Monograph

Conductometry – Conductivity Measurement

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Metrohm

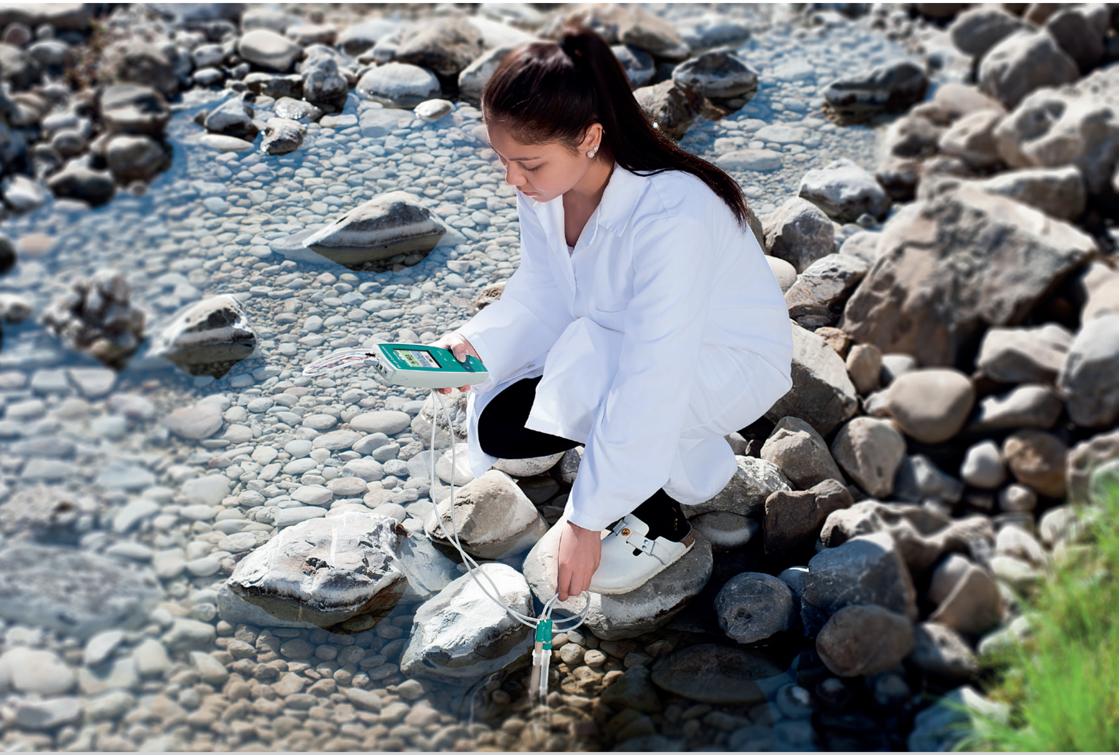
Table of contents

Foreword

The measurement of electrical (electrolytic) conductivity – conductometry – can look back on a long tradition. Conductivity measurements were already being made more than 100 years ago. For many decades Metrohm has provided suitable measuring instruments and suitable accessories for its customers. This monograph is concerned solely with the measurement of conductivity in solutions.

Although conductivity measurements are carried out frequently, they have never achieved the wide range of application of potentiometry (e.g., pH, ion, redox measurements). The reason for this may be that in conductometry there is no generally valid equation (such as, for example, the Nernst equation) that permits the appropriate calculations. On the contrary, in conductometry experience, experiments and comparative measurements come to the fore instead of calculations.

This monograph is intended to provide a basic familiarization course in conductometry in a short time. Help is provided by the alphabetically arranged terms and definitions as well as the practical examples.



Terms / definitions

Activity

In water and polar solvents ionic compounds dissociate into their single ions (e.g., NaCl → $Na^+ + Cl^-$). At normal concentrations, strong electrolytes (e.g., HCl, K_2SO_4) are completely dissociated, but weak electrolytes (e.g., NH_3, CH_3COOH) are always incompletely dissociated. However, strong electrolytes behave as if an incomplete dissociation were present. This is caused by the fact that interactions (associations) occur between the oppositely charged ions and these reduce the chemical potential. For this reason the electrical conductivity is not a linear function of the concentration. The effective concentration (c) is known as the activity. (Of course, these interactions also occur with weak electrolytes, but can normally be neglected because of the low ionic concentration.)

Activity coefficient

In real ionic solutions the interaction (association tendency) causes the «mass action» of the ions to be smaller than would be expected from the weight present. The stoichiometric concentration c must therefore be multiplied with a correction factor so that the mass action law continues to remain valid. This concentration-independent factor is known as the **activity coefficient a_i**, the effective concentration as the activity (see section *Activity* on page 5).

Amount-of-substance concentration

c(X) amount-of-substance concentration of substance X in mol/L, e.g., c(KCl) = 0.01 mol/L.

Ash

The ash content of sugars can be determined by measuring the electrical conductivity. This method is much more rapid than the ashing process itself and provides usable results. The theoretical basis is that the majority of the ash components consist of electrolytes, whereas the sugar itself is a non-electrolyte. This means that the electrical conductivity of sugar solutions is practically only determined by their ash content.

Determination

5.0 g sugar is dissolved in dist. H_2O, the solution made up to 100 mL and mixed. The electrical conductivity is measured at 20 ± 0.1 °C → K_5

$$\% \text{ ash} = K_5 \times 0.0018$$

% ash:	Ash content in sugar in %
K_5:	Electrical conductivity in µS/cm of the 5% sugar solution
0.0018:	Conversion factor measured conductivity to ash content

Calibration

See chapter *Calibration* on page 27.

Calibration solutions

These solutions are used for calibrating conductivity measuring cells, i.e. for determining the cell constant. See also chapter *Calibration* on page 27.

Calibration solutions are solutions whose electrical conductivity γ is known exactly. It is best to use so-called secondary standards. These are certified and can be directly traced to standard reference materials (e.g., National Institute of Standards and Technology – NIST, USA).

Examples of available standards are:
Conductivity standard κ = 12.87 mS/cm (25 °C), Metrohm No. 6.2301.060.

Conductivity standard κ = 100 µS/cm (25 °C), Metrohm No. 6.2324.010 (250 mL) or 6.2324.110 (5 × 30 mL sachets).
Sources for standards with electrical conductivities <100 µS/cm are, for example:

- Hamilton (5–100 µS/cm, accuracy ±1%)
- Reagecon, Shannon (Ireland) **www.reagecon.com** (1–100 µS/cm)

Figure 1: Examples of calibration solutions provided by Metrohm

Carbon dioxide

One of the major interference for conductivity measurements in water samples is carbon dioxide. Compared to other gases, carbon dioxide is relatively soluble in water with a solubility of up to 0.2%, depending on the temperature. Carbon dioxide reacts with water according to the following reaction:

$$CO_2 + 2\ H_2O \rightleftarrows HCO_3^- + H_3O^+ \quad pK_a = 6.5$$

In solution with a higher pH value the formed hydrogen carbonate reacts with water to form carbonate.

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \quad pK_a = 10.5$$

To minimize the influence of dissolved carbon dioxide the following points should be considered:

- Samples should be measured as soon as possible after sampling
- Between sampling and measurement the sample should be stored in closed sample vessel containing a minimal amount of air
- Small, high measuring vessels should be used (minimization of surface area) or a flow-through-cell should be used for measurements
- The stirring rate should be low (no uptake of air)
- Stirring should only be used for mixing the sample before the measurement
- If the conductivity is very low the measurement should be carried out under an atmosphere of nitrogen

Cell constant

In principle, most instruments for measuring electrical conductivity are instruments for measuring the resistance R_X or the conductance $G_X = 1/R_X$ of a measuring cell filled with sample.

The relationship to the electrical conductivity γ, the real subject of interest, is provided by the cell constant c, which depends on the geometrical dimensions of the measuring cell:

$$\gamma = \frac{c}{R_X} = c \times G_X$$

The unit of the electrical conductivity is S/cm.

In a two-plate measuring cell the cell constant c is obtained from the area A and the distance l between the plates:

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

The unit of the cell constant is cm^{-1}.

Because the distribution of the field lines is not ideal, this calculated value does not agree exactly with the effective cell constant of the measuring cell. The effective value of c can only be determined by calibration; see chapter *Calibration* on page 27.

Charge number

The charge number z_i gives the charge of the particular ion including its sign.

Examples:

$NaCl \rightarrow Na^+ + Cl^-$ $z_+ = +1; z_- = -1$

$CaCl_2 \rightarrow Ca^{2+} + 2\ Cl^-$ $z_+ = +2; z_- = -1$

$K_3PO_4 \rightarrow 3\ K^+ + PO_4^{3-}$ $z_+ = +1; z_- = -3$

Conductance

The conductance G is the reciprocal of the electrical resistance (1/R) and has the unit Siemens (S) = Ω^{-1}. The electrical conductivity is obtained by multiplying the conductance with the cell constant. Conductivity titrations only require the measurement of conductance G.

Conductivity cells

See chapter *Measuring cells* on page 24.

Conductivity standards

See section *Calibration solutions* on page 6.

Conductivity titration

See section *Conductometric titrations* on page 8.

Conductivity water

Term (introduced by W. Ostwald) for highly pure water with very low intrinsic conductivity. It expresses the fact that such a water is suitable even for demanding studies in the field of electrical conductivity (e.g., preparation of conductivity standards). The term also applies to the ultrapure water used in the pharmaceutical industry. See chapter *Conductivity measurements in demineralized water according to USP guidelines* on page 37 for the determination of the conductivity in such water.

