Practical description of how to measure conductivity

Laboratory environment

A Guide to Conductivity Measurement

Theory and Practice of Conductivity Applications

METTLER TOLEDO

Contents

Contents

1. Introduction

Electrical conductivity has been measured in practice for more than 100 years and it is still an important and widely used analytical parameter today. The high reliability, sensitivity, fast response, and the relatively low cost of the equipment make conductivity a valuable, easy-to-use tool for quality control. Electrical conductivity is a non-specific sum parameter over all dissolved ionic species (salts, acids, bases, and some organic substances) in a solution. This means that this technique is unable to differentiate between diverse kinds of ions. The reading is proportional to the combined effect of all ions in the sample. Therefore, it is an important tool for monitoring and surveillance of a wide range of different types of water (pure water, drinking water, natural water, process water, etc.) and other solvents. It is also used to determine the concentrations of conductive chemicals.

This guide provides all the important basics that are necessary for a good understanding of conductivity measurement. Furthermore, all the important factors that influence the measurement and possible sources of errors are discussed. This booklet is not limited to theoretical aspects. It also contains a substantial practical part with step-by-step tutorials and guidelines for reliable calibration and measurements, descriptions of specific applications, and a section with answers to frequently asked questions.

The main goal of this conductivity guide is to disseminate knowledge and understanding of this analytical technique, which will lead to more accurate and reliable results.

2. Theory

Electrical conductivity is the ability of a material to carry an electrical current. The term conductivity can also be used in other contexts (e.g., thermal conductivity). For simplicity, in this guide the term "conductivity" is always used in the sense of electrical conductivity.

The transport of electricity through matter always requires the presence of charged particles. Conductors can be classified into two main groups based on the nature of the charged particle. Conductors in the first group consist of a lattice of atoms with an outer shell of electrons. The electrons in this 'electron cloud' can dissociate freely from their atom and transport electricity through the lattice and therefore also through the material. Metals, graphite, and a few other chemical compounds belong to this group.

The conductors in the second group are so-called ionic conductors. In contrast to the conductors of the first group the current flow is not caused by freely moving electrons but by ions. Thereby the charge transfer in electrolytes is always linked to the transport of matter. Conductors in the second group consist of electrically charged and moveable ions and are called electrolytes. Ionization occurs by dissolving in a polar solvent (such as water) or through melting.

**2.2 Definition of
Conductivity**

According to Ohm's law (1) the voltage (V) set up across a solution is proportional to the flowing current (I):

$$V = R \times I \qquad (1)$$

R = resistance (ohm, Ω)
V = voltage (volt, V)
I = current (ampere, A)

The resistance (R) is a constant of proportionality and can be calculated with the measured current flow if a known voltage is applied:

$$R = \frac{V}{I} \qquad (2)$$

Conductance (G) is defined as the inverse of resistance:

$$G = \frac{1}{R} \qquad (3)$$

G = conductance (siemens, S)

To measure the resistance or the conductance of a sample, a so-called measuring cell is required. The measuring cell consists of at least two poles with opposite charge. The term electrode is used as a synonym for pole and the poles together form a measuring cell. The cell and the insulating body holding it together are called the sensor.

The reading depends on the geometry of the measuring cell, which is described with the cell constant (K). This is the ratio of the distance (l) and area (A) of the poles:

$$K = \frac{l}{A} \qquad (4)$$

K = cell constant (cm^{-1})
l = distance between the electrodes (cm)
A = effective cross-sectional area of electrolyte between the electrodes electrodes (cm^2)

The conductance can be transformed into the standardized conductivity (κ), which is independent from the setup of the measuring cell. This is done by multiplying the conductance by the cell constant:

$$\kappa = G \times \frac{l}{A} = G \times K \qquad (5)$$

κ = conductivity (S/cm)

2.3 Conductivity of Solutions

Pure solvents are non-conducting and therefore have a conductivity near zero. Only dissolved solids with ionic or very polar bonds enable the solution to conduct electricity. The impact of dissolved ions is discussed in section 2.3.1. Also absolutely pure water contains some ions and therefore conducts electricity. This effect is caused by self-ionization of water and is described in section 2.3.2.

2.3.1 Dissolved Ions   The dissolving of solids and the forming of ions is called electrolytic dissociation. It is a prerequisite that electricity can be conducted in the solvent. Some examples of electrolytic dissociation are as follows:

NaCl	→	Na^+ + Cl^-
HCl	→	H^+ + Cl^-
CH_3COOH	→	CH_3COO^- + H^+

A distinction is made between strong and weak electrolytes. Strong electrolytes like sodium chloride dissociate completely to form sodium and chloride ions. In contrast, weak electrolytes like acetic acid dissociate incompletely. This means that the electrolyte solution contains ionic acetate (CH_3COO^-) and protons (H^+), and also non-ionic acetic acid (CH_3COOH).

The dissociation is strongly temperature-dependent and can be quantified with the dissociation rate or the dissociation constant. Only the dissociated, ionic parts are relevant for the conductivity.

The contribution of an ion to the conductivity depends on its concentration, its charge and its mobility. The conductivity of a sample can be expressed as a function of concentrations of dissolved ions and their electrochemical properties:

$$\kappa = \sum_i c_i Z_i \lambda_i \qquad (6)$$

c = concentration [mol/L]
Z = charge number
λ = equivalent conductance [S*cm²/mol]

The equivalent conductance is a specific attribute of every kind of ion. It depends not only on the ion type, but also on the concentration and the temperature.

Equivalent Conductance λ (25 °C, in H_2O, very high dilution)			
Cations	[S*cm²/mol]	Anions	[S*cm²/mol]
H^+	349.8	OH^-	198.6
Li^+	38.7	Cl^-	76.4
Na^+	50.1	HCO_3^-	44.5
NH_4^+	73.4	½ CO_3^{2-}	69.3
½ Mg^{2+}	53.1	NO_3^-	71.5
½ Ca^{2+}	59.5	½ SO_4^{2-}	80.0

Table 1 Equivalent conductance of different ion types

The equivalent conductance increases with the charge number and decreases with the size. The expected values can differ from the measured values, which are listed in Table 1. For example, the small lithium ion is much less conductive than the bigger ammonium ion. This is because the size of the solvated ion, and not the size of the ion, is the determining factor. A smaller, highly charged ion can attract more water molecules and build up a bigger solvation shell than a bigger and less charged ion. The very high conductance of a proton (H^+) and hydroxide (OH^-) also stands out. The transport mechanism of these two ions is not based on ionic migration. Protons are easily transferred from hydronium (H_3O^+) to surrounding H_2O or from H_2O to hydroxide (OH^-). The charge is transported mainly by the fast electron swap and not through the slower migration of the ions (see Figure 1).
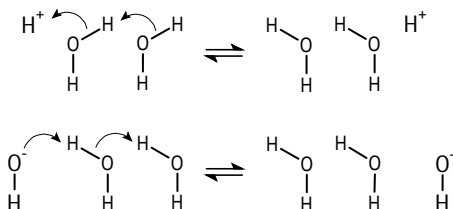

Figure 1: Charge Transport Mechanism of Protons and Hydroxides

As already mentioned, equivalent conductance is not a fixed value. With increasing concentration, the equivalent conductance decreases, because there is an increasing interference of contrariwise moving ions. In case of weak electrolytes, the equivalent conductance also decreases due to the lower dissociation rate at higher concentrations.

Temperature influences the equivalent conductance in a different manner. Higher temperature increases the motion of the particles and lowers the viscosity of the solvent. This leads to increased mobility of the ions and a higher conductivity. In the case of weak electrolytes, a higher temperature raises the dissociation rate and therefore also the conductivity.

The conductivity of a solution depends on different parameters, which interact in diverse ways. The important parameters of the conductivity can be summarized as followed:
- Type of dissolved electrolyte (ionic charge, ionic radius, ionic mobility)
- Concentration of the dissolved electrolyte
- Dissociation degree of the electrolyte
- Solvent (viscosity, permittivity)
- Temperature

2.3.2 Self-ionization of Water

Ionic parts in a solvent which increase the conductivity of a solution are not always external substances. They can also be produced by the solvent itself. An example is pure water without any impurities, which has a conductivity of 0.055 µS/cm. The conductivity is caused by hydronium (H_3O^+) and hydroxide (OH^-) which are created through the self-ionization of water. The equilibrium of this reaction is strongly on the water side and only two of a billion water molecules are in ionic configuration. The influence of the self-ionization is quite small but must be considered for pure water measurements.
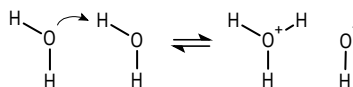

Figure 2 Self-ionization of water

2.4 Measuring Principle   Basically a conductivity measuring cell consists of an electrode pair, the so-called poles, to which a voltage is applied. The meter measures the flowing current and calculates the conductivity (see section 2.2). This is a very simplified way to explain the measuring principle. In reality, there are some important aspects, which must be considered.
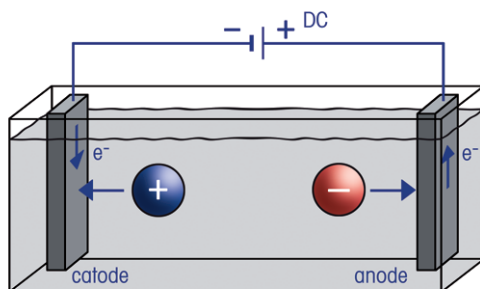
Figure 3 Schematic set-up of a conductivity measuring cell

When a direct current (DC) is applied to the electrodes, the positively charged ions (cations) migrate to the negatively charged electrode (cathode). Analogous to this, the negatively charged ions (anions) move in the inverse direction to the positively charged (anode) (see Figure 3). This can lead to an accumulation of ions near the electrode surface and to chemical reactions. This electrolysis affects the composition of the solution and therefore also the conductivity. To prevent the undesirable electrolysis reactions, alternating current (AC) is used for the conductivity measurement. With the alternating current the ions do not migrate in one direction, they oscillate with the rhythm of the applied frequency about their positions (see Figure 4).

