coefficient (θ)

By measuring the conductivity of a sample at temperature T_1 close to T_{ref} and another temperature T_2, you can calculate the temperature coefficient by using the following equation:

$$\theta = \frac{(K_{T2} - K_{T1}) * 100}{(T_2 - T_1) * K_{T1}}$$

T_2 should be selected as a typical sample temperature and should be approximately 10°C different from T_1. The temperature coefficients of the following electrolytes generally fall into the ranges shown below:

Acids	1.0 to 1.6% / °C
Bases	1.8 to 2.2% / °C
Salts	2.2 to 3.0% / °C
Drinking water	2.0% / °C
Ultra pure water	5.2% / °C

Non-linear temperature correction

The linear temperature correction is not suitable for many aqueous liquids and the temperature dependency can only be described by non-linear functions such as the non-linear function for natural waters, i.e. for ground water, surface water, drinking water and waste water. The principle of this correction is that the conductivity measured at the sample temperature is corrected to 25°C to give K_{25}.

$K_{25} = f_{25}$ (T) * KT

f_{25} (T) is the temperature correction factor used for the conversion of conductivity values of natural water from T to 25°C.

The conductivity meter calculates f_{25} (T) from a 4-degree polynomial equation. This equation fits the conductivity variations against temperature for natural water stated in "Natural Water temperature correction (ISO/DIN 7888), The non-linear correction is defined by ISO/DIN7888 standard and is applicable for measurements between 0 and 35.9°C.

5.3 TDS measurement

TDS measurements in the pulp and paper industry measure accurately and easily the total organic and inorganic dissolved solids in water. What is TDS and how is it measured? The TDS (Total Dissolved Solids) corresponds to the total weight of cations, anions and the non-dissociated dissolved species in one litre of water.

The standard method to determine TDS is to evaporate a defined (water) sample to dryness at 180°C, under strict laboratory conditions, and carefully weigh the amount of dry solids remaining. The precision of the standard method depends on the nature of the dissolved species. The TDS method in a typical conductivity meter offers a quicker and easier way of determining TDS by measuring the conductivity, then using a conversion factor to give TDS readings.

Determination of the TDS Factor

Perform a calibration using a standard of known TDS, (STD). The TDS factor is calculated as follows:

$$\text{TDS factor} = \frac{\text{TDS(STD)}}{\text{K}_{18}\text{(STD)}}$$

TDS(STD) is expressed in mg/L.

K_{18}(STD) = Conductivity of the standard corrected to 18°C (in µS/cm).

The conductivity of the standard measured is corrected to 18°C using the corresponding temperature correction table.

For "normal" water, the TDS factor calculated should be within 0.50 to 0.70. The TDS factor calculated by the conductivity meter also provides information about the qualitative ionic composition of the water sample. If the TDS factor is out of the 0.55 to 0.7 range, the TDS calibration should be considered as suspect and must be repeated. If a TDS factor below 0.55 is confirmed, the sample probably contains a significant concentration of a constituent that cannot be measured (e.g. ammonia or nitrite). A TDS factor above 0.8 may indicate the presence of a large amount of poorly dissociated calcium and sulphate ions.

Calculating the sample TDS

The sample conductivity is measured at the sample temperature (0 to 99°C) and corrected to 18°C. The sample TDS (SMP) is calculated from the sample conductivity corrected at 18°C, K_{18} (SMP):

TDS (SMP) (in mg/L) = TDS factor * K_{18} (SMP).

TDS values between 4 and 20000 mg/L can be displayed.

Note: *To obtain the most accurate measurements, it is recommended to perform the standard and sample measurements at the same temperature. Such TDS measurements are accurate as long as the composition of the samples varies only slightly.*

5.4 Salinity measurement

Salinity is a measurement without units corresponding to the weight of dissolved salts in seawater. The salinity is calculated from an empirical relationship between the conductivity and the salinity of a seawater sample. Oceanographic Tables and Standards endorsed by UNESCO/SCOR/ICES/IAPSO are used for the calculation. Salinity measurements are performed with no direct temperature correction. The calculation is valid for salinity values in the range 2 to 42 at a sample temperature of –2 to +35°C.

Calibration

The calibration is carried out using a standard seawater solution κ_{15} (STD) (salinity = 35, conductivity equals 42.896 mS/cm at 15°C). The conductivity of the sample is measured at the sample temperature T. The conductivity of standard seawater κ_T (STD) is calculated from the following equation:

κ_T (STD) = f (T) * κ_{15} (STD)

The conversion factor f (T) is calculated from a 4-degree polynomial formula.

Salinity of the sample

At the sample temperature T, the sample conductivity measured is κ_T (SMP). Salinity is calculated from the equation below combined with a 5-degree polynomial formula:

$R = \kappa_T$ (SMP) / κ_T (STD)

5.5 Demal solution

In 1940, Jones and Bradshaw determined the demal definition as the weight of KCl/weight of the solution. As the molar weight is redefined from time to time, there is a need to redefine the conductivity for a given molarity of KCl solution. Using a given mass in a defined mass of water means that the determined conductivity of these solutions will not change over time. Below are the mass of KCl Conductivity at 25°C per 1000 g of solution for three demal solutions:

1 D	71.1352 g	111.3 mS/cm
0.1 D	7.4191 g	12.85 mS/cm
0.01 D	0.745263 g	1408 µS/cm

The conductivity of the demineralised water used must not exceed 2 µS/cm. Correction for air buoyancy must be applied to the weighing. Reference for the preparation of standards: *OIML "The International Organisation of Legal Metrology" Recommendation No. 56, June 1980*.