Conductometer

See chapter *Measuring instruments* on page 23.

Conductometric titrations

In addition to colored indicators, conductivity measurement is one of the oldest methods for indicating titration endpoints.

As all the ions present contribute to the conductivity at each point in the titration, typical V-shaped titration curves are obtained.
Below you see an example titration curve for the titration of HCl with NaOH.

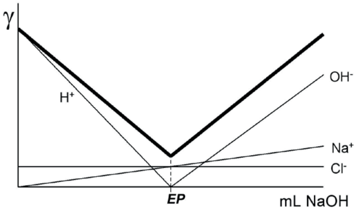


Figure 2: Exemplary titration curve for a conductivity titration (bold lines) including individual contribution of the different ions (thin lines)

Contact-free methods

As the name says, in these methods (for measuring the electrical conductivity) there are no contacts between the measuring cell electrodes and the sample. These methods are frequently called «electrode-free», which is, of course, incorrect. Two basic methods are used:

1. Capacitive method
See under section *High-frequency measurement* on page 12.

2. Inductive method
Here, the sample forms a coupling loop between two windings of a transformer that are magnetically shielded from each other. Measuring frequencies of 50–500 Hz are used in this case. There is a correlation between the electrical conductivity of the sample and the voltage transferred from the primary to the secondary winding over a very wide range. This means that it is possible to evaluate the measured values by using the cell constant.

Contact-free methods have the advantage that the measured values can never be falsified by polarization. There are also no corrosion or contamination problems with the electrodes. However, the cost and complexity of the necessary apparatus are considerably higher when compared with those for «normal» instruments.
For this reason such methods are used, if at all, mostly for industrial applications.

Convection

One of the three mechanisms (convection, migration, diffusion) by which ion transport can take place is convection – ions travel as a result of liquid flow, e.g., thermal convection (temperature gradient).

Degree of dissociation

Quantity that describes the extent to which dissociation occurs. It represents the ratio between the free ions and the total molecules present in the solution and is expressed either relatively or as a percentage (1 or 100% means complete dissociation, 0.5 or 50% means that only half the molecules are dissociated). Strong electrolytes such as HCl, HNO_3, H_2SO_4, NaOH, KOH and their salts are always completely dissociated in aqueous solution.

Dependency of electrical conductivity

The electrical conductivity of a solution depends on:

- The **number of ions**: The more ions a solution contains, the higher its electrical conductivity.
- In general on the **ionic mobility**, which in turn depends on
  - the *type of ion*: The smaller the ion, the more mobile it is and the better it conducts. H_3O^+, OH^-, K^+ and Cl^- are very good conductors. If hydration occurs (the ion surrounds itself with water molecules that make it larger), then the conductivity is reduced.
  - the *solvent*: The more polar a solvent is, the better the dissolved compounds it contains can ionize. Water is an ideal solvent for ionic compounds. In alcohols ionization decreases as the chain length increases (methanol > ethanol > propanol). In nonpolar organic solvents (e.g., chlorinated and non-chlorinated hydrocarbons) practically no ionization occurs.
  - the *temperature*: In contrast to solids, in solutions the electrical conductivity increases as the temperature increases by 1 – 9% per °C, depending on the ion.
  - the *viscosity*: As the viscosity increases, the ionic mobility and therefore the electrical conductivity decreases.

Dielectric constant D

In electrochemistry the dielectric constant is important wherever opposite charges act on each other. Examples are dissociation or ionic interaction. The larger the relative dielectric constant ($D_{vacuum} = 1$), the better the ionic compounds dissociate in the particular solvent. A few examples:

Table 1: Different dielectric constants for various solvents

Solvent	D (20 °C)
Formamide	110
Water	80
Methanol	34
Ethanol	25
Acetone	21
Propanol	19
Chloroform	4.8
Hexane	1.9

Diffusion

One of the three mechanisms (convection, migration, diffusion) by which ion transport can take place is diffusion – ions travel as a result of differences in chemical potential (concentration gradients). Diffusion is described quantitatively by Fick’s laws.

Dissociation

In solvents with a high dielectric constant (polar solvents) ionic compounds break down into freely mobile single ions, e.g.,

$$KCl \rightarrow K^+ + Cl^-$$

A different type of dissociation occurs when a chemical compound with a heteropolar bond is dissolved in a protic solvent, e.g.,

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

The most important solvent for dissociation is water. It has a high dielectric constant and is polar.

Ionic solutions are electrically conductive and decompose when a direct current is applied (electrolysis).

Ionic solutions are also known as electrolytes. Both strong and weak electrolytes occur; these are differentiated by their degree of dissociation.

Dissociation constant

This quantity is used to describe the ionic equilibrium in aqueous solutions of weak electrolytes and is defined by the following equation:

$$K_d = \frac{c_a^x \times c_b^y}{c_{a_x b_y}}$$

K_d: Dissociation constant
c_a: Concentration of substance a in mol/L
c_b: Concentration of substance b in mol/L
$c_{a_x b_y}$: Concentration of substance $c_{a_x b_y}$ in mol/L

K increases as the degree of dissociation increases and therefore represents a usable quantity for describing the strength of a weak acid or weak base.

The negative common logarithm of K is also known as the pK_d value; $pK_d = -\log(K_d)$. As all dissociation equilibria are temperature-dependent this also applies to K_d and pK_d.

Dosimat

Metrohm term for motor-powered piston burets. Dosimats are high-precision universal dosing devices that can be controlled manually or remotely. Dosimats are equipped with so-called Exchange Units.

Figure 3: Metrohm 805 Dosimat

Dosino

Metrohm term for a stepper-motor-controlled drive for precise dosing in small spaces. Dosing Units are attached to the dosing drive by a quick-action coupling and screwed directly onto the reagent bottle.

Figure 4: Metrohm 800 Dosino

Electrical conductivity

According to ISO 7888 and DIN EN 27888 the electrical conductivity γ is equal to the reciprocal of the electrical resistance (conductance G) multiplied by the cell constant c:

$$\gamma = \frac{1}{R} \times \frac{l}{A} = G \times c$$

γ: Electrical conductivity in S/cm
R: Resistance in Ω
l: Distance between plates in a two-plate measuring cell in cm
A: Area of the plates in a two-plate measuring cell in cm^2
G: Conductance in S
c: Cell constant in cm^{-1}

The electrical conductivity is normally expressed in µS/cm or mS/cm (12.88 mS/cm = 1288 mS/m; 5 µS/cm = 500 µS/m). In American usage the terms mhos and µhos are frequently encountered.

Electrolytes

Electrolytes are substances that, in solutions or melts, undergo heterolytic dissociation into ions that conduct the electrical current. Electrolytes include acids, bases and salts.

Strong electrolytes dissociate completely, weak electrolytes only partially.

Emulsions

Emulsions («water in oil» or «oil in water») normally belong to the group of non-electrolytes. Migration of ions in an electric field and the resulting electrical conductivity do not occur. However, a technical effect can be used for measurement – this is charge transport in an electric field. According to Coehn’s law, two phases that are immiscible are characterized by the occurrence of surface charges. The phase with the higher dielectric constant (water) assumes a positive charge, that with the lower one (oil) a negative charge. According to Dahms, G.H. *et al.* is the stability of the emulsion at its maximum when the viscosity is at its maximum, at the same time the lowest "electrical conductivity" is measured. This means that under defined measuring conditions conclusions can be drawn about the stability of emulsions.

Equivalent conductivity

The equivalent conductivity Λ^* is a quantity that is primarily used in theoretical studies. It can be obtained from the molar conductivity Λ and the electrochemical valence n_e:

$$\Lambda^* = \frac{\Lambda}{n_e}$$

The electrochemical valence n_e can be calculated for a molecule that dissociates into ν_- anions and ν_+ cations with the corresponding charge numbers z_- and z_+ as follows:

$$n_e = \nu_- \times z_- = \nu_+ \times z_+$$

Examples:
$NaCl \rightarrow Na^+ + Cl^-$; $\nu_+ = \nu_-$; $n_e = 1$
$AlCl_3 \rightarrow Al^{3+} + 3\ Cl^-$; $\nu_+ = 1$ and $z_+ = 3$; $n_e = 3$

Gauging / Gauging solution

These terms have been replaced by the terms calibration solution and conductivity standards, respectively.

High-frequency measurement

This term is used in connection with capacitive, contact-free methods for measuring the electrical conductivity. It refers in particular to the relatively high frequencies (3–100 MHz) used for this type of measurement.

The special measuring cells are constructed so that two ring-shaped metal electrodes are attached to the outer wall of a non-metallic cell body (e.g., glass beaker).

The electric field penetrates the cell body and is influenced by the properties of the sample that it contains.

A major component of all instruments used for measuring the high-frequency conductivity is an oscillating circuit. The contact-free measuring cell is located parallel to the rotary condenser of the oscillating circuit. If resonance tuning is carried out during the measurement (maximum value of voltage U), then evaluation is carried out by the reactive component method. In contrast, if after resonance tuning has been carried out the value of U is divided by the conductance G, the evaluation takes place according to the active component method. Both types of evaluation require calibration with different conductance standards and also produce different calibration curves.

In comparison with the classical method, high-frequency measurement has practically no advantages; this is why it has never been able to establish itself on the market.

Hydration

In an aqueous solution all the ions are surrounded by a sheath of oriented water dipoles (hydration sheath). This phenomenon is known as hydration.

