Manual of Electrochemical Analysis

Part 3

Electric Conductivity
Measuring Electric Conductivity in Aqueous Solutions

What is Electric Conductivity?

Aqueous solutions of salts or other substances based on ionic band linkage conduct electrical current, as they contain more or less freely mobile ions. The decomposition of an electrovalent linkage into ions (in fusion or solution) is described as electrolytic dissociation. Electrolytic dissociation is not an effect of the electrical current, but rather the prerequisite for the electric conductivity of a fusion or a solution. An electrolyte is a substance that consists of ions in its solid state or which decomposes easily into ions when it is dissolved and which is therefore subject to electrolytic dissociation. Although slightly inaccurate, solutions of these electrolytes are also described as electrolytes and not (more precisely) as electrolyte solutions.

All substances that conduct electrical current have a measurable electrical resistance. The electrical resistance determines the strength of a current that flows through the circuit at a specific voltage. It is defined as the ratio of the voltage between the ends of a conductor to the strength of the current in the conductor. Ohm's law describes this linear dependence of the current intensity $I$ on the voltage $U$ on the conductor.

$$I = \frac{U}{R}$$

The resistance $R$ is dependent on the geometry (length $l$ and area $A$) of the conductor and the specific electric conductivity $\kappa$:

$$R = \frac{l}{\kappa \cdot A}$$

The electric conductance $G$, as an inversion of ohmic resistance $R$, also depends on the spatial dimensions (length $l$ and cross-section area $A$) of the conductor.

$$G = \frac{1}{R} = \frac{A}{\kappa \cdot l}$$

The electric (more accurately, electrolytic) conductivity $\kappa$ is substance-specific and in an aqueous solution it serves as a parameter for the concentration of dissolved ions. The specific resistance $\rho$, as an inversion of the electric conductivity, is also a substance-specific variable.

$$\rho = \frac{1}{\kappa}$$

To determine the electric conductivity, a precisely known current is applied to a conductor and the voltage drop that depends on the resistance or conductance of the conductor is measured. Hence, the resistance or conductance are directly accessible, the specific resistance or electric conductivity are then determined from this, taking account of the geometry of the conductor.
Table 1: Several examples of the electric conductivity of various substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature / °C</th>
<th>$\kappa$ / S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>20</td>
<td>$6 \times 10^5$</td>
</tr>
<tr>
<td>Copper</td>
<td>20</td>
<td>$5.8 \times 10^5$</td>
</tr>
<tr>
<td>Iron</td>
<td>20</td>
<td>$1.1 \times 10^5$</td>
</tr>
<tr>
<td><strong>Molten salt</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl, molten</td>
<td>850</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Aqueous acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 molar HCl</td>
<td>25</td>
<td>$1.07 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$, conc.</td>
<td>25</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>1 molar acetic acid</td>
<td>25</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$10^{-3}$ molar HCl</td>
<td>25</td>
<td>$4.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>$10^{-3}$ molar acetic acid</td>
<td>25</td>
<td>$4.1 \times 10^{-5}$</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water with traces of CO$_2$</td>
<td>25</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>Pure water</td>
<td>18</td>
<td>$4 \times 10^{-8}$</td>
</tr>
<tr>
<td><strong>Organic Solvents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>18</td>
<td>$6 \times 10^{-8}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>18</td>
<td>$1.35 \times 10^{-9}$</td>
</tr>
<tr>
<td>Hexane</td>
<td>18</td>
<td>$10^{-18}$</td>
</tr>
<tr>
<td>Xylene</td>
<td>18</td>
<td>$10^{-18}$</td>
</tr>
</tbody>
</table>

**Current Conduction and Conductivity Measurement in Aqueous Solutions**

In metallic conductors free electrons conduct current, but in aqueous solutions this takes place via dissolved anions and cations. On the electrode there is a phase boundary between the solution and the metal where both forms of electrical conduction are linked.

As shown in Table 1, the conductivity of aqueous solutions covers a bandwidth of 4 decades, but it is clearly distinct from the conductivity of metallic conductors and organic substances. Even traces of ions will increase the conductivity of pure water by several decades. Correspondingly, electric conductivity is used as a measure for the purity of water. In many measuring tasks it is used as a cumulative parameter for measuring dissolved inorganic substances.

