A Guide to On-line Conductivity Measurement

Theory and Practice
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Electrical conductivity has been measured for more than 100 years and it is still an important and widely used analytical parameter today. The high reliability, sensitivity, fast response, and relatively low cost of the equipment make conductivity a valuable, easy-to-use tool for quality control. In some applications, the same measurement is made as resistivity which is the inverse of conductivity and with reciprocal units.

Electrical conductivity is a non-specific sum parameter, responding to all dissolved ionic materials (salts, acids, bases, and some organic substances) in solution. Conductivity is unable to differentiate the kinds of ions. The measurement 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 the basics for a good understanding of conductivity and resistivity measurement. Important factors that influence the measurement and possible sources of error are discussed. Both theoretical and practical aspects are covered to enable reliable calibration and measurement in various applications.

1. Introduction
2. Theory

2.1 Electrical Conductivity – Basic Information

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). In this guide the term “conductivity” always refers to 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 (primarily metals) consist of a lattice of atoms with an outer shell of electrons. The electrons in this ‘electron cloud’ can dissociate freely from their atoms and transport electricity through the lattice and therefore also through the bulk material. Metals, graphite, and a few other chemical compounds belong to this group.

The conductors in the second group are electrolytes, with ions carrying the charge. The charge transfer in electrolytes is always linked to the transport of matter as ions. Ionization occurs by dissolving a substance in a polar solvent (such as water) or through melting.

2.2 Definition of Conductivity

According to Ohm’s law (1) the voltage (V) applied across a solution is proportional to the current (I) flowing through the solution

\[ V = R \times I \]  

(1)

\[ R = \text{resistance (ohm, } \Omega) \]

\[ V = \text{voltage (volt, } V) \]

\[ I = \text{current (ampere, } A) \]

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

\[ R = \frac{V}{I} \]  

(2)

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

\[ G = \frac{1}{R} \]  

(3)

\[ G = \text{conductance (siemens, } S) \]
To measure the resistance or the conductance of a sample, a measuring cell is required. The measuring cell consists of at least two electrically conductive electrodes (sometimes called poles) with opposite charge. The electrodes together form a measuring cell. The cell and the support body together make up the sensor.

The conductance measured depends also on the geometry of the measuring cell, which is described by the cell constant (K). This is the ratio of the distance between electrodes (l) and the effective cross-sectional area of electrolyte (A) between the electrodes:

\[
K = \frac{l}{A}
\]  

(4)

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

The conductance can be transformed into the conductivity (\(\kappa\)), which is independent of the particular measuring cell. This is done by multiplying the conductance by the cell constant:

\[
\kappa = G \times \frac{l}{A} = G \times K
\]  

(5)

\( \kappa \) = conductivity \((\text{S/cm})\)

Resistivity is the reciprocal of conductivity:

\[
\rho = \frac{1}{\kappa}
\]  

(6)

\( \rho \) = resistivity \((\Omega \cdot \text{cm})\)

### 2.3 Conductivity of Solutions

Most pure solvents are non-conducting and have a conductivity near zero. Dissolved solids with ionic or very polar bonds dissociate and enable the solution to conduct electricity. The impact of dissolved ions is discussed in section 2.3.1. Also, water dissociates into ions to a very small degree and therefore even absolutely pure water has some conductivity. This dissociation of water is described in section 2.3.2.
2.3.1 Dissolved Ions

The dissolution of materials that form ions is called electrolytic dissociation. Some examples of electrolytic dissociation are as follows:

NaCl → Na⁺ + Cl⁻
HCl → H⁺ + Cl⁻
CH₃COOH ⇌ CH₃COO⁻ + H⁺

There is a distinction between strong and weak electrolytes. Strong electrolytes like sodium chloride and hydrochloric acid dissociate completely to form sodium and chloride ions or protons and chloride ions. In contrast, weak electrolytes like acetic acid dissociate only partially, symbolized by the two-way arrow above. This means that the electrolyte solution contains ionic acetate (CH₃COO⁻) and protons (H⁺), and also non-ionic acetic acid molecules (CH₃COOH). The dissociation is strongly temperature-dependent and can be quantified with a dissociation constant. Only the dissociated, ionic portion contributes to the conductivity.

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

$$\kappa = \sum_i c_i Z_i \lambda_i$$  \hspace{1cm} (7)

c = ion concentration [mol/L]
Z = ion charge number
\lambda = equivalent ionic conductance [S•cm²/mol]

The equivalent ionic conductance is a specific attribute of each type of ion. It depends not only on the ion type, but also on the concentration and the temperature.
The equivalent conductance generally increases with the charge number and decreases with the size. However, the predicted values can differ from the actual measured values listed in Table 1. For example, the small lithium ion is much less conductive than the larger ammonium ion. This is because the size of the solvated ion, and not the size of the ion itself, is the determining factor in mobility. A smaller, highly charged ion like lithium can attract more water molecules and build up a bigger solvation shell than a bigger and less charged ion. The very high conductances of a proton (H\(^+\)) and hydroxide ion (OH\(^-\)) also stand out. The transport mechanism of these two ions is not based on ionic migration. Protons are easily transferred from hydronium (H\(_3\)O\(^+\)) to surrounding H\(_2\)O or from H\(_2\)O to hydroxide (OH\(^-\)). The charge is transported primarily by the fast electron swap and not through the slower migration of the ions. For this reason, acids and bases are much more conductive than salts which can be important in understanding the significance of conductivity values in many applications.

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

<table>
<thead>
<tr>
<th>Equivalent Conductance (\lambda) [25 °C, in H(_2)O at very high dilution]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cations</strong> [S•cm(^2)/mol]</td>
</tr>
<tr>
<td>H(^+)</td>
</tr>
<tr>
<td>Li(^+)</td>
</tr>
<tr>
<td>Na(^+)</td>
</tr>
<tr>
<td>NH(_4)(^+)</td>
</tr>
<tr>
<td>(\frac{1}{2}) Mg(^{2+})</td>
</tr>
<tr>
<td>(\frac{1}{2}) Ca(^{2+})</td>
</tr>
</tbody>
</table>

Table 1: Equivalent conductance of different ion types
Temperature also influences the equivalent conductance. Higher temperature increases the motion of the particles and lowers the viscosity of the solvent. This leads to increased mobility of ions and to higher conductivity. Because viscosity is a property of the solvent, the mobility of all ions tends to have the same increase with temperature which simplifies temperature compensation for general purpose measurements. However, in the case of weak electrolytes, a higher temperature may also change the amount of dissociation and therefore influence the conductivity further. This complicates temperature compensation.

