Conductivity
Theory and Practice

Preface

The importance of conductivity

Conductivity measurement is an extremely widespread and useful method, especially for quality control purposes.

Surveillance of feedwater purity, control of drinking water and process water quality, estimation of the total number of ions in a solution or direct measurement of components in process solutions can all be performed using conductivity measurements.

The high reliability, sensitivity and relatively low cost of conductivity instrumentation makes it a potential primary parameter of any good monitoring program. Some applications are measured in units of resistivity, the inverse of conductivity. Other applications require the measurement of total dissolved solids (TDS), which is related to conductivity by a factor dependent upon the level and type of ions present.

Conductivity measurements cover a wide range of solution conductivity from pure water at less than 1×10^{-7} S/cm to values of greater than 1 S/cm for concentrated solutions.

In general, the measurement of conductivity is a rapid and inexpensive way of determining the ionic strength of a solution. However, it is a non-specific technique, unable to distinguish between different types of ions, giving instead a reading that is proportional to the combined effect of all the ions present.

This booklet

The subject of this booklet is the measurement of conductivity, i.e. the ability of an aqueous solution to carry an electrical current. Reliable and accurate measurements depend on a number of factors: the concentration and mobility of ions, presence of organic alcohols and sugars, valence of ions, temperature, etc.

The scope of this booklet is to discuss the theoretical aspects of conductivity, the factors that influence the reliability of the measurement, and the techniques. Sections covering the applications, rules for reliable measurements and frequently asked questions have been included to make this a comprehensive review of the importance of conductivity measurements.

Contents

Theory of conductivity

What is conductivity?

Conductivity is the ability of a solution, a metal or a gas - in brief all materials - to pass an electric current. In solutions the current is carried by cations and anions whereas in metals it is carried by electrons.

How well a solution conducts electricity depends on a number of factors:

- Concentration

- Mobility of ions

- Valence of ions

- Temperature

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

How is conductivity measured?

Conductivity may be measured by applying an alternating electrical current (I) to two electrodes immersed in a solution and measuring the resulting voltage (V). During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor.
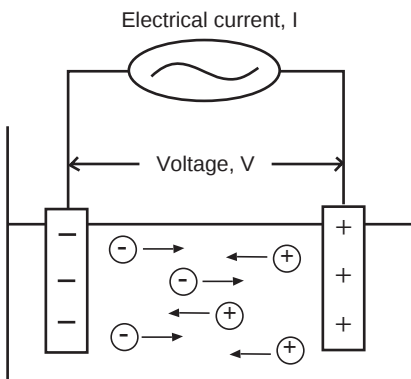
Fig. 1: Migration of ions in solution

What is a conductive solution?

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

Strong electrolytes

Strong electrolytes are substances that are fully ionised in solution. As a result, the concentration of ions in solution is proportional to the concentration of the electrolyte added. They include ionic solids and strong acids, for example HCl.

Solutions of strong electrolytes conduct electricity because the positive and negative ions can migrate largely independently under the influence of an electric field.

Weak electrolytes

Weak electrolytes are substances that are not fully ionised in solution. For example, acetic acid partially dissociates into acetate ions and hydrogen ions, so that an acetic acid solution contains both molecules and ions. A solution of a weak electrolyte can conduct electricity, but usually not as well as a strong electrolyte because there are fewer ions to carry the charge from one electrode to the other.

Definition of terms

Resistance

The resistance of the solution (R) can be calculated using Ohm's law (V = R x I).

$$R = V/I$$

where:

V = voltage (volts)

I = current (amperes)

R = resistance of the solution (ohms)

Conductance

Conductance (G) is defined as the reciprocal of the electrical resistance (R) of a solution between two electrodes.

$$G = 1/R \ (S)$$

The conductivity meter in fact measures the conductance, and displays the reading converted into conductivity.

Cell constant

This is the ratio of the distance (d) between the electrodes to the area (a) of the electrodes.

$$K = d/a$$

K = cell constant (cm^{-1})
a = effective area of the electrodes (cm^2)
d = distance between the electrodes (cm)

Conductivity

Electricity is the flow of electrons. This indicates that ions in solution will conduct electricity. Conductivity is the ability of a solution to pass current. The conductivity reading of a sample will change with temperature.

$$\kappa = G \bullet K$$

κ = conductivity (S/cm)
G = conductance (S), where G = 1/R
K = cell constant (cm^{-1})

Resistivity

This is the reciprocal of the conductivity value and is measured in ohm•cm. It is generally limited to the measurement of ultrapure water, the conductivity of which is very low.

Calibration

Determination of the cell constant required to convert conductance readings into conductivity results.

Standard solution

A solution of known conductivity that is used to calibrate the conductivity measuring chain.

Reference temperature

Conductivity readings are often referenced to a specific temperature, typically 20°C or 25°C, for comparative purposes.

Automatic temperature correction

Algorithms for automatic conversion of sample conductivity to a reference temperature.

Cable correction

The cable correction takes into account the cable resistance and the cable capacitance.

$$Gm = \frac{Gs}{1 + (Rc \cdot Gs)}$$

Gm = measured conductance (siemens)

Gs = solution conductance (siemens)

Rc = cable resistance (Ω)

- **Cable resistance**

    A cable has a given length, therefore a given resistance. It induces error on the result when the resistance of the solution is low, i.e. at high conductivity.

    The cable resistance only influences measurements with 2 or 3-pole cells. For the 4-pole cells the cable resistance has no influence, so if during programming of the conductivity meter a value is demanded, enter zero.

- **Cable capacitance**

   A cable of a given length has a given capacity. The cable capacitance influences low conductance measurements (below 4 µS). Entering a value of cable capacitance in the conductivity meter allows this influence to be corrected.

   Note: a cable capacitance below 350 pF will have no influence on measurements performed using Radiometer Analytical conductivity meters.

Total Dissolved Solids (TDS)

This is the measure of the total concentration of ionic species of a sample. Its magnitude is relative to the standard solution used to calibrate the meter.

TDS factor

Conductivity readings are converted to TDS readings by multiplication with a known mathematical factor. The factor depends on the reference material used to prepare the standard.

Salinity

Salinity is a measurement without unit corresponding to the weight of dissolved salts in seawater.