It is possible to relate the conductance of solutions of pure substances to their concentration.

$$\Lambda = \frac{\kappa}{c}$$
In this case $\Lambda$ is described as molar conductance with the unit S\cdot cm²/mol. As ions have different charges $n$, we can deduce the following:

$$\Lambda_{\text{eq}} = \frac{\kappa}{c \cdot n}$$

By comparing the conductance of solutions of various electrolytes with common anions or cations, KOHLRAUSCH discovered the law of independent migration of ions.

$$\Lambda = \lambda_+ + \lambda_-$$

The ions' contribution to electric conductivity depends on their charge and on their mobility in the solution. Thus, to describe a type of ion X we use the ion equivalent conductivity $\lambda(X)$. The values stated in literature for $\lambda(X)$ are temperature-related and generally apply to infinite dilution. Ion equivalent conductivity only plays a major role in the examination of clean water and boiler feed water.

The hydroxyl ion (OH⁻) and especially the proton (H⁺) stand out from the other ions that are listed in Table 2 because of their much higher equivalent conductivity. This can be attributed to an ion migration mechanism that differs from other ions.

Table 2: Equivalent conductivity of various ions at 25°C

<table>
<thead>
<tr>
<th>Cations</th>
<th>$\lambda_+^0$ [S\cdot cm²/mol\cdot z]</th>
<th>Anions</th>
<th>$\lambda_-^0$ [S\cdot cm²/mol\cdot z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>349.8</td>
<td>OH⁻</td>
<td>198.6</td>
</tr>
<tr>
<td>Li⁺</td>
<td>38.7</td>
<td>F⁻</td>
<td>55.4</td>
</tr>
<tr>
<td>Na⁺</td>
<td>50.1</td>
<td>Cl⁻</td>
<td>76.4</td>
</tr>
<tr>
<td>K⁺</td>
<td>73.5</td>
<td>Br⁻</td>
<td>78.1</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>77.8</td>
<td>I⁻</td>
<td>76.8</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>77.3</td>
<td>NO₃⁻</td>
<td>71.5</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>61.9</td>
<td>ClO₄⁻</td>
<td>67.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>73.4</td>
<td>ClO₃⁻</td>
<td>64.6</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>53.1</td>
<td>HCO₃⁻</td>
<td>44.5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>59.5</td>
<td>SO₄²⁻</td>
<td>80.0</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>63.6</td>
<td>C₂O₄²⁻</td>
<td>74.2</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>53.6</td>
<td>Acetate⁻</td>
<td>40.9</td>
</tr>
</tbody>
</table>

If the opposing influences of the particles towards one another are too great conductivity can decline as the concentration increases, since the ions increasingly restrict each other's mobility.
According to Figure 1 it is not the ions themselves that migrate, instead there is a charge transfer because of the continuous breaking up and reformation of O-H bonds. As only one proton "leaps" from a molecule to a neighboring molecule, we also speak of a "leap mechanism".

As can be seen in Figure 2, if the electrolyte concentration is low we have an almost linear connection between the conductivity and the electrolyte concentration. Because of the very good linear dependency and the unproblematic handling potassium chloride (KCl) solutions are a favored standard for calibrating measuring instruments and conductivity cells.
How is Electric Conductivity Measured?

The Conductivity Cell

A two-electrode conductivity cell (Kohlrausch conductivity cell) generally comprises two solid-state electrodes positioned opposite one another (usually coal, graphite, platinized platinum or non-rusting steel). Important is that the cell is constructed in such a way that the electric field is prevented from spreading throughout the entire measuring vessel. This is achieved by arranging the electrodes in a glass or plastic cylinder which is perforated in several places. Apart from a few exceptions, by using suitable equipment with conductivity cells it is possible to measure most conductivities with cell constants between 0.1 cm\(^{-1}\) and 10 cm\(^{-1}\). Porous layers such as platinized platinum, coal or graphite can adsorb constituents of the measuring solution. This leads to prolonged set-up times with concentration leaps. This effect does not occur when smooth electrodes are used.

Besides cell constants, a conductivity cell’s suitability for a measuring task also depends on the occurrence of polarization on the surface of the electrode. We understand this to mean all effects that occur on the interface between metal and solution when current is flowing. A resistance is formed (polarization resistance) that can severely adulterate the result of the measurement. These decrease with increasing measuring frequency and electrode surface. Smooth platinum electrodes have especially high resistances. The least effect is achieved with electrodes made from platinized platinum.

The susceptibility of electrode materials for carry-over effects from one measuring solution to the next is exactly opposed to its polarization tendency. Hence, we cannot talk of a “better” or “worse” electrode material. The choice of electrode is based on the specific measuring task. In the case of a four-electrode conductivity cell the polarization resistances are not recorded so that the cell constants remain valid across a larger measurement range. Compared to the two-electrode conductivity cell the four-electrode cell is also less sensitive to contamination. The conductivity cells PY-C01 – PY-C03 offered by Sartorius are four-electrode conductivity cells with platinum electrodes. This guarantees easy cleaning and a long life for the sensors.