The conductivity of a solution depends on several parameters, which sometimes have interactions. The important influences on conductivity can be summarized as follows:
- Type of dissolved electrolyte (ionic charge, ionic radius, ionic mobility)
- Concentration of the dissolved electrolyte
- Dissociation degree of the electrolyte
- Solvent (viscosity)
- Temperature

2.3.2 Dissociation of Water

Pure water without any impurities has a conductivity of 0.055 µS/cm and resistivity of 18.18 Mohm•cm at 25 °C. This small conductivity is caused by hydronium (H$_3$O$^+$) and hydroxide (OH$^-$) ions which exist from the dissociation of water. The equilibrium of this dissociation is strongly on the water side and only two out of a billion water molecules are in ionic form. The influence of this dissociation is insignificant in general purpose measurements but is dominant in pure water. The degree of dissociation of water is very temperature dependent which requires extra consideration in temperature compensating pure water measurements.

![Figure 1: Dissociation of water](image-url)
2.4 Measuring Principle

A conductivity measuring cell consists of an electrode pair, to which a voltage is applied. The instrument measures the flowing current and calculates the conductivity (see section 2.2). However, this is an oversimplified explanation of the measuring principle.

When a direct current (DC) is applied to the electrodes, the positively charged ions (cations) migrate toward the negatively charged electrode (cathode) and the negatively charged ions (anions) move toward the positively charged electrode (anode) (see Figure 2). This can lead to an accumulation of ions near the electrode surfaces, giving a condition called polarization and causing chemical reactions. This electrolysis affects the composition of the solution and therefore also the conductivity. To prevent the undesirable polarization and 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 about their positions with the rhythm of the applied frequency (see Figure 3).

Figure 2: Schematic set-up of a conductivity measuring cell

Figure 3: 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 electrodes and the solution when a current is applied are summarized as polarization. The main effect is the formation of a double layer of ions that impedes the mobility of the ions near the surface. This layer has the same effect as contamination of the electrode surface and causes an additional resistance. Polarization negatively influences the measurement of samples with moderate to high electrolyte concentration and reduces the linearity at the upper end of the range (see Figure 4). 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 polarization.
- Optimizing the electrode surface: By roughening the surface of the electrodes, their surface area is increased, the current density is reduced and therefore polarization is also reduced (see section 2.5.4).
- Using a 4-electrode conductivity cell: This kind of conductivity cell is much less influenced by polarization effects (see section 2.5.2)

![Figure 4: Negative impact of polarization and capacitances on the conductivity reading](image)

The linearity at the low end of the scale is limited by the impact of capacitance (see Figure 4). Two electrodes in a non-conductive medium behave like a capacitor. When a DC voltage is applied to these electrodes, no electricity can flow. The capacitive resistance is infinitely high and the conductance is zero. However, when an AC voltage is applied to the electrodes, the capacitive resistance drops and the conductance
rises correspondingly. Even more important in process measurements, a long cable connecting the sensor to the measuring instrument can add very significant capacitance. The influence of capacitances can be reduced or prevented by:

- Adjusting the measuring frequency: The lower the measuring frequency, the lower the impact of capacitance.
- Using a conductivity cell with low capacitance: The smaller the electrodes’ area and the greater the distance (l) between the electrodes, the lower the capacitance. However, this is not a viable option because for measurements in a low conductivity range, cells with a low cell constant (large electrode area and small distance between the electrodes) are required to keep the resistance low enough for reliable measurement.
- Using a special circuit and cable: Measurement system designs with careful signal handling can reduce the effects of cable capacitance.
- Using digital sensors: With measuring circuit and analog-to-digital conversion built into the sensor, there is negligible distance for the AC measurement signal to travel, so cable capacitance is eliminated. Only a robust digital signal is transmitted over the long cable to the instrument.

The optimal measuring frequency depends on the measuring range. Therefore, the frequency is adopted to the conductivity of the sample. In general, low frequencies are applied at low conductivities, where polarization effects are insignificant and capacitance is a concern. High frequencies are applied at high conductivities enabling the polarization effects to be reduced.

State of the art conductivity measuring circuits adjust the measuring frequency and voltage automatically based on the range being measured. The algorithms used for these adjustments vary among instrument manufacturers which results in widely varying measurement range specifications for a particular cell constant. METTLER TOLEDO Thornton UniCond™ digital sensors have been optimized for exceptionally wide rangeability.
Given the diversity of applications, it is not surprising that there is no single measurement technology which is ideal for every situation. The following three technologies are used for process conductivity measurement:

- 2-electrode conductivity cell
- 4-electrode conductivity cell
- Inductive conductivity cell

### 2.5 Conductivity Sensor Types

#### 2.5.1 2-electrode Conductivity Cell

Classical 2-electrode conductivity cells consist of two parallel plates. The plates are supported by a structural insulator(s) which protects them from mechanical damage and reduces the errors caused by field effects. Early designs used platinum electrodes which were vulnerable to bending, resulting in changes in the cell constant with only minor mishandling. (see Figure 5a). A more recent and now widely used concentric design originally developed by Thornton and associates in the 1960s uses a center electrode which is encircled by a second outer electrode (see Figure 5b). These concentric sensors are manufactured from robust materials such as titanium, stainless steel or Monel and are very resistant to changes in cell constant, mechanical damage or temperature influences.

![Figure 5a and 5b: 2-electrode conductivity cell designs](image)

The forte of the 2-electrode conductivity cell is measuring low to medium conductivity with high accuracy. The measuring range for a METTLER TOLEDO Thornton digital UniCond 2-electrode 0.1 cm⁻¹ sensor shown in Figure 5b is from 0.02 µS/cm up to 50,000 µS/cm. It is an excellent general purpose sensor for use throughout water treatment systems due to this wide rangeability. Applications of a 2-electrode sensor are for accurate measurements from non-aqueous solvents and ultra-pure water up to saline solutions.
2.5.2 4-electrode Conductivity Cell

Four-electrode conductivity sensors work with an additional electrode pair (see Figure 6). There are different configurations of 4-electrode cell but the functional principle is the same.

The outer electrodes are the current electrodes to which AC is applied. They are driven in the same manner as the 2-electrode sensor. The inner measuring electrodes are placed in the electric field of the current electrodes and measure the voltage with a high impedance amplifier. The current flowing through the outer electrodes and the solution can be accurately measured by the circuit. If the voltage across the inner electrodes and the current are known, the resistance and conductance can be calculated. To obtain the conductivity, the conductance must be multiplied by the cell constant of the inner electrodes (see section 2.2).

The advantage of the 4-electrode sensor lies in the fact that there is negligible current flowing through the inner electrodes where the measurement is made. Therefore, no polarization effects occur which would otherwise influence the measurement. The 4-electrode conductivity cell is also less sensitive to measuring errors through electrode fouling.