The conductivity meter

A typical conductivity meter applies an alternating current (I) at an optimal frequency[1] to two active electrodes and measures the potential (V). Both the current and the potential are used to calculate the conductance (I/V). The conductivity meter then uses the conductance and cell constant to display the conductivity.

$$\text{Conductivity}^{2)} = \text{cell constant} \times \text{conductance}$$

Note: the current source is adjusted so that the measured potential (V) is equal to the reference potential (Er) (approximately ± 200 mV).
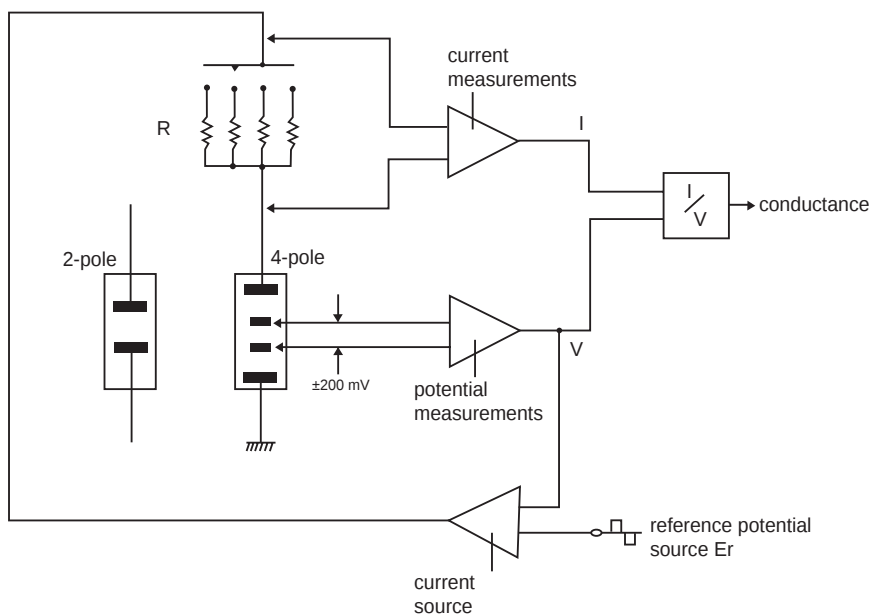
Fig. 2: Simplified conductivity meter diagram

1) Measuring frequencies of a typical conductivity meter

94 Hz in 4.000 µS and 40.00 µS ranges
46.9 kHz in 400.0 mS and 2.000 S ranges

2) at sample temperature

Conductivity cells

2-pole cell

In a traditional 2-pole cell, an alternating current is applied between the 2 poles and the resulting voltage is measured. The aim is to measure the solution resistance (Rsol) only. However the resistance (Rel) caused by polarisation of the electrodes and the field effect interferes with the measurement, and both Rsol and Rel are measured.

Methods of reducing the effects of polarisation are explained on page 16.
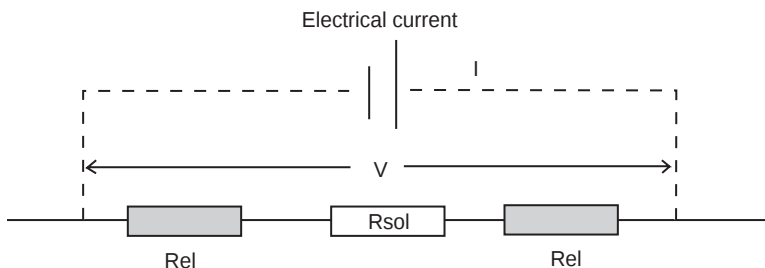
Fig. 3: Simplified diagram of a 2-pole conductivity cell

3-pole cell

The 3-pole cell is not as popular now as it has been replaced by the 4-pole one. The advantage of this design was that the third pole which was linked to pole 1 allowed the field lines to be guided and confined in an optimal manner, limiting dispersion in the measurement and minimising influences on the measurement such as beaker volume and position of the cell in the beaker (field effect). It guarantees a better reproducibility when determining the cell constant and therefore more reproducible results.

4-pole cell

In a 4-pole cell, a current is applied to the outer rings (1 and 4) in such a way that a constant potential difference is maintained between the inner rings (2 and 3). As this voltage measurement takes place with a negligible current, these two electrodes are not polarised ($R_2 = R_3 = 0$). The conductivity will be directly proportional to the applied current.

The geometry of 4-pole cells with an outer tube minimises the beaker field effect, due to the measurement volume being well defined within the tube. The position of the conductivity cell in the measuring vessel or the sample volume therefore has no influence on the measurement.
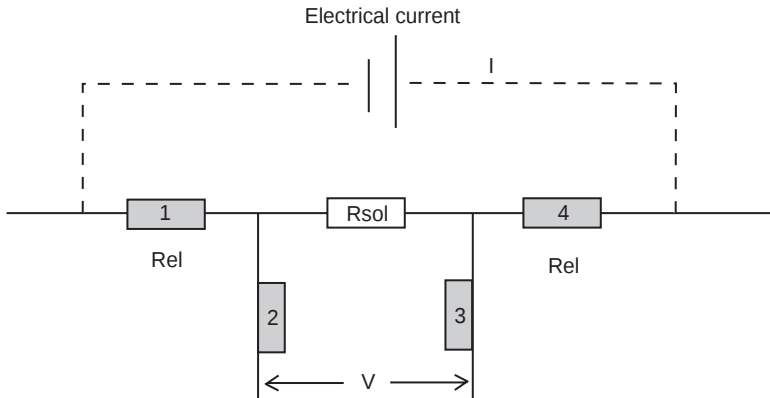
Fig. 4: Simplified diagram of a 4-pole conductivity cell

Platinised cells

Covering the cell poles (plates or rings) with a layer of platinum black is another way to minimise polarisation effects and avoid error on the measurement. The surface of the pole is increased, the current density is decreased, therefore the polarisation effect is less.

Consequently, the cell constant is linear over 2-3 decades towards the higher conductivity range.

The platinum black must not be damaged or scratched, as this will modify the surface of the poles and therefore the cell constant.

However, one minor disadvantage of platinised cells is that the cell constant tends to drift faster than the constant of non-platinised cells.

It is advisable to use platinised cells only in non-viscous samples, without suspensions and to perform frequent calibrations.

Flow-through cell

Flow-through type conductivity cells are designed for flow measurements and measurements in small sample volumes. These measurements can be performed in a closed liquid system protected from air.

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

A circulation cell can be used in two ways:

• circulation: the solution flows non-stop during the measurement.

• pipette: a quantity of solution is drawn into the cell. This technique is ideal for small sample volumes.

Select the right conductivity cell

2-pole or 4-pole cell?