Figure 4: Different migration of ions when DC or AC is applied to the measuring cell

Even when using AC the accumulation of ions is not fully eliminated. All effects which occur at the boundary surface of the sensor and the solution when a current is applied are summarized as polarization. The main cause is the formation of a double layer that affects the mobility 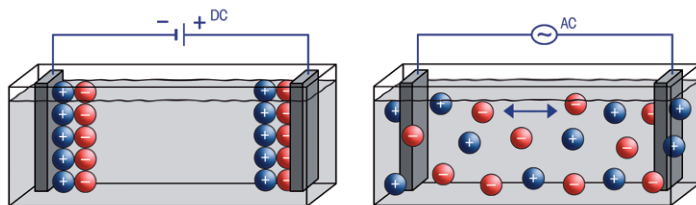of the ions. This layer has the same effect as contamination of the electrode surface and causes an additional resistance.

Polarization effects negatively influence the measurement of samples with middle to high electrolyte concentration and limit the linearity at the upper end of the scale (see Figure 5). Polarization effects can be reduced or prevented by:

- Adjusting the measuring frequency: The higher the measuring frequency, the shorter the time for the ions to accumulate at an electrode and to build up a double layer. Using a high measuring frequency minimizes the influence of polarization effects.
- Optimizing the electrode surface: By increasing the surface area of the electrode, the current density is reduced and therefore also the polarization effects (see section 2.5.3).
- Using a 4-pole conductivity cell: This kind of conductivity cell is not influenced by polarization effects (see section 2.5.2)
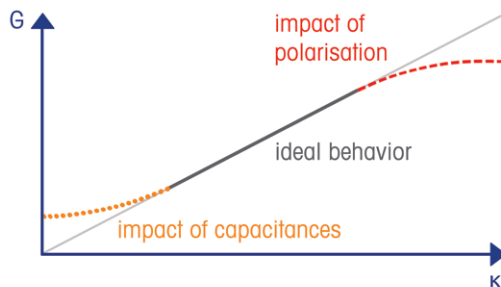
Figure 5: Negative impact of polarization and capacitances on the conductivity reading

The linearity at the other end of the scale is limited by the impact of capacitances (see Figure 5). Two electrodes in a non-conductive medium behave like a capacitor. When a DC is applied to these electrodes, no electricity can flow. The capacitive resistance is infinitely high and the conductance is zero. However, when an AC is applied to the electrodes,

the capacitive resistance drops and the conductance rises corresponding-ly. The influence of capacitances can be reduced or prevented by:

- Adjusting the measuring frequency: The lower the measuring frequen-cy, the lower the impact of the capacitances.
- Using a conductivity cell with low capacitance: The smaller the electrode's area (A) and the bigger the distance (l) between the elec-trodes, the lower the capacitance. However, this is not really an option because for measurements in a low conductivity area, cells with a low cell constant (large electrode area and small distance between the electrodes) are required. In some situations, the ca- pacitance of the cable between the electrodes and the measuring circuit may be more significant and should be minimized and/or compensated by the equipment design.

The optimal measuring frequency depends on the measuring range. Therefore, the frequency has to be adapted to the conductivity of the sample. In general, low frequencies are applied at low conductivities, where polarization effects are insignificant. High frequencies are applied at high conductivities enabling the polarization effects to be reduced. State of the art conductivity meters adjust the measuring frequency automatically. The algorithm used for the adjustment of the measuring frequency varies between manufacturers of conductivity meters.

2.5 Conductivity Sensor

Given the diversity of the applications, it is not surprising that there is no single measurement technology which is ideal for every situation. The following three technologies are established on the market:

- 2-pole conductivity cell
- 4-pole conductivity cell
- Inductive conductivity measuring cell

The inductive measuring cells are mainly used for inline measurement for process control in industrial plants. For that reason only the 2- and 4-pole conductivity cells are discussed in the following sections.

2.5.1 2-pole Conductivity Cell

Classical 2-pole conductivity cells consist of two plates. Normally, the plates are surrounded by an outer tube which protects them from mechanical damage and reduces the errors caused by field effects (see Figure 6). There are also other designs of 2-pole cells. Another

widely used construction type is a pin which is encircled by the second electrode (see Figure 6). These sensors are manufactured from robust materials such as stainless steel or titanium and are much less susceptible to mechanical damage. The easy setup of the 2-pole cell allows miniaturized measuring cells to be constructed. These micro sensors also enable measurement of small amounts of sample.

Figure 6: Schematics of a 2-pole conductivity cell

The strength of the 2-pole conductivity cell is measuring low conductivity with high accuracy. A typical measuring range goes from 0.001 µS/cm up to 1000 µS/cm. The main applications of a 2-pole cell are the conductivity measurement of pure water, highly diluted aqueous solutions, and non-aqueous solutions.

2.5.2 4-pole Conductivity Cell

This further development of the conductivity cell works with an additional electrode pair (see Figure 7). There are different layouts of 4-pole cell but the functional principle is always the same:
• The outer poles are the current poles to which an AC is applied. They are driven in the same manner as the 2-pole sensor. The inner measuring poles are placed within the electric field of the current poles and measure the voltage by using a high impedance amplifier.

The current flowing through the outer poles and the solution can be accurately measured by the circuit. If the voltage across the inner poles and the current are known, the resistance and the conductance can be calculated. To obtain the conductivity, the conductance must be multiplied by the cell constant of the inner poles (see section 2.2).

The advantage of the 4-pole sensor lies in the fact that there is very little current flowing in the inner poles where the measurement is taken.

Thereby no polarization effects occur which influence the measurement. The 4-pole conductivity cell is also less sensitive to measuring errors through fouling.
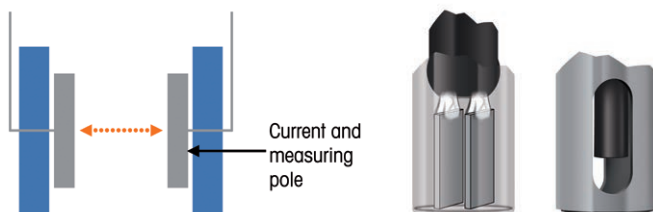

Current pole   Measuring pole
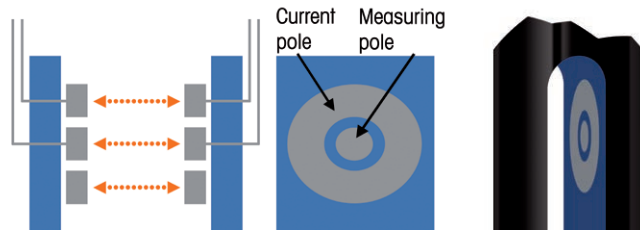
Figure 7: Schematics of a 4-pole conductivity cell

The strength of a 4-pole conductivity cell is measuring conductivity over a wide measuring range from 10 µS/cm up to 1000 mS/cm with excellent linearity. The main applications of this sensor type are measurements over expanded midrange conductivity as found in seawater, wastewater or diluted acids or bases.

2-pole Cell	4-pole Cell
• High accuracy at low conductivities • Easy setup of the cell allows a miniaturized cell to be constructed to also measure small sample amounts.	• Polarization effects do not influence the measurement of high conductivity samples, therefore it is suitable for high conductivity measurements • Good linearity over a very wide conductivity range (several decades) • Less influenced by surface contamination

Table 2 : Advantages of 2-pole and 4-pole cell

2.5.3 Material   Different materials are used to build conductivity cells. Platinum, platinized platinum, graphite, stainless steel, and titanium are qualified materials for the electrodes, while epoxy and glass are often used as shaft material. With steel and titanium, it is also possible to produce the electrodes and shaft in one piece.

Important characteristics of the materials used are:
• Chemical resistance
• Mechanical resistance
• Polarization resistance
• Carry-over effect

Chemical reactions between the sensor material (especially the electrodes) and the sample are highly undesirable because this leads to incorrect measurements and to a permanent change of the cell. The cell can also be destroyed by mechanical influences. Electrodes which are built from a material with a low mechanical strength like platinum or graphite are normally surrounded with a more robust material which makes the electrode less sensitive to mechanical damage.

The surface texture of the electrode has an influence on the polarization resistance. Porous or roughened surfaces have a lower interface resistance and therefore a reduced polarization effect. Uncoated platinum electrodes have very high resistance; electrodes made of platinized platinum have the lowest.

Porous layers such as platinized platinum or graphite can adsorb some parts of the sample, which leads to a carry-over effect and a longer response time if solutions with different concentrations are measured. These effects are contrary to the polarization resistance of the electrode material. Depending on the requirements, an electrode material with a low polarization resistance, large carry-over effect and longer response time or an electrode material with a high polarization resistance, a small carry-over effect and short response time can be chosen.

2.5.4 Selecting the Right Sensor

Choosing the right conductivity sensor is a decisive factor in obtaining accurate and reliable results. As shown in the previous sections, the different construction types and materials used lead to sensors with a variety of strengths and weaknesses. Therefore, it does not make sense to speak of good or bad sensors. The right sensor is the one which fits the needs of the application best.

A basic requirement is that no chemical reactions occur between the sample and the sensor. For chemically reactive samples, glass and

platinum are often the best choice because they have the best chemical resistance of all commonly used cell materials. For field application and also a lot of laboratory applications, the mechanical stability of the sensor is a more important factor. A conductivity sensor with an epoxy body and graphite electrodes is often used, as this has been shown to be extremely durable and it also has good chemical resistance. For low reactive aqueous solutions and organic solvents, the use of cells made of steel or titanium is often a good alternative.

The next point which should be considered in order to select an optimal sensor is the cell constant and the construction type. A suitable cell constant correlates with the conductivity of the sample. The lower the expected conductivity of the sample, the smaller the cell constant of the sensor should be. Figure 8 shows a set of samples and the range of recommended cell constants which should be used for the measurement. To make a decision between a 2-pole cell and a 4-pole cell the following rough-and-ready rule can be used: For low conductivity measurements, a 2-pole cell should be used. For mid to high conductivity measurements a 4-pole cell is preferred, especially for measurements over a wide conductivity range.