![Figure 6: Digital 4-electrode conductivity cell with temperature sensor in a polymer body](image)

The strength of a 4-electrode conductivity cell is measuring conductivity over a high range from 10 µS/cm up to 1000 mS/cm. The main applications of this sensor type are medium to high conductivity measurements as found in seawater, cleaning solutions, process waters and acids and bases used for ion exchange regeneration. The flat surfaces make it less vulnerable to fouling by suspended solids. The fifth metal electrode shown in Figure 6 contains the temperature sensor.
2.5.3 Inductive Conductivity Cell

An inductive sensor is constructed like a pair of transformer coils where the solution to be measured is the core of the transformer. The parallel coils are closely spaced and embedded within a polymer body like a donut which is immersed into the solution (see Figure 7). There are no electrodes and usually no metal contacting the solution. One coil is energized with AC and the signal induced into the second coil is related to the conductivity of the solution flowing through and around the sensor. The cell constant is determined by the diameter of the hole, among other factors.

Inductive sensors are suitable for medium to very high conductivity measurements and because there are no electrodes, they are not subject to any polarization or fouling problems. However, the electrical field of measurement goes around the outside of the donut as well as through the hole so space should be allowed around the sensor to maintain the integrity of the cell constant. As a result, inductive sensors are normally mounted in large pipes or submerged in open tanks. Where piping or other physical barriers encroach on the measurement field, in-situ calibration is required to account for the altered cell constant and the sensor must always be mounted with the same orientation. With no wetted metal parts and with bodies of PEEK or PFA polymer, inductive sensors have excellent chemical resistance.

![Figure 7: Inductive conductivity sensor with measuring coils and temperature sensor sealed within a polymer body](image)

<table>
<thead>
<tr>
<th>Advantages</th>
<th>2-electrode Cell</th>
<th>4-electrode Cell</th>
<th>Inductive Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>- High accuracy at low conductivity</td>
<td>- Medium to high conductivity measurements</td>
<td>- Medium to very high conductivity measurements</td>
<td></td>
</tr>
<tr>
<td>- Low to medium range conductivity measurements</td>
<td>- Little influence from surface contamination</td>
<td>- No influence of surface contamination</td>
<td></td>
</tr>
<tr>
<td>- Compact mounting</td>
<td>- Compact mounting</td>
<td>- Excellent chemical resistance</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Advantages of the three types of conductivity sensors
Different materials are used in conductivity cell construction. Titanium, stainless steel, Monel, Hastelloy, graphite, platinum and platinized platinum are used for electrodes while PEEK, CPVC, PFA, other polymers and glass are used as structural and insulating materials. Important characteristics of wetted materials are chemical and temperature resistance (to process fluids as well as to sanitization, cleaning or related maintenance conditions), mechanical durability and ability to condition electrode surfaces to minimize polarization.

Chemical reactions between the sensor materials (especially the electrodes) and the sample fluid are highly undesirable because they would cause errors and permanently alter the cell and possibly alter the sample.

The surface texture of the electrode has an influence on the polarization resistance. Rough surfaces have a reduced polarization effect. However, if electrode surfaces are overly roughened or porous, the hold up and slow leaching of ionic impurities would cause very slow response in pure water measurements.

Choosing the right conductivity sensor is important to obtain accurate and reliable results. The different construction types and materials provide a variety of choices that can be optimized for a given application. In addition, a compatible process connection is required.

A basic requirement is that no chemical reactions occur between the sample and the sensor. For process applications the mechanical stability and pressure rating of the sensor are important factors. Titanium electrodes with PEEK polymer insulator have been found to be mechanically stable and chemically resistant in virtually all 2-electrode applications.

The sensor cell constant and construction type must also be considered. A suitable cell constant covers the conductivity range of the sample. Traditionally, the lower the expected conductivity of the sample, the lower the cell constant should be. However, recent digital sensor developments have greatly expanded the rangeability of low constant 2-electrode sensors to where a 2-electrode $0.1 \text{ cm}^{-1}$ UniCond sensor
can measure from ultrapure water to sea water. Figure 8 shows a sampling of applications and the sensor types which cover their ranges. To select a sensor these generalizations apply: for low to medium conductivity measurements, a 2-electrode sensor should be used. For mid to high conductivity measurements a 4-electrode or inductive sensor may be needed, especially for measurements at the highest end of the conductivity range. Inductive sensors are preferred for highest conductivity ranges, where suspended solids may foul electrodes, and where large piping or tanks are available for housing those large sensors.

Figure 8: Applications and ranges of various METTLER TOLEDO Thornton sensor types (other 2E sensor ranges are more limited)

<table>
<thead>
<tr>
<th>Conductivity (µS/cm)</th>
<th>Resistivity (Ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>100 M</td>
</tr>
<tr>
<td>10</td>
<td>10 M</td>
</tr>
<tr>
<td>100</td>
<td>1 M</td>
</tr>
<tr>
<td>1000</td>
<td>100k</td>
</tr>
<tr>
<td>10k</td>
<td>100k</td>
</tr>
<tr>
<td>100k</td>
<td>1000k</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

Conductivity is 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 may remain constant (see section 2.3.1). In pure waters, the ion concentration also increases due the effect of temperature on the dissociation of water. This adds further to the change in conductivity with temperature.

Every conductivity result must therefore be specified with a temperature or be temperature compensated, usually to the industry standard of 25 °C. 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. Because con-
ductivity is typically used as a surrogate for concentration, readings are referred to or compensated to a reference temperature, which allows the results of measurements at various temperatures to be compared against a standard value.

Because the temperature dependence of various samples, especially of pure waters, can be different, various methods have been developed to accommodate these effects. In the pharmaceutical industry, final on-line water quality specifications have limits based on tables of uncompensated conductivity vs. temperature, which eliminates any ambiguity of temperature compensation. Measuring instruments for these applications often have these pharmaceutical limit tables built in to enable convenient alarming as the limits are approached. Nevertheless, most pharmaceutical conductivity measurements in the treatment systems upstream of the final water going to production use temperature compensated measurements for simpler performance comparisons. (See 3.6.1)

In other industries, temperature compensated measurements are expected. METTLER TOLEDO Thornton has developed a “Standard” temperature compensation algorithm that closely matches the dissociation as well as changing viscosity characteristics of ultrapure water and also covers widely varying amounts of neutral mineral contamination. This Standard compensation is applicable all the way up to highly saline waters. It is therefore used throughout desalination and pure water treatment systems as well as for ultrapure water and general purpose monitoring.