Advantages	Disadvantages
2-pole cell	
Easier to maintain	Field effects - cell must be positioned in the centre of the measuring vessel
Use with sample changer (no carryover)	Only cells with no bridge between the plates
Economical	Polarisation in high conductivity samples
Recommended for viscous media or samples with suspension	Calibrate using a standard with a value close to measuring value Measurement accurate over 2 decades
4-pole cell	
Linear over a very large conductivity range	Unsuitable for micro samples; depth of immersion 3 to 4 cm
Calibration and measurement in different ranges	Unsuitable for use with a sample changer
Flow-through or immersion type cells	
Ideal for high conductivity measurements	
Can be used for low conductivity measurements if cell capacitance compensated	

Conductivity cells and measuring range

The number of poles and whether they are platinised or not influences the measurement. The measurement range over which the cell stays linear gets broader as the number of poles increases. Platinised poles also contribute to increasing the measurement span in which the cell is linear.
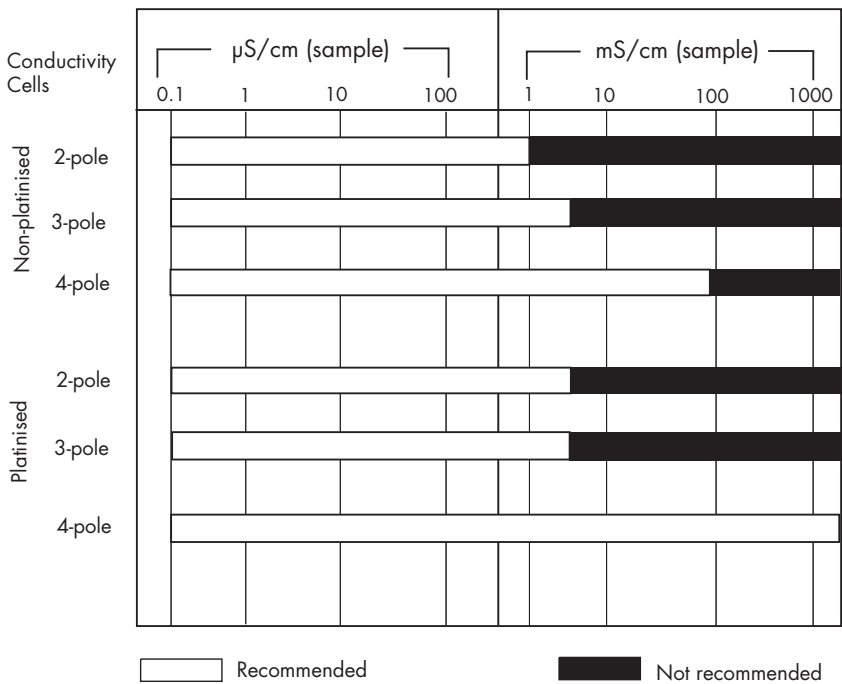
Fig. 5: Guidelines for choosing a cell corresponding to your measuring range

Conductivity values at 25°C

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

What influences the measurement?

The accuracy of conductivity measurements can be influenced by the following factors:

- Polarisation
- Contamination
- Geometry
- Cable resistance
- Cable capacitance
- Frequency change
- Temperature

Polarisation

Applying an electrical current to electrodes in solution may cause an accumulation of ionic species near the electrode surfaces and chemical reactions at the surfaces. Thus, a polarisation resistance arises on the electrode surface, which may lead to erroneous results as it is a parasitic component to the solution resistance.
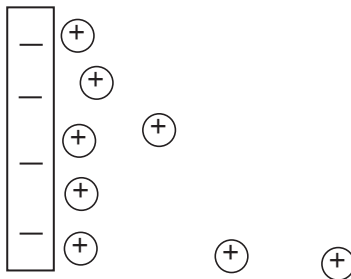
Fig. 6: Accumulation of ionic species at electrode surface

Preventing polarisation

Polarisation effects can be reduced or prevented by:

- **Applying an alternating current**: the measuring current will flow through the double layer capacitance (Cdl) of the electrodes instead of building up a voltage drop across the electrode surface due to the solution resistance (Rsol). Rel is then much smaller than Rsol.

- **Adjusting the measuring frequency**: the frequency has to be adapted to the conductivity of the sample. Low frequencies are applied at low conductivities, where polarisation is negligible compared to the solution resistance (Rsol). High frequencies are applied at high conductivities, where the solution resistance (Rsol) is low in order to minimise the polarisation resistance (Rel).
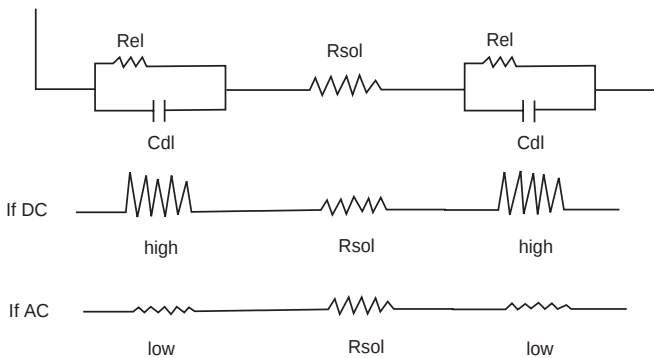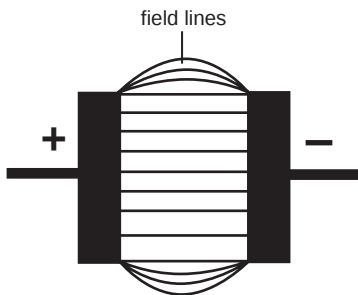
Fig. 7: Polarisation resistance

- **Optimising the electrode areas**: increasing the active surface area of the electrodes with a layer of platinum black reduces the current density and consequently the polarisation effect.

- **Using a 4-pole conductivity cell**: polarisation resistance has no influence on the measurement.

Contamination of electrode surfaces

Deposits on the electrode surface of a 2-pole cell have a similar effect to polarisation errors, i.e. the conductivity reading is lower than usual. These effects can also be prevented with a 4-pole conductivity cell.

Geometry related errors - field effects

field lines

Errors are also caused by field effects - the part of the measuring field that falls outside the geometric space of the 2-pole cell. These field lines can affect the measurement if something inter-feres with the field lines, such as the beaker walls.

3 and 4-pole conductivity cells are de-signed to minimise this effect. If the entire measuring field is contained with-in the body of the cell, then field errors cannot be caused by the beaker wall.

Frequency change

Low frequencies are applied at low conductivities, where the polarisation resistance is negligible compared to resistance of the solution. They also contribute to reducing the cable capacitance effect, which is greater when the conductivity is low (high solution resistance).

High frequencies are applied at high conductivities, where the solution resistance is low.

In most conductivity meters, the frequency is automatically increased with increasing conductance of the sample, to avoid polarisation errors at high conductivity.

Cable resistance

A cable has a given length, therefore a given resistance. The cable resistance induces error on the result and must be taken into account.

Compensate the cable resistance when:

• solution resistance is low (below 50 Ω), i.e. for high conductivity measurements,

• performing measurements using 2 or 3-pole cells,

The cable resistance of a cell is normally specified by the manufacturer.

Note: for 4-pole cells the cable resistance has no influence if during programming of the conductivity meter, a value is demanded, enter zero.

Cable capacitance

A shielded cable of a given length has a given capacity. When the measured conductance is low (below 4 µS), the cable capacitance is not negligible and must be taken into account.

Compensate the cable capacitance when:

• using a 4-pole cell,

• measuring low conductivities,

• the cable capacitance of the conductivity cell is greater than 350 pF,

The cable capacity is normally specified by the manufacturer.

Measuring conductivity

Determination of the cell constant

Calibration is important because the result is the correct value of the cell constant in your working conditions.

The cell constant is a factor that is used to convert the measured conductance to conductivity (see "Definition of terms").