Interionic interaction

In infinitely dilute solutions no electrostatic attraction can occur between the oppositely charged anions and cations of a dissolved electrolyte. This condition would occur for an ion i at the hypothetical concentration $c_i = 0$, which can only be achieved by extrapolation.

As the concentration increases the ions move closer together. This causes an interaction between the ions in which each cation is surrounded by a cloud of anions. In the same way each anion is surrounded by a cloud of cations. Interionic interaction is particularly important for strong electrolytes.

Ionic mobility l_i

The product of the migration speed u_i and the Faraday constant F is the ionic mobility. u_i refers to a uniform field with a field strength of 1 V/cm. The distance covered by an ion i is expressed in cm. The ionic mobility depends on the temperature and the concentration. It usually refers to 25 °C and an infinite dilution (measurement series extrapolated to $c_i = 0$).

Some examples:

Table 2: Different ionic mobilities for different cations and anions

Cation	l_+ (cm^2 / Ω)	Anion	l_- (cm^2 / Ω)
H^+	350	OH^-	199
Li^+	39	Cl^-	76
Na^+	50	NO_3^-	71
K^+	74	CH_3COO^-	41
½ Mg^{2+}	53	½ SO_4^{2-}	80
½ Ca^{2+}	60	½ CO_3^{2-}	69

Ionic product of water

Water undergoes a self-dissociation known as autoprotolysis:

$$2\ H_2O \rightarrow H_3O^+ + OH^-$$

As a result of this self-dissociation, pure water has an electrical conductivity of 0.055 µS/cm at 25 °C or 0.039 µS/cm at 20 °C. Please note the high temperature coefficient of 5.8% per °C!

Ionic strength

The ionic strength is a measure of the interionic interaction occurring in the solution of an electrolyte. It is determined solely by the concentration c_i and charge z_i of the ions, and not by their characteristic features. The following applies for the ionic strength:

$$J = \frac{1}{2}\sum c_i \times z_i^2$$

The calculation of the ionic strength J of a known molar concentration c_i of a particular electrolyte is simplified by the fact that there is a multiplication factor for each type of electrolyte. It is calculated for 1-molar solutions and can then be used generally:

Table 3: Calculation factors for the ionic strenght for different salt types

Type of salt	Example	Factor
1,1	KCl	1
1,2	K_2SO_4	3
2,2	$MgSO_4$	4
1,3	K_3PO_4	6

The ionic strength is obtained by multiplying the particular molar salt concentration by this factor.

Example:
$c(MgSO_4) = 0.0025$ mol/L
$J = 4 \times 0.0025$ mol/L $= 0.01$ mol/L

Ions

Ions are positively or negatively charged atoms or molecules that are formed by dissociation from compounds with ionogenic or heteropolar bonds. In an electric field the positively charged ions (cations) migrate to the cathode (negative pole), negatively charged ions (anions) to the anode (positive pole).
In dilute solutions anions and cations migrate independently without any interactions in an electric field.

Kohlrausch cells

See chapter *Measuring cells* on page 24.

Kohlrausch's square-root law

This law for strong electrolytes links the molar conductivity Λ_c with the square root of the concentration c according to:

$$\Lambda_c = \Lambda_0 - A\sqrt{c}$$

Λ_c: Molar conductivity in S cm^2/mol
Λ_0: Limiting conductivity in S cm^2/mol
A: Constant
c: Concentration in mol/L

The equation states that the molar conductivity extrapolated to infinite dilution decreases as a function of the square root of the concentration. The constant A depends on the type of electrolyte.

Limiting conductivity

Λ_0 is the limiting equivalent conductivity or limiting conductivity for short. Λ_0 is the sum of the limiting conductivities of the cations (λ_0^+) and anions (λ_0^-) (law of independent ionic migration).
For Λ see definition under the section *Equivalent conductivity* on page 12.

Limiting conductivity of some ions in water at 25 °C are given in table 4.

Mass concentration

β(X) mass concentration of the substance X in g/L, e.g., β(NaCl) = 2.5 g/L

Mass fraction

w(X) mass fraction of the substance X in %, e.g., w(NaOH) = 25%

Table 4: Limiting conductivity of some ions in water at 25 °C

Cations	Limiting conductivity ($S \times cm^2 \times mol^{-1}$)	Anions	Limiting conductivity ($S \times cm^2 \times mol^{-1}$)
H_3O^+	349.8	OH^-	197.0
NH_4^+	73.7	SO_4^{2-}	80.8
K^+	73.5	Br^-	78.4
Ba^{2+}	63.2	I^-	76.5
Ag^+	62.2	Cl^-	76.4
Ca^{2+}	59.8	NO_3^-	71.5
Mg^{2+}	53.1	ClO_4^-	68.0
Na^+	50.1	F^-	55.4
Li^+	38.6	CH_3COO^-	40.9

Measuring cell

See chapter *Measuring cells* on page 24.

Measuring frequency

For conductivities the measuring frequency has a decisive influence on the correctness of the measured conductance G. Interfering polarization effects can be reduced by increasing the measuring frequency, which equates to extending the usable measuring range. However, at high frequencies the parasitic capacitances of the electrode and electrode cable cause interference, which manifests itself in turn in an increase in measurement error at low conductances. The following basic principles apply, though they are always a compromise:

- At low conductances, measurements are made at a lower frequency. The polarization is normally small, allowing a low measuring frequency. At the same time, the measuring error due to the parasitic capacitances is reduced.
- At high conductances, measurements are made at a higher frequency. As a result, the polarization is reduced; the effect of the parasitic capacitances at high conductances is of minor importance.

Measuring range

The usable measuring range depends on the type of conductivity measuring cell (platinized/nonplatinized, multi-pole measuring cell), the cell constant and the measuring frequency. Unfortunately, no universal measuring cell exists for the whole usable range. This is why Metrohm offers measuring cells with different cell constants. Table 7 on page 25 under *Conducitivity measuring cells* shows the different cells for different ranges.

Migration

One of the three mechanisms (convection, migration, diffusion) by which ion transport can take place – ions travel (or are transported) in an electric field (field gradient).

Migration speed

Electrical conductivity in aqueous solutions takes place by the charge transport of the ions. This means that anions and cations can be differentiated by their direction of movement (in a direct current field). The migration speed w_i of an ion is obtained from the force F_i acting on the ion and the friction F_{fi} inhibiting the migration.

The force F_i is produced by electrostatic attraction (Coulomb’s law). On the other hand, the friction F_{fi} depends on the ionic radius r_i and the viscosity η of the solution.

If E is the field strength and if the ion z_i carries electron charges e_0, then the following applies for the migration speed w_i:

$$W_i = \frac{F_i}{F_{f_i}} = \frac{z_i \times e_0 \times E}{300 \times 6\pi \times r_i}$$

If w_i is divided by the field strength E, the resulting migration speed u_i for a field of 1 V/cm is:

$$u_i = \frac{w_i}{E}$$

Typical values for u_i are about 10^{-4} cm/s. If u_i is multiplied by the Faraday constant F, we obtain the ionic mobility l_i.
The sum of the ionic mobilities of the anions and cations of an electrolyte produces the molar conductivity Λ.

Molar conductivity

The molar conductivity Λ is defined as the quotient of the specific conductivity γ and the concentration c (mol/L) of the dissolved substance:

$$\Lambda = \frac{1000 \times \gamma}{c}$$

The unit of the molar conductivity is S cm^2/mol.

Multi-electrode measurement technique

Errors in measurement results due to polarization are most likely to occur if other electrode materials (e.g., steel) are used instead of platinized platinum electrodes. With the multi-electrode measurement technique this polarization can be disregarded, as it hardly affects the measurement result. This multi-electrode measurement technique is an extension of the classical two-conductor measurement technique. Instruments and sensors with four, five or seven electrodes are available.

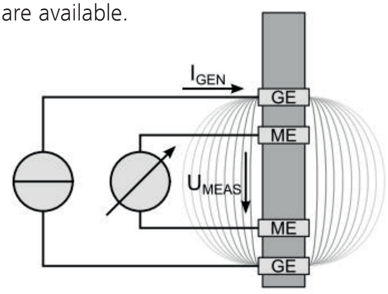


Figure 5: Schematic of the setup for the measurement with the four-electrode technique

All these forms of multi-electrode measurement are based on the same principle of the four-electrode measurement. Separate electrode pairs are used for introducing the generator current I_{GEN} and recording the measurement voltage U_{MEAS}. The generator current I_{GEN} is brought into the solution via the outer generator electrodes GE. The flowing current in the solution causes a drop in voltage U_{MEAS} on the inner measuring electrodes ME. From these two values the conductance G can be calculated:

$$G = \frac{I_{GEN}}{U_{MEAS}}$$

Because only a negligibly small current flows through the measuring electrodes ME when the measurement voltage U_{MEAS} is being recorded, there is no polarization here. By contrast, it is quite possible for polarization to occur on the generator electrodes GE as a result of the introduction of the generator current. However, because of the separation of generator electrodes and measurement electrodes, as described above, this has no effect on the measurement.

A variant of the four-electrode measurement is the five-electrode measurement. An additional generator electrode splits the generator current in the solution symmetrically. If a suitable cuvette is used, measurement is possible irrespective of the immersion depth.