Other more specialized compensation algorithms are available in METTLER TOLEDO Thornton transmitters as shown in Table 3.
Temperature Compensation Algorithm | Application
--- | ---
Standard | Ultrapure water to highly saline waters, suitable throughout desalination and pure water treatment systems
None | Uncompensated measurement to meet final pharmaceutical water monitoring requirements
Linear % per °C setting | Special processes usually involving acids or bases; can be referenced to 20 or 25 °C
Ammonia | Power industry cycle chemistry samples containing ammonia and/or amines
Cation | Power industry cycle chemistry samples that have passed through a cation exchanger and contain trace acids
Light 84 | Same as Standard but with slight differences using earlier 1984 pure water data published by T.S. Light
Standard 75 °C | Same as Standard but referenced to 75 °C for specialized microelectronics UPW applications
Alcohol | Pure water containing approximately 50% isopropyl alcohol
Glycol | Pure water containing approximately 50% isopropyl alcohol, or 100% isopropyl alcohol (selectable)

Table 3: Conductivity temperature compensation algorithms available in METTLER TOLEDO Thornton transmitters

In METTLER TOLEDO Thornton transmitters, when direct chemical concentration readout is selected, the unique temperature characteristics of that particular chemical are used for compensation regardless of the temperature compensation setting.

### 2.6.1 Linear Temperature Correction

For the temperature correction of medium and highly conductive solutions, linear temperature compensation may provide best accuracy. The following equation is used to determine the coefficient experimentally:

\[
\kappa_{T_{\text{ref}}} = \frac{\kappa_T}{1 + \frac{\alpha}{100\%} \times (T - T_{\text{ref}})}
\]  

(8)
It relates the temperature coefficient $\alpha$ which expresses the conductivity variation in $\%$/°C. The $\alpha$-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 process temperature. Then the $\alpha$-value can be calculated according to equation (9):

$$\alpha = \frac{(\kappa_{T_2} - \kappa_{T_1}) \times 100\%}{(T_2 - T_1) \times \kappa_{T_1}}$$ (9)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature Coefficient $\alpha$(%/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>1.0 - 1.6</td>
</tr>
<tr>
<td>Bases</td>
<td>1.8 - 2.2</td>
</tr>
<tr>
<td>Salts</td>
<td>2.0 - 3.0</td>
</tr>
<tr>
<td>Drinking water</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 4: Typical temperature coefficients of various electrolyte types

**2.7 Interferences with Conductivity Measurements**

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

**2.7.1 Dissolved Gases**

Besides solids and liquids, gases can also be dissolved in the sample and form ions which influence the conductivity. 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$_2$CO$_3$) which dissociates in a first step to bicarbonate (HCO$_3^-$) and in a second step to carbonate (CO$_3^{2-}$) (Figure 9). Carbon dioxide is readily soluble in water, with the reaction equilibrium strongly on the CO$_2$ side and only about 0.2% of the molecules react to form carbonic acid. Under standard conditions, the impact of the carbon dioxide in ambient air increases the conductivity reading by approximately 1 µS/cm.
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 is achieved using an in-line measurement or a continuously flowing sample through a well-sealed sample line and sensor flow housing. Static grab sample measurements are unreliable. At higher conductivity levels (> 50 to 100 µS/cm), the effect of carbon dioxide becomes negligible and these precautions are unnecessary.

If a bubble adheres to an active electrode surface, it increases the measured resistance and lowers the conductivity reading. Unstable signals can be an indication of air bubbles in the sensor—building up and being washed away. Bubbles are prone to form spontaneously in makeup water treatment processes where the water may be warming up and/or the pressure may be dropping, both of which will reduce gas solubility. It is also possible to have significant amounts of CO$_2$ released after primary cation exchange. Bubbles may be detected by tapping the sensor to see if the conductivity reading rises temporarily which can be caused by bubbles being dislodged and washed down stream. This kind of problem can be corrected by increasing the flow rate through the sensor to prevent bubbles large enough to affect measurements from adhering to sensor surfaces.
2.7.3 Coating of the Electrode Surface

Undissolved or slowly precipitating solids or oils 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. An example is biofouling of the cell. Periodic cleaning and/or high flowrates can prevent this kind of problem (see section 3.5).

2.7.4 Geometry Related Errors – Field Effects

With some sensor designs, parts of the electrical measuring field fall outside the geometric space of the conductivity sensor itself. Any interference with these field lines affects the conductivity measurement. A main source of interference is the wall of piping if the sensor is placed too close or in too small diameter pipe. Generally, concentric 2-electrode conductivity sensors have their field lines well-contained and do not experience this effect. Process 4-electrode and inductive conductivity sensors have field lines well-outside their own dimensions and must be installed allowing sufficient space for them. In some cases it is necessary to do an in-situ process calibration in order to reduce the errors caused by field effects. Generally, conductive metallic surface interference will cause positive errors and insulating polymer surface interference will cause negative errors.
3. Practical Considerations

Conductivity is measured over a wide range of applications. This section of the guide provides application know-how. First, general operation for calibration, verification, and conductivity measurements including the special case of low conductivity measurement is described. Next, maintenance and storage of conductivity sensors are discussed. Finally, important applications are described in detail.

3.1 Calibration and Verification

To make an accurate, temperature compensated conductivity measurement, calibration is required for the measuring circuits for conductivity and temperature and for the cell constant and the temperature transducer such as an RTD (resistance temperature detector).

3.1.1 Measuring Circuit Calibration

The measuring circuits for all conductivity and temperature ranges of METTLER TOLEDO Thornton instruments are factory calibrated and certified to NIST-traceable resistances. With conventional measuring systems the measuring circuits are located in the transmitter and may have long cable runs to the sensor. Long cable lengths add capacitance and resistance that can affect the measurement so the measuring circuit calibration should make accommodation for the cables where possible. With digital UniCond sensors the measuring circuits are built into the sensors with fixed, very short internal wiring so there are no cable challenges. In either case, modern electronics are generally quite stable but annual verification is recommended and can be accomplished by METTLER TOLEDO Thornton service personnel or by using traceable resistance plant standards for all conductivity and temperature ranges.

3.1.2 Sensor Calibration

The nominal cell constant is used in choosing the correct sensor for the range to be measured but production tolerances on the cell constant can be too wide to ensure accurate measurements. Therefore, each sensor is individually calibrated and certified at the METTLER TOLEDO Thornton factory. Because temperature has such a large influence in compensation, the RTD is also individually calibrated to support high accuracy.

Certified cell constants of METTLER TOLEDO Thornton sensors are determined as part of the manufacturing process at the factory. The exact cell constant is listed on the certificate of accuracy and is also either stored in digital UniCond sensor memory or is printed on the label of a conven-
tional analog sensor. Similar calibration is performed and certified at the factory for the RTD to enable accurate temperature measurement and compensation. METTLER TOLEDO Thornton certified cell constants and temperature calibration factors have traceability to ASTM and NIST, and to ultrapure water for 2-electrode sensors.

The cell constant can change slightly with time. Contamination and deposits or slight physical or chemical alteration of the electrodes affect the cell constant. It is advisable to perform a verification to check that the cell constant is still valid at least annually and more frequently if measuring potentially fouling or corrosive samples.

Verification and calibration can be accomplished in three ways.
1. The sensor may be returned to the factory for recalibration.
2. The sensor may be compared with a reference measuring system on site, either by METTLER TOLEDO service personnel or using a traceable plant standard system.
3. The sensor may measure a traceable standard conductivity solution and have its temperature sensor calibrated to a reference thermometer.