Conductivity* ($S \bullet cm^{-1}$) = cell constant (cm^{-1}) x conductance (S)

It is determined by the geometry of the cell, but in practical terms can only be measured using a standard of known conductivity, for example KCl 0.01 D solution.

The cell constant changes with time. Some modifications can occur due to contamination or due to physical-chemical modification in case of platinised cells. It is therefore recommended to calibrate the cell at least once a week. However, if you use a platinised cell, it is advisable to perform a daily conductivity measurement in a standard. If the result obtained is in accordance with the theoretical value, continue your measurements. If not, your cell needs to be cleaned (if non-platinised) or replatinised (if platinised).

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

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

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

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

Conductivity measurements

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

Low conductivity measurements (pure water)

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

Principle of pure water measurements

According to USP

The conductivity partly depends on the pH, the temperature and the amount of atmospheric carbon dioxide, which has been dissolved in the water to form ions (intrinsic conductivity). The conductivity also depends on the chloride, sodium and ammonium ions considered as water impurities (extraneous conductivity). The conductivity (intrinsic and extraneous) of the water is measured and compared to values listed in a table to evaluate if the studied water is suitable or not for use in pharmaceutical applications. If the sample fails Stage 1, additional tests have to be performed (Stages 2 and 3) in order to determine if the excessive conductivity value is due to intrinsic factors or extraneous ions. The main requirement is that the cell constant be known with an uncertainty better than ±2%.

According to the European Pharmacopoeia

The cell consists of two parallel platinum plates at a defined distance. It is confined within a glass jacket with two pipe connectors enabling measurement in flow mode. This cell is calibrated using a conductivity standard of 26.6 µS/cm at 20°C, which is traceable to NIST[1]. All measurements are made with a precision conductivity meter using AC current at a low frequency.

[1] NIST = National Institute of Standards and Technology

High conductivity measurements

High conductivity measurements are performed when samples are water solutions, highly concentrated in dissociated species, i.e. salts, acids and bases. The conductivity method is used to control the concentration of pure or mixed solutions. For example, the conductivity method is preferred to pH measurements in production plants of concentrated acids or bases.

Temperature effect

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

The concept of reference temperature was introduced to allow the comparison of conductivity results obtained at different temperature. The reference temperature is usually 20°C or 25°C. The conductivity meter measures the actual conductivity and temperature and then converts it to the reference temperature using a temperature correction function and displays the conductivity at the reference temperature.

It is mandatory to always associate the temperature together with a conductivity result. If no temperature correction is applied, the conductivity is the value taken at measurement temperature.

For temperature correction different options can be selected:

• Linear function

• Non-linear function for natural waters according to ISO/DIN7888.

• No correction

To perform correct conductivity measurements, it is recommended to use a temperature sensor or a conductivity cell with built-in temperature sensor.

For high accuracy measurement, it is necessary to thermostat samples, so that the same temperature is used for the calibration and measurement.

Linear temperature correction

In moderately and highly conductive solutions, temperature correction can be based on a linear equation involving a temperature coefficient (θ). The coefficient is usually expressed as a conductivity variation in %/°C.

Linear temperature correction is used, e.g. for saline solutions, acids and leaching solutions.

$$\kappa_{Tref} = \frac{100}{100 + \theta \bullet (T - T_{ref})} \bullet \kappa_T$$

where:

κ_{Tref} = Conductivity at T_{ref}

κ_T = Conductivity at T

T_{ref} = Reference temperature

T = Sample temperature

θ = Temperature coefficient

Note that the correction is accurate only within a limited temperature range around T_1 and T_2. The figure below shows : $T_1 = 26°C$, $T_2 = 14°C$ and $T_{ref} = 25°C$.
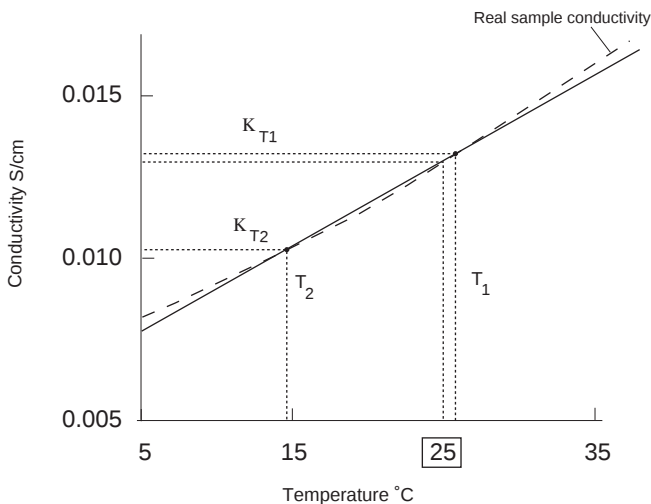
Fig. 8: Conductivity versus temperature

The greater the difference between T and $T_{ref,}$ the higher the risk of error.

Determination of the temperature coefficient (θ)

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

$$\theta = \frac{(\kappa_{T2} - \kappa_{T1}) \cdot 100}{(T_2 - T_1) \cdot \kappa_{T1}}$$

T_2 should be selected as a typical sample temperature and should be approximately 10°C different from T_1.

The temperature coefficients of the following electrolytes generally fall into the ranges shown below:

Acids:	1.0 - 1.6%/°C
Bases:	1.8 - 2.2%/°C
Salts:	2.2 - 3.0%/°C
Drinking water:	2.0%/°C
Ultrapure water:	5.2%/°C

Non-linear temperature correction

The linear temperature correction is not suitable for many aqueous liquids under test and the temperature dependency can only be described by non-linear functions such as the non-linear function for natural waters, i.e. for ground water, surface water, drinking water and waste water.

The principle of this correction is that the conductivity measured at the sample temperature is corrected to 25°C to give K_{25}.

$$K_{25} = f_{25} (T) \cdot K_T$$

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

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

[1] Bibliography: WAGNER, R. Temperaturkorrekturfaktoren für die elektrische Leitfähigkeit von Wässern. Z. Wasser - Abwasserforsch. (2) 1980".

Measurement techniques
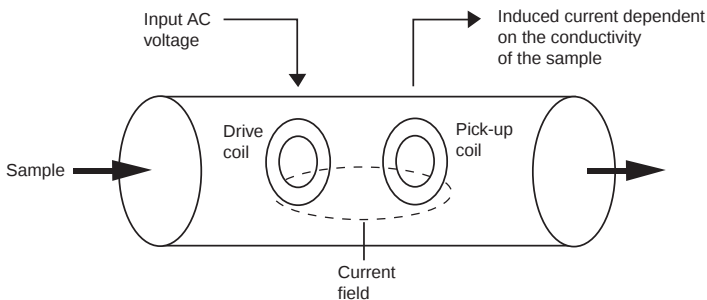
Contacting conductivity

Contacting conductivity uses a cell with two metal or graphite electrodes in contact with the electrolyte solution. An AC current is applied to the electrodes by the conductivity meter, and the resulting AC voltage.

