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Conductivity Handbook

MEASUREMENT TECHNIQUE THEORY AND TIPS FOR PRACTICAL APPLICATION

WTW
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More than 70 years of experience



Conductivity measurement has a long tradition with our WTW® brand and is marked out by edge cutting innovations which continue to shape conductivity measurement today. For example, the development of the four electrode measurement cells of the TetraCon® series 30 years ago resulted in a universal measurement cell which still sets the benchmark today. Conductivity is mostly measured in industrial applications, from ultrapure water to concentrated salt solutions, acids and alkalis. In environmental measurements it is used, for example, to determine the salinity in brackish and sea water.

With this handbook we want to help the user get to know the **basics of measurement**, make **reasons and procedures** clearer to the user, and, last but not least, provide **practical tips** for handling and maintenance. We are happy to be at your disposal at any time, just give us a call!

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SECTION 1
Fundamentals

The specific electric conductivity and electrical conductance are a measure of the property of a solution, metal or gas, in short, all materials, to conduct electricity. In solutions the current is provided by cations and anions, and by electrons in metals. If a substance has a high conductance value G the electrical respectivly ohmic resistance R is low.
The electrical conductance G is the inverse of the resistance

$$G = \frac{1}{R}$$

R with the unit Ohm (Ω) and G with the unit Siemens (S). At this point a look ahead to the measurement technology makes sense. In order to measure the electrical conductance, voltage is applied to electrode pairs and the current is measured. During this the cations are attracted to the negative electrodes (cathodes), and the anions to the positive ones (anodes), with the solution thus representing an electrical conductor. A conductor is defined by its length and diameter. The smaller the distance L between electrodes and the greater the electrode surface A the greater the measured current at the same electrolyte concentration and same voltage (Fig. 1).

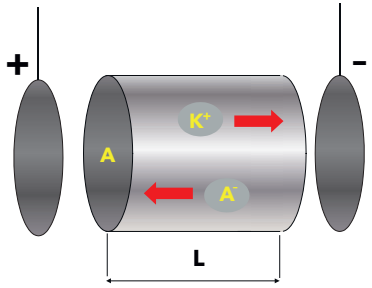


Fig. 1 Representation of an electrical conductor

The electrical conductance G arises from the relationship:

$$G = \gamma \cdot \frac{A}{l} = \frac{1}{\rho} \cdot \frac{A}{l}$$

with A as the electrode surface, l as the distance between electrodes, γ as the specific conductivity and ρ as the specific resistance. γ and ρ are material constants with the units S/m and Ω m. This relationship makes clear the context between specific conductivity γ and the conductance G. For the specific conductivity, besides γ, σ and particularly K are commonly used as symbols.

The quotient of the length and area is the cell constant K (resulting in the unit m-1).

$$K = \frac{l}{A}$$

If the cell constant is known, the specific conductivity can be correspondingly determined from the measured conductance and depicts the result of the conductivity measurement.

1.1 Conductivity cells

Generally conductivity cells consist of electrode pairs to which a voltage is applied. The current is measured and the conductivity calculated.

This is however a highly simplified explanation. The voltage applied is an alternating voltage in order to reduce polarization effects.
The polarization of a conductivity cell means effects which occur on the interface between metal and fluid during current flow and which appear to alter the conductivity of the solution. If voltage is applied to an electrode a capacitor layer (double layer) is created because the electrode attracts inversely charged ions.

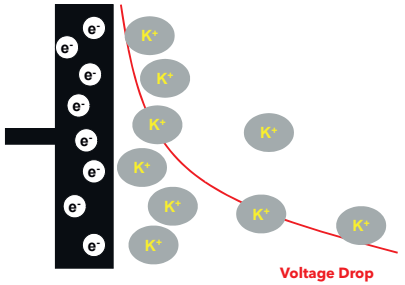


Fig. 2 Polarization effect

With increasing distance of the electrode in the solution, the effective voltage continues to drop further. Polarization effects can be reduced or prevented by applying an alternating voltage and by optimizing the electrode surfaces. In an alternating field, inhomogeneous charge distribution as shown in Fig. 2 cannot form so easily because the ions are alternately attracted by the two electrodes. Cations and anions oscillate about their location with the applied frequency. This effect can be compared to a tug-of-war between two equally strong teams.