Using the third option, the reading must be within the limit of sensor tolerance plus standard solution tolerance or a calibration adjustment should be made. The calibration or verification should be performed near the conductivity measurement range of the process. The following procedure is recommended:

Calibration/Verification Procedure

**IMPORTANT:** Always use fresh standard solutions. Keep the standard solution bottle capped tightly except when dispensing it to prevent contamination and preserve its integrity throughout the shelf life.

1. Connect the sensor to the instrument. Select ‘Standard’ temperature compensation mode or ‘None’ if the exact conductivity of the standard solution is known at the test temperature.
2. If the sensor has been dry, soak it in clean water for 2 hours before proceeding.
3. Thoroughly rinse the sensor, the stirring bar if used and the container that will hold the standard solution several times with deionized water to remove any process solution and suspended solids and then shake off any leftover droplets.

4. Rinse the sensor, a certified thermometer and container with a small amount of the standard solution and discard it.

5. Immerse the thermometer and sensor in the standard solution to cover the active measuring area of the sensor and eliminate all air bubbles from that area by agitating or tapping the sensor on the container. With all 2-electrode sensors, the vent holes in the side must be completely covered.

   **IMPORTANT:** 4-electrode sensors must be suspended at least 1 inch (25 mm) above the bottom of the container while measuring and calibrating to obtain valid results. Inductive sensors must have at least 1.2 inches (30 mm) of fluid around the sensor donut.

6. Measure the thermometer temperature, conductivity and conductivity sensor temperature of the standard, allowing time for all readings to reach equilibrium. Stirring can help to reach equilibrium sooner but must not generate any bubbles.

7. If the sensor temperature is outside of tolerance, perform a sensor temperature calibration/adjustment at the instrument according to its instruction manual.

8. a. If ‘Standard’ temperature compensation is active then compare the conductivity reading directly to the certified 25°C value of the standard solution.

   b. If the reading is not temperature compensated, then apply a 2%/°C temperature correction to the certified value of the standard and compare that to the reading. For example, if the certified standard value is 100.43 µS/cm at 25 °C and the measured temperature is 23.2 °C then the certified value at that temperature is calculated as: $100.43 \times [1 + (0.02 \times (23.2 - 25.0))] = 96.81$ µS/cm.

9. If outside of tolerance, perform a sensor cell constant calibration/adjustment at the instrument according to its instruction manual.

**3.1.3 Standard Solutions**

METTLER TOLEDO provides a complete range of standard solutions and guarantees the quality of unopened standard solution bottles for a period of one year from the date of manufacture (6 months for 25 µS/
cm standard). The expiration date is located on the product label and certificate. Standard solutions should be stored at normal ambient temperatures and protected from direct sunlight.

<table>
<thead>
<tr>
<th>Conductivity Standard</th>
<th>Accuracy</th>
<th>Shelf Life</th>
<th>Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 µS/cm, 500 mL, HCl</td>
<td>± 3%</td>
<td>6 mo</td>
<td>58 078 001</td>
</tr>
<tr>
<td>100 µS/cm, 500 mL, KCl</td>
<td>± 1%</td>
<td>12 mo</td>
<td>58 078 002</td>
</tr>
<tr>
<td>1000 µS/cm, 500 mL, KCl</td>
<td>± 1%</td>
<td>12 mo</td>
<td>58 078 003</td>
</tr>
<tr>
<td>10,000 µS/cm, 500 mL, KCl</td>
<td>± 1%</td>
<td>12 mo</td>
<td>58 078 004</td>
</tr>
<tr>
<td>100,000 µS/cm, 500 mL, KCl</td>
<td>± 1%</td>
<td>12 mo</td>
<td>58 078 005</td>
</tr>
</tbody>
</table>

*Table 5: METTLER TOLEDO Thornton Conductivity standard solutions*

**Pure Water Verification/Calibration**

The 25 µS/cm standard with ± 3% accuracy is intended only for verification of measurement near the pure water range. For best accuracy of calibration, the 100 µS/cm standard which has ±1% accuracy should be used. The consistent linearity of METTLER TOLEDO Thornton measuring systems between 100 µS/cm and pure water provides much better accuracy than can be obtained using standards less than 100 µS/cm.

*Conductivity standards*

Conductivity standard solutions provide an easy way to calibrate or verify the cell constant. However, conductivity standard solutions are more vulnerable to errors from contamination or 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 CO₂ when in contact with air. Their values can change easily, especially the lower conductivity standards. Also, a slight change in temperature may have a large impact on the conductivity so using temperature compensation during calibration is generally the best practice.
3.2 Measurement

Before conductivity measurements can be made, the cell constant and temperature calibration factor must be stored in the measuring instrument (see section 3.1). With traditional analog sensors, the factory certified cell constant and temperature factor from the sensor certificate or label are entered manually using the instrument menus. Smart sensors and UniCond sensors with Intelligent Sensor Management (ISM™) have the factory cell constant and temperature calibration factor stored within the sensor. This data is automatically transferred to the measuring instrument when these sensors are connected.

Sensor Installation

Choose a sensor with compatible materials, process connection, temperature and pressure ratings and measurement range for the installation including cleaning and sanitization conditions. Locate the sensor in an active flowing part of the process stream in a horizontal or up-flow piping run, preferably with the flow directed at the end for a 2-electrode sensor. Alternatively, locate the sensor in a flow chamber that will have reliable and representative side stream sample flowing through it, discharging from the top.

Do not mount the sensor in the top of a partially filled pipe or in downward flowing pipe where air gaps or bubbles could collect in the measuring area of the sensor. Do not mount the sensor in the bottom of a pipe that carries suspended solids which could collect in the sensor (see Figure 10).

![Figure 10: Preferred sensor monitoring configurations](image-url)
3.3 Low Conductivity Measurements

Measurements of samples with conductivity lower than 10 μS/cm require special care. As noted in section 2.7.1 carbon dioxide from the atmosphere greatly influences the conductivity measurement at this low level. The following precautions are recommended:

- Install the sensor directly in the pure water pipeline or tank if possible.
- If a side stream measurement is necessary, use stainless steel sample tubing to the sensor flow chamber. If flexible tubing is needed, use a short length (< 2 m) of low permeability polymer tubing such as PVDF or nylon and a relatively high sample flowrate (> 200 mL/min). Be sure any connections of fittings, valve, flowmeter, etc. in the sample line are absolutely air tight to prevent ingress of air.
- In ultrapure water (18 Mohm•cm quality) measurements using sample lines, significant contamination of the sample by air including CO₂ is a common problem. It can be detected by changing the sample flowrate. At higher flowrates, any air contamination will be diluted by the additional water, causing lower conductivity or higher resistivity readings which are more accurate. See the above precautions to eliminate this problem.