Sometimes standards or norms contain requirements concerning the conductivity sensor. If a conductivity measurement is performed according to such a standard, then the chosen senor must completely fulfill all the described requirements.
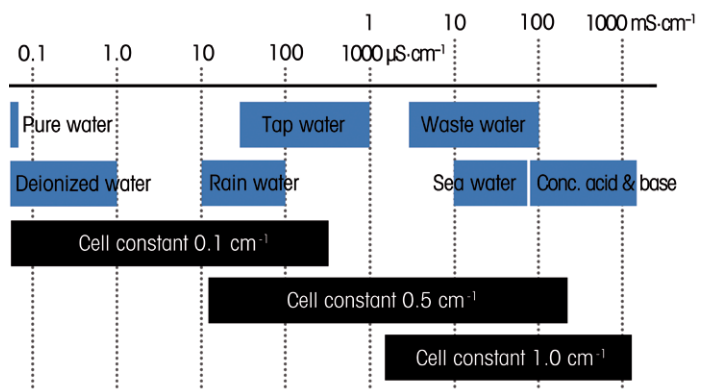
Figure 8: Set of samples and recommended cell constants

Furthermore, there are some special sensors with a very low cell constant for a high precision measurement or with a small shaft diameter which allow conductivity measurements in small sample vessels. Table 3 gives an overview over the METTLER TOLEDO laboratory conductivity sensor portfolio. For further information, please check: **www.electrodes.net**

		Configuration	Cell Constant	Measuring Range	Sensor Name
Generalist		4 platinum pole glass shaft	0.80 cm^{-1}	0.01-500 mS/cm	InLab® 710
		4 graphite pole epoxy shaft	0.57 cm-1	0.01-1000 mS/cm	InLab® 731 InLab® 738
Specialist Specialist	**Pure Water and high Precision**	2 titanium pole titanium shaft	0.01 cm^{-1}	0.0001-1000 µS/cm	InLab® Trace
		2 steel pole steel shaft	0.105 cm^{-1}	0.001-500 µS/cm	InLab® 741 InLab® 742
		2 platinum pole glass shaft	0.06 cm^{-1}	0.1-500 µS/cm	InLab® 720
	Micro	2 platinum pole glass shaft	1.0 cm^{-1}	0.01-100 mS/cm	InLab® 751-4mm
		2 platinum pole glass shaft	1.0 cm^{-1}	0.01-112 mS/cm	InLab® 752-6mm
	Bio-ethanol	2 platinum pole glass shaft	0.1 cm^{-1}	0.1-500 µS/cm	InLab® 725

Table 3: Conductivity sensor portfolio of METTLER TOLEDO

2.6 Temperature Effects

Conductivity measurements are strongly temperature-dependent. As the temperature of a sample increases, the viscosity of the sample decreases which leads to increased mobility of the ions. Therefore, the observed conductivity of the sample also increases even though the ion concentration stays constant (see section 2.3.1). Every conductivity result must be specified with a temperature, otherwise it is worthless. For example, the conductivity of 0.01 molar potassium chloride at 20 °C is 1278 µS/cm but at 25 °C it is 1413 µS/cm. This means that it does not make sense to compare measurements performed in the same sample but at different temperatures. For this reason, the readings refer to a reference temperature, which makes the results comparable. The reference temperature is usually 25 °C, sometimes 20 °C is also used.

Not all temperature correction is the same
Temperature correction for conductivity measurements should not be confused with temperature compensation in pH measurements. In a conductivity measurement, the displayed conductivity value is the calculated conductivity at the desired reference temperature. So the temperature effect of the sample is corrected. With pH measurement, the pH at the actual temperature (e.g., 27 °C) is displayed. Here temperature compensation involves adapting the slope of the pH electrode to the actual temperature being measured. In this case, the temperature effect of the electrode is corrected.

It is inefficient to adjust the temperature of all samples to the reference temperature with an expensive temperature control system. Hence in practice, the conductivity meter measures the conductivity at the current temperature (e.g., 27 °C) and converts the measurement value with user selectable temperature correction algorithms to the desired reference temperature. As conductivity measurement and temperature measurement are connected, all METTLER TOLEDO conductivity sensors have an integrated temperature sensor.

As temperature plays a key role in determining the conductivity measured, it is important to know the temperature dependence (= change in

the conductivity per °C) of the measured sample. The temperature dependence of every sample is different and can vary strongly at different temperatures and different ion concentrations.

To simplify the complex relationship between conductivity, temperature and ion concentration, different temperature correction methods have been developed to accommodate users:
- Linear
- Non-linear
- Pure water
- None

Depending on the sample in which conductivity is measured, one of the methods listed above is chosen. For medium to strongly conducting solutions, a linear temperature correction mode is used. Natural water has a higher temperature dependence and the use of the non-linear correction is recommended. For pure water, which has the highest temperature dependence, METTLER TOLEDO has specially developed a unique and very accurate pure water algorithm which is based on the extensive knowledge and experience of THORNTON, a leading company in ultrapure water analytics. These temperature correction methods are described in the following sections.

2.6.1 Linear Temperature Correction

For the temperature correction of medium and highly conductive solutions, the following linear equation is often used:

$$\kappa_{Tref} = \frac{\kappa_T}{1 + \dfrac{\alpha}{100\%} \times (T - T_{ref})} \qquad (7)$$

It involves the temperature coefficient α which expresses the conductivity variation in %/ °C. The α-values are listed in literature or are determined experimentally. For empirical determination two conductivity measurements are performed, one at the reference temperature, a second at the sample temperature. Then the α-value can be calculated according to equation (8):

$$\alpha = \frac{(\kappa_{T2} - \kappa_{T1}) \times 100\%}{(T_2 - T_1) \times \kappa_{T1}} \qquad (8)$$

Example: Determination of the temperature coefficient α
The conductivity of the sample is measured without temperature compensation ($\alpha = 0$) at two different temperatures, T1: chosen reference temperature, T2: actual temperature of the sample. A 0.01 molar KCl solution is used as an example. Upon measuring, the following conductivity values are obtained:
Measurement 1: 1413 μS/cm at 25 °C
Measurement 2: 1698 μS/cm at 35 °C

$$\alpha = \frac{(1698\ \mu S/cm - 1413\ \mu S/cm) \times 100\%}{(35\ °C - 25\ °C) \times 1413\ \mu S/cm} = \underline{\underline{2.017\ \%/°C}}$$

These values are then entered in equation (8) to calculate the temperature coefficient.

Example: Linear temperature correction
The KCl solution of the previous example is measured again and following result is obtained:
Measurement 3: 1996 μS/cm at 45 °C

This value is corrected to the reference temperature (25 °C) by using equation (7) and the calculated α-value:

$$\kappa_{Tref} = \frac{1996\ \mu S/cm}{1 \times \dfrac{2.017\ \%/°C}{100\%} \times (45°C - 25°C)} = \underline{\underline{1422\ \mu S/cm}}$$

The corrected value of 1422 μS/cm is slightly different from the true value of 1413 μS/cm. This error is caused by the fact that the α-value for an electrolyte is not constant. It depends on the concentration of an electrolyte and the temperature.

	α [%/C]		
Temp [°C]	**0.001 mol/L KCl**	**0.01 mol/L KCl**	**0.1 mol/L KCl**
0	1.81	1.81	1.78
15	1.92	1.91	1.88
35	2.04	2.02	2.03
45	2.08	2.06	2.02
100	2.27	2.22	2.14

Table 4: Dependency of the α-value of KCl solutions on the concentration and temperature for $T_{ref} = 25$ °C.

As Table 4 shows, the α-value varies at different temperatures. There-fore, the α-value should be determined in a similar temperature range as the sample temperature. For measurements over a wide temperature range, the typical approach is to use an average coefficient. One option for determining the average α-value is to use the least square method to fit the straight line to the data.

The typical temperature coefficients of different samples are given in Table 5.

Sample	**Temperature Coefficient α (%/°C)**
Acids	1.0 – 1.6
Bases	1.8 – 2.2
Salts	2.2 – 3.0
Drinking water	2.0
Pure water	2.3 – 7.4

Table 5: Typical temperature coefficients of various substance groups

2.6.2 Non-linear Correction

For aqueous samples, non-linear functions are more suitable for tem-perature correction than the linear temperature correction mode. The most important is a non-linear function for natural waters such as ground water, surface water, drinking water, and waste water.

The described correction mode is defined in the ISO/DIN 7888 standard. The measured conductivity at the sample temperature (κ_T) is corrected to 25 °C to get $\kappa_{25\,°C}$ by using the following equation:

$$\kappa_{25°C} = f_{25}(T) \times \kappa_T \qquad (9)$$

$f_{25}(T)$ is the temperature correction factor which is used for the adjustment of the conductivity values of natural waters from the sample temperature (T) to the reference temperature (25 °C). The non-linear correction mode works in a temperature range from 0 °C to 35.9 °C. All used correction factors are stored in the METTLER TOLEDO conductivity meters and are listed in Appendix 6.1. To obtain the results for a reference temperature of 20 °C, the corrected result must be divided by a factor of 1.116:

$$\kappa_{20°C} = \frac{\kappa_{25°C}}{1.116} \qquad (10)$$

2.6.3 Pure Water
As shown in Table 5, the temperature coefficient α of pure water varies strongly. The main reason for this is that the self-ionization of the water molecules is more temperature dependent than the conductivity which is caused by other ions. Given that in pure water samples nearly no contaminant ions exist, the α-value is mainly influenced by the self-ionization of the water. In other samples, the concentration of the contaminant ions is many times higher than the concentration of the ions from the self-ionization of the water. Thereby the high temperature dependency is suppressed and the α-value becomes more linear.

An exact temperature correction in pure water is quite challenging. It can be assumed that the conductivity is the sum of the water (self-ionization) and the conductivity caused by the ionic impurities. Figure 9 shows the schematic functionality of how the temperature compensation of pure water works. Point 1 is the measured conductivity at 80 °C of the sample with a sodium chloride concentration of 100 µg/L. The conductivity meter subtracts the intrinsic conductivity of the water, which is well known, from this value and the conductivity originating from the sodium chloride is obtained (Point 2). In a next step, the conductivity meter converts the conductivity of sodium chloride at 80 °C into the conductivity of sodium chloride at 25 °C (Point 3).