The higher the applied frequency, the lower the polarization effects that can be expected. Because the measuring frequency at high conductivity is device related restricted, a suitable electrode material must be used, usually graphite or stainless steel.

The „classical" conductivity cell consists of an electrode pair with a measurement range which is, however, generally restricted to low conductivity. Despite high frequency and the selection of low-polarizing materials, polarization effects cannot be avoided when measuring higher ion concentrations. Polarization effects generally lead to the display of apparently lower measured values.

An enhanced development is provided by the four-electrode TetraCon® measuring cell from WTW®. It has a voltage electrode pair in addition to the current electrode pair. As a result, the ohmic voltage drop is determined in the solution with current flowing through it. The conductivity value of the solution results from the known current and measured voltage drop. This measuring method is not affected by polarization resistances. Moreover, a four-electrode cell is insensitive to measuring errors that result from contamination.

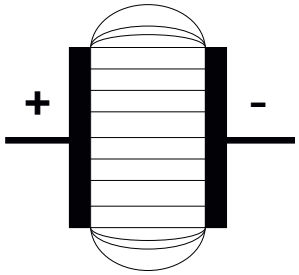


Fig. 3 Field line stray fields at the edges

The cell constant K cannot be determined by purely „measuring" the electrode distance and area. Although the flux lines in the area directly between the electrodes appear linear, at the edges stray fields form and the electrode area relevant for the measurement is larger than the actual geometric area (Fig. 3). This effect is encountered when the cells are calibrated. The cell constant is determined using a calibration solution with known conductivity, usually a 0.01 mol/L KCl solution. This is described in more detail later.

1.2 Temperature compensation

Conductivity is a parameter that is strongly dependent on temperature. A 0.01 molar potassium chloride solution is presented here as an example. The conductivity of this solution at 20 °C is 1278 µS/cm, whereas, at 25 °C, it is 1413 µS/cm. As a result, values of the same sample measured at different temperatures cannot be compared in practice. For this reason, the reference temperature was introduced. It is usually 20 °C or 25 °C. Conductivity measurements are normally conducted as follows: the meter records the actual conductivity and temperature, converts it to the reference temperature using a temperature compensation function and displays the conductivity at the reference temperature. Conductivity measurements and temperature measurement are intrinsically related. Thus modern WTW conductivity cells have built-in temperature sensors.

Depending on the type of sample, different temperature compensation functions must be used.

- Linear function
- Non-linear function (nlF) for natural waters according to EN 27 888 [1]
- Non-linear function for ultrapure water (additional consideration of the intrinsic conductivity of the water)
- Non-linear functions for special solutions
- No compensation

Figure 4 illustrates the measuring principle of conductivity measurements for a sample (e.g. wastewater) using nlF temperature compensation.

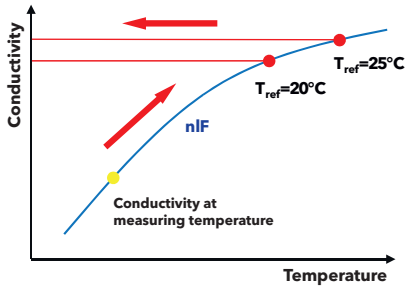


Fig. 4 Measuring principle for conductivity measurement for a sample with nlF temperature compensation

Linear functions are used, e.g. for salt solutions, acids and alkalines. However, the linear dependency is not suitable for many aqueous liquids. The temperature dependency can only be described by non-linear functions. The non-linear function for natural waters, i.e. for ground water, surface water, drinking water and wastewater is an example of this.
Selected values are listed in the following table as an example of typical conductivity:

	Conductivity at 25 °C
Ultrapure water	0.055 µS/cm
De-ionized water	1 µS/cm
Rain water	50 µS/cm
Drinking water	500 µS/cm
Industrial wastewater	5 mS/cm
Seawater	50 mS/cm
1 mol/L NaCl	85 mS/cm
1 mol/L HCl	332 mS/cm

Even the ultrapure water has a conductivity. This has its origin in the intrinsic dissociation of water that, according to the solubility product, forms oxonium and hydronium ions.