3.4 Maintenance and Storage

Conductivity sensors require little maintenance but the electrodes must be clean. If there is a build-up of solids inside the measuring cell, carefully remove it by soaking in a suitable detergent, solvent or dilute acid. A light touch with a soft cotton swab may also be used on titanium, Monel, Hastelloy and stainless steel electrodes but do not scrub electrode surfaces. Do not touch the surfaces of graphite or platinized electrodes. Rinse the sensor well with deionized water.

Cleaned conductivity sensors can be left wet in their flow chambers for many days. However, during longer plant shutdowns it is good practice to remove and dry the sensor to prevent bio-growth.
3.5 Alternative Units of Measurement

The most common units of conductivity measurement are micro- and milli- siemens per centimeter (µS/cm and mS/cm). However, some countries and organizations adhere to the SI unit recommendation that only prefix symbols that represent the number 10 raised to a power that is a multiple of 3 should be used. That policy precludes the use of centimeter; the meter is used instead. Therefore be vigilant in reading conductivity data (and in configuring on-line instrumentation with a choice of display units) to distinguish units of milli- and micro- siemens per meter (mS/m and µS/m). For comparison, 1 µS/m = 0.01 µS/cm.

3.5.1 Resistivity

In the case of measurements in ultrapure water in the microelectronics industries or organic solvents, resistivity units are usually preferred to conductivity. Resistivity is the inverse of conductivity (see equation 10). Pure water has a conductivity of 0.055 µS/cm, which corresponds to a resistivity of 18.18 MΩ•cm.

\[ \rho = \frac{1}{\kappa} \]  

(10)

ρ = resistivity [MΩ•cm]

3.5.2 TDS

Total Dissolved Solids (TDS) is the total weight of solids (cations, anions and other dissolved substances) in a weight of water, usually expressed in parts-per-million or parts-per-billion. This parameter is often used for the analysis of water in cooling towers, industrial boilers, and environmental testing.

The fundamental way to determine TDS is a gravimetric method. A defined weight of a sample is evaporated until dry and the residue is weighed. The ratio as ppm is the TDS value of the sample. This is the formal method, but is very time-consuming.

Conductivity offers a quicker and easier alternative for approximating TDS. The conductivity reading can be converted to TDS by multiplying by a TDS factor. To obtain reliable results two important points must be considered:
- Only solids that produce ions when dissolved in water raise the 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 and the other without sugar. Because sugar is non-conductive, both will have a similar conductivity, but the TDS of the coffee with sugar is much higher.
- Equal weights of different ionic solids give different conductivity values.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Conductivity Equivalent</th>
<th>TDS Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1 ppm TDS = 2.04 µS/cm</td>
<td>0.49</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1 ppm TDS = 1.49 µS/cm</td>
<td>0.67</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>1 ppm TDS = 1.36 µS/cm</td>
<td>0.74</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1 ppm TDS = 1.06 µS/cm</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Table 6: Conductivity equivalent and TDS factor of different salts

For these reasons, reliable TDS measurements by conductivity are only obtained when most of the dissolved solids are ionic or when the ionic and non-ionic materials are present in a reasonably consistent ratio. This applies for most natural and treated waters.

The critical step for a TDS measurement with a conductivity transmitter is to define the TDS factor to be 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 follows:

\[
TDS \text{ factor} = \frac{TDS}{\kappa_{25^\circ C}} \tag{11}
\]

The measured conductivity (in µS/cm) is corrected to 25°C by using Standard temperature compensation.

- Make the assumption that the conductivity is caused by a single salt. A TDS factor which is based on the conductivity equivalent of potassium chloride (KCl) or sodium chloride (NaCl) is frequently used for the TDS calculation (see Table 6).
• The TDS factor for the mineral content of natural waters normally lies between 0.55 and 0.70. A TDS factor of 0.65 is often used for these samples.

\[ TDS (mg/L) = TDS \text{ factor} \times \kappa_{25^\circ C} \] \hspace{1cm} (12)

Uncertainty in the TDS factor is an additional source of error. Therefore, the error of a TDS determination is higher than that of a conductivity measurement. If reasonable assumptions are made, the typical error is less than 15%.

Different measuring instruments have different ways of configuring the TDS conversion. Consult the instrument manual for instructions on entering the conversion factor.

### 3.5.3 Concentration

In binary solutions (one electrolyte and water) conductivity can be used to give a direct readout of the electrolyte concentration in percent by weight, because the compensated conductivity is directly related to the concentration. Each electrolyte possesses a unique conductivity/concentration relationship (see Figure 11). For many electrolytes, the conductivity curve reaches a maximum value, and then reverses its slope. Concentration can be inferred on the increasing or the decreasing part of the curve if the concentration is confined to one of those regions. Conductivity cannot be used to infer concentration near the peak of the curve, since it has no way of determining on which side it is measuring.

![Figure 11: Conductivity versus concentration curves of different electrolytes at 25 °C](image)
For concentration measurements, the conductivity of the solution as a function of the concentration and temperature of the electrolyte must be known. For most of the reagents used in ion exchange regeneration and food, beverage and pharmaceutical clean-in-place processes, the temperature/concentration algorithms are stored in the memory of METTLER TOLEDO transmitters. For any other reagent, concentration readout can be obtained if custom data points for that reagent are entered into a matrix in the transmitter.

3.6 Specialized Industry Measurements

Conductivity is a non-specific measurement but in particular applications it can take on a particular significance. Following are industry-unique methods of sample conditioning, measuring and interpreting conductivity.

3.6.1 Pharmaceutical Waters

Water is the most frequently used raw material in the production of pharmaceuticals as a solvent, ingredient, reagent and for cleaning and laboratory use. The various pharmacopoeias prescribe several quality specifications for compendial waters such as Purified Water and Water for Injection, with which pharmaceutical manufacturers must demonstrate compliance. Conductivity is one of two prescribed chemical tests which monitors impurities. Depending on the country and required water quality, the specifications vary slightly. Pharmacopoeias include:

- United States Pharmacopoeia: USP
- European Pharmacopoeia: EP
- Chinese Pharmacopoeia: ChP
- Indian Pharmacopoeia: IP

In recent years, there has been a harmonization effort among the pharmacopoeias. Some common specifications were adopted, but there are still differences. Table 7 shows an overview of the conductivity specifications for two different water qualities.
Practical Considerations

Conductivity

Table 7: Overview of the on-line conductivity limits referred to in different pharmacopoeias