To finish, the meter adds the conductivity of water at 25 °C and the conductivity of sodium chloride at 25 °C to get the corrected conductivity of the sample (Point 4).
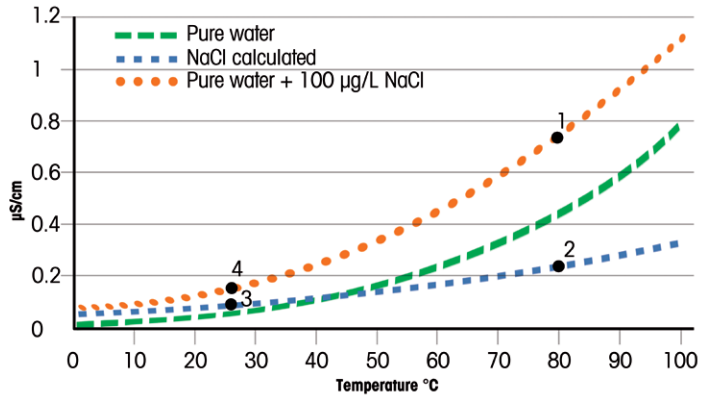
Figure 9: Schematic functionality of the temperature correction of pure water with a sodium chloride impurity of 100 µg/L.

Due to the fact that there is only one kind of impurity in the example, the correction shown looks quite easy. In reality the situation is much more complex because there are many different impurities in different concentrations and each with its own temperature behavior. For an accurate temperature correction in pure water, METTLER TOLEDO has implemented a unique temperature correction mode in the premium conductivity meters, which is based on an algorithm developed by THORNTON, a leading company in pure water analytics with many years of proven experience. This so-called pure water mode compensates conductivity values in the range from 0.005 to 5.00 µS/cm and a temperature range from 0 °C to 50 °C to the reference temperature of 25 °C. When the conductivity reading exceeds 5.00 µS/cm in the pure water mode, the algorithm blends into a linear compensation mode with $\alpha = 2.00\%/°C$.

2.6.4 None Every temperature corrected result is burdened with possible errors caused by the temperature correction. The better the temperature correction mode, the smaller the error. The only way eliminate these errors is not to use any temperature correction mode at all. Instead, the tempera-

ture of the sample must be adjusted to the required reference temperature, which needs additional equipment and time.

There are some standards, such as USP <645>, which prohibit the use of temperature correction methods and stipulate uncorrected conductivity measurements instead. For measurements corresponding to these standards, the temperature correction mode has to be switched off. In the case of conductivity meters which only come with a linear temperature correction mode, it is often not possible to switch this off. However, using an α-value of 0%/°C, the linear temperature mode behaves as if it is switched off.

Table 6 provides an overview of METTLER TOLEDO's laboratory conductivity meters and the supported temperature correction modes.

	None	Linear	Non-linear	Pure water
SevenExcellence S700, S470,…				
SevenCompact S230	✓	✓	✓	✓
SevenGo Duo pro SG78				
SevenGo pro SG7	✓	✓	✓	
FiveEasy FE30, FEP30				
FiveGo FG3	✓	✓		

Table 6: Supported temperature correction mode of METTLER TOLEDO's conductivity meters.

2.7 Interferences with the Conductivity Measurement

Conductivity measurements can be affected by several factors. The four most important ones are discussed in this chapter.

2.7.1 Dissolution of Gaseous Substances

Besides solid and liquid substances, gaseous substances can also be dissolved in the sample and form ionic species which influence the conductivity measurement. Carbon dioxide (CO_2) is the only gas in normal ambient air that can have a significant influence on the conductivity

measurement. In water, dissolved carbon dioxide forms carbonic acid (H_2CO_3) which dissociates in a first step to hydrogen carbonate (HCO_3^{2-}) and in a second step to carbonate (CO_3^{2-}) (Figure 10). The carbon dioxide reaction equilibrium is strongly on CO_2-side and only around 0.2% of the molecules react to carbonic acid. Under standard conditions, the impact of the carbon dioxide can increase the conductivity reading by approximately 1 µS/cm in total.
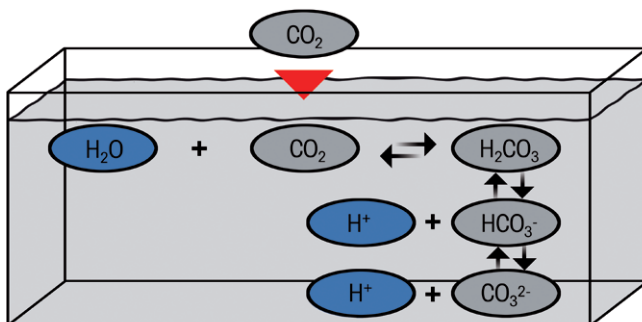
Figure 10 Dissociation of carbon dioxide in water

At low conductivity measurements (<10 µS/cm) carbon dioxide can strongly influence the result. For reliable results, it is important to prevent the sample from coming into contact with air. This can be achieved by the use of a flow cell or the use of chemically inert gases, such as nitrogen or helium, to blanket the sample surface (see section 3.4).

2.7.2 Air Bubbles Even a tiny air bubble which adheres to the electrode surface increases the resistance of the sample within the cell and lowers the conductivity reading. Unstable signals can be an indication of air bubbles in the measuring cell. Before every measurement (and also every calibration and verification) it should be ensured that there are no air bubbles inside the cell. Remove bubbles by tapping the sensor or alternately raising and lowering the sensor to flush them out.

Dissolved air in cold water becomes less soluble when it gets warmer. This may produce bubbles within a measuring cell and can cause the problems mentioned above.

2.7.3 Coating of the Electrode Surface

Undissolved or slowly precipitating solids in the sample can build up a coating on the electrodes of the conductivity cell. This layer can cause poor cell response and erroneous readings. A well-known example is the bio-fouling of the cell. Correct cleaning prevents this kind of problem (see section 3.5).

2.7.4 Geometry Related Errors – Field Effects

The active part of the conductivity measurement within the electrolyte in and around the cell is described by field lines. Any interference with these field lines affects the conductivity measurement. A main source of interference is the wall or the bottom of the sample vessel if the sensor is placed too close to them. The ideal placement of sensor is centrally and 25 mm above the bottom of the container. Some conductivity cells are designed to minimize this negative effect. If the entire field is contained within the measuring cell, then there can be no blockage of the field lines and therefore no errors from this source.
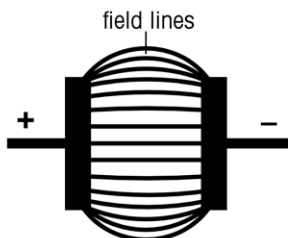
field lines

Figure 11 Field lines of a 2-pole-cell

3   Code of Best Practice

Conductivity is measured in a wide range of different applications. The second part of this guide provides a lot of application know-how. First, a general operation mode for calibration, verification, and conductivity measurements including the special case of low conductivity measurement is described. Furthermore, the maintenance and storage of conductivity sensors is discussed. In the following chapters, the most important applications are described in detail.

All METTLER TOLEDO conductivity meters provide further measurement modes beside conductivity measurements. Table 7 gives an overview of the measurements modes which are supported by a meter. TDS, salinity, conductivity ash, and bioethanol measurements are described in detail in section 3.6.

	Conduc-tivity (µS/cm, mS/cm)	TDS (mg/L, g/L)	Salinity (psu)	Resis-tivity (MΩ·cm)	Conduc-tivity Ash (%)	Bio-ethanol (µS/m, mS/m)
SevenExcellence SevenCompact	✓	✓	✓	✓	✓	✓
SevenGo Duo pro SevenGo pro	✓	✓	✓	✓		
FiveEasy FiveGo	✓	✓	✓			

Table 7: Supported temperature correction mode of METTLER TOLEDO's conductivity meters.

3.1 Calibration and Verification

Before a conductivity measurement can be performed, the cell constant must be known or determined. This factor is required to convert the measured conductance into the conductivity (see section 2.2). Every conductivity cell has its own cell constant. METTLER TOLEDO uses two different kinds of cell constants: Nominal and certified cell constants. The nominal cell constant helps you to choose the right sensor. Due to the production process, the cell constants have a wide tolerance and the nominal cell constant has an accuracy of only ± 20%. Before a measurement, the exact cell constant has to be determined by so-called calibration. The measurement of a standard with a known conductivity value is a reliable way to determine the cell constant of a sensor (see equation 5).

Certified cell constants are determined after the manufacturing process directly at the plant. With a maximum uncertainty of ± 2%, they are accurate enough and can be used for measurement. The exact cell constant is listed in the quality certificate and is printed on the cable of the sensor. For ISM sensors, the cell constant is also stored on the sensor chip.

METTLER TOLEDO's InLab 73x, as well the InLab 710, and InLab 720 conductivity sensors are delivered with a nominal cell constant only. For these sensors, the cell constant must be determined prior to a conductivity measurement by performing a calibration. The InLab 74x and InLab Trace are delivered with a certified cell constant that was determined after manufacturing by calibration with traceability according to ASTM and NIST.

The cell constant can change with time. Contamination and deposits or physical or chemical modification of the measuring cell affect the cell constant. It is advisable to perform a verification to check if the cell constant is still valid prior to a conductivity measurement. For this purpose, the conductivity of a standard solution is measured. The reading must be within the predefined limits (e.g., ± 2% of the standard solution).

In summary, sensors with a nominal cell constant must be calibrated before the first use. For sensors with a known cell constant, verification is adequate. If the measured value in the verification is outside the limit, the sensor must be re-calibrated.

Conductivity standards

Conductivity standard solutions provide an easy way to calibrate or verify the cell constant. Note that conductivity standard solutions are more vulnerable to contamination and dilution than pH buffer solutions. The buffering capacity of pH standards tends to resist pH change and makes them much more forgiving of mishandling. Conductivity standards on the other hand are directly affected by dilution, contamination or the influence of CO_2 when in contact with air; their values change readily, especially the lower conductivity standards. Helpful usage tips for the standard solution handling are given in section 3.2.