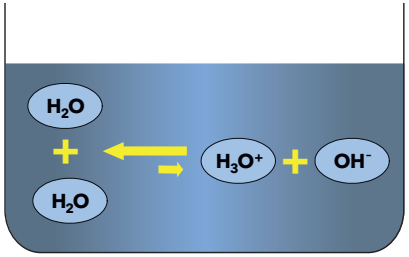


Fig. 5 Intrinsic dissociation of water

SECTION 2

Calibration and analytical quality assurance

2.1 Calibration

First a preliminary remark: The terms calibration and adjustment are often used synonymously. Strictly speaking, calibration describes a comparison with set points. The determined values must lie within specified tolerances. Adjustment means an active change of settings.

Compared to pH measurement and oxygen measurement, the measuring cell does not change by the measurement procedure in conductivity measurements. At least, this is the case if the cell is used correctly. The measuring cell is made of stainless steel, platinum or graphite electrode pairs that are chemically resistant and whose geometry is determined by the cell constant.

The measuring cells are delivered from the factory with a specified and tested cell constant and the user can start measuring without any need for prior determination of the cell constant.

The production-dependent tolerances of the cell constant lie between 1.5 % and 2 %. If highly precise measurements are required, the cell constant can be precisely adjusted using potassium chloride solutions (Fig. 6). This generally applies to new cells or when a cell is changed. In its area of application the cell constant is an inalterable measurement defined by the mechanical parameters of distance and area, as well as via the surface roughness. A calibration with more than one standard solution therefore does not make sense.



Fig. 6 Control standards for conductivity cells

To do this, the use of commercially available KCl solutions is recommended as there is no danger of error as a result of dilution or contaminated substances (KCl or water).

Calibration of the conductivity cell is to be understood in the sense of checking, and not in the sense of adjustment, as any change of the cell constant is usually caused by contamination. It is not logical to adjust the cell to the current contamination. It is better to clean the cell.

EN 27 888 recommends regular testing at least every six months. The standard calibration solution that corresponds to the cell constant must be used to do this.
All standard conductivity solutions contain highly defined, low amounts of dissolved salt in order to create a specific conductivity value. They are highly sensitive to contamination, dilution and evaporation if stored in an open vessel and thus immediately lose their characteristics.

Please note:

- All conductivity standards are only permitted for single use
- They must be disposed after use
- Only store in closed vessels
- Do not use beyond the expiry date

The solutions to be used are potassium chloride solutions of different concentrations (see Table below).

For the measurement range up to 2 µS/ cm, that is, only for the ultrapure water such as boiler feed water or de-ionized water, no contamination is to be expected. There are specific standards available for this conductivity measurement

Measuring range	Electrode material	Recommended standard solution $C_{(KCl)}$ [mol/L]	Electrical conductivity at 25°C [mS/cm]
≤ 200 µS/cm	Steel	-	5 µS/cm
≤ 2 mS/cm	Platinum, graphite	0.01	1.413

Table: Recommended standard solution depending on electrode material and measurement range

range which strongly reduce carbon dioxide contamination from the air through the partial replacement of the water by suitable organic fluids such as glycerin. They are, however, only intended for single use and must be handled with great care in order to avoid contamination. Exposure to the air must be limited to a few minutes, something which, however, does not present a problem due to the little time it takes to complete the measurement.

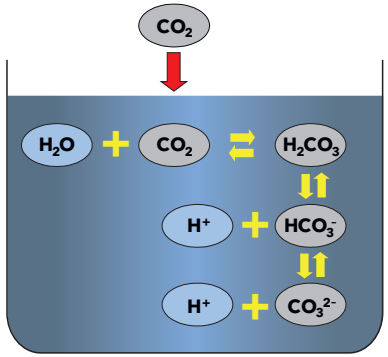


Fig. 7 Impact of CO2 from the air on the standard solution

Considering the effect of carbon dioxide applies to calibration as well as to the actual measurement (see Fig. 7). It should be performed under the absence of air or using an inert gas

To check an ultrapure water measurement cell, a simple functional test is the most useful. If the cell provides plausible values for de-ionized water, interference can be essentially excluded.