This technique can measure down to pure water conductivity. Its main drawback is that the cell is susceptible to coating and corrosion, which drastically decreases the reading. In strongly conductive solutions there can also be polarisation effects, which result in non-linearity of measurements.

Toroidal "Inductive" conductivity

A toroidal conductivity measurement is made by passing an AC current through a toroidal drive coil, which induces a current in the electrolyte solution, see figure below. This induced solution current, in turn, induces a current in a second toroidal coil, called the pick-up toroid. The amount of current induced in the pick-up toroid is proportional to the solution conductivity.

The main advantage of toroidal conductivity is that the toroidal coils are not in contact with the solution. They are either encased in a polymeric material or are external to a flow through cell.

One of the main disadvantages of toroidal conductivity measurements is that it lacks the sensitivity of contacting measurement. Toroidal sensors are also typically larger than contacting sensors, and the solution current induced by the toroid occupies a volume around the sensor. Hence, toroidal sensors need to be mounted in a larger pipe.

Rules for reliable measurements

Reliable measurement results can be obtained when you follow these simple rules:

Calibrate frequently

The cell constant value is an important factor of conductivity measurements. You must be sure of the cell constant value before starting measurements.

It is impossible to recommend a given calibration interval for conductivity cells as the interval will depend on the application, the samples and the operating conditions in use.

It is recommended to check the cell constant regularly especially when using a platinised cell, due to increased risk of contamination or physical-chemical modification of the platinum layer.

Temperature and stirring conditions

It is recommended to thermostat if you want accurate measurements.

The temperature and stirring conditions during the calibration must be as close as possible to the conditions used during the measurement.

Note: for conductivity measurements the conductivity reading can be expressed at the measuring temperature or at a reference temperature using a temperature correction factor.

Position of conductivity cell

Make sure that all the poles of the conductivity cell are completely covered by the sample. Always position a 2-pole cell in the centre of the measuring vessel.

Low conductivity measurements

- use a flow-through cell, to avoid atmospheric contamination from carbon dioxide,

- use cells with low cell constant, 1 cm^{-1} or lower,

- use non-platinised cells for easier cleaning and faster response,

- make sure that your instrument is able to apply an appropriate measuring frequency.

High conductivity measurements

- Use platinised cells to avoid polarisation errors, preferably 4-pole cells.

- Use cells with a high cell constant (1 cm^{-1}) or higher if possible.

- Do not dilute samples in order to bring them into measuring range. Conductivity is not proportional to concentration at high levels.

- Make sure that your instrument is able to apply an appropriate measuring frequency.

Traceability

Using one of Radiometer Analytical's Demal range of certified conductivity standards to calibrate your measuring chain guarantees that your conductivity measurements are traceable to NIST. Our Cofrac accredited laboratory produces pH and conductivity standards with certificates of traceability and conformity.

Metrology

To comply with ISO 9001 and ISO 17025 requirements, our Metrology Department can supply calibration and verification certificates.

[1] NIST = National Institute of Standards and Technology

Recommendations for maintenance and storage

Make sure that your cell is clean

Between measurements, rinse the cell with deionised water. If the cell has been exposed to a solvent immiscible with water, clean it with a solvent miscible with water e.g. ethanol or acetone and rinse carefully with water.

In the event of deposits on the cell, dip the cell in ○RENOVO•N, Normal Cleaning Solution for approximately 1 hour. Rinse thoroughly with distilled water after cleaning.

Store the conductivity cell carefully

Before storing the cell, rinse it carefully in deionised water.

- Short-term storage: in deionised water.

- Long-term storage: in deionised water or store dry.

After long-term storage, condition the cell for 8 hours in deionised water, before use.

Handle platinised cells carefully

Do not touch the black platinum layer of the platinised cells.

To rinse the platinised cells, it is recommended to dip the cell several times in a beaker of demineralised water.

Be careful when rinsing platinised cells using deionised water from a water bottle. The force of water could remove some of the platinum layer and consequently modify the cell constant.

Applications of conductivity measurements

Conductivity measurements

Measuring conductivity simply detects the presence of ions in solution and is therefore a non-specific measurements. Conductivity applications encompass for instance monitoring of water purity, drinking water and process water quality. It is also a rapid and inexpensive way of determining the ionic strength of a solution.

The conductivity κ is calculated using the conductance G and the cell constant K:

$$\kappa = G \bullet K \ (S/cm)$$

Resistivity measurements

Resistivity measurements are used as a reliable indicator of ionic water quality, especially for ultrapure water (UPW) and more generally when a resistivity value is preferred to a conductivity value, for example when checking for water contamination in organic solvents.

The resistivity of a solution is calculated on the basis of the conductance G compensated for the cable resistance, cable capacitance and cell constant of the conductivity cell used. The resistivity ρ is calculated as follows:

$$\rho = \ \frac{1}{\kappa} \ \ \Omega \bullet cm^{-1}$$

TDS measurements

TDS measurements in the pulp and paper industry measure accurately and easily the total organic and inorganic dissolved solids in water.

What is TDS and how is it measured?

The TDS (Total Dissolved Solids) corresponds to the total weight of cations, anions and the undissociated dissolved species in one litre of water.

The standard method[1] to determine TDS is to evaporate a measured sample of water to dryness at 180°C, under strict laboratory conditions, and carefully weigh the amount of dry solids remaining. The precision of the standard method depends on the nature of the dissolved species.

The TDS method in a typical conductivity meter offers a quicker and easier way of determining TDS by measuring the conductivity, then using a conversion factor to give TDS readings.

Determination of the TDS Factor

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

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

TDS(STD) is expressed in mg/l.

$\kappa_{18}(\text{STD})$ = conductivity of the standard corrected to 18°C (in μS/cm). The conductivity of the standard measured is corrected to 18°C using the corresponding temperature correction table.

[1] Standard methods for the examination of water and wastewaters, 18th Edition 1992 (Editors: Arnold E. Greenberg, Leonore S. Clesceri, Andrew D. Eaton), part 2540C page 2-55.

For "normal" water, the TDS factor calculated should be within 0.50 to 0.70.

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

Calculating the sample TDS

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

$$\text{TDS (SMP) (in mg/l)} = \text{TDS factor} \bullet \kappa_{18} \text{(SMP)}.$$

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

Note: to obtain the most accurate measurements, it is recommended to perform the standard and sample measurements at the same temperature.

Such TDS measurements are accurate as long as the composition of the samples varies only slightly.

Concentration measurements

Since the charge of the ions in solution facilitates the conductance of electrical current, the conductivity of a solution is highly (but not totally) proportional to its ion concentration. As conductivity is a non-specific technique, concentration calculation using conductivity measurements is valid for samples containing only the species of interest.

The first step to measuring concentration is to know the conductivity of the solution as a function of the concentration of the specie of interest. This data can come from published conductivity vs. concentration curves for electrolytes, or from laboratory measurements.