Furthermore, a slight change in temperature may have a big impact on the accuracy. During conductivity sensor calibration or verification, special care should be taken to establish accurate measuring conditions.

The calibration or verification should be performed under the same conditions as the conductivity measurement (e.g., stirred/not stirred, flow cell) with the conductivity standard in a similar concentration range. The following procedure is recommended:

Preparation
1. Select the correct conductivity cell (see section 2.5.4)
2. Connect the sensor to the conductivity meter

Calibration/Verification Procedure
IMPORTANT:
Always use fresh standard solutions.
1. Thoroughly rinse the sensor and the container that will hold the standard solution several times with deionized water to remove any contamination and then shake off any leftover droplets.
2. Rinse the sensor and container with a small amount of the standard solution and discard it.
3. Fill the container with fresh standard solution.

4. Immerse the sensor in the standard solution. The measuring cell and the vent holes in the side of some sensors must be completely covered.
5. Eliminate all air bubbles by agitating or tapping the sensor.
6. **Calibration:** Perform a sensor calibration according to the instruction manual. The meter calculates the new cell constant automatically.
   Verification: There are two different ways to perform the verification. One way is to use no temperature correction mode and compare the reading with the value of the standard solution at the measured temperature, which is listed on the bottle or the quality certificate of the standard solution. The other way is to use a linear temperature mode. The required α-values of the standard solutions are listed in Appendix 6.2. The reading can be directly compared with the value of the certified standard solution.

   Stirring can help to get the result faster but must not generate any bubbles.

7. Dispose of all used standard solutions. Never pour standards back into the original bottle.

3.2 Standard Solutions Usage Tips

METTLER TOLEDO is committed to providing a complete range of standard solutions and guarantees the quality of unopened bottles for a period of two years from the date of manufacture. The expiration date is located on the product label following "Lot, Exp.:" or "Unopened storage until:". The warranty period covers up to the last day of the month stated. The quality of the standard solution is not guaranteed beyond the expiration date under any circumstances. A detailed test certificate may be obtained by visiting www.mt.com/buffer and entering the lot number found on the bottle.

Due to unforeseeable circumstances beyond our control, the only guarantee offered is for the quality of the standard solution in a previously unopened bottle that is fully within the two-year period from its date of manufacture. The following tips are a guideline to optimize the usefulness of a standard solution while in use in the laboratory. Following these simple tips helps to ensure that measurements will be precise and accurate when the standard solution is used.

The prerequisites are a properly maintained cell, cable, and meter.

- Standard solutions beyond their expiration date or with expected contamination should never be used.
- Standard solutions should be replaced with a new bottle after they have reached the expiration date.
- The date of the first opening should be marked on the bottle of the standard solution.
- Standard solutions should never be diluted or mixed with standard solutions from different manufacturers.
- Dispensed standard solution should be use promptly and never be poured back into the original bottle.
- Standard bottles should always be kept sealed to ensure that no contaminants can enter the solution bottle.
- Standard solutions should be stored at normal ambient temperatures and protected from direct sunlight.

3.3 Measurement Before a conductivity measurement can be performed, the cell constant must be known (see section 3.1). If a calibration was carried out prior to the measurement, then the value of the cell constant is already stored in the meter. ISM sensors store the cell constant directly on the sensor chip. The cell constant is directly transferred to the meter, when the ISM sensor is connected. If a non-ISM sensor is used, the cell constant must be entered manually into the meter.

Measurement Procedure

1. Thoroughly rinse the sensor and the container that will hold the sample solution several times with deionized water to remove any contamination and then shake off any leftover droplets.
2. Rinse the sensor and container with the sample two or three times and discard the used sample.
3. Fill the container with fresh sample solution.
4. Immerse the sensor in the sample. The measuring cell and the vent holes in the side of some sensors must be completely covered.
5. Eliminate all air bubbles from that area by agitating or tapping the sensor.
6. Perform a conductivity measurement according to the instruction manual. Stirring can help to get the result faster but must not generate any bubbles. If a temperature compensation mode is active, the

conductivity reading will be directly corrected to the preset reference temperature.

3.4 Low Conductivity Measurements

Measurements of samples with conductivity lower than 10 µS/cm need a special procedure. As mentioned in section 2.7.1 carbon dioxide from the atmosphere greatly influences the conductivity measurement at this low level. To get reliable conductivity results below 10 µS/cm, the following two approaches are recommended:

Inert gas:
The sample is protected by an inert gaseous layer of nitrogen or helium to prevent contamination from the atmosphere. This allows the use of normal dip cells to measure samples in the range of 1 to 10 µS/cm.

Flow cell:
A closed system like a flow cell enables the influence of carbon dioxide to be fully excluded. This is the best practice to measure samples with a conductivity lower than 10 µS/cm. However, samples with higher conductivity may also be measured in this manner.

For non-pressurized samples, flow cells can be used with a peristaltic or a membrane pump, given that they are completely sealed systems. With other types of pumps, the sample or standard comes into contact with the pump which can lead to contamination and erroneous readings. For sample and standards, the flow must not introduce any air bubbles.
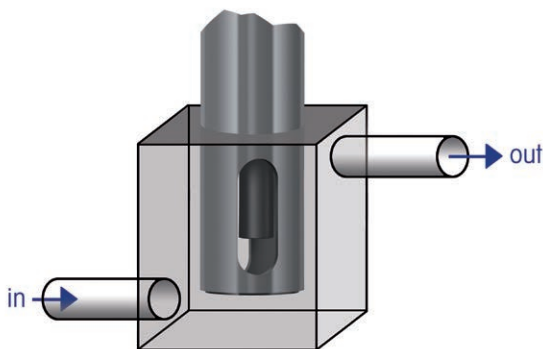

Figure 12: Schematic of a flow cell

Contamination from one sample to another or from calibration standard to sample can cause incorrect readings. Rinsing between each measurement helps to avoid this contamination. To decrease the volume of sample or standard solution that is being wasted for rinsing purposes, the cell and tubes can be rinsed with deionized water in between. The following steps are recommended:

1. Rinse thoroughly with deionized water (high flow rate recommended)
2. Rinse with sample or standard
3. Measure sample or calibrate with standard
4. Start at point 1 again

METTLER TOLEDO offers certified standard solutions with a conductivity of 10 µS/cm and lower. These standards are only intended for checking the reading of low conductivity measurement, because they are easily affected by any mishandling. For best accuracy of low conductivity calibrations, the 84 µS/cm standard should be used. The consistent linearity of METTLER TOLEDO measuring systems between 84 µS/cm and low conductivity values provides much better accuracy than is typically obtained by using standard solutions with conductivity below 84 µS/cm.

3.5 Maintenance and Storage

Conductivity sensors do not need much maintenance; there are only a few points which must be considered. The most important point is to ensure that the cell is clean. The sensor should be rinsed with deionized water after every measurement. If the sensor has been exposed to a sample immiscible with water, it should be cleaned with a solvent miscible with water e.g., ethanol or acetone and carefully rinsed afterwards with deionized water. If there is a build-up of solids inside the measuring cell, carefully remove it with a cotton bud soaked in detergent solution, and then rinse the sensor with deionized water (Caution: Sensors with platinized poles should never be cleand mechanically, as this could damage the sensors).

Cleaned conductivity sensors should be stored as follow:
Short-term storage (< 1 day): dry or in deionized water
Long-term storage (> 1 day): dry
Ensure that the plugs are kept free of moisture and dirt.

Contrary to other electrochemical sensors like pH sensors, conductivity sensors do not age. Therefore, the lifetime of a conductivity sensor fully depends on the handling. The following three points should always be considered:

1. To prevent static damage to the meter, avoid touching the measuring cell of the sensor. Always disconnect the sensor from the meter before cleaning.
2. Do not use harsh chemicals or abrasive material for cleaning.
3. Do not use the sensor outside the recommended temperature range. Irreparable damage may occur to the sensor.

3.6 Specific Applications

3.6.1 TDS   Total Dissolved Solids (TDS) corresponds to the total weight of solids (cations, anions and undissociated dissolved substances) in one liter of water (mg/L). This parameter is often used for the analysis of water in different areas e.g., in the pulp and paper industry, cooling towers, industrial boilers, and environmental testing.

The traditional way to determine the TDS is a gravimetric method. A defined volume of a sample is evaporated under strict laboratory conditions until dry and the residue left is weighed. This is generally the best method, but very time-consuming.

Conductivity offers a quicker and easier alternative for determining the TDS. The conductivity reading can be converted to TDS by multiplying with a TDS-factor. To get reliable results two important points must be considered:

- Only solids that produce ions when dissolved in water cause conductivity. Solids that do not yield ions do not influence the conductivity, but they influence the true TDS value of a solution.This can be illustrated with two cups of coffee one with, the other without sugar. Both have a similar conductivity, but the TDS of the coffee with sugar is around 500 times higher.
- Equal weights of different ionic solids leads to different conductivity values.

Salt	Conductivity Equivalent	TDS Factor
NaCl	1mg/L TDS = 2.04 µS/cm	0.49
Na_2SO_4	1mg/L TDS = 1.49 µS/cm	0.67
$CaSO_4$	1mg/L TDS = 1.36 µS/cm	0.74
$NaHCO_3$	1mg/L TDS = 1.06 µS/cm	0.91

Table 8 Conductivity equivalent and TDS factor of different salts

Due to these two reasons, reliable TDS measurements with the conductivity meter are only possible when the main part of the dissolved solids is ionic. This applies for natural water and treated water. Furthermore, the TDS measurements are accurate as long as the composition of the samples varies only slightly.