When checking cells for a conductivity range smaller than 200 µS/cm use the specific standard solutions available from Xylem Analytics. These can be obtained with 100 µS/cm or with 5 µS/cm for the ultrapure water range (nominal values at 25 °C). It is important to work without temperature compensation when calibrating; the certificates in the deliveries contain the temperature curve for comparison. It is recommended to carry out calibrations at 25 °C.
For the measurement range up to 2 mS/cm it is possible and recommended to use the 0.01 mol/L KCl solution.

Within the measurement range up to 300 mS/cm a simple check (not calibration!) can be carried out where the 3 molar KCl solution is used for the pH measurement. The result should lie within the order of magnitude of 300 mS/cm.

2.1.1 Adjusting and checking the cell constant

Conductivity measurements are extremely sensitive to ionic contamination. Therefore, the cleaned or new conductivity cell should be rinsed with standard solution before it is submersed in the standard solution. For laboratory measurement cells such as the TetraCon® 325, it is recommended to submerse the sensor directly in the freshly opened calibration standard bottles to prevent contamination by the sample vessel. If this is not possible, the vessels to be used should be rinsed with standard solution.

A special case is presented by stray field cells. The electrodes are attached to the front of the shaft (e.g. TetraCon® 700 for online measurement). The cell constant depends on the size and type of the stray field. The stray field is influenced by limitations such as the base of the vessel or of the mounting tube. As a result, the adjustment or checking of the sensor in a mounting tube must be performed while it is installed. In other cases, a minimum distance to the vessel wall must be maintained. The measured value must be independent of the size of the vessel or the volume of standard solution.

If the cell constant is adjusted to raise the measuring accuracy (not to compensate for contamination!), it is important to check whether the conductometer has an automatic calibration function as is the case in modern WTW® conductometers.

If it does, it is sufficient to submerse the cell in 0.01 mol/L KCl solution and to start the adjustment process (Fig. 8). The background to this is that the temperature compensation function of the standard calibration solution is stored in the meter. During this process, the meter measures the conductivity and changes the calculated cell constant in such a way that the corresponding conductivity of the standard solution is reached at the selected reference temperature. After this is completed, the adjusted cell constant is displayed.

In meters without automatic calibration, this process is performed by the user. In this case, the user must ensure that adjustment takes place in the thermostatic state (Fig. 9). The control solution and measuring cell must be at the reference temperature. The background for adjusting the cell constant is the same. The cell constant is changed so that, at the reference temperature, the nominal conductivity is achieved as closely as possible. As closely as possible because the resolution of the cell constant is not often high enough to enable an adjustment to the exact value (e.g. 1413 µS/cm for 0.01 molar KCl solution at 25 °C).

Note:
If the conductivity cells continue to be submersed in the standard calibration solution after the adjustment is complete and the meter is switched to the normal measuring mode using, e.g. an nIF temperature compensation function, this usually results in a different measured value. (Reason: A different temperature compensation function!)

If a control measurement only is performed with the standard calibration solution and without adjustment of the cell constant, the correct temperature compensation function must be considered. The value of the linear temperature compensation for the 0.01 molar KCl solution is 1.9 %/K at a reference temperature of 20 °C and 2.1 %/K for a reference temperature at 25 °C

Alternatively, the control solution can be thermostatted precisely to the reference temperature where adjustment of the corresponding temperature compensation function is no longer required.



Fig. 8 Automatic calibration function

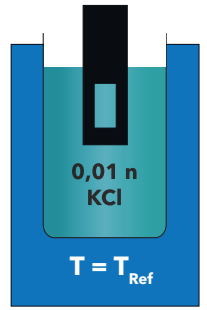


Fig. 9 No automatic calibration function

If the conductivity cell is changed, the new cell constant must be entered in the conductometer! This does not apply to measurement systems that work with digital conductivity cells; for these the cell constants are saved in the measurement cell's electronics and are automatically transferred when changing the meter.

2.1.2 Testing the conductometer

The primary measurement of the conductance is the resistance. The classical function of a conductometer can be tested using certified test resistors. To do this, we provide a set of six different resistors that are connected to the meter instead of the measuring cell (Fig. 10). This type of qualification is particularly required in context with measurements according to pharmacopoeia.