<table>
<thead>
<tr>
<th></th>
<th>USP</th>
<th>EP</th>
<th>JP</th>
<th>ChP</th>
<th>IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified Water</td>
<td>1.3 µS/cm</td>
<td>5.1 µS/cm</td>
<td>on-line: 1.3 µS/cm</td>
<td>5.1 µS/cm (1 stage)</td>
<td>1.3 µS/cm (3 stage)</td>
</tr>
<tr>
<td></td>
<td>(3 stage)</td>
<td>(1 stage)</td>
<td>off-line: 2.1 µS/cm</td>
<td>(3 stage)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>off-line: 2.1 µS/cm</td>
<td>1.3 µS/cm</td>
<td>off-line: 2.1 µS/cm</td>
<td>1.3 µS/cm (3 stage)</td>
<td>1.3 µS/cm (3 stage)</td>
</tr>
</tbody>
</table>

Water for Injection

<table>
<thead>
<tr>
<th></th>
<th>USP</th>
<th>EP</th>
<th>JP</th>
<th>ChP</th>
<th>IP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.3 µS/cm</td>
<td>1.3 µS/cm (3 stage)</td>
<td>on-line: 1.3 µS/cm</td>
<td>1.3 µS/cm (3 stage)</td>
<td>1.3 µS/cm (3 stage)</td>
</tr>
<tr>
<td></td>
<td>(3 stage)</td>
<td>(3 stage)</td>
<td>off-line: 2.1 µS/cm</td>
<td>(3 stage)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>off-line: 2.1 µS/cm</td>
<td>1.3 µS/cm</td>
<td>off-line: 2.1 µS/cm</td>
<td>1.3 µS/cm (3 stage)</td>
<td>1.3 µS/cm (3 stage)</td>
</tr>
</tbody>
</table>

The 3 stage testing noted in Table 7 allows water to be further tested against laboratory criteria if it should fail to meet the on-line conductivity limit. Off-line laboratory tests have higher conductivity limits that include saturation with air containing CO₂.

Table 8: Requirements for conductivity instrumentation for pharmaceutical water

<table>
<thead>
<tr>
<th>Specification</th>
<th>USP, EP, JP, ChP, and IP</th>
</tr>
</thead>
</table>
| Conductivity sensor and cell constant accuracy | Verification by: Cell constant must be known within ± 2%.  
  - 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 instrument calibration    | Conductivity cell is replaced with NIST (or equivalent national authority) traceable ± 0.1% resistor. |
| Instrument resolution                  | 0.1 µS/cm                                                                                 |
| Instrument accuracy (at 1.3 µS/cm)     | ± 0.1 µS/cm                                                                               |
| Temperature compensation               | None                                                                                      |
| Temperature accuracy                   | ± 2 °C                                                                                   |
Note that pharmacopeial and other regulatory specifications are subject to change. Consult the applicable pharmacopeia for current requirements.

**3.6.2 Power Industry Cycle Chemistry**

Conductivity measurements in the steam power generation industry have a particular significance depending on the sample conditioning applied ahead of the measurement. Often these on-line measurements are made on the same sample, flowing sequentially to three sensors with sample conditioning components between them. Because the composition of these samples is different from general purpose applications, special temperature compensation algorithms are included in transmitter firmware that accounts for both the changing dissociation of water and its interaction with the ionization of ammonia, amines and acids found in these samples. (See Table 3.)

**Specific Conductivity** is the direct conductivity measurement of a sample, usually containing ammonia and/or amines with a conductivity in the range of 2 to 15 µS/cm and is closely related to the pH. It is frequently used to control the ammonia or amine feed. ‘Ammonia’ temperature compensation is used for this measurement.

**Cation Conductivity** is the measurement of conductivity after the sample has passed through a cation exchange resin cartridge that removes any ammonia and amines, usually in a range < 0.5 µS/cm. It measures total anion concentration, e.g. ppb levels of chlorides, sulfates, bicarbonates, acetates, formates. This measurement is also known as acid conductivity or conductivity after cation exchange. ‘Cation’ temperature compensation is used for this measurement.

**Degassed Cation Conductivity** is the measurement of conductivity after both the cation exchange cartridge and a degassifier, usually in a range < 0.5 µS/cm. It measures total anion concentration except for bicarbonate which has been removed in the degassifier as CO₂. It is a more specific indication of the more corrosive anions and is valuable during plant startups and in units where CO₂ intrusion is significant. This measurement is also known as degassed acid conductivity. ‘Cation’ temperature compensation is used for this measurement.
Calculation of pH is possible because of the close relationship between specific conductivity and pH in cycle chemistry samples. The small cation conductivity value is used to trim the calculation for the effect of small amounts of anions. This function is provided in transmitters measuring specific and cation conductivity and results are typically more accurate than pH electrode measurements under normal operating conditions. However, under upset conditions such as an acid leak from a condensate or makeup demineralizer, if the pH goes below 7, the calculation will produce very large errors. Therefore an electrode measurement is always recommended as a safety backup to the calculation.

3.6.3 Industrial Boiler Neutralized Conductivity Measurement

Industrial boiler water treatment sometimes specifies a conductivity measurement on a grab sample that has been neutralized with a weak acid such as gallic or citric to eliminate the high conductivity of hydroxide ions. This measurement is a more accurate estimate of total dissolved solids for controlling boiler blowdown. However, it is always lower than a direct on-line conductivity measurement so the measurements cannot be compared. Neutralized conductivity measurement is always made off-line and should use standard temperature compensation in a portable or laboratory instrument.
4 Frequently Asked Questions

When do I need to perform a calibration or a verification?
METTLER TOLEDO Thornton process conductivity sensors and transmitters are factory calibrated and certified valid for one year from installation unless measurement is in samples that could deposit solids or otherwise foul the electrodes or insulator of the sensor. It is recommended to verify accuracy and make calibration adjustments if necessary on an annual basis.

Complete calibration for highest accuracy measurements consists of calibrating the temperature and conductivity measuring circuits, the temperature transducer and the cell constant. Measuring circuit calibration is accomplished using NIST-traceable resistances provided in calibration modules specifically designed for Thornton transmitters and for the measuring circuits within UniCond sensors. Calibration of the temperature transducer should be done using a certified thermometer standard. Calibration of the cell constant should be done very carefully with a clean sensor, certified standard(s) and good technique as described in the transmitter’s manual. Calibrations can be performed by METTLER TOLEDO service personnel or by returning equipment to the factory. See section 3.1.

Which temperature compensation mode should be used?
The default and appropriate setting for normal water treatment, general purpose and ultrapure water monitoring applications is the Thornton ‘Standard’ setting which provides very accurate compensation across a very wide range of measurement.

Pharmaceutical water monitoring requiring conformance to USP <645> or similar pharmacopoeia requirements should be set to ‘None’.