Over large conductivity ranges, conductivity will increase with concentration, but may reach a maximum and then decrease with increasing concentration. When using conductivity measurement to determine the concentration, it is important to work at constant temperature for calibration and measurements as the shape of the conductivity vs. concentration curve will change with temperature.

Necessary conditions

With the help of conductivity vs. concentration data, the following conditions are necessary to perform a concentration measurement:

• There must be a measurable change in conductivity over the desired concentration range.

• Conductivity must either increase or decrease with concentration. If a maximum or minimum is present in the desired concentration range, concentration cannot be measured (see below).
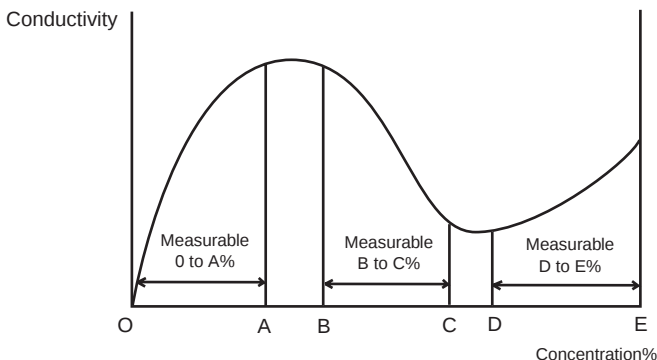
Fig. 9: Conductivity versus concentration

To calculate a sample concentration, the conductivity meter must be calibrated against 1 to 3 standards of known concentration. At the end of the calibration, a formula expressing the concentration as a function of the conductivity measured is determined. The sample concentration is calculated from the sample conductivity measured and the coefficients obtained during calibration.

Determination of the concentration coefficients

A calibration using 1 to 3 standards of known concentration is performed.

For each standard:

- The conductivity of the standard is measured at the standard's temperature.

- The conductivity of the standard is corrected to a reference temperature T_{ref} (linear correction or natural water correction as for a conductivity measurement).

At the end of the calibration, the conductivity meter calculates and displays the A_0, A_1 and A_2 coefficients of the following equation:

$$C = A_0 + A_1 \bullet \kappa_{Tref} + A_2 \bullet (\kappa_{Tref})^2$$

C = concentration

κ_{Tref} = conductivity corrected to the T_{ref} reference temperature.

If:

1-point calibration, A_1 is calculated, A_0 and A_2 are equal to 0.

2-points calibration, A_0 and A_1 are calculated, A_2 = 0.

Note: all the measurements of the standards must be performed at the same temperature. To obtain the most accurate measurements, it is recommended to thermostat the standards and the samples at the reference temperature T_{ref}.

Determination of the sample concentration

The conductivity of the sample is measured at the sample's temperature then corrected to a reference temperature T_{ref} to give κ_{Tref} (linear correction or "Natural water" correction as for a conductivity measurement).

The sample concentration C_{SMP} is then calculated using the following equation:

$$C_{SMP} = A_0 + A_1 \bullet \kappa_{Tref} + A_2 \bullet (\kappa_{Tref})^2$$

A_0 , A_1 and A_2 are the coefficients determined during method calibration.

Limitations of the concentration method

For some samples with high concentrations, the conductance = f (concentration) curve may show a maximum. This can lead to major measurement errors as shown below for the example of HCl.

For HCl, a maximum around 860 mS is obtained for a concentration of about 19% (see the curve below). Two calibrations have been performed using 3 standards each. The two calibration curves obtained are represented as dashed lines on the conductance = f (concentration) curve.
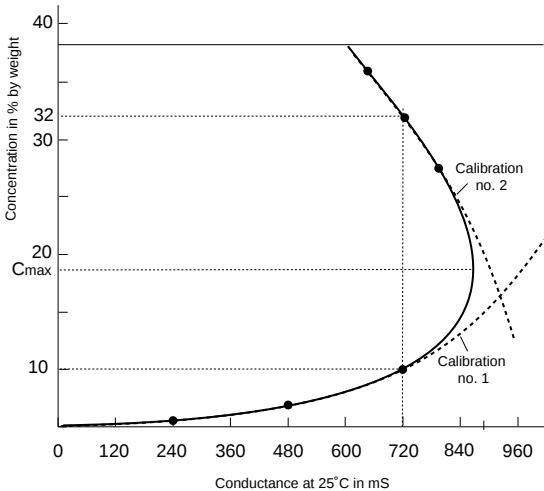
Fig. 10: Concentration versus conductance for a HCl solution

- 34 -

When performing measurements on a 32% HCl sample using calibration no. 1, the conductivity meter measures a conductance of 720 mS and finds a concentration of 10% instead of 32%. The correct result (32%) is obtained if sample measurements are performed using calibration no. 2.

Recommendations:

To obtain accurate measurements in concentrated samples, some precautions must be taken:

1. For the sample analysed, you must know if the conductance = f (concentration) curve shows a maximum for the conductance. If it is the case, the concentration value C_{max} must be known.

2. A calibration on 3 standards must be performed with the following recommendation: the 3 standard concentrations must be greater or less than the C_{max} value.

3. Make sure that the change in conductivity is only due to the specie of interest. As conductivity is a non-selective measurement, conductivity change due to any other species would lead to misinterpretation of the concentration results.

Salinity measurements

Salinity is a measurement without unit corresponding to the weight of dissolved salts in seawater.

The salinity is calculated from an empirical relationship between the conductivity and the salinity of a seawater sample. Oceanographic Tables and Standards endorsed by UNESCO/SCOR/ICES/IAPSO are used for the calculation.

Salinity measurements are performed with no direct temperature correction. The calculation is valid for salinity values in the range 2 to 42 at a sample temperature of -2 to +35°C.

Determination of the sample salinity

Calibration

The calibration is carried out using a standard seawater solution κ_{15} (STD) (salinity = 35, conductivity equals 42.896 mS/cm at 15°C).

The conductivity of the sample is measured at the sample temperature T. The conductivity of standard seawater κ_T (STD) is calculated from the following equation:

$$\kappa_T \text{ (STD)} = f\text{ (T)} \bullet \kappa_{15}\text{ (STD)}$$

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

Salinity of the sample

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

$$R = \kappa_T \text{ (SMP)} / \kappa_T \text{ (STD)}$$

Build the system to suit your needs

Radiometer Analytical SAS offers complete conductivity measuring systems comprising, conductivity meters, cells, temperature sensors and conductivity standards to ensure you obtain accurate and reproducible measurements every time.

✓ Choose the right conductivity meter

The CDM230 Conductivity Meter has the following features to simplify routine tasks:

- Conductivity, Resistivity, Salinity, TDS, Concentration.

- Measurement capability in 7 measuring ranges (0.001 µS to 2 S).

- Stored conductivity values of standards against temperature allow the CDM230 to automatically determine cell constant.

- Dedicated range for low conductivity measurements (0 to 4 µS).

- For water samples: the conductivity value of pure water can be subtracted automatically from the measured value according to ASTM D1125-91.

- Linear and non linear temperature correction (natural water following ISO/DIS 7888).