Fig. 10 Set with traceable and certified precision resistances

Digital conductivity cells can be checked via comparative measurements with traceable and certified reference systems or with a corresponding system calibration (see below). This type of qualification is also particularly required in context with pharmacopoeia measurements.

If the measured values displayed are within the tolerance specified in the certificate, the functional safety is met. If the displayed values are outside the tolerance, the meter must be sent for adjustment. Our test set enables testing within the scope of the ISO 9000. It enables the traceability of the measured values to national standards.

2.2 Derived measured parameters

Additional parameters can be derived from the conductivity, partially via a simple conversion, and partially through the introduction of additional parameters. Below you can find a brief list of the most important values:

2.2.1 Salinity

Salinity is an auxiliary value for the measurement of oxygen dissolved in seawater. The reason for this is that the solubility of oxygen reduces in the presence of further dissolved materials. As this dependency is known and tabulated, the salinity value can be used for compensation for the comparison of the dissolved oxygen concentration. The salinity is a dimensionless value determined from the mass of the dissolved salt in the mass of water (g/kg). Xylem Analytics uses the IOT (International Oceanographic Tables) [2] to calculate salinity. For IDS multiparameter meters with two and three channels, in the case of the simultaneous connection of a conductivity and oxygen electrode (also in the multiparameter depth sonde) it is possible to select the compensation directly from the menu. It is then automatically calculated in the background. For all other oxygen measurements the value can be manually set in the equipment. Correction is recommended from a salinity of 1 %.

2.2.2 Total Dissolved Solids (TDS) Filtrate

In order to conclude to the amount of the salt dissolved in comparable samples, a conductivity measurement can be used following suitable sample preparation with a corresponding calibration. For this a filtered sample is weighted from the salt residue remaining after evaporation.

The principle for this measurement is that this determined mass can be adjusted to the measured conductivity via a proportional factor that can be adjusted between 0.40 and 1.00. Following this the concentration of dissolved salts in similar samples of comparable composition can be directly read on the meter via the conductivity measurement. The base temperature compensation is usually the nlF.

2.2.3 Specific resistance

The specific resistance is merely the mathematic reciprocal value of the specific conductivity. Its unit is thus Ohm × cm with the corresponding derived prefixes (kOhm × cm, MOhm × cm). In some industries it is provided in place of the specific conductivity, particularly in the measurement of ultrapure water (0.055 µS/cm at 25°C corresponds to around 18.2 MOhm × cm).



Fig. 11 Benchtop conductivity meter, Multi 9630 IDS (WTW®)

SECTION 3

Measurement and analytical quality assurance

3.1 Which measuring cell is required for which application?

As in pH measurement, the selection of the most suitable conductivity cell depends on the application. It is also true that the effort required is greater, the cleaner the sample to be examined. A number of examples have been included to illustrate this, but it is also important to note that a wide number of special cells are available:
The standard TetraCon® 325 conductivity cells have graphite electrodes in four conductor technology and are, thus, insensitive to contamination and easy to clean; their application is in routine analysis where the measuring range lies between 1 µS/ cm and 2 S/cm. If a measurement is to be made in ultrapure water such as boiler feed water or ion exchange water, it is necessary to use a flow-through vessel. Contact with the air must be excluded. The reason for this is the carbon dioxide in the air that in turn forms carbonic acid in water and leads to a change in the conductivity. Two electrodes are available depending on the measuring range required.

3.2 A special tip and for recapitulation

Two points are often overlooked in the measurement of conductivity:
The result is usually referred to the reference temperature. Mostly, this is 25 °C. If the reference temperature is set to 20 °C in the meter, a very different value is obtained that has nothing to do with incorrect measurement, but simply has a different reference.

To calculate the conductivity at the reference temperature, the meter converts from the current sample temperature using a characteristic function. If this function does not correspond to the sample, an incorrect value is obtained. If, for example, a saline solution is to be tested, a linear function is required and not the non-linear function for natural waters.

These two points should be taken into consideration in every measurement, set correctly and also documented according to the AQA.

3.3 Drift control

Drift control, as with pH and oxygen, does not apply in the case of conductivity measurement as the displayed measured value is the current measured value. The time-determining factor is the temperature and the associated compensation, and it can take a little while for a measuring cell to cool down from air temperature to, for example, that of the water of a mountain stream. Precisely this is taken into account as part of drift control.