The four-electrode conductivity cell represents an improvement over the two-electrode cell. The conductivity cell comprises two current electrodes and two voltage electrodes. The electric current enters the solution via the current electrodes, the current intensity is known. The voltage drop in the aqueous solution is determined with very high impedance by the voltage electrodes. The exact geometric form of the electrode arrangement is generally unknown, so that the cell constant is determined by using standard solutions. The electrodes are arranged as rings on a glass form. The outer electrode forms, made of plastic, limit the influences of the measuring vessel and protect the glass form from being damaged.

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1 A porous layer consisting of electrolytically separated platinum on a platinum electrode
The Measuring Device

Conductivity measuring devices are also known as conductometers. They differ from conventional resistance meters (ohmmeters) by using alternating voltage instead of direct voltage. A measurement carried out with direct voltage changes the electrode surface and the composition of the solution. On the other hand, if alternating current is used these changes do not occur; the charge carriers only oscillate within the frequency of the alternating current (the most common frequency is 50 Hz).

Conductometers measure current intensity I and voltage U. The conductance G or (after entering the cell constant) the conductivity \( \kappa \) are calculated according to Ohm's law (see above). High-performance conductometers such as Sartorius PP-20 and PP-50 allow cell constants of between 0.1 cm\(^{-1}\) and 10 cm\(^{-1}\) to be set.

Indicating the Conductivity of Aqueous Solutions

The result of a resistance measurement in an aqueous solution can be indicated in various ways. If it is directly displayed as resistance, the measured values are within the range of \( k \Omega \) and \( M \Omega \). As described in the chapter "What is electric conductivity", the conductivity is calculated from the measured resistance.

\[
\kappa = \frac{1}{R \cdot A}
\]

Unit equation: \( \frac{m}{\Omega \cdot m^2} = \frac{S \cdot m}{m^2} = \frac{S}{m} \)

The derived SI unit of conductivity is consequently \( \Omega^{-1}/m^{-1} \) or \( S/m \). In practice we usually work with the units mS/cm or \( \mu S/cm \):

- 1 S/m = 0.01 S/cm = 10 mS/cm = 10,000 \( \mu S/cm = 10^4 \mu S/cm \)
- 1 S/cm = 1,000 mS/cm = 1,000,000 \( \mu S/cm \)

If we base our results on the fact that the measured conductivity was caused solely by sodium chloride, we can calculate the NaCl concentration directly from the conductivity.

Salinity is a cumulative parameter especially used to indicate the salt concentration in sea water. As a rule, sea water has a uniform composition of salts. In addition to NaCl it contains MgSO\(_4\), CaSO\(_4\), CaCO\(_3\) and MgBr\(_2\). The average total concentration is approx. 3%, however, especially the salt concentration of inland seas and seas that are almost landlocked deviates considerably from the average. For instance the Baltic Sea only contains 1% salt, while the Dead Sea has around 30%. The salt concentration is here given in g/kg or ppm and is consequently dimensionless. In the calculation based on the tables carbonates are converted into oxides, and halides into chlorides.

For specific problems one requires very exact indications of salinity. Determination is carried out under strictly controlled boundary conditions. In particular the exact temperature must be known and it must remain constant (± 0.003 K). Calibration is carried out with standard sea water (salinity \( S = 35.000 \)) or with an aqueous KCl solution (32.4356 g KCl in 1,000 g water).

If the composition of the solid matter dissolved in the water is constant, a factor gained by drying a known volume of water (solid matter factor) can be used to make a direct conversion into the concentration of dissolved solid matter (TDS\(^2\))

The conductometers from Sartorius support all the described evaluations, a selection is made in the device menu.

\(^2\) TDS: Total Dissolved Solid
Temperature Dependence and Temperature Compensation

The conductivity of an electrolyte depends very much on the temperature, as the mobility of the ions and the number of dissociated molecules are temperature-related. To compare measured values they must be converted into a defined temperature. Currently the reference temperature is usually 25°C. To indicate the conductivity the temperature must be stated as follows \( \kappa(\vartheta) \). \( \kappa(25) \) which represents the conductivity measured at or converted to 25°C. The temperature relation of conductivity depends on the type and quantity of the dissolved substance and is between 1% and 5% per °C. With the conductometers from Sartorius the temperature coefficient can be entered in the calibration menu.

As opposed to the pH measuring technology, in conductivity measurement the term temperature compensation describes the conversion of a conductivity measured at a specific temperature to the conductivity at a reference temperature. The compensation of the temperature influence relates to the measuring medium, not to the conductivity cell.