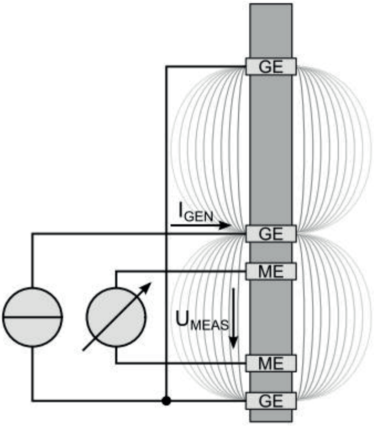


Figure 6: Schematic of the setup for the measurement with the five-electrode technique.

Non-electrolytes

In contrast to electrolytes, non-electrolytes release no freely mobile anions and cations and therefore make no contribution to the electrical conductivity in aqueous solutions.

Typical representatives of this group are, for example, alcohols, urea, sugar (raw sugar), nonionic surfactants and emulsions.

Electrolytic contaminants may contribute to electrical conductivity – see section *Ash* on page 5.

However, higher concentrations of non-electrolytes may influence the viscosity of the solution, which also affects the ionic mobility.

Oscillometry

See section *High-frequency measurement* on page 12.

Ostwald's dilution law

This law applies to weak electrolytes considering the law of mass action and the degree of dissociation of the weak electrolyte. The following relation between the dissociation constant and the molar conductivity is obtained.

$$K_c = \frac{c \times \Lambda_c^2}{\Lambda_0 (\Lambda_0 - \Lambda_c)}$$

K_c: Dissociation constant in mol/L

c: Concentration in mol/L

Λ_c: Molar conductivity in S cm^2/mol

Λ_0: Limiting conductivity in S cm^2/mol

With this equation the dissociation constants of weak electrolytes can be obtained from conductivity measurements.

Platinization

Platinization is the deposition of finely dispersed platinum (platinum black) on bare platinum electrodes. It is an important feature of all classical conductivity measuring cells and is used to avoid polarization effects (and the measuring errors they cause), particularly at higher electrical conductivities.
With multi-pole technology a higher linearity range can be guaranteed than with conventional measuring cells. Therefore, multi-pole conductivity measuring cells do not need any additional platinization, making them more robust and easier to look after.

Polarization

In the measurement of electrical conductivity a number of technical measurement effects that produce incorrect measured values are grouped together under polarization. Their source lies at the electrode/solution boundary. Of chief interest here are the polarization resistance, which is in series with R_X (resistance of the solution), and the polarization capacity, which is also in series. Interference by polarization usually results in too low electrical conductivities being measured.
With the two-electrode method polarization depends mainly on the current density at the electrodes. However, this current density can be kept negligibly small if platinized measuring cells are used together with a suitable, not too low measuring frequency.

Reference temperature

The electrical conductivity measured at a given temperature is converted to a reference temperature. The conversion is carried out (usually automatically) by using the temperature coefficient.
The normal reference temperatures are 20 °C and 25 °C.

Salinity

Applications exist in which it is not the electrical conductivity that is of interest, but rather the total content of the dissolved salts. Separation into the individual ions cannot be achieved by measuring the conductivity, as each type of ion makes a different contribution to the total conductivity. An example of such an application is the salinity of seawater. Absolute salinity (S_A) is the ratio of the mass of the dissolved material in seawater to the mass of the seawater. Because this cannot be measured directly in practice, the practical salinity scale, PSS-78 that uses conductivity measurement as the basis for calculation, has been defined by the UNESCO. A seawater with conductivity at 15 °C the same as that of a 32.4356 g/kg KCl solution has a salinity value of 35 according to the

definition. Further information on the practical salinity scale and the calculation of the salinity can be found under the fellowing website:
http://salinometry.com/pss-78/

Solvents, non-polar

Non-polar (also known as aprotic) solvents have no self-dissociation. Molecules with ionic bonding only decompose in them to form ions on rare occasions.
Examples of acidic non-polar solvents are:
pyridine, dimethylformamide (DMF), dimethylsulfoxide (DMSO).

Examples of neutral non-polar solvents are:
acetone, methyl isobutyl ketone (MIBK), acetonitrile, nitrobenzene, ethers, hydrocarbons and chlorinated hydrocarbons.

«Normal» conductometers are not suitable for non-polar solvents such as chlorinated and non-chlorinated hydrocarbons, insulation oils or petrochemical products. In order to measure the electrical conductivity (insulation properties) of such products, special instruments are required. These work with voltages in the kV range and with special measuring cells.

Solvents, polar

Polar (also known as amphiprotic) solvents have an appreciable self-dissociation. In such solvents molecules with ionic bonding are prone to dissociate and to form ions (the higher the dielectric constant, the better).
The most polar solvent is water:
$2\ H_2O \rightleftarrows H_3O^+ + OH^-$
Alcohols also belong to the protic solvents,
e.g., $2\ CH_3OH \rightleftarrows CH_3OH_2^+ + CH_3O^-$

Examples of acidic polar solvents are:
formic acid, glacial acetic acid, cresols, phenol.

Examples of basic polar solvents are:
ethylenediamine, benzylamine, butylamine.

Examples of neutral polar solvents are:
methanol, ethanol, isopropanol, ethylene glycol, ethylene glycol monomethyl ether.

Specific conductivity

Earlier term for electrical conductivity γ (EN and ISO standard). It was known as κ and had the same unit, i.e. S/cm (from conductance G × cell constant c).

Specific resistance

The specific resistance ρ is the reciprocal of the specific conductivity κ – electrical conductivity γ – with the unit $\Omega \times$ cm.
In earlier days it was usual in water purification plants to express the water quality in these units. 1 µS/cm corresponds to a specific resistance of 1 M$\Omega \times$ cm.

TDS (total dissolved solids)

A sample contains suspended and dissolved solids, and of these only the dissolved solids can pass through a glass fiber filter (e.g., Millipore AP-40, Whatman 934-AH, Gelman type A/E, or equivalent). The conventional way for determining TDS is by weighing the dried sample residue on the filter and expressing the determined mass in relation to 1 liter of sample. It is considerably easier to measure the conductivity of the dissolved salts in unfiltered sample. The conductivity is then converted into TDS by means of a factor. This factor depends on the way in which the result is to be expressed. If, for example, TDS is to be expressed as 0.01 M NaCl, the factor is 0.51, because 0.01 M NaCl has a mass concentration of 584 mg/L and a theoretical conductivity of 1156 µS/cm.

Temperature coefficient

$$\alpha(\Theta-25)=\frac{1}{\gamma_{25}}\left(\frac{\gamma_{\Theta}-\gamma_{25}}{\Theta-25}\right)\times 100$$

$\alpha(\Theta-25)$: Temperature coefficient in %/°C
γ_{25}: Conductivity at reference temperature; here 25 °C, in S/cm
γ_{Θ}: Conductivity at solution temperature in S/cm
Θ: Temperature of the solution in °C
100: Conversion factor to obtain %

25 and Θ °C are temperatures at which the electrical conductivities have been measured. The temperature coefficient can be given as reciprocal Kelvin or % per °C. The temperature coefficient depends primarily on the ions contained in the solution and seldom shows a linear behavior. We recommend that it is determined automatically by the 856 Conductivity Module in conjunction with the ***tiamo*** software.

See also under chapter *Determination of the temperature coefficient* α *of c*(Na_2SO_4) *= 0.05 mol/L* on page 30.

Temperature compensation

See section *Reference temperature* on page 18.

Temperature dependency

The temperature dependency of electrical conductivity can be explained by observations concerning the migration speed of the ions in an electric field. See section *Walden's rule* on page 22.
This can be used to explain at least the positive temperature coefficient. However, the quantitative relationships are complicated and calculations are therefore practically impossible. Even with uniform substances (e.g., KCl solutions) the temperature coefficient changes with the concentration. In mixtures all the ions contribute to a new, mixed temperature coefficient. If high accuracy is required, the temperature coefficient must therefore be determined experimentally.

See also sections *Reference temperature* on page 18, *Temperature coefficient* on page 20 and *Determination of the temperature coefficient* α *of* *c*(Na_2SO_4) *= 0.05 mol/L* on page 30.

Transference number

The transference numbers n_+ and n_- describe the current fraction transported by the cation and anion, respectively.

$$n_+ = \frac{\Lambda_+}{\Lambda} = \frac{u_+}{u_+ + u_-}$$

$$n_- = \frac{\Lambda_-}{\Lambda} = \frac{u_-}{u_+ + u_-}$$

n_+: Transference number of cations
n_-: Transference number of cations
Λ_+: Molar conductivity of cations in S cm^2/mol
Λ_-: Molar conductivity of anions in S cm^2/mol
Λ: Molar conductivity in S·cm^2/mol
u_+: Migration speed of cations
u_-: Migration speed of anions

Experimental determination of the transference numbers allows the calculation of the ionic conductivities and ionic mobilities.

Validation

Validation is the systematic checking of analysis procedures and/or measuring devices with the aim of ensuring that, if defined SOPs (Standard Operating Procedures) are observed, reliable and reproducible results and measurements will be obtained. See also chapter *Calibration* on page 27.

Table 5: Electrical conductivity of KCl solutions at two different reference temperatures

c(KCl)	20 °C	25 °C
0.001 mol/L	133 µS/cm	147 µS/cm
0.010 mol/L	1.28mS/cm	1.41 mS/cm
0.100 mol/L	11.67 mS/cm	12.87 mS/cm

Viscosity

The (dynamic) viscosity η is the property of a liquid to resist (by internal friction, thickness) the mutual laminar displacement of two neighboring layers. For Newtonian liquids at a given temperature, η is a material constant with the SI unit Pascal per second (Pa/s). An interesting feature in connection with the measurement of conductivity is that, as the viscosity increases, the ionic mobility and therefore the electrical conductivity decrease and vice versa. See also section *Walden's rule* on page 22.