The most challenging step for a TDS measurement with a conductivity meter is to define the TDS factor used. There are different approaches for this:
• Perform a calibration using a standard of known TDS or a sample from which the TDS was determined gravimetrically. The TDS factor is calculated as follow:

$$TDS\ factor : \frac{TDS}{\kappa_{25°C}} \qquad (11)$$

The measured conductivity (in µS/cm) is corrected to 25 °C by using a temperature correction mode.
• Assume that the conductivity is caused by a single salt. Typically, a TDS factor which is based on the conductivity equivalent of potassium chloride (KCl) or sodium chloride (NaCl) is used for the TDS calculation (see Appendix 6.3).
• The TDS factor for natural water normally lies between 0.55 and 0.70. A TDS factor of 0.65 is often used for these samples.
TDS measurements are performed in the same way as a conductivity measurement. The meter corrects the reading to the reference temperature according the selected temperature correction mode. Then the meter calculates the TDS using the following formula:

$$TDS\,(mg/L) = TDS\ factor \times \kappa_{25°C} \qquad (12)$$

The TDS factor is an additional source of error. Therefore, the error of a TDS determination is higher than that of a conductivity measurement. Typically, the error is less than 15%.

3.6.2 Concentration Measurements

In binary solutions (one electrolyte and water) conductivity can be used to measure the electrolyte concentration, because the conductivity is directly proportional to the concentration. Each electrolyte possesses a unique conductivity curve (see Figure 13). For most electrolytes, the conductivity curve reaches a maximum value, and then reverses its slope. Conductivity can be measured on the increasing or the decreasing part of the curve. Conductivity cannot be used to measure concentration in the region near the peak of the curve, since two different concentration values have the same conductivity.
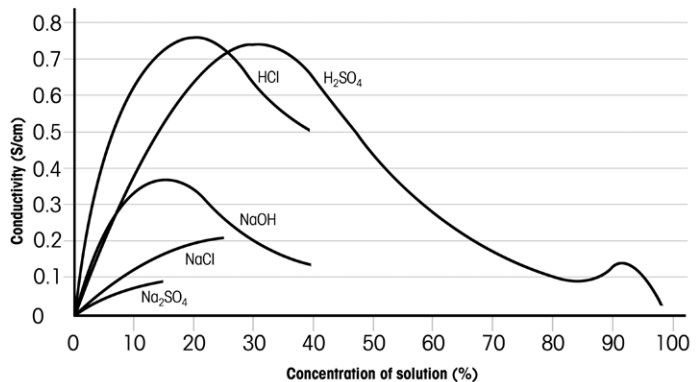
Figure 13: Conductivity versus concentration curves of different electrolytes

For concentration measurements, the conductivity of the solution as a function of the concentration of the electrolyte of interest must be known. This data can come from literature or from laboratory measurements. It is recommended to work at constant temperature for calibration and measurements because the shape of the curve changes with temperature. There must be a measurable change in conductivity over the concentration range, and the conductivity must be increasing or decreasing over the range (see Figure 14). Every measurable area requires separate determination of the slope and the intercept.
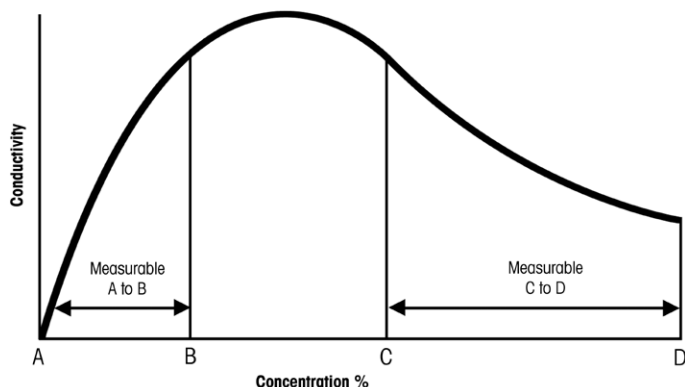
Figure 14: Conductivity versus concentration curve with measureable areas of NaOH

For concentration measurements, calibration using two or more standards of known concentration must be performed in advance. In this guide, only the two-point calibration is described. The first step is to measure the conductivity of the two standard solutions with known concentration. Then the slope (equation 13) and the intercept (equation 14) of the calibration curve are calculated using the following equations:

$$m = \frac{y_2 - y_1}{x_2 - x_1} \qquad (13)$$

$$b = y_1 - m \times x_1 \qquad (14)$$

m   slope
y_1, y_2 conductivity of standard 1 and 2
x_1, x_2 concentration of the standard 1 and 2
b   intercept

In a second step, the conductivity of the sample is measured and then the concentration is calculated using the following equation:

$$x = \frac{(y - b)}{m} \qquad (15)$$

y   conductivity of the sample
x   concentration of the sample

3.6.3 Salinity   Salinity (S) is a measurement without a unit corresponding to the weight of dissolved salts in seawater. There are different definitions of salinity. Normally the UNESCO 1978 definition is used. Even though salinity is a dimensionless number, often the unit psu (practical salinity unit) is used. The salinity is calculated from an empirical relationship between a seawater sample and KCl solution (32.4356 g/kg) at a temperature of 15 °C and standard atmospheric pressure. When the ratio of the two conductivity readings is one, then the salinity is exactly 35. In other words, 1 psu is approximately equal to the salt content of 1 g/L.

The formula is quite complex (equation 16), but all the calculations are done by the meter itself. When the salinity mode of the conductivity meter is selected, the measurements are performed as a conductivity measurement.

$$S = \sum_{j=0}^{5} a_j R_T^{j/2} - \frac{(T-15)}{1+k(T-15)} \sum_{j=0}^{5} b_j R_T^{j/2} \qquad (16)$$

$$R_T = \frac{R_{Sample}(T)}{R_{KCl}(T)}$$

$a_0 = 0.0080$	$b_0 = 0.0005$	$k = 0.00162$
$a_1 = -0.1692$	$b_1 = -0.0056$	
$a_2 = 25.3851$	$b_2 = -0.0066$	
$a_3 = 14.0941$	$b_3 = -0.0375$	
$a_4 = -7.0261$	$b_4 = 0.0636$	
$a_5 = 2.7081$	$b_5 = -0.0144$	

Sometimes the older definition, the natural sea water scale (UNESCO 1966b), is still used. The salinity S_{ppt} of a sample in ppt (parts per thousand) is calculated by using the following formula for a temperature of T = 15 °C and at standard atmospheric pressure:

$$S_{ppt} = -0.08996 + 28.2929729\,R + 12.80832\,R^2 - 10.67869\,R^3 + 5.98624\,R^4 - 1.32311\,R^5 \quad (17)$$

R   = κ_{sample}/κ with T =15 °C

κ_{sample} =   conductivity of the sample

κ =   42.914 mS/cm (Conductivity of Copenhagen Seawater Standard)

If the conductivity is not measured at 15 °C, equation 18 can be applied for 10 °C < T < 31 °C:

$$R = R_T + 10^{-5} R_T (R_T - 1)(T - 15)(96.7 - 72.0\,R_T + 37.3\,R_T^{\,2} - (0.63 + 0.21 R_T^{\,2})(T - 15)) \quad (18)$$

RT   = $\kappa_{sample}\,(T) / \kappa\,(T)$

3.6.4 Ultrapure Water   Water is the most frequently used raw material for the production of pharmaceuticals. For the use of water, pharmacopoeias prescribe several quality specifications, with which pharmaceutical manufacturers must demonstrate compliance. Conductivity is one of the main parameters, which allows the monitoring of all ionic impurities. Depending on the country and required water quality, the specifications vary slightly.

The most important pharmacopoeias are:

United States Pharmacopoeia: USP
European Pharmacopoeia: EP
Japanese Pharmacopoeia: JP
Chinese Pharmacopeia: ChP
Indian Pharmacopoeia: IP

Over the years, harmonization of specifications have been partly adopted, but there are still differences. Table 10 shows an overview of the conductivity specifications for two different water qualities.

Conductivity (µS/cm at 25 °C)	USP	EP	JP	ChP	IP
Purified Water	1.3 µS/cm (3 stage)	5.1 µS/cm (1 stage)	on-line: 1.3 µS/cm off-line: 2.1 µS/cm	5.1 µS/cm (1 stage)	1.3 µS/cm (3 stage)
Water for Injection	1.3 µS/cm (3 stage)	1.3 µS/cm (3 stage)	on-line: 1.3 µS/cm off-line: 2.1 µS/cm	1.3 µS/cm (3 stage)	1.3 µS/cm (3 stage)

Table 10 Overview of the conductivity limits referred to in different pharmacopoeias

Meter Requirements	
Specification	USP, EP, JP, ChP, and IP requirements
Conductivity sensor and cell constant accuracy	Cell constant must be known within ± 2%. Verification by: - Direct method: Using a solution of known conductivity (certified conductivity standard). - Indirect method: Comparing with a cell of known or certified cell constant.
Electrode material	Suitable material
Conductivity meter calibration	Conductivity cell is replaced with NIST (or equivalent national authority) traceable resistor. The reading must be accurate to ± 0.1% of the stated value
Instrument resolution	0.1 µS/cm
Instrument accuracy (at 1.3 µS/cm)	0.1 µS/cm
Temperature compensation	None
Temperature accuracy	± 2 °C

Table 11 Requirements for the conductivity meter

The most widespread test is the three-stage method according to USP <645>, which is described in detail in the following section.

Three-stage Method for <645>

This method contains three stages of different measurements. Testing stops at the first stage that passes. If all three stages fail, the water does not meet requirements. The general requirements for the conductivity meter are listed in Table 11.

IMPORTANT: Switch-off the temperature correction.

Stage 1
Measure the non-temperature-compensated conductivity and temperature. The measurement may be performed online (with flow cell) or offline (with sample bottle). Round the temperature down to the next lowest 5 °C interval. Look up the Stage 1 limit for that temperature (see Table 12). If the measured conductivity is not greater than the limit in the table, the water meets the requirements for <645>. If the conductivity is higher than the table value, proceed with Stage 2.