Other settings and their applications are identified in Table 3.
What effect does flowrate have on conductivity measurement?
With good instrumentation, the measurement of conductivity is unaffected by sample flowrate. However, the flowrate can influence the actual conductivity of pure water samples which will then show up in the measurement. If a sample line or fittings allow traces of air including CO\textsubscript{2} to diffuse or leak into the sample it will raise the conductivity (lower the resistivity). Under these conditions, an increase in flowrate will dilute the CO\textsubscript{2} ingress and lower the conductivity (raise the resistivity) which is an excellent way to identify this kind of sample degradation. Low flow-rates can also allow trace contaminants dissolving off sample line and fitting surfaces to accumulate and produce the same results. Depending on the particular installation issues, this condition can be mitigated or eliminated by measuring in-line, by tightening sample tubing fittings, by increasing the sample flowrate, by using a shorter length of sample tube or by using non-gas-permeable (stainless steel) sample tubing.

For less pure samples, if the water is saturated with air and bubbles form on the electrode surfaces, the measurement will read too low a conductivity value. This condition is likely to occur in water treatment systems where the water is warming up and/or dropping in pressure as it passes through treatment components. If the flowrate is increased sufficiently for increased turbulence to strip off the bubbles, or if tapping on the sensor or the pipe holding it dislodges the bubbles, the conductivity measurement will go back up to its real value. This condition should be resolved by using a higher flowrate or by relocating the sensor to a more turbulent flow area of the piping.

How do I clean a conductivity sensor?
Sensors use chemically resistant materials and can be cleaned with most dilute detergents, acids or other solvents appropriate to remove the fouling coating. **WARNING:** Use appropriate precautions if using hazardous cleaning materials. For coatings between metal electrodes, light wiping with a cotton swab may help. However, do not use a brush or scrubbing action and do not touch graphite or platinized platinum electrodes as this would smooth the intentionally roughened surface and result in erroneously low conductivity readings.
What is the shelf life of certified conductivity standard solutions?
METTLER TOLEDO Thornton guarantees the accuracy of most unopened standard solutions for a period of one year from the date of manufacture. The 25 µS/cm standard has a shorter shelf life of 6 months. The expiration date is printed on the product label.

What is the general life expectancy of a conductivity sensor?
Conductivity sensors are basically mechanical and do not age in the same way as electrochemical sensors such as pH electrodes. Conductivity sensor lifetime is not limited as long as it is not subjected to excessive temperature or pressure, corrosive chemicals, mishandling, mechanical damage or fouling.

Can conductivity be measured in non-aqueous solutions?
Some organic substances have dissociative properties that allow conductivity measurement. Compounds like benzene, alcohols, and petroleum products generally have very low conductivity. It should be recognized that an increase in conductivity can indicate either an increase in ionic contamination or an increase in water content that allows increased dissociation, or both. This may make the significance of the measurement rather ambiguous. METTLER TOLEDO Thornton conductivity equipment is suitable for aqueous samples or non-aqueous samples with low water content. For the very lowest conductivity ranges, a sensor with 0.01 cm\(^{-1}\) cell constant should be used. With organic solvents be sure to confirm chemical compatibility with sensor materials.
## 5 Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternating current (AC)</td>
<td>Flow of electric charge which periodically reverses direction.</td>
</tr>
<tr>
<td>Anion</td>
<td>A negatively charged ion such as chloride, sulfate, bicarbonate.</td>
</tr>
<tr>
<td>Calibration</td>
<td>Empirical determination of the cell constant by measuring a standard solution or comparing with standard equipment.</td>
</tr>
<tr>
<td>Cation</td>
<td>A positively charged ion such as sodium, calcium, ammonium.</td>
</tr>
<tr>
<td>Cell constant $K \ [\text{cm}^{-1}]$</td>
<td>Theoretically: $K = \frac{L}{A}$; The ratio of the distance between the electrodes ($L$) to the effective cross-sectional area of the sample between the electrodes ($A$). The cell constant is used to transform a conductance measurement into the conductivity value and is determined by calibration.</td>
</tr>
<tr>
<td>Conductance $G \ [\text{S}]$</td>
<td>The ability of a material to conduct electricity. It is the reciprocal of electrical resistance.</td>
</tr>
<tr>
<td>Conductivity $\kappa \ [\mu \text{S/cm}]$</td>
<td>Conductance for a standardized cell. The measured conductance is multiplied by the cell constant to obtain the conductivity ($\kappa = G \cdot K$).</td>
</tr>
<tr>
<td>Direct current (DC)</td>
<td>Flow of electric charge in only one direction.</td>
</tr>
<tr>
<td>Electrode</td>
<td>One of 2 or 4-electrodes to which a current is applied to measure the conductivity. The electrodes are in direct contact with the sample solution and form the measuring cell. An electrode is also called a pole.</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Aqueous solution of acids, bases and/or salts which are able to conduct electricity.</td>
</tr>
<tr>
<td>Field effects</td>
<td>Measurement errors caused by part of the conductivity measuring field outside the geometric space of the measuring cell that encounters physical interference such as by a pipe wall.</td>
</tr>
</tbody>
</table>
Fouling: Formation of gelatinous or oily coating, colloidal masses or bacterial growth in the measuring cell. These deposits can negatively influence the conductivity measurement if they coat the electrodes or may positively influence high purity conductivity measurement if they coat insulator surfaces.

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 with a defined probability.

Measuring cell: The 2 or 4 electrodes held together with an insulating structure.

Polarization: Accumulation of ionic species near electrode surfaces due to applying electrical current in an electrolyte. A polarization resistance arises at the electrodes, which may lead to erroneous results.

Pole: Synonym for electrode.

Reference temperature: The temperature to which conductivity measurements are compensated (usually 20°C or 25°C) using a temperature compensation algorithm.

Resistance Ω [ohm]: Property of a conductor that opposes the flow of current through it.

Resistivity $\rho$ [MΩ·cm]: Resistivity is the inverse of conductivity ($\rho = 1 / \kappa$). Resistivity values are frequently preferred to conductivity for measurements in ultrapure water or organic solvents, especially in the microelectronics industries.
<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>The concentration of soluble minerals (mainly salts of alkali metals) in water.</td>
</tr>
<tr>
<td>Standard solution</td>
<td>A solution containing a known amount of ionic substance that produces a precisely known conductivity.</td>
</tr>
<tr>
<td>TDS [ppm]</td>
<td>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. Conductivity is sometimes used as a convenient surrogate measurement to obtain an estimate of TDS.</td>
</tr>
<tr>
<td>Temperature compensation mode</td>
<td>The selected algorithm to convert the measured conductivity to a reference temperature (usually 25 °C). A compensated measurement is a temperature-independent indication of water quality that enables comparison with industry specifications. Because the temperature dependence differs from one kind of sample to another, the compensation mode should be selected based on the application. For on-line pharmaceutical water specifications, temperature compensation is not used; instead, both the uncompensated conductivity and the temperature must be reported and be within tabular limits established by the pharmacopoeia.</td>
</tr>
<tr>
<td>Verification</td>
<td>Checking the conductivity reading by measuring a standard solution.</td>
</tr>
</tbody>
</table>

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