Walden’s rule

In its general form this rule states that the product of the ionic mobility l_i of an ion and the viscosity η of a solvent is constant:

$$l_i \times \eta = K$$

An increase in the viscosity results in a reduction of the ionic mobility (and therefore the electrical conductivity) and vice versa.

Water, intrinsic conductivity

Kohlrausch recognized already about 150 years ago that even the most thorough purification of water by distillation resulted in an intrinsic conductivity that could not be lowered any further. The cause is the self-dissociation of the water, which is also known as autoprotolysis:

$$2\ H_2O \rightleftarrows H_3O^+ + OH^-$$

This self-dissociation depends very strongly on the temperature. Examples are shown in table 6.

Table 6: Correlation between the measured conductivity from the self-dissociation of water and the temperature

°C	µS/cm
0	0.010
18	0.038
25	0.060
34	0.090
50	0.170

The very large temperature coefficient is striking. Between 18 °C and 25 °C it is 8.3% per °C!

Measuring instruments

Instruments for measuring electrical conductivities, also known as conductometers, are instruments for measuring complex resistances with alternating voltages. (In contrast to the measurement of purely ohmic resistances of metallic conductors, liquids, together with the measuring cell, constitute a whole network of resistances and capacitances). Almost ohmic conditions can be obtained, however, by selecting the right measuring frequency, cell constant and measuring cell material. Under these conditions the electrical conductivity can be determined from the measured resistance.

Figure 7: Metrohm 912 Conductometer and 856 Conductivity Module

Conductivity measuring cells

These measuring cells, also known as Kohlrausch cells, normally have two platinized platinum electrodes. By selecting the area and the distance between the two electrodes it is possible to vary the cell constant of such measuring cells within wide limits. Platinizing the electrodes greatly reduces the risk of obtaining incorrect measured values due to polarization. It also has a favorable effect on the usable measuring range. Uncoated, i.e. non-platinized, measuring cells should only be used for low electrical conductivities (<20 µS/cm).

However, platinization also has its disadvantages. Platinized measuring cells are susceptible to encrustation, inclusions and also growth of algae, bacteria or mold. They also dry out during prolonged storage or the platinization gradually breaks down. As a result of these effects the cell constant changes and has to be redetermined from time to time (and, of course, after every replatinization process).
Some suggestions for treating and preparing the platinized conductivity measuring cells:

- Place measuring cells that have been stored dry in acetone for approx. 30 min. Then rinse well with dist. H_2O and place in dist. H_2O for 2–3 h.
- Frequently used measuring cells should be stored in dist. H_2O.
- Less frequently used measuring cells should be stored in 20% ethanol or stored dry (prevents biological growth).
- Always rinse the measuring cell well with dist. H_2O after use.

Thanks to multi-electrode technology, measuring cells with a wide linearity range are now available without platinization. They can be stored in a dry environment. They are very easy to clean: if necessary, the protective cap can be removed and the sensor cleaned with a cloth moistened with ethanol or the rings can be polished with the polishing set (6.2802.000).

Figure 8: Conducitvity measuring cells offered by Metrohm

The following table holds the information on which conductivity cell Metrohm offers for its instruments.

Table 7: Offered conductivity measuring cells by Metrohm and their measuring range

Device	**Plug**	**Measuring range**			
		very low	low to medium	medium to high	very high
		<300 µS/cm	5 µS/cm to 20 mS/cm	5 µS/cm to 100 mS/cm	100 µS/cm to 1000 mS/cm
856	N	6.0916.040 (1.2 m cable) 	6.0915.100 (1.2 m cable) 6.0920.100 (2 m cable) 	6.0915.130 (1.2 m cable) 6.0920.130 (2 m cable) 	6.0901.260 (1 m cable) + adapter 6.2103.160 

Device	**Plug**	**Measuring range**			
		very low	low to medium	medium to high	very high
		<300 µS/cm	5 µS/cm to 20 mS/cm	15 µS/cm to 250 mS/cm	100 µS/cm to 1000 mS/cm
912/914	O	6.0918.040 (1.2 m cable) 		6.0917.080 (1.2 m cable) 	6.0919.140 (1.2 m cable) 

Examples of measuring cells

Figure 9: Stainless-steel measuring cell with integrated Pt1000 temperature sensor (c = 0.1 cm^{-1})

Figure 10: 5-ring conductivity measuring cell with integrated Pt1000 temperature sensor (c = 1.0 cm^{-1} or c = 0.7 cm^{-1})

Figure 11: Flow-through measuring vessel 6.1420.100 for flow-through measurements with the conductivity measuring cell 6.0916.040

Figure 12: Flow-through cell 6.2763.000 for flow-through measurements with the 5-ring conductivity measuring cells 6.0915.100 or 6.0920.100

Calibration

GLP (Good Laboratory Practice) requires, among other things, that the accuracy and precision of analytical instruments are checked regularly on the basis of SOPs (Standard Operating Procedures).
Calibration is used to validate the whole system that is needed for performing the measurements. In our case, this means that the instrument and used measuring cell(s) must be calibrated from time to time.
The following test procedures should be considered as guidelines. The limits they contain are merely examples. Depending on the accuracy required for the measuring system, it may be necessary for these limits to be redefined in your own SOPs.

A) Checking the instrument

Regular checking of the instrument in accordance with the manufacturer's specification / standard requirements is recommended.

B) Checking the conductivity measuring cell with calibration solution

It is assumed that the conductivity measuring cell is in a clean – and, in the case of platinized cells, also well-conditioned – state.
The measuring vessel is rinsed thoroughly, first with ultrapure water and then with calibration solution. It is then filled with the calibration standard and thermostated at 25 °C.
The measuring cell is first immersed several times in the calibration solution and then positioned in it so that the upper openings at the sides are completely immersed in the liquid. Any air bubbles that are present inside the measuring cell can be removed by swirling and tapping. The conductometer is switched on and the measuring temperature and reference temperature are entered on the instrument. Gentle stirring (e.g., setting 3) during measurement is recommended. When the temperature is constant, measuring can be started.
Various methods can be chosen to check the cell constant:

- Determination of the cell constant with a calibration solution and then determination with a second calibration solution (within the specified range of the measuring cell) → The difference between the two cell constants (measurement error) should be no more than 2%.
- Determination of the cell constant with a calibration solution and measurement of the conductivity of a second calibration solution → The measured value for the second standard should deviate from the certified value by no more than 2% (e.g., 12.87 ± 0.25 mS/cm at 25.0 +/- 0.2 °C).

Practical applications

Determination of the cell constant c

General

Metrohm conductivity cells are supplied with the cell constant printed on their box and certificate. Use of the cells may cause the cell constant to change. Therefore, for high-precision measurements, the cell constant must be checked or redetermined from time to time. KCl solutions of a known concentration are used for these determinations.

For example:
c(KCl) = 0.1000 mol/L (Metrohm No. 6.2301.060)
The conductivity of this solution is:
– at 20 °C: 11.66 mS/cm
– at 25 °C: 12.87 mS/cm

Additionally Metrohm offers a conductivity standard with 100 µS/cm (Metrohm No. 6.2324.010 or 6.2324.110)
The conductivity of this solution is:
– at 20 °C: 90.9 µS/cm
– at 25 °C: 100.0 µS/cm

Certified conductivity standards with a wide range (1 µS/cm–100 mS/cm) are sold, for example, by Reagecon, Ireland; **www.reagecon.com**

Example of a determination at 25 °C

Instruments and accessories

- Conductometer e.g., 856 incl. Touch Control, 2.856.0110
- Magnetic stirrer, 2.801.0010
- Conductivity measuring cell, e.g., 6.0915.100
- Titration vessel lid, 6.1414.010
- Titration vessel with thermostat jacket, 6.1418.250

Reagents

- c(KCl) = 0.1000 mol/L, 6.2301.060
- Ultrapure water

Settings of parameters

For entering the data of the standard correctly into the software, please proceed as follows:

- In case no temperature sensor is connected enter the actual temperature
- Enter temperature coefficient for the actual temperature depending on the reference temperature (α20 or α25)
- Enter conductivity of standard at reference temperature (not actual one!)

The following two examples illustrate this for a 100 µS/cm standard with an actual temperature of 30 °C, and with reference temperatures of 20 °C and 25 °C, respectively:

Measuring temperature: 30 °C
Reference temperature: 25 °C
Temperature coefficient: 2.0%/°C
Conductivity (at T_{ref}) = 25 °C 100 µS/cm

Measuring temperature: 30 °C
Reference temperature: 20 °C
Temperature coefficient: 2.2%/°C
Conducitivty (at T_{ref}) = 20 °C 90.9 µS/cm

The same procedure is applied for the 12.87 mS/cm standard.

Procedure

The measuring cell is rinsed with deionized water. The titration vessel is first rinsed with c(KCl) = 0.1000 mol/L and then filled up with this solution. The measuring cell is also rinsed with c(KCl) = 0.1000 mol/L and inserted into the titration vessel. With the help of the thermostat, the liquid in the titration vessel is brought to 25.0 °C with gentle stirring. Care must be taken to ensure that there are no air bubbles inside the measuring cell. For the calibration the measuring temperature and reference temperature are entered as 25 °C and the temperature compensation is switched off.
After that, the calibration is started.