✓ Ensure correct cell positioning and reproducible stirring conditions

The positioning of a 2-pole conductivity cell in the beaker is essential for accurate results due to the influence of the field lines on the measurements (see page 17). The SAM7 Sample Stand includes an electrode holder for safe and consistent positioning of electrodes via the unique bayonet concept and also has fixed reproducible stirring speeds.

✓ Select the appropriate cell for your application

Different types of conductivity cells exist, the following criteria will help you determine your selection:

- Measuring range (high or low conductivity): a 4-pole cell covers a wide measurement range whereas a platinised cell is recommended for high conductivity measurements. Order the 4-pole CDC565 with epoxy body (part no. E61M003) or the 2-pole platinised cell with built-in temperature sensor, CDC641T (part no. B15B001). The CDC566T (part no. E61M010) also has an epoxy body together with a temperature sensor.

- Sample type and sample volume: a flow-through cell, CDC511T (part no. E61M009), is recommended for measurements in pure water as it protects the sample from carbon dioxide in air. The pipette version of this cell can be used for small sample volumes.

✓ Use certified conductivity standards

No conductivity measurement can be more precise than the standards used for the calibration. To ensure optimum accuracy time after time, calibrate your system with solutions that are fully traceable to national standards.

Two types of conductivity standards exist, certified or economical. If your laboratory is involved in an accreditation, certification or quality procedure, it is recommended to use certified standards. The range of certified conductivity standards prepared by Radiometer Analytical is fully traceable to SI units via Standard Reference Materials manufactured by NIST[1]. The first three standards in the table below are manufactured and calibrated according to the internationally recognised Demal scale laid down by the OIML[2] (Recommendation No. 56).

Certified conductivity standard solutions

Type	Value*	Qty	Part no.
KCl 1 D	111.3 mS/cm ±0.5% at 25°C	500 ml	S51M001
KCl 0.1 D	12.85 mS/cm ±0.35% at 25°C	500 ml	S51M002
KCl 0.01 D	1408 µS/cm ±0.5% at 25°C	500 ml	S51M003
NaCl 0.05%	1015 µS/cm ±0.5% at 25°C	500 ml	S51M004
KCl 26.6	26.6 µS/cm ±2.5% at 20°C	250 ml	S51M012

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

[1] NIST = National Institute of Standards and Technology
[2] OIML = International Organisation of Legal Metrology

All of our certified standard solutions come in sealed containers guaranteeing conductivity values for a full two years (KCl 26.6 comes in a glass bottle with a guaranteed shelf life of 1 year). All standards are delivered with a Cofrac Verification Certificate and a Certificate of Conformity and Traceability drawn up according to ISO Guide 31.

Economical KCl Solutions

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

What is a Demal solution?

Definition

In 1940, Jones and Bradshaw determined the demal definition as the weight of KCl/weight of the solution.

KCl Demal solutions

mass of KCl/1000 g of solution

As the molar weight is redefined from time to time, there is a need to redefine the conductivity for a given molarity of KCl solution. Using a given mass in a defined mass of water means that the determined conductivity of these solutions will not change over time.

Solution type	mass of KCl / 1000 g of solution	Conductivity at 25°C
1 D	71.1352 g	111.3 mS/cm
0.1 D	7.4191 g	12.85 mS/cm
0.01 D	0.745263 g	1408 µS/cm

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

✓ Correct reading to reference temperature

Conductivity measurements are strongly temperature dependent. Add a temperature sensor to your system for automatic temperature measurements and temperature correction of the conductivity to a reference temperature. You can use, the T201 (part no. E51M001), or a conductivity cell with built-in temperature sensor, e.g. CDC641T (part no. B15B001).

Pure water conductivity measurements

Dedicated USP offer

Radiometer Analytical has created a complete conductivity package for pure water measurements complying with USP standard requirements including, in addition to the CDM230 Conductivity Meter:

• CDC511T, 4-pole flow-through cell with built-in temperature sensor.

• Calibration certificate stating the cell constant value within ±2%.

• Certified calibration standard KCl 0.01D, 1408 µS/cm at 25°C.

• Epoxy tube for the cell for stage 2 measurements.

• pH meter and pH electrode with calibration certificates, for stage 3 measurements.

Refer to the article "Conductivity measurements on pure water according to the recommendations of the US Pharmacopoeia".

Dedicated EP offer

Radiometer Analytical has created an application kit for water conductivity by the European Pharmacopeia, including:

• CDC641T 2-pole cell with built-in temperature sensor.

• Flow-through cell adapter.

• Certified conductivity standard, 26.6 µS at 20°C.

Refer to the application note "Pure water conductivity measurements, according to the European Pharmacopoeia".

To comply with ASTM D1125-91

Conductivity samples at or below 1.0 µS/cm may require the deduction of the contribution of pure water conductivity, which may be considered as a blank. This occurs because the conductivity of pure water is a large fraction of the overall sample conductivity.

The CDM230 Conductivity Meter calculates the theoretical conductivity of pure water at the sample temperature using a 4-degree polynomial equation given by ASTM D1125-91 and applicable between 0 and 100°C. The CDM230 then subtracts the conductivity of pure water (0.055 µS/cm at 25°C) from the conductivity measured and displays the difference.

Visit our **MeterLab**® **Resource Centre** at
www.radiometer-analytical.com
to consult the above articles and find out more about our products.

FAQs

My conductivity readings appear to be incorrect. What could be wrong?

When calibrating or taking conductivity measurements, the conductivity cell has to be totally submerged. If not, calibration or reading will be affected. If incorrectly calibrated, all subsequent readings will be out of specification.

Do not immerse the air escape hole of 4-pole cells.

How often do platinum cells need to be replatinised?

Some platinum electrodes are coated with platinum black during manufacture. This coating is extremely important to cell operation, especially in solutions of high conductivity. Electrodes are platinised to avoid errors due to polarisation leading to inaccurate readings.

Cells should be inspected periodically and after each cleaning. If the platinum black coating appears to be wearing or flaking off the electrode, the cell should be replatinised or replaced. It is recommended to have the cell replatinised approximately every six months, contact your Radiometer Analytical representative for details.

Can conductivity be measured in non-aqueous solutions?

Many substances possess some dissociative properties. Generally organic compounds (such as benzene, alcohols, and petroleum products) have very low conductivities. We recommend using a non platinised glass cell. The CDM230 Conductivity Meter offers a 1 nS/cm resolution on the 4 µS range.

What is the guarantee of traceability as indicated on the certificate supplied with each bottle of certified conductivity standard?

Each bottle comes with its two certificates.

The verification certificate states accreditation by Cofrac and therefore guarantees that the product is a CRM (certified reference material) fully traceable to a primary standard.

The conformity certificate is drawn up according to ISO Guide 31 and gives full traceability information as well as the composition and preparation of the standard and recommendations for storage and use.

What is the confidence level of Radiometer Analytical conductivity standards?