3.4 Cleaning the cells

Warm water with some household detergent has proved itself as a suitable cleaning agent for organic contamination, alcohol may also be used. Carbonate deposits are best cleaned using ten-percent citric acid. It is possible to clean graphite, steel or polished platinum electrodes mechanically using a soft brush. However, make sure that the surface of the electrodes is not scratched! Never use hard objects such as screwdrivers.

3.5 Storing the measuring cells

Cells made of polished platinum, steel or graphite will be stored in a dry place.

SECTION 4

New measurement technologies & specific applications

4.1 Intelligent Digital Sensors – IDS

For some years we also offer intelligent sensors for conductivity measurement where the signal processing takes place in the sensor and no longer in the meter. The IDS sensors (= intelligent digital sensors), alongside the digitally processed measurement signals, provide further important parameters as part of comprehensive data sampling, such as description, serial number, calibration status, and additionally for conductivity the saved cell constant as well as the selected temperature compensation. The advantage of this relocation of the measurement function is evident:

1. Without restrictions cable lengths of up to 100 m are possible, as well as the use of wireless modules.
2. The sensors can be used without issue or re-calibration with different meters from the IDS MultiLine® or inoLab® Multi IDS series.

The meters themselves provide all the necessary options for calibration, data sampling, display and data transfer, as well as conversion into derived measured parameters such as specific resistance, TDS or salinity conductivity.

4.2 Pharmacopoeia conductivity measurements

Conductivity is a simple quality parameter for the determination of the quality of ultrapure water for pharmaceutical applications, but also for other quality assessments for the use of aqueous solutions in pharmaceutical production. Additional regulations exist for these cases which can be found in the corresponding pharmacopoeia. Below a short extract is provided with key data that is to be taken into account during conductivity measurement. [3]

In general there are just a few points to be taken into account:

1. **The measuring meter:** The minimum resolution of a measurement meter must be 0.1 µS/cm in the lowest measurement range. The measurement meter must be checked with resistances displaying a precision of 0.1 % of the respective nominal value.
2. The conductivity cell must be made from a **chemically-resistant material** and the **precision of the cell constant** must be at least 2 %.
3. **(Certified) test solutions** must be used to check the system.
4. The **meter** (in the case of analog sensors) must occasionally be **tested** with specific test resistances.



Fig. 12 Portable conductivity meter, Multi 3630 IDS (WTW®)

Bibliography

[1] DIN EN 27888, Water quality; determination of electrical conductivity, 11/93

[2] The practical salinity scale, UNESCO 1978

[3] Cited from Pharm. Eu., 9th Edition

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Xylem Analytics is a leading manufacturer of premium laboratory, process and field analytical measurement technology for the water & wastewater, marine & coastal, food, environmental, chemical and pharmaceutical markets. We offer sensors, meters and systems that enable the greatest possible flexibility in use due to their modular design. Our range of premium products is constantly expanding through ongoing developments to improve energy savings, process efficiency and compliance with increasingly strict specifications. Our in-depth application knowledge gives our customers confidence that we are the right partners to develop solutions for their needs.

Xylem Lab Solutions, part of Xylem Analytics, is at the forefront of analysis, measurement and monitoring with its diverse product brands. The remarkable history of groundbreaking innovations and many years of experience provide our customers with the best laboratory and field measurement technology for a variety of industries.

Portfolio Webpage

Xylem |ˈzīləm|

1) The tissue in plants that brings water upward from the roots;
2) a leading global water technology company.

We're a global team unifi ed in a common purpose: creating advanced technology solutions to the world's water challenges. Developing new technologies that will improve the way water is used, conserved, and re-used in the future is central to our work. Our products and services move, treat, analyze, monitor and return water to the environment, in public utility, industrial, residential and commercial building services settings. Xylem also provides a leading portfolio of smart metering, network technologies and advanced analytics solutions for water, electric and gas utilities. In more than 150 countries, we have strong, long-standing relationships with customers who know us for our powerful combination of leading product brands and applications expertise with a strong focus on developing comprehensive, sustainable solutions.

For more information on how Xylem can help you, go to **www.xylem.com**

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