If no thermostat is available, the following procedure can be used. The measuring cell and the solutions used are prepared in exactly the same way. The measurements are also performed in a closed measuring/titration vessel. Instead of thermostatting, a Pt1000 temperature sensor (e.g., 6.1110.100) is connected if a cell with integrated Pt1000 is not being used. The parameters in the conductometer software also remain the same with the exception of the temperature coefficient, which is entered as 2.11% / °C.

The cell constant is calculated automatically as follows:

New cell constant = theoretical conductivity / measured conductance

Example:
Theoretical conductivity = 12.87 mS/cm
c(KCl) = 0.1000 mol/L at 25 °C)
Measured conductance = 19.067 mS
12.87 mS cm^{-1}/19.067 mS = c =
0.675 cm^{-1}

Determination of the temperature coefficient α of $c(Na_2SO_4) = 0.05$ mol/L

As explained in the theoretical section, the conductivity of ionic solutions is extremely temperature-dependent and this dependency is rarely linear. This is why we recommend that the temperature coefficient (TC) in the temperature range of interest is recorded automatically with the 856 Conductivity Module with ***tiamo***.

Instruments and accessories

- 856 Conductivity Module with ***tiamo,*** 2.856.0210
- 801 Magnetic Stirrer, 2.801.0010
- Conductivity measuring cell with temperature sensor (Pt1000), e.g., 6.0915.100
- Thermostat (available from third party providers)
- Titration vessel lid, 6.1414.010
- Titration vessel with thermostat jacket, 6.1418.250

Reagents

- $c(Na_2SO_4) = 0.05$ mol/L
- Ultrapure water

Procedure

The conditioned measuring cell is rinsed with ultrapure water and with Na_2SO_4 solution. Sufficient Na_2SO_4 solution is filled into the measuring vessel and the measuring cell inserted with no air bubbles.

In ***tiamo***, method Meas TC Cond is loaded and adapted. The stirrer is switched on and the solution is heated to approx. 45 °C with the help of the thermostat. The automatic determination is started and the solution is allowed to cool down slowly (not faster than 1 °C / min) or, starting at room temperature, it is heated up slowly. Before starting the ***tiamo*** method, ensure that the temperature is below or above the temperature range which is used for the temperature coefficient determination.

General remarks concerning conductivity measurements

The measuring cell

- The cell constant should match the solution being measured. Low conductivities require the use of a low cell constant, high conductivities a high one:
    - $c \approx 0.1\ cm^{-1}$ for poorly conducting solutions, such as fully or partially demineralized water
    - $c \approx 1\ cm^{-1}$ for moderately conducting solutions, such as drinking water, surface water, ground water and wastewater
    - $c \approx 10\ cm^{-1}$ for solutions with good conductivity, such as seawater, rinsing water, physiological solutions, etc.
    - $c \approx 100\ cm^{-1}$ for solutions with very good conductivity, such as brine, acids, alkalis, electroplating baths, etc.
- The measuring cell must be well conditioned/prepared. Platinized measuring cells stored dry must be placed in acetone for 30 min. Then they are rinsed with ultrapure water and allowed to stand in this water for at least 2 h, but preferably overnight. Frequently used measuring cells are stored in ultrapure water or 20% ethanol (to prevent the growth of microorganisms). Measuring cells that are used only occasionally should be stored dry.
  Stainless-steel or five-ring measuring cells are generally stored dry.
- Contaminated measuring cells cannot be used for conductivity measurements and must be cleaned. After cleaning they should be rinsed thoroughly with ultrapure water. Possible sources of contamination are:
    - Deposits of calcium carbonate or barium sulfate: Rinse with HCl. In the case of $BaSO_4$ immerse the cell overnight in a solution of $w(Na_2EDTA) = 10\%$ in $c(NaOH) = 0.1$ mol/L with stirring.
    - Fat and oil residues: Rinse with acetone. In severe cases, saponify with ethanolic $c(NaOH) = 1$ mol/L at approx. 40 °C.
    - Proteins: Place in $w(pepsin) = 5\%$ in $c(HCl) = 0.1$ mol/L for 1–2 h.

The instrument

- Temperature coefficient: If known, set on the instrument, otherwise determine it. Another possibility is to use a thermostat and to perform the measurement at the reference temperature, which means that this setting is not necessary.
- Temperature: It is best to use a measuring cell with an integrated temperature sensor. Otherwise, connect a separate temperature sensor or use a thermometer – in the latter case the measuring temperature must be entered on the instrument.

- Cell constant: Enter the cell constant indicated on the measuring cell or, preferably, redetermine the cell constant by way of calibration.
- Reference temperature: This is normally 25.0 °C; for some applications 20.0 °C is stipulated or preferred. Any reference temperatures can be entered on the conductometer.

The measurement

Only use clean measuring cells. It is best to rinse them, prior to measuring, with the solution to be measured. Immerse the measuring cell in the measuring solution to an adequate depth and make sure it is bubble-free. The lateral openings must be fully immersed. Immerse and withdraw the measuring cell a few times. Wait for the measuring cell and solution to reach a constant temperature.

Conductivity measurement in water

Wastewater, ground water, mineral water, surface water and drinking water

The reference temperature is normally 25.0 °C. In order to avoid errors due to incorrect selection of the temperature coefficient (TC), it is either recommended or stipulated that the sample solution is thermostated at 25.0 °C. If this is not desirable, a TC can be entered according to the table below or the «DIN» template can be selected. The latter setting is suitable for water that contains mainly calcium and hydrogen carbonate ions as well as small amounts of magnesium, sulfate, chloride and nitrate ions.

Table 8: Temperature coefficients in dependence of the sample temperature

Sample temperature	TC in % / °C
5–10 °C	2.62
10–15 °C	2.41
15–20 °C	2.23
20–25 °C	2.08
25–30 °C	1.94
30–35 °C	1.79

Demineralized water

Because of possible interferences, a special procedure must be selected for water with a conductivity of <5 µS/cm. This applies to water with a conductivity <1 µS/cm in particular! The main interferences are:

– entrainment of CO_2 (or other «conducting» gases) from the atmosphere;
– leaching of traces of Na and Ca from the glassware used.

Both interferences cause the settings to drift and ultimately excessively high, i.e. incorrect, conductivities are obtained. We recommend the following procedures to eliminate such interferences as far as possible:

- Version 1
  Perform flow-through measurements. Because of the small volume of the measuring setup we recommend use of conductivity measuring cell 6.0916.040 (stainless steel, integral Pt1000 temperature sensor) screwed into flow-through vessel 6.1420.100. The water is allowed to flow through the measuring setup and the conductivity is determined in the usual way.

- Version 2
  Measurement is carried out in as large a volume as possible. Nitrogen or argon should be passed through and over the solution, which should also be stirred. If possible, use a closed or covered setup.

Please note the high TC (approx. 5.8%/ °C) of such water samples!

TDS

Applications exist in which it is not the conductivity that is of interest, but rather the total content of the dissolved salts. Separation into the individual ions cannot be achieved by measuring the conductivity, as each type of ion makes a different contribution to the total conductivity. For this reason, in this determination, the conductivity of the sample solution is compared with that of pure NaCl solutions and the corresponding NaCl concentration is stated. The conductometer software performs this conversion automatically, if the calculation is programmed accordingly. Also see section *TDS (total dissolved solids)* on page 20.

Conductometric titrations

For conductometric titrations the cell constant does not normally need to be known. A conductivity measuring cell is used as measuring electrode. Thermostatting is not required for simple titrations – room temperature is adequate. Alterations in conductivity caused by temperature variations are of virtually no consequence.

Example of a TBN titration of motor oil according to IP400

Instruments and accessories used

- 856 Conductivity Module with software ***tiamo,*** 2.856.0210
- 801 Magnetic stirrer, 2.801.0010
- 2 x Dosino, 2.800.0010
- 50 mL Dosing unit, 6.3032.250
- 10 mL Dosing unit, 6.3032.210
- Conductivity measuring cell made of stainless steel, c = 0.1 cm^{-1}, with Pt1000 (plug N), 6.0916.040
- Cable USB A – mini-DIN 8-pin, 6.2151.000

Reagents

- c(HCl) in 2-propanol = 0.1 mol/L
- Toluene
- 2-propanol

Procedure

The weighed sample is dissolved in a mixture of 50% toluene, 49.5% 2-propanol, and 0.5% ultrapure water. The resulting solution is titrated to the endpoint at room temperature with standard alcoholic HCl solution. The endpoint is determined by a change in the slope of the curve, (conductivity/volume of added titrant).

- Weigh sample into a clean and dry tared beaker.
- Add 75 mL solvent.
- Immerse conductivity measuring cell into the titration vessel, activate stirrer and wait 30 s. Then start the titration with c(HCl) = 0.1 mol/L in 2-propanol. Parameters: 10 s intervals, volume increment of 0.1 mL.
- After titration rinse the buret tip and sensor with solvent until no oil is visible. Then rinse the sensor with ultrapure water followed, again, by solvent. (Parameters and examples of results can be found in AB-405 and AN-T-098.)