The certified value of Radiometer Analytical's certified conductivity standards is given with an expanded uncertainty to guarantee a confidence level of 95%. It is printed on the bottle and mentioned on the certificates.

What is the shelf life of the certified conductivity standards?

Radiometer Analytical's range of Demal certified conductivity standards (1 D, 0.1 D and 0.01 D) are delivered in airtight tins to protect them from evaporation and microbiological growth. This guarantees the tolerance on their nominal values for two years from the date of production. This guarantee also applies to the 0.05% NaCl standard.

Note: Once opened use within 3 months.

How can the cell constant accuracy required by the USP be obtained?

USP states that the cell constant must be known with an uncertainty which is better than ± 2%.

The cell constant is a factor that is used to convert the measured conductance to conductivity. It is determined by the geometry of the cell, but in, practical terms, can only be measured using a standard of known conductivity value. The expanded uncertainty of the cell constant results from the contribution of uncertainties from all variables that are used in the determination of that constant. The prime source of uncertainty is the uncertainty of the conductivity standard solution. In other words, a cell constant can never be more accurate than the standard used for calibration.

Taking into account all other contributions to the cell constant uncertainty (and using rules from GUM[1]) the uncertainty of the standard solution has to be less than ±1%, to be able to determine a cell constant to within ±2%.

[1]GUM: Guide to the expression of uncertainty

Which conductivity standard can I use to ensure that the cell constant can be determined to within ± 2%?

Radiometer Analytical produces a KCl 0.01D conductivity standard which has a certified conductivity value of 1409 µS/cm ± 0.5% at 25°C, traceable to internationally recognised Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST). This means that there is a 95% confidence level for the true value of the conductivity standard to be 1409 µS/cm ± 7 µS/cm at 25°C. For such a low uncertainty contribution, the uncertainty associated to the cell constant determination can be reduced to less than 1%.

This cannot be achieved using lower conductivity standards as their relative uncertainty increases greatly for low conductivity values.

Must I calibrate my cell with a standard whose value is close to that of the samples?

- Yes, if the cell is a 2-pole one, as its behaviour, due to polarisation, is not linear over the whole conductivity range (see European Pharmacopeia)

- Not necessary when using a 4-pole cell as its geometry prevents polarisation influence on the measurements (refer to indications of USP).

Conductivity tables

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

Temp. (°C)	KCl[2] 1 D	KCl[1] 0.1 D	KCl[1] 0.01 D
0	65.14	7.13	0.773
1	66.85	7.34	0.796
2	68.58	7.56	0.820
3	70.32	7.77	0.843
4	72.07	7.98	0.867
5	73.84	8.20	0.891
6	75.62	8.42	0.915
7	77.41	8.64	0.940
8	79.21	8.86	0.965
9	81.03	9.08	0.989
10	82.85	9.31	1.014
11	84.68	9.54	1.039
12	86.54	9.76	1.065
13	88.39	9.99	1.090
14	90.26	10.22	1.116
15	92.13	10.46	1.142
16	94.02	10.69	1.168
17	95.91	10.93	1.194
18	97.81	11.16	1.220
19	99.72	11.40	1.247
20	101.63	11.64	1.273
21	103.56	11.88	1.300
22	105.49	12.12	1.327
23	107.42	12.36	1.354
24	109.36	12.61	1.381

Temp. (°C)	KCl[2) 1 D	KCl[1) 0.1 D	KCl[1) 0.01 D
25	111.31	12.85	1.409
26	113.27	13.10	1.436
27	115.22	13.35	1.464
28		13.59	1.491
29		13.84	1.519
30		14.09	1.547
31		14.34	1.575
32		14.59	1.603
33		14.85	1.632
34		15.10	1.660
35		15.35	1.688
36		15.61	1.717
37		15.86	1.745
38		16.12	1.774
39		16.37	1.803
40		16.63	1.832
41		16.89	1.861
42		17.15	1.890
43		17.40	1.919
44		17.66	1.948
45		17.92	1.977
46		18.18	2.007
47		18.44	2.036
48		18.70	2.065
49		18.96	2.095
50		19.22	2.124

[1] Reference: "Organisation Internationale de Métrologie Légale (OIML)", Recommendation no. 56 and "The National Institute of Standards and Technology (NIST)", Journal of Solution Chemistry, Vol. 20, no. 4 1991.

[2] For the Demal KCl solution: extrapolation of the NIST results from OIML conductivity values at 0°C, 18°C and 25°C.

Table 2: Conductivity (in mS/cm) of various molar concentrations of KCl solutions

Temp. (°C)	KCl 1M	KCl 10^{-1}M	KCl 2×10^{-2}M	KCl 10^{-2}M
0	65.41	7.15	1.521	0.776
1	67.13	7.36	1.566	0.800
2	68.86	7.57	1.612	0.824
3	70.61	7.79	1.659	0.848
4	72.37	8.00	1.705	0.872
5	74.14	8.22	1.752	0.896
6	75.93	8.44	1.800	0.921
7	77.73	8.66	1.848	0.945
8	79.54	8.88	1.896	0.970
9	81.36	9.11	1.945	0.995
10	83.19	9.33	1.994	1.020
11	85.04	9.56	2.043	1.045
12	86.89	9.79	2.093	1.070
13	88.76	10.02	2.142	1.095
14	90.63	10.25	2.193	1.121
15	92.52	10.48	2.243	1.147
16	94.41	10.72	2.294	1.173
17	96.31	10.95	2.345	1.199
18	98.22	11.19	2.397	1.225
19	100.14	11.43	2.449	1.251
20	102.07	11.67	2.501	1.278
21	104.00	11.97	2.553	1.305
22	105.94	12.15	2.606	1.332
23	107.89	12.39	2.659	1.359
24	109.84	12.64	2.712	1.386
25	111.80	12.88	2.765	1.413
26	113.77	13.13	2.819	1.441

Temp. (°C)	KCl 1M	KCl 10^{-1}M	KCl 2×10^{-2}M	KCl 10^{-2}M
27	115.74	13.37	2.873	1.468
28		13.62	2.927	1.496
29		13.87	2.981	1.524
30		14.12	3.036	1.552
31		14.37	3.091	1.581
32		14.62	3.146	1.609
33		14.88	3.201	1.638
34		15.13	3.256	1.667
35		15.39	3.312	
36		15.64	3.368	

Table 3: Average temperature coefficients of standard electrolyte solutions expressed as %/°C of the conductivity value at 25°C

Temp. range °C	KCl 1 M	KCl 0.1 M	KCl 0.01 M	Saturated NaCl
15 - 25	1.725	1.863	1.882	1.981
15 - 25 - 35	1.730 (15 - 27°C)	1.906	1.937 (15 - 34°C)	2.041
25 - 35	1.762 (25 - 27°C)	1.978	1.997 (25 - 34°C)	2.101

Table 4: Conductivity (in µS/cm) values of a 0.05% NaCl solution

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

Notes

MeterLab® is a registered trademark of Radiometer Analytical SAS

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