USP <645> Stage 1 Requirements			
For non-temperature compensated conductivity measurements			
Temperature (°C)	Maximum Conductivity (µS/cm)	Temperature (°C)	Maximum Conductivity (µS/cm)
0	0.6	55	2.1
5	0.8	60	2.2
10	0.9	65	2.4
15	1.0	70	2.5
20	1.1	75	2.7
25	1.3	80	2.7
30	1.4	85	2.7
35	1.5	90	2.7
40	1.7	95	2.9
45	1.8	100	3.1
50	1.9		

Table 12 Stage 1 maximum conductivity limits

Stage 2

Adjust the temperature of the sample to 25 ± 1 °C and stir or agitate until the conductivity stops rising and is equilibrated with ambient air. The reading must not exceed 2.1 µS/cm

Stage 3

Add saturated KCl solution (0.3 mL/100 mL) to the sample from stage 2 and measure the pH value. The conductivity reading from stage 2 must not exceed the allowed conductivity for that pH (see Table 13)

USP <645> Stage 3 pH and Conductivity Requirements	
pH	Maximum Conductivity (µS/cm)
5.0	4.7
5.1	4.1
5.2	3.6
5.3	3.3
5.4	3.0
5.5	2.8
5.6	2.6
5.7	2.5
5.8	2.4
5.9	2.4
6.0	2.4
6.1	2.4
6.2	2.5
6.3	2.4
6.4	2.3
6.5	2.2
6.6	2.1
6.7	2.6
6.8	3.1
6.9	3.8
7.0	4.6

Table 13 Stage 3 maximum conductivity limits

3.6.5 Resistivity In the case of low conductivity measurements such as checking ultra-pure water or organic solvents, sometimes resistivity is preferred to a conductivity value. Resistivity is the inverse of conductivity (equation 19). Pure water has a conductivity of 0.055 µS/cm, which corresponds to a resistivity of 18.18 MΩ·cm.

$$\rho = \frac{1}{\kappa} \qquad (19)$$

ρ = resistivity [MΩ·cm]

3.6.6 Conductivity Ash The ash content is an important quality parameter for sugar and its precursors to quantify the inorganic impurities. After incineration of sugar products at 550 °C, the solid residue is weighed to calculate the ash content. Similar to TDS measurements, conductivity provides a much faster alternative to estimate the ash content. If the ash content is determined by conductivity then it is called conductivity ash. The International Commission for Uniform Methods of Sugar Analysis (ICUMSA) defined two standards for the conductivity ash determination. A certain amount of the sugar sample is dissolved in a definite amount of deionized water with a known conductivity. Then the conductivity of the solution is measured. The temperature of the solution must be between 15 °C and 25 °C. SevenExcellence and SevenCompact provide a special conductivity ash mode, which directly reports the result in percent. With other meters, the result can be calculated according to the following formulas:

• ICUMSA GS2/3-17 for refined sugar products:
  Dissolve 28 g of the sample in 100 g of deionized water with a known conductivity. The conductivity ash is calculated using the following formula:

$$\%(m/m) = 0.006 \times \left(\frac{\kappa_1}{1 + 0.026 \times (T - 20)} \right) - 0.35 \times \left(\frac{\kappa_2}{1 + 0.026 \times (T - 20)} \right) \times K \qquad (20)$$

- ICUMSA GS 1/3/4/7-13 for raw sugar, brown sugar, juice, syrup and molasses:
  Dissolve 5 g of the sample in 100 mL of deionized water with a known conductivity. The conductivity ash is calculated using the following formula:

$$\%(m/V) = 0.0018 \times \left(\frac{\kappa_1}{1+0.023 \times (T-20)} \right) - \left(\frac{\kappa_2}{1+0.023 \times (T-20)} \right) \times K \qquad (21)$$

κ_1: conductivity of the solution in µS/cm
κ_2: conductivity of the used deionized water in µS/cm
T: temperature in °C (must be between 15 °C and 25 °C)
K: cell constant

3.6.7 Bioethanol   Bioethanol can contain ionic impurities at trace level. These impurities increase the risk of corrosion, which can lead to engine damage when it is used as fuel or as part of a fuel mixture. Conductivity is a non-specific sum parameter related to the concentration and mobility of all ions in a solution. The higher the conductivity level, the higher the corrosive ion content in the fuel. The equipment necessary for such determination is inexpensive and simple to use even on-site. Therefore, conductivity is a key indicator of the overall quality of bioethanol.

An important standard for conductivity measurements in bioethanol is the NBR 10547 (Fuel Ethanol – Determination of Electrical Conductivity) which was defined by Brazilian Association of Technical Norm (ABNT). To measure the conductivity according to this standard, the following points must be considered:

Equipment:
- Conductivity meter with a minimum resolution of 1 µS/m (0.01 µS/cm).
- Platinum conductivity cell with a cell constant of 0.10 ± 0.02 cm^{-1} including an integrated or external temperature probe with a resolution of 0.1 °C.

- Thermostat to adjust the temperature of the sample to 25 ± 0.1 °C.
- Certified conductivity standard with a conductivity of 500 µS/m (5 µS/cm) or less.
- Sample vessel made from glass, plastic or stainless steel.

Calibration:

For the calibration, the temperature correction mode of the conductivity meter must be switched off. The temperature of the standard sample is adjusted to 25 °C with the thermostat. Agitate smoothly to achieve temperature equilibrium. Stop agitating and wait for two minutes before taking the conductivity reading. The sample temperature must be 25 ± 0.5 °C. The resulting cell constant must be between 0.08 and 0.12 cm^{-1}

Measurement:

For the measurement, there are two possibilities:

- Adjust the temperature of the sample to 25 ± 0.5 °C
- Use the linear temperature correction mode with a temperature correction coefficient of 2.2%/°C.

Agitate the sample smoothly to uniform temperature. Stop agitating and wait for two minutes before taking the conductivity reading. To fulfill the specifications the result must not be greater than or equal to 500 µS/m (5 µS/cm).

4 Frequently Asked Questions

How do I select the right sensor?
Checking the following three criteria will help you to choose the right
sensor.
1. Chemical stability: There must be no chemical reaction between the
   sensor material and the sample.
2. Construction type:
   2-pole sensor: Best for low conductivity measurements
   4-pole sensor: Best for mid to high conductivity measurements
3. Cell constant: Use a sensor with a low cell constant (0.01–0.1 cm^{-1})
   for low conductivity measurements and a sensor with a higher cell
   constant (0.5–1.0 cm^{-1}) for mid to high conductivity measurements.

At **www.electrodes.net**, you can find all the necessary information
about METTLER TOLEDO's sensors.

**What is the difference between a nominal and a certified cell
constant?**
The cell constant can vary widely due to the production process. The
nominal cell constant has an accuracy of only ± 20% and helps you
to choose the right sensor. It is too inaccurate and cannot be used for
conductivity measurements. Sensors with a nominal cell constant must
be calibrated first.

Certified cell constants are determined after the manufacturing process
directly at the plant with traceability according to ASTM and NIST. With
a maximum uncertainty of ± 2% they are accurate enough and can be
used for conductivity measurement. The certified cell constant is stated
on the quality certificate, printed on the sensor cable, and stored on the
ISM sensor chip.

When do I need to perform a calibration or a verification?
If the exact cell constant is not known, then calibration must be per-
formed. When the exact cell constant is known, then a verification is
sufficient. This is the case with sensors with a certified cell constant or
sensors which have been previously calibrated.

Which temperature correction mode should be used?
Depending on the measured sample, different temperature correction modes should be used:
Linear: Medium to high conducting solutions (use a correct
              α-value)
Non-linear: Natural water
Pure water: Ultrapure water
None: Temperature-controlled samples; conductivity measure-
             ments according to certain standards (e.g., USP <645>)

Should the sample for the conductivity measurement be stirred or not?
In unstirred solutions, measurement drift is possible. In general, conductivity measurements in stirred samples are preferred. The exception is low conductivity samples where stirring can increase exposure to air and carbon dioxide contamination.

IMPORTANT: Use the same stirring conditions for both calibration or verification and measurement.

How do I clean a conductivity sensor?
The sensor should be rinsed after every measurement with deionized water. If the sensor has been exposed to a sample immiscible with water, it should be cleaned with a solvent miscible with water e.g., ethanol or acetone and carefully rinsed afterwards with deionized water. If there is a build-up of solids inside the measuring cell, carefully remove it with a cotton bud soaked in detergent solution, and then rinse the sensor with deionized water (Caution: Sensors with platinized poles should never be cleand mechanically, as this could damage the sensors).

How to store a conductivity sensor?
Cleaned conductivity sensors should be stored as follow:
Short-term storage (< 1 day): dry or in deionized water
Long-term storage (> 1day):   dry

What is the shelf life of the certified conductivity standards?

METTLER TOLEDO guarantees the quality of unopened standard solutions for a period of two years from the date of manufacture. Standards with a conductivity value lower than 100 µS/cm have a shorter shelf life (84 µS/cm: 1 year; 10 µS/cm: 6 months). The expiration date is printed on the product label. The warranty period covers up to the last day of the month stated.

What is the general life expectancy of a sensor with a certified cell constant?

Conductivity probes do not age in the same way as pH electrodes. Their lifetime is not limited as long as their measuring cell is not attacked by any harsh chemicals, mishandling, mechanical damage or fouling. The lifetime mostly depends on the usage and handling of the sensor. Proper cleaning and storage increase the lifetime of the sensor.

Can conductivity be measured in non-aqueous solutions?

Yes, it is possible. Organic substances also have dissociative properties. Organic compounds like benzene, alcohols, and petroleum products generally have very low conductivity. It should be recognized that an increase in conductivity can indicate an increase in ionic contamination and/or an increase in water content that allows increased dissociation. METTLER TOLEDO conductivity equipment is mainly developed for aqueous samples or non-aqueous samples with low water content. Before measuring non-aqueous samples first check the resistance of the sensor material.