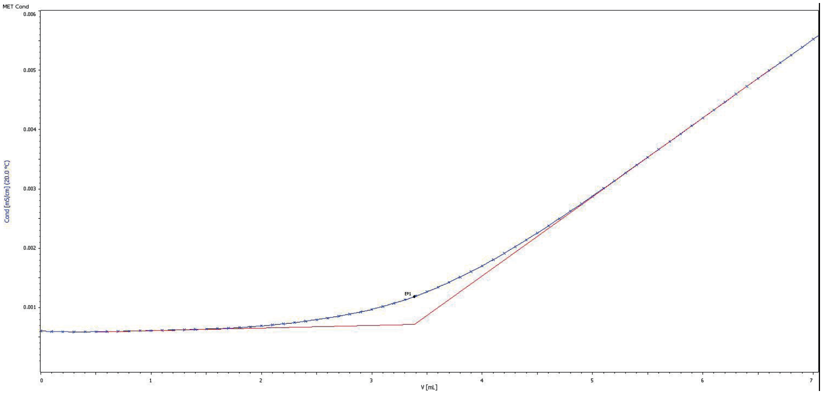


Figure 13: Example of a conductometric titration curve

Evaluation

The evaluation is done automatically by ***tiamo.***

Calculation

$$\mathrm{TBN} = \frac{V_{EP1} \times c_{HCl} \times f \times M_A}{m_s}$$

TBN: Total base number in mg KOH/g sample

V_{EP1}: Titrant consumption in mL to reach the first equivalence point

C_{HCl}: Concentration of titrant in mol/L; here c(HCl) = 0.1 mol/L

f: Correction factor (titer) without unit

M_A: Molar mass of KOH; 56.106 g/mol

m_s: Sample weight in g

Further literature on this topic can be accessed using the Application Finder under
www.metrohm.com/applications

- *Application Bulletin AB-405 – Determination of the total base number in petroleum products*
- *Titration Application Note AN-T-098 – Conductometric determination of TBN in petroleum products according to IP 400*

Conductivity measurements in demineralized water according to USP guidelines

The electrical conductivity of ultrapure water is measured according to USP Method 645 (US Pharmacopeia; USP 33–NF 28) with a conductivity measuring cell with cell constant $c = 0.1\ cm^{-1}$. Procedure Step 1 is intended for online measurement, though it can also be performed offline in a suitable vessel.

Sample

Ultrapure water from a «Barnstead Nanopure» unit, Application Lab, Herisau.

Reagents

Hamilton conductivity standard, 5 µS/cm ± 5%

Instruments and accessories used

856 Conductivity Module with Touch Control, 2.856.0110
(or) 856 Conductivity Module with ***tiamo***, 2.856.0210
Conductivity measuring cell (stainless steel), $c = 0.1\ cm^{-1}$, 6.0916.040
801 Magnetic Stirrer, 2.801.0010
Titration vessel, 6.1418.250
Titration vessel lid, 6.1414.010
Thermostat bath

Optionally for flow-through measurement:
843 Pump Station Membrane, 2.843.0020
Remote box MSB, 6.2148.010
Connection cable, 6.2141.290
Flow-through cell, 6.1420.100

Sample preparation

Water is taken from the «Nanopure» unit. The first 500 mL is discarded. One liter is then filled into an amber glass bottle (thoroughly rinsed) and the bottle placed in a thermostat bath for 1 h at 25 °C.

Preparing the measuring setup

The instrument must be checked according to the technical specifications and manufacturer's instructions. The cell constant (c) can be verified by two methods:

- directly with a conductivity standard or
- indirectly by comparison with a conductivity cell with a known, validated cell constant (precision ± 2%).

In case a new calibration of the cell constant is necessary the following procedure can be applied. The cell constants of the conductivity measuring cells are determined at 25 °C with 100 mL conductivity standard (Hamilton 5 µS/cm) in a closed, thermostatted titration vessel. When the conductivity standard has reached the specified temperature of 25.0 °C, the cell constant is determined in accordance with the procedure described under: *Determination of the cell constant* on page 28. For this, the temperature compensation on the conductometer is switched off. The newly determined cell constant is entered on the conductometer or imported by this / saved in the software (configuration).

Measuring with the flow-through cell

In the case of flow-through measurement the measuring system must be rinsed first with 500 mL «sample». Further sample is pumped through the closed system and the electrical conductivity is measured.

Calculations

$$c_{new} = \frac{\gamma_{theor.}}{G}$$

c_{new}: New cell constant
$\gamma_{theor.}$: Electrical conductivity in S/cm
G: Conductance in S

Remarks

USP Monograph 645 sets standards for the quality control of ultrapure waters using electrochemical conductivity measurements. The conductivity test according to USP 645 is a «three-step test». The requirements have been met when the conductivity of the tested water has reached <1.3 µS/cm at 25 °C. If this value is exceeded, this leads to the second step.

In this case, the water is thermostatted in an open vessel at 25 °C with stirring and the CO_2 equilibrium (absorption from the atmosphere) is awaited. The electrical conductivity of the solution is measured and the temperature is compensated. If $\gamma > 2.1$ µS/cm, the third step must be carried out.

The water sample from step two is treated with a small amount of KCl, in order to ensure a stable pH value.

The measured electrical conductivity must be less than a value specified in a table. If the value in the table is exceeded, then the conditions of the USP test have not been fulfilled.

Summary/Procedure

In practice the electrical conductivity of water from ultrapure water units is determined according to USP monographs for conductivity measurements (645), as follows:

1. The conductometer is checked according to the manufacturer's instructions.
2. The cell constant of the conductivity measuring cell is determined at 25 °C.
3. The temperature compensation on the conductometer is switched off in the parameters.
4. The electrical conductivity and temperature of the sample are measured.
5. The value is compared with the Table 9 on page 39 (USP requirements):
6. If the electrical conductivity (at the corresponding temperature) is not greater than the value given in the table 9, then the USP requirements have been fulfilled. However, if the measured electrical conductivity is greater than the corresponding table value, then step two under «Remarks» must be carried out.

USP 645 Requirements – Ultrapure water

(without temperature compensation)

Table 9: Comparison table for the conducitivy depended on the temperature as per USP 645

Temp. / °C	µS / cm	Temp. / °C	µS / cm
0	0.6	55	2.1
5	0.8	60	2.2
10	0.9	65	2.4
15	1.0	70	2.5
20	1.1	75	2.7
25	1.3	80	2.7
30	1.4	85	2.7
35	1.5	90	2.7
40	1.7	95	2.9
45	1.8	100	3.1
50	1.9		

Automated procedure

With the MATi 14 system Metrohm offers a fully automated solution for the determination of the conductivity as per USP 645.

For more information have a look at AB-428 - Automatic conductometry in water samples with low electrical conductivity in accordance with USP<645> which can be downloaded from **www.metrohm.com/applications**.

Appendix

Literature

Below a list of additional literature for further information is given. All Metrohm application literature can be downloaded from **www.metrohm.com/applications**

- Metrohm Application Bulletin AB-102
  Conductometry
- Metrohm Application Bulletin AB-428
  Automatic conductometry in water samples with low electrical conductivity in accordance with USP<645>
- Metrohm Application Note AN-T-098
  Conductometric determination of TBN in petroleum products according to IP 400
- Metrohm Application Note AN-T-139
  Standardization of barium acetate as the titrant for conductometric sulfate titration
- Metrohm Application Note AN-T-154
  Titration of alpha acids in hops products in accordance with EBC 7.4
- Metrohm Application Note AN-T-155
  Titration of alpha acids in hops extracts in DMSO/ethanol
- United States Pharmacopeia Convention, Inc.
  USP<645>
- Kunze, U.R., Schwedt, G.
  Grundlagen der quantitativen und qualitativen Analyse
  Wiley-VCH, Weinheim 2002, ISBN 3-527-30858-X
- Dahms, G.H., Jung, A., Seidel, H.
  Predicting emulsion stability with focus on conductivity analysis, Cosmetics & Toiletries Manufacture Worldwide 2003, p. 223-228
- Donald T. Sawyer et al.
  Electrochemistry for chemists
  John Wiley & Sons, New York 1995, ISBN 0-471-59468-7

- Öhme, F., Bänninger, R.
  ABC der Konduktometrie
  «Chemische Rundschau» offprint, 1979 (out of print)
- DIN EN 27888
  Water quality – Determination of electrical conductivity
- ISO 7888
  Water quality – Determination of electrical conductivity
- AOAC, Method 973.40
  Specific conductance of water
- UNESCO technical papers in marine science 36: Tenth report of the joint panel on oceanographic tables and standards (UNESCO 1981)

Electrical conductivity of organic acids at 25 °C

% formic acid	mS/cm	% acetic acid	mS/cm
5	6.22	5	1.36
10	8.26	10	1.76
15	9.86	15	1.82
20	11.1	20	1.82
25	11.4	25	1.71
30	11.8	30	1.58
40	11.1	40	1.23
50	9.78	50	0.840
60	7.92	60	0.521
70	5.92	70	0.270
80	3.92	80	0.093
90	1.95		
100	0.32		

M(HCOOH) = 46.026 g/mol
$M(CH_3COOH)$ = 60.052 g/mol

Electrical conductivity of hydrogen bromide and hydrogen chloride at 25 °C

% HBr	mS/cm	% HCl	mS/cm
5.09	239	2.03	202
9.16	409	6.00	506
15.3	603	10.0	698
20.4	706	15.2	821
25.3	787	19.0	849
30.5	828	20.3	844
32.5	833	24.8	809
35.5	833	29.9	737
37.5	825	33.0	688
40.7	801	36.0	638

M(HBr) = 80.912 g/mol
M(HCl) = 36.461 g/mol

Electrical conductivity of nitric acid at 25 °C

% HNO_3	mS/cm	% HNO_3	mS/cm
3.06	176	45.1	775
4.89	270	49.9	719
8.99	454	55.0	659
14.0	631	60.0	597
18.1	741	70.1	442
24.0	830	80.1	239
28.0	852	88.5	80.0
33.1	859	92.6	70.6
36.3	844	99.5	48.8
40.0	819		