Certified conductivity standard solutions

Type	Value[5]	Quantity	Part. No.
KCl 1 D	111.3 mS/cm ±0.5% at 25°C	500 mL	S51M001
KCl 0.1 D	12.85 mS/cm ±0.35% at 25°C	500 mL	S51M002
KCl 0.01 D	1408 µS/cm ±0.5% at 25°C	500 mL	S51M003
NaCl 0.05%	1015 µS/cm ±0.5% at 25°C	500 mL	S51M004
KCl 26.6	26.6 µS/cm ±2.5% at 25°C	250 mL	S51M012

Economical KCl solutions

Type	Value	Quantity	Part. No.
KS910	0.1 M KCl (12.88 mS/cm at 25°C)	500 mL	C20C250
KS920	0.01 M KCl (1.413 mS/cm at 25°C)	500 mL	C20C270
KS930	0.001 M KCl (148 µS/cm at 25°C)	500 mL	C20C282

[5] Tolerance specified taking into account the expanded uncertainty with k=2.

Table 7 Conductivity (in mS/cm) of demal concentrations of 1 D, 0.1 D and 0.01 D KCl solutions

Temp. (°C)	KCl[2] 1 D	KCl[1] 0.1 D	KCl[1] 0.01 D
0	65.14	7.13	0.773
1	66.85	7.34	0.796
2	68.58	7.56	0.820
3	70.32	7.77	0.843
4	72.07	7.98	0.867
5	73.84	8.20	0.891
6	75.62	8.42	0.915
7	77.41	8.64	0.940
8	79.21	8.86	0.965
9	81.03	9.08	0.989
10	82.85	9.31	1.014
11	84.68	9.54	1.039
12	86.54	9.76	1.065
13	88.39	9.99	1.090
14	90.26	10.22	1.116
15	92.13	10.46	1.142
16	94.02	10.69	1.168
17	95.91	10.93	1.194
18	97.81	11.16	1.220
19	99.72	11.40	1.247
20	101.63	11.64	1.273
21	103.56	11.88	1.300
22	105.49	12.12	1.327
23	107.42	12.36	1.354
24	109.36	12.61	1.381
25	111.31	12.85	1.409
26	113.27	13.10	1.436
27	115.22	13.35	1.464
28		13.59	1.491
29		13.84	1.519
30		14.09	1.547
31		14.34	1.575
32		14.59	1.603
33		14.85	1.632
34		15.10	1.660
35		15.35	1.688
36		15.61	1.717
37		15.86	1.745
38		16.12	1.774
39		16.37	1.803
40		16.63	1.832
41		16.89	1.861
42		17.15	1.890
43		17.40	1.919
44		17.66	1.948
45		17.92	1.977
46		18.18	2.007
47		18.44	2.036
48		18.70	2.065
49		18.96	2.095
50		19.22	2.124

Table 8 Conductivity (in mS/cm) of various molar concentrations of KCl solutions

Temp. (°C)	KCl 1M	KCl 10^{-1}M	KCl 2 x 10^{-2}M	KCl 10^{-2}M
0	65.41	7.15	1.521	0.776
1	67.13	7.36	1.566	0.800
2	68.86	7.57	1.612	0.824
3	70.61	7.79	1.659	0.848
4	72.37	8.00	1.705	0.872
5	74.14	8.22	1.752	0.896
6	75.93	8.44	1.800	0.921
7	77.73	8.66	1.848	0.945
8	79.54	8.88	1.896	0.970
9	81.36	9.11	1.945	0.995
10	83.19	9.33	1.994	1.020
11	85.04	9.56	2.043	1.045
12	86.89	9.79	2.093	1.070
13	88.76	10.02	2.142	1.095
14	90.63	10.25	2.193	1.121
15	92.52	10.48	2.243	1.147
16	94.41	10.72	2.294	1.173
17	96.31	10.95	2.345	1.199
18	98.22	11.19	2.397	1.225
19	100.14	11.43	2.449	1.251
20	102.07	11.67	2.501	1.278
21	104.00	11.97	2.553	1.305
22	105.94	12.15	2.606	1.332
23	107.89	12.39	2.659	1.359
24	109.84	12.64	2.712	1.386
25	111.80	12.88	2.765	1.413
26	113.77	13.13	2.819	1.441
27	115.74	13.37	2.873	1.468
28		13.62	2.927	1.496
29		13.87	2.981	1.524
30		14.12	3.036	1.552
31		14.37	3.091	1.581
32		14.62	3.146	1.609
33		14.88	3.201	1.638
34		15.13	3.256	1.667
35		15.39	3.312	
36		15.64	3.368	

Table 9 Conductivity (in µS/cm) values of a 0.05% NaCl solution

Temp. (°C)	Conductivity	Temp (°C)	Conductivity
0	540.40	27	1056.53
1	557.73	28	1077.54
2	575.20	29	1098.67
3	592.79	30	1119.92
4	610.53	31	1141.30
5	628.40	32	1162.80
6	646.40	33	1184.41
7	664.55	34	1206.15
8	682.83	35	1228.00
9	701.26	36	1249.96
10	719.82	37	1272.03
11	738.53	38	1294.21
12	757.37	39	1316.49
13	776.36	40	1338.89
14	795.48	41	1361.38
15	814.74	42	1383.97
16	834.14	43	1406.66
17	853.68	44	1429.44
18	873.36	45	1452.32
19	893.18	46	1475.29
20	913.13	47	1498.34
21	933.22	48	1521.48
22	953.44	49	1544.71
23	973.80	50	1568.01
24	994.28		
25	1014.90		
26	1035.65		

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