5   Glossary

Alternating current (AC):	Flow of electric charge which periodically reverses direction.
Anion:	A negatively charged ion.
Calibration:	Empirical determination of the cell constant by measuring a standard solution.
Cation:	A positively charged ion.
Cell constant K [cm^{-1}]:	Theoretical: $K = l / A$; The ratio of the distance between the electrodes (l) to the effective cross-sectional area of electrolyte between the poles (A). The cell constant is used to transform the conductance into the conductivity and is determined by calibration. The difference between the theoretical and real cell constant is caused by field lines.
Conductance G [S]:	The ability of material to conduct electricity. It is the reciprocal of electrical resistance.
Conductivity κ [μS/cm]:	Conductance for a standardized cell. The measured conductance is multiplied by the cell constant to obtain the conductivity ($κ = G*K$).
Direct current (DC):	Flow of electric charge in only one direction.
Electrode:	Synonym for pole.
Electrolyte:	Aqueous solution of acids, bases or salts which are able to conduct electricity.
Field effects:	The part of the measuring field that falls outside the geometric space of the measuring cell. If something interferes with the field lines (e.g., beaker wall) the measurement is affected.
Fouling:	Formation of gelatinous coating, colloidal masses or bacterial growth in the measuring cell. These deposits negatively influence the conductivity reading.

Ion:	An atom or molecule with an electrical charge that is positive (cation) or negative (anion) as a result of having lost or gained electrons.
Measurement uncertainty:	Range of possible values within which the true value of the measurement lies at a defined probability.
Measuring cell:	The 2 or 4 poles together are called the measuring cell.
Polarization:	Applying an electrical current to electrodes in solution may cause an accumulation of ionic species near the electrode surfaces. Thus, a polarization resistance arises at the electrode surface, which may lead to erroneous results.
Pole:	One of 2- or 4-poles to which a current is applied to measure the conductivity. The pole is in direct contact with the sample solution and forms the measuring cell together with the other poles. A pole is also called an electrode.
Quality certificate:	Certifies that a product system or parts thereof meet a desired level of quality within agreed tolerances and that traceability is guaranteed within the complete production process.
Reference temperature:	Conductivity measurements are strongly temperature-dependent. The measured values are converted to a reference temperature (usually 20 °C or 25 °C) by using a temperature correction mode. This makes the results comparable.
Resistance Ω [ohm]:	Property of a conductor due to which it opposes the flow of current through it.

Resistivity ρ [MΩ·cm]:	Resistivity is the inverse of conductivity ($\rho = 1 / \kappa$). Resistivity values are sometimes preferred to a conductivity value in low conductivity applications such as measurements in ultrapure water or organic solvents.
Salinity:	The concentration of soluble mineral (mainly salts of the alkali metals or of magnesium) in water.
Standard solution:	A solution containing a precisely known amount of a substance or, in this case, an exactly known conductivity.
TDS [mg/L]:	Total Dissolved Solids is a measure of the amount of all dissolved non-volatile substances contained in a liquid and is usually expressed in mg/L or ppm.
Temperature correction mode:	Methode used to convert the measured value according to a preselected equation to the desired reference temperature. Adjusting the sample temperature is then not necessary.
Verification:	Check the conductivity reading by performing a measurement in a standard solution.

6   Appendix

6.1 Temperature Correction Factors f_{25} for Non-linear Correction

°C	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	1.918	1.912	1.906	1.899	1.893	1.887	1.881	1.875	1.869	1.863
1	1.857	1.851	1.845	1.840	1.834	1.829	1.822	1.817	1.811	1.805
2	1.800	1.794	1.788	1.783	1.777	1.772	1.766	1.761	1.756	1.750
3	1.745	1.740	1.734	1.729	1.724	1.719	1.713	1.708	1.703	1.698
4	1.693	1.688	1.683	1.678	1.673	1.668	1.663	1.658	1.653	1.648
5	1.643	1.638	1.634	1.629	1.624	1.619	1.615	1.610	1.605	1.601
6	1.596	1.591	1.587	1.582	1.578	1.573	1.569	1.564	1.560	1.555
7	1.551	1.547	1.542	1.538	1.534	1.529	1.525	1.521	1.516	1.512
8	1.508	1.504	1.500	1.496	1.491	1.487	1.483	1.479	1.475	1.471
9	1.467	1.463	1.459	1.455	1.451	1.447	1.443	1.439	1.436	1.432
10	1.428	1.424	1.420	1.416	1.413	1.409	1.405	1.401	1.398	1.384
11	1.390	1.387	1.383	1.379	1.376	1.372	1.369	1.365	1.362	1.358
12	1.354	1.351	1.347	1.344	1.341	1.337	1.334	1.330	1.327	1.323
13	1.320	1.317	1.313	1.310	1.307	1.303	1.300	1.297	1.294	1.290
14	1.287	1.284	1.281	1.278	1.274	1.271	1.268	1.265	1.262	1.259
15	1.256	1.253	1.249	1.246	1.243	1.240	1.237	1.234	1.231	1.228
16	1.225	1.222	1.219	1.216	1.214	1.211	1.208	1.205	1.202	1.199
17	1.196	1.93	1.191	1.188	1.185	1.182	1.179	1.177	1.174	1.171
18	1.168	1.166	1.163	1.160	1.157	1.155	1.152	1.149	1.147	1.144
19	1.141	1.139	1.136	1.134	1.131	1.128	1.126	1.123	1.121	1.118
20	1.116	1.113	1.111	1.108	1.105	1.103	1.101	1.098	1.096	1.093
21	1.091	1.088	1.086	1.083	1.081	1.079	1.076	1.074	1.071	1.069
22	1.067	1.064	1.062	1.060	1.057	1.055	1.053	1.051	1.048	1.046
23	1.044	1.041	1.039	1.037	1.035	1.032	1.030	1.028	1.026	1.024
24	1.021	1.019	1.017	1.015	1.013	1.011	1.008	1.006	1.004	1.002
25	1.000	0.998	0.996	0.994	0.992	0.990	0.987	0.985	0.983	0.981
26	0.979	0.977	0.975	0.973	0.971	0.969	0.967	0.965	0.963	0.961
27	0.959	0.957	0.955	0.953	0.952	0.950	0.948	0.946	0.944	0.942
28	0.940	0.938	0.936	0.934	0.933	0.931	0.929	0.927	0.925	0.923
29	0.921	0.920	0.918	0.916	0.914	0.912	0.911	0.909	0.907	0.905
30	0.903	0.902	0.900	0.898	0.896	0.895	0.893	0.891	0.889	0.888
31	0.886	0.884	0.883	0.881	0.879	0.877	0.876	0.874	0.872	0.871
32	0.869	0.867	0.866	0.864	0.863	0.861	0.859	0.858	0.856	0.854
33	0.853	0.851	0.850	0.848	0.846	0.845	0.843	0.842	0.840	0.839
34	0.837	0.835	0.834	0.832	0.831	0.829	0.828	0.826	0.825	0.823
35	0.822	0.820	0.819	0.817	0.816	0.814	0.813	0.811	0.810	0.808

**6.2 Temperature
Coefficients
(α-values) for
METTLER TOLEDO's
Conductivity
Standards**

Conductivity standard 12.88 mS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	1.81%/°C	1.97%/°C
10 °C	1.84%/°C	2.01%/°C
15 °C	1.86%/°C	2.04%/°C
20 °C	1.88%/°C	2.05%/°C
25 °C	1.91%/°C	2.07%/°C
30 °C	1.93%/°C	2.10%/°C
35 °C	1.95%/°C	2.13%/°C

Conductivity standard 1413 µS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	1.83%/°C	1.99%/°C
10 °C	1.85%/°C	2.02%/°C
15 °C	1.88%/°C	2.05%/°C
20 °C	1.91%/°C	2.08%/°C
25 °C	1.94%/°C	2.11%/°C
30 °C	1.97%/°C	2.14%/°C
35 °C	2.00%/°C	2.18%/°C

Conductivity standard 500 µS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	1.85%/°C	2.01%/°C
10 °C	1.87%/°C	2.04%/°C
15 °C	1.94%/°C	2.15%/°C
20 °C	1.94%/°C	2.15%/°C
25 °C	1.94%/°C	2.15%/°C
30 °C	1.94%/°C	2.15%/°C
35 °C	2.05%/°C	2.23%/°C

Conductivity standard 84 µS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	1.84%/°C	2.00%/°C
10 °C	1.88%/°C	2.04%/°C
15 °C	1.95%/°C	2.16%/°C
20 °C	1.95%/°C	2.16%/°C
25 °C	1.95%/°C	2.16%/°C
30 °C	1.95%/°C	2.16%/°C
35 °C	2.01%/°C	2.21%/°C

Conductivity standard 10 µS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	1.94%/°C	2.11%/°C
10 °C	1.93%/°C	2.08%/°C
15 °C	2.05%/°C	2.27%/°C
20 °C	2.06%/°C	2.29%/°C
25 °C	2.06%/°C	2.30%/°C
30 °C	2.06%/°C	2.30%/°C
35 °C	2.14%/°C	2.36%/°C

Conductivity standard 5 µS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	1.98%/°C	2.18%/°C
10 °C	2.04%/°C	2.26%/°C
15 °C	2.06%/°C	2.30%/°C
20 °C	2.06%/°C	2.30%/°C
25 °C	2.06%/°C	2.30%/°C
30 °C	2.06%/°C	2.30%/°C
35 °C	2.14%/°C	2.36%/°C

Conductivity standard 1.3 µS/cm

Measuring temperature	α at T_{Ref} = 25 °C	α at T_{Ref} = 20 °C
5 °C	2.42%/°C	2.75%/°C
10 °C	2.46%/°C	2.81%/°C
15 °C	2.46%/°C	2.81%/°C
20 °C	2.46%/°C	2.81%/°C
25 °C	2.23%/°C	2.81%/°C
30 °C	2.00%/°C	2.54%/°C
35 °C	2.15%/°C	2.57%/°C

6.3 Conductivity to TDS Conversion Factors

Conductivity	TDS KCl		TDS NaCl	
at 25 °C	ppm value	factor	ppm value	factor
84 µS/cm	40.38	0.5048	38.04	0.4755
447 µS/cm	225.6	0.5047	215.5	0.4822
1413 µS/cm	744.7	0.527	702.1	0.4969
1500 µS/cm	757.1	0.5047	737.1	0.4914
8974 µS/cm	5101	0.5685	4487	0.5000
12'880 µS/cm	7447	0.5782	7230	0.5613
15'000 µS/cm	8759	0.5839	8532	0.5688
80 mS/cm	52'168	0.6521	48'384	0.6048

www.mt.com/pH
For more information