M(HNO_3) = 63.013 g/mol

Electrical conductivity of phosphoric acid at 25 °C

% H_3PO_4	mS/cm	% H_3PO_4	mS/cm
5	31	40	222
10	61	45	232
15	91	50	233
20	122	55	224
25	152	60	210
30	180	70	169
35	204	80	98

M(H_3PO_4) = 97.995 g/mol

Electrical conductivity of sulfuric acid (and oleum) at 25 °C

% H_2SO_4	mS/cm	% H_2SO_4 (SO_3)	mS/cm
3.93	177	53.5	555
7.00	308	58.4	471
10.0	426	63.1	380
14.6	586	72.3	223
19.8	717	85.9	124
25.3	798	95.4	124
29.4	825	98.0	94.7
34.3	819	100.0	10.46
39.1	781	101.5	32.05
43.9	714	103.8	34.50
48.7	640	105.1	28.84

$M(H_2SO_4) = 98.07$ g/mol
$M(SO_3) = 80.06$ g/mol

Electrical conductivity of potassium and sodium hydroxide at 25 °C

% KOH	mS/cm	% NaOH	mS/cm
5	225	5	197
10	360	10	353
15	407	15	478
20	395	20	567
25	342	25	618
30	266	30	624
35	209	35	595
40	169	40	525

M(KOH) = 56.106 g/mol
M(NaOH) = 39.997 g/mol

Electrical conductivity of ammonia solutions at 25 °C

% NH_3	mS/cm	% NH_3	mS/cm
1.04	0.821	15.2	0.810
3.73	1.176	18.6	0.625
5.26	1.275	23.2	0.419
7.46	1.236	27.3	0.286
9.52	1.142	31.0	0.197
11.5	1.035		

M(NH_3) = 17.030 g/mol

Electrical conductivity of lithium chloride at 25 °C

% LiCl in H_2O	mS/cm	% LiCl in ethanol	mS/cm
2.5	45.4	2.5	3.648
5.0	82.6	5.0	4.565
7.5	112.5	7.5	6.565
10.0	135.6	10.0	4.035
12.5	142.6	12.5	3.139
15.0	148.6	15.0	2.541

M(LiCl) = 42.394 g/mol

Electrical conductivity of potassium and sodium chloride at 25 °C

(own measurements)

% KCl	mS/cm	% NaCl	mS/cm
5	68.9	5	70.3
10	134.0	10	118.8
15	197.8	15	164.2
20	250.2	20	196.8
25	299.6	25	220.2

M(KCl) = 74.551 g/mol
M(NaCl) = 58.443 g/mol

Electrical conductivity of potassium and sodium nitrate at 20 °C

g/L KNO_3	mS/cm	g/L $NaNO_3$	mS/cm
1.01	1.236	0.85	1.025
2.02	2.405	1.70	2.00
5.05	5.745	4.25	4.775
10.1	10.94	8.50	9.11
20.2	20.62	17.0	17.19
50.5	46.6	42.5	38.7

$M(KNO_3)$ = 101.103 g/mol
$M(NaNO_3)$ = 84.995 g/mol

Electrical conductivity of calcium and magnesium chloride at 20 °C

g/L $CaCl_2$	mS/cm	g/L $MgCl_2$	mS/cm
0.555	1.085	0.476	1.030
1.11	2.088	0.952	1.982
2.77	4.90	2.38	4.64
5.55	9.26	4.76	8.76
11.1	17.39	9.52	16.38
27.7	39.35	23.8	36.55

$M(CaCl_2)$ = 110.99 g/mol
$M(MgCl_2)$ = 95.211 g/mol

Electrical conductivity of magnesium and sodium sulfate at 20 °C

g/L $MgSO_4$	mS/cm	g/L Na_2SO_4	mS/cm
0.602	0.798	0.71	1.015
1.204	1.42	1.42	1.925
3.010	2.98	3.55	4.39
6.020	5.20	7.10	8.22
12.04	12.04	14.2	14.97
		35.5	31.3

$M(MgSO_4)$ = 120.36 g/mol
$M(Na_2SO_4)$ = 142.04 g/mol

Electrical conductivity of ammonium chloride and sodium carbonate at 20 °C

g/L NH_4Cl	mS/cm	g/L Na_2CO_3	mS/cm
0.535	1.275	0.53	1.010
1.07	2.50	1.06	1.883
2.675	6.02	2.65	4.220
5.35	11.57	5.30	7.670
10.7	22.25	10.6	13.81
26.75	52.9	26.5	28.70

$M(NH_4Cl)$ = 53.491 g/mol
$M(Na_2CO_3)$ = 105.989 g/mol

Electrical conductivity of sodium chloride and phosphoric acid solutions at 20 °C

% w/v NaCl	mS/cm	$c(H_3PO_4)$ in mol/L	mS/cm
5	65	0.05	7.5
10	113	0.10	10.2
15	148	0.50	32
20	175	1.00	57
25	191	2.00	110
		3.00	165
		4.00	190
		5.00	210

$M(NaCl)$ = 58.443 g/mol
$M(H_3PO_4)$ = 97.995 g/mol

Electrical conductivity of potassium chloride solutions at 20 °C and 25 °C

c(KCl) in mol/L	µS/cm at 20 °C	µS/cm at 25 °C
0.0005	67	74
0.001	133	147
0.005	654	720
0.010	1280	1410
0.020	2510	2770
0.050	6060	6700
0.100	11670	12900
0.200	22440	24800

M(KCl) = 74.551 g/mol
1 mS/cm = 1000 µS/cm
1 µS/cm = 0.001 mS/cm

Electrical conductivity and temperature coefficient (TC) of potassium chloride solutions at various temperatures

°C	mS/cm 0.1 mol/L	TK (α) in % per °C 0.1 mol/L	mS/cm 0.01 mol/L	TK (α) in % per °C 0.01 mol/L
18	11.19	2.06	1.225	2.07
19	11.34	2.06	1.251	2.11
20	11.67	----	1.278	----
21	11.91	2.06	1.305	2.11
22	12.15	2.06	1.332	2.11
23	12.39	2.06	1.359	2.11
24	12.64	2.07	1.386	2.11
25	12.88	2.07	1.413	2.11

M(KCl) = 74.551 g/mol

Electrical conductivity of water – temperature coefficient (TC) as a function of sample temperature

Sample temperature in °C	TK (α) in % per °C
5–10	2.62
10–15	2.41
15–20	2.23
20–25	2.08
25–30	1.94
30–35	1.79

- The reference temperature for water samples is normally 25 °C.
- The above values refer to water samples containing mainly calcium hydrogen carbonate ions and small amounts of magnesium, sulfate, chloride and nitrate ions.

Electrical conductivity of salt solutions – temperature coefficient (TC) as a function of the salt content

Salt	TC at 5%	TC at 10%	TC at 15%	TC at 20%	TC at 25%
NH_4Cl	1.98	1.86	1.71	1.61	1.54
NH_4NO_3	2.03	1.94	----	1.79	----
$(NH_4)_2SO_4$	2.15	2.03	----	1.93	----
$BaCl_2$	2.14	2.06	2.00	1.95	----
$CaCl_2$	2.13	2.06	2.02	2.00	2.04
$Ca(NO_3)_2$	2.18	2.17	----	----	2.18
KBr	2.06	1.94	----	1.77	----
KCl	2.01	1.88	1.68	1.66	----
KNO_3	2.08	2.05	2.02	1.97	----
K_2SO_4	2.16	2.03	----	----	----
LiCl	2.23	2.18	----	2.20	----
$MgCl_2$	2.22	2.20	----	2.37	----
$MgSO_4$	2.26	2.41	2.52	2.69	2.88
$NaCH_3COO$	2.51	2.59	----	2.93	----
Na_2CO_3	2.52	2.71	2.94	----	----
NaCl	2.17	2.14	2.12	2.16	2.27
$NaNO_3$	2.21	2.17	----	2.15	----
Na_2SO_4	2.36	2.49	2.56	----	----
$AgNO_3$	2.18	2.17	----	2.12	----
$ZnSO_4$	2.25	2.23	2.28	2.41	2.58

TC (α) in % per °C, at 18 °C

Requirements of USP 645 for ultrapure water

(without temperature compensation)

Temp. / °C	µS/cm	Temp. / °C	µS/cm
0	0.6	55	2.1
5	0.8	60	2.2
10	0.9	65	2.4
15	1.0	70	2.5
20	1.1	75	2.7
25	1.3	80	2.7
30	1.4	85	2.7
35	1.5	90	2.7
40	1.7	95	2.9
45	1.8	100	3.1
50	1.9		

TC (% per °C) calculated from the above values:

0–20 °C	2.73%
20–40 °C	3.24%
40–60 °C	3.86%
60–80 °C	4.07%
80–100 °C	4.35%

Dependency of the electrical conductivity of dist. H_2O and KCl solutions, on the measuring frequency (at 25 °C and c = approx. 1 cm^{-1})

(own measurement)

Solution	300 Hz	2.4 kHz
dist. H_2O	1.12 µS/cm	1.59 µS/cm
c(KCl) = 0.001 mol/L	147 µS/cm	151 µS/cm
c(KCl) = 0.01 mol/L	1.35 mS/cm	1.41 mS/cm
c(KCl) = 0.1 mol/L	11.03 mS/cm	12.90 mS/cm
c(KCl) = 1 mol/L	45.37 mS/cm	96.18 mS/cm

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