The electric conductivity of most diluted salt solutions and natural water changes in an almost linear manner so that the following applies

\[
\kappa_{\vartheta} = \kappa_{25} \left[ 1 + \frac{\alpha_{25}}{100} (\vartheta - 25) \right]
\]

\( \alpha_{25} \) for natural water is approx. 2%/K. In the case of a non-linear connection between \( \kappa \) and \( \vartheta \) \( \alpha_{25} \) itself is temperature dependent; more complex equations are necessary for the calculation, e.g. higher degree polynomials. As a rule one can describe all practically occurring temperature dependencies with 4th degree polynomials. For simple cases (minor temperature differences) the user can enter the temperature coefficient \( \alpha_{25} \). In standard solutions the manufacturer usually states \( \alpha_{25} \) on the label or the package leaflet.
Determining the Cell Constants

The variable I/A is described as cell constant $K$. Generally it cannot simply be determined from the geometric dimensions, therefore the conductivity cells are calibrated. To do this the conductivity cell is immersed in an aqueous salt solution with a precisely known conductivity and the conductance is then determined. This procedure is repeated with several standard solutions. In this way you obtain in the range of medium and low conductivities, a linear characteristic curve that is extensively independent of the temperature with the rise $1/K$. Figure 3 shows an example of a conductivity cell with a cell constant of around 1 cm$^{-1}$.

![Figure 3](image.png)

Figure 3: Plotting the conductance against the conductivity to determine the cell constants.

The measuring points lie within a small range around the characteristic curve. Therefore, for many practical cases a 1 point calibration is adequate. In modern conductometers this calculation is carried out automatically and the cell constant is stored for the subsequent test evaluation.

$$K = \frac{\kappa_{(Standardsolution)}}{G_{(Display)}}$$

Compared to the slope of pH electrodes, the cell constant has more long-term stability. Most changes occur through microscopic deposits on and damage to the electrode surface.
Conductivity Standards

Conductivity standards are salt solutions for which the conductivity and the temperature dependence of the conductivity are known. Because of the almost ideal linear connection between concentration and electric conductivity and the good handling, as a rule KCl solutions are used. The manufacturers usually guarantee the accuracy of their standards to ± 1% of the indicated value. Through the absorption of CO₂ from the air and the evaporation of water the conductivity slowly increases once a standard solution has been opened. This effect is especially pronounced in standards with low conductivity. Because of this the bottles with standard solutions must always be tightly closed as soon as any standard has been removed. A standard used to measure the cell constant must NEVER be poured back into the bottle.

<table>
<thead>
<tr>
<th>KCl concentration / mol/l</th>
<th>κ(18°C) / µS/cm</th>
<th>κ(20°C) / µS/cm</th>
<th>κ(25°C) / µS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>98,220</td>
<td>102,100</td>
<td>118,000</td>
</tr>
<tr>
<td>0,1000</td>
<td>11,190</td>
<td>11,670</td>
<td>12,880</td>
</tr>
<tr>
<td>0,01000</td>
<td>1,225</td>
<td>1,278</td>
<td>1,413</td>
</tr>
<tr>
<td>0,001000</td>
<td>127.1</td>
<td>132.6</td>
<td>146.9</td>
</tr>
</tbody>
</table>

The most common conductivity standards are solutions with a conductivity of 12,880 µS/cm, 1,413 µS/cm and 147 µS/cm. In addition, Sartorius offers a conductivity standard with a conductivity of 84 µS/cm to calibrate conductivity cells for clean water. For special applications (high-purity water) standards with 5 and 1.3 µS/cm are also available from suppliers. These standards can be used for a maximum of 3 months and must be handled extremely carefully, as just the slightest contamination can render the standard unusable.
The Traceability of Standard Solutions to International Standards

Like all standards used to calibrate and rectify measuring instruments, these conductivity standards can also be traced back to international standards. Traceability describes a completely documented chain of reference measurements with which the connection between normal and used standard is established. The measuring inaccuracy for every reference measurement is known and this is used to state the tolerance of the used standard.

\[ \kappa = G \cdot K \]
The Actual Conductivity Measurement

If the cell constant of the conductivity cell is stored in the conductometer by calibration or manual entry, the samples can be measured. For this purpose the conductivity cell is rinsed with sample solution and immersed so that it is completely filled with sample solution. When the display of the measured value has stabilized (after approx. 1 minute) the measured value can be read. Modern devices such as the PP series from Sartorius have a display within the display that signals when a stable measured value has been reached. After each measurement the conductivity cell should be rinsed out with deionized water. If the cell is to be stored for some time the plastic protective cover should be unscrewed and the cell should be dried with soft, absorbent paper, the protective cover should then be screwed on again.

Conductivity Measurement Applications

Purity control

If a pure substance only shows minimum intrinsic conductivity, contamination with electrolytes can be detected by determining the conductivity. In this way oxidation products in methanol can be detected by directly measuring the conductivity. On the other hand, chloride in crude oil is extracted by shaking the sample out with deionized water and the chloride concentration is determined via the increase in conductivity in the water.

Controlling the Purity of Water

The function of a desalination plant is monitored by measuring the electrolytic conductivity. Pure water has a minimum electrolytic conductivity in the pH range of 6.8 to 7.2. As shown in Table 1, even small quantities of ions considerably increase conductivity.

This is the basis of conductivity measurement to control deionization plants. When the ion exchanger is exhausted or if there is a defect in the reverse osmosis plant this is reliably detected via the conductivity. In sets of regulations such as DIN standards or USP the purity of water for various purposes is defined, among other things, via conductivity.

As the conductivity of mineral waters generally does not change very much, the conductivity measurement can be used to monitor sources and filling processes. A large increase in conductivity can then be attributed to external contamination.

Conductivity Titration

The conductivity that is measured in an electrolyte solution depends on the type and concentration of the ions. Consequently the conductivity measurement represents a sensitive method of determining the end point of a titration. The change in conductivity is especially pronounced in reactions where an insoluble precipitate forms. The precipitate draws free ions from the solution, for example when titrating magnesium sulfate with barium hydroxide:

\[
\text{Mg}^{2+} + \text{SO}_4^{2-} + \text{Ba}^{2+} + 2 \text{OH}^- \rightarrow \text{Mg(OH)}_2 \downarrow + \text{BaSO}_4 \downarrow
\]

or sodium chloride with silver nitrate

\[
\text{Na}^+ + \text{Cl}^- + \text{Ag}^+ + \text{NO}_3^- \rightarrow \text{Na}^+ + \text{AgCl} \downarrow + \text{NO}_3^-
\]

Other reactions can also be tracked with conductivity measurement. If there is a clear difference in the equivalence conductivity of the reacting ions we also see here a characteristic curve which can be used to indicate the end point of a titration. This particularly applies to the neutralization reaction, as the protons and hydroxide ions with their high equivalence conductivity (see Table 2) react to non-conductive water. As long as the reaction is taking its course the conductivity drops, when the standard solution is in surplus the conductivity rises again (see Figure 4). By plotting the conductivity against the quantity of standard solution that is used it is possible to determine the quantity of standard solution that was required to complete the reaction.

3 USP: United States Pharmacopoeia

4 Titration: Volumetric analysis of a dissolve substance. To a sample with an unknown concentration a reagent solution with a known concentration is added until the sample has completely reacted. The concentration of the sample is calculated from the volume of the reagent solution that was consumed.
Figure 4: Conductivity during the titration of a strong acid with a strong base.
Short Instructions for Measuring Electric Conductivity

Preparing the Measurement

- Choose a conductivity cell that is suitable for the expected conductivity and the material to be measured (liquid, gel, suspension,..)
- Rinse the conductivity cell with deionized water and dab dry with soft, lint-free paper (laboratory cloth).
- Connect the conductivity cell to the measuring device according to the operating instructions.
- Calibrate the conductivity cell
- Select suitable standards for the desired measuring range.
- Always calibrate in the temperature range in which you are measuring.
- Select the "conductivity" mode on the measuring device.
- Prepare standard solution in a suitable vessel.
- Immerse the conductivity cell in the standard solution, remove and allow the solution to drain.
- Immerse and drain the conductivity cell at least three times.
- Immerse the conductivity cell and remove air bubbles by gently tapping the cell.
- Change to the calibration menu with the "Standardize" button and enter the conductivity of the standard at the prevailing temperature (stated on the label or package leaflet).
- The cell constant can be called up with the “Cal Data” key.
- Proceed in the same way with other standards.

Measuring the sample

- Place prepared sample in a suitable vessel.
- Rinse the conductivity cell with deionized water.
- Dab the cell dry.
- Immerse the conductivity cell in the sample, remove and allow the solution to drain.
- Immerse and drain the conductivity cell at least three times.
- Immerse the conductivity cell and remove air bubbles by tapping the cell carefully.
- Wait until the reading has stabilized
- Remove the conductivity cell from the sample, rinse with deionized water and dab dry.
- Store the conductivity cell in a dry place.
For your own notes: