

Conductometry

Branch

General analytical chemistry; water, wastewater, environmental protection; pharmaceutical industry; petrochemistry, biofuels; food, stimulants, beverages, flavors; biochemistry, biology; energy, power plants

Keywords

Conductometry; five-ring conductivity measuring cell; stainless steel cell; USP 645; IP 400; branch 1; branch 2; branch 4; branch 5; branch 7; branch 8; branch 16; 6.0915.100; 6.0915.130; 6.0916.040

Summary

This bulletin contains two parts. The first part gives a short theoretical overview while more details are offered in the Metrohm Monograph Conductometry. The second, practice-oriented part deals with the following subjects:

- Conductivity measurements in general
- Determination of the cell constant
- Determination of the temperature coefficient
- Conductivity measurement in water samples
- TDS – Total Dissolved Solids
- Conductometric titrations

Theoretical part

General

The following considerations apply exclusively to solutions containing ions.

Conductometry concerns the conductivity of electrolytes. The resistance of a solution is measured by applying an alternating voltage to the measuring cell (if direct current were applied, electrolytic processes occurring within the solution could alter the resistance). The 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 an ion, the more mobile it is and the better it conducts. Hydronium, hydroxide, potassium and chloride ions are very good conductors. If hydration occurs (the ion surrounds itself by water molecules that make it larger), then the conductivity is reduced.
 - the solvent: the more polar a solvent, the easier it is for ionic compounds to dissociate. Water is an ideal solvent for ionic compounds. In alcohols, the relative degree of dissociation decreases as the chain length increases (methanol > ethanol > propanol). In nonpolar organic solvents (e.g. chlorinated and non-chlorinated hydrocarbons) practically no dissociation occurs.
 - the temperature: in contrast to solids, in solution the conductivity increases as the temperature increases by 1...9% per °C, depending on the ion. (Moderately conducting solutions such as drinking water: 2%/°C).
 - the viscosity: as the viscosity increases, the ionic mobility and therefore also the electrical conductivity decrease.

Measuring the electrical conductivity

The electrical conductivity 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 :	conductivity (S cm ⁻¹ or S m ⁻¹)
R :	resistance (Ω (Ohm))
G :	conductance (1/R), (S (Siemens) = Ω^{-1})
l :	length of measuring path (cm or m)
A :	cross sectional area (cm ² or m ²)
c :	cell constant (l/A), (cm ⁻¹ or m ⁻¹)

The electrical conductivity is usually expressed in $\mu\text{S/cm}$ or mS/cm (e.g. $12.88 \text{ mS/cm} = 1288 \text{ mS/m}$; $5 \text{ }\mu\text{S/cm} = 500 \text{ }\mu\text{S/m}$).

The electrical conductivity strongly depends on the temperature. The value measured at a given temperature is therefore often converted to a reference temperature. The usual reference temperatures are $20 \text{ }^\circ\text{C}$ and $25 \text{ }^\circ\text{C}$. The conversion is done applying the temperature coefficient α .

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

$25 \text{ }^\circ\text{C}$ and $\Theta \text{ }^\circ\text{C}$ are temperatures at which the electrical conductivities have been measured. The temperature coefficient can be given as reciprocal Kelvin or % per $^\circ\text{C}$.

The temperature coefficient depends mainly on the ions that are in the solution but its behavior is seldom linear.

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 (α_{20} or α_{25})
- Enter conductivity of standard at reference temperature (not actual one!)

The following two examples illustrate this for a $100 \text{ }\mu\text{S/cm}$ standard with an actual temperature of $30 \text{ }^\circ\text{C}$, and with reference temperatures of $20 \text{ }^\circ\text{C}$ and $25 \text{ }^\circ\text{C}$, respectively:

- Measuring temperature: $30 \text{ }^\circ\text{C}$
- Reference temperature: $25 \text{ }^\circ\text{C}$
- Temperature coefficient: $2.0\%/^\circ\text{C}$
- Conductivity (at $T_{\text{ref}} = 25 \text{ }^\circ\text{C}$): $100 \text{ }\mu\text{S/cm}$

- Measuring temperature: $30 \text{ }^\circ\text{C}$
- Reference temperature: $20 \text{ }^\circ\text{C}$
- Temperature coefficient: $2.2\%/^\circ\text{C}$
- Conductivity (at $T_{\text{ref}} = 20 \text{ }^\circ\text{C}$): $90.9 \text{ }\mu\text{S/cm}$

The same procedure is applied for the 12.88 mS/cm standard.

Measuring setup

The standard measuring setup consists of a conductometer, the conductivity cell with an inbuilt temperature sensor and a magnetic stirrer. For highest precision, a closed vessel that can be thermostatted is recommended.

A classical conductivity measuring cell has two platinum electrodes. By selecting the surface area of and the distance between the two electrodes it is possible to vary the cell constant of such measuring cells within wide limits. Uncoated, i.e. non-platinized, conductivity measuring cells should only be used for conductivities $< 20 \text{ }\mu\text{S/cm}$. For higher conductivities platinized conductivity measuring cells or modern sensors like five-ring conductivity measuring cells – which need no platinization – are used. The conductivity measuring cells are characterized by their cell constant c . For low conductivities, cells with a small cell constant (e.g. stainless steel conductivity measuring cell) are used while cells with higher cell constants serve to measure higher conductivities.

The cell constant should match the solution being measured.

- $c \approx 0.1 \text{ cm}^{-1}$ for poorly conducting solutions, such as fully or partially demineralized water
For organic solvents see *Comments*
- $c \approx 1 \text{ cm}^{-1}$ for moderately conducting solutions, such as drinking water, surface water, ground water and wastewater
- $c \approx 10 \text{ cm}^{-1}$ for solutions with good conductivity, such as seawater, rinsing water, physiological solutions, etc.
- $c \approx 100 \text{ cm}^{-1}$ for solutions with very good conductivity, such as brine, acids, alkalis, electroplating baths, etc.

Practical part

1. General remarks concerning conductivity measurements

Preparing /handling the conductivity measuring cell

- The measuring cell must be well conditioned/prepared. Platinized measuring cells stored dry must be placed in acetone for 30 min. 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 and recommended cleaning:
 - Deposits of calcium carbonate or barium sulfate: Rinse with HCl. In the case of BaSO₄ immerse the cell overnight in a stirred solution of w(Na₂EDTA) = 10% in c(NaOH) = 0.1 mol/L.
 - 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.

Preparing the instrument

- *Temperature coefficient*: If known, enter it into software configuration, otherwise determine it with *tiamo*TM. 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 integral 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 packaging 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.

Performing the measurement

- Only use clean measuring cells. It is best to rinse them, prior to measuring, with the solution to be measured. The lateral openings of the conductivity measuring cell must be fully immersed. Immerse and withdraw the measuring cell a few times (e.g. three) in the measuring solution to remove adhering air bubbles. Wait for the measuring cell and solution to reach a constant temperature

2. Determination of the cell constant c

Use of the conductivity measuring 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.

Instruments

- Conductometer
- Magnetic stirrer
- Titration vessel with thermostat jacket
- Thermostat (third party provider)

Electrodes

- Conductivity measuring cell

Reagents

- Ultrapure water

Standards

Conductivity standard 100 µS/cm	6.2324.x10
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or

Conductivity standard 12.88 mS/cm	6.2301.060
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Procedure

The measuring cell is rinsed with ultrapure water. The titration vessel is first rinsed with conductivity standard and then filled up with the standard. The measuring cell is also rinsed with conductivity standard and inserted into the titration vessel. With the help of the thermostat, the standard 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. Therefore, the conductivity measuring cell is dipped three times into the solution prior to measurement to remove adhering air bubbles. A calibration method is created in the control software of the conductometer. Here 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 as described above. The measurements are also performed in a closed measuring/titration vessel. Instead of thermostating, a Pt1000 temperature sensor is connected, if a cell with integral 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 described in the theoretical part.

Calculation

The cell constant is calculated automatically by the conductometer software, as follows:

$$c = \frac{\text{theoretical conductivity}}{\text{measured conductance}}$$

3. Determination of the temperature coefficient (TC) α of $c(\text{Na}_2\text{SO}_4) = 0.05 \text{ mol/L}$

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 TC in the temperature range of interest is recorded automatically with the 856 Conductivity Module with *tiamo*TM.

Instruments

- 856 Conductivity Module with *tiamo*TM
- Magnetic stirrer
- Titration vessel with thermostat jacket
- Thermostat (third party provider)

Electrodes

- Conductivity measuring cell with temperature sensor

Reagents

- Ultrapure water

Solutions

$c(\text{Na}_2\text{SO}_4) = 0.05 \text{ mol/L}$	7.10 g Na_2SO_4 or 16.11 g $\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$ are dissolved in ultrapure water and made up to 1000 mL.
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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.

The 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 method, ensure that the temperature of the solution is outside the heating range.

4. Conductivity measurement in water

Instruments

- Conductometer
- Magnetic stirrer
- Titration vessel with thermostat jacket
- Thermostat (third party provider)

Electrodes

- Conductivity measuring cell with temperature sensor

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 thermostatted at 25.0 °C. If this is not desired, a TC can be entered or in the case of water the «DIN» template can be selected. It is suitable for water that contains mainly calcium and hydrogen carbonate ions as well as small amounts of magnesium, sulfate, chloride and nitrate ions.

DeminerIALIZED water

Because of possible interferences, a special procedure must be selected for water with a conductivity of < 5 $\mu\text{S/cm}$. This applies to water with a conductivity < 1 $\mu\text{S/cm}$ 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 excessively high 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 using the stainless steel conductivity measuring cell (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

The 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!!

5. Total dissolved solids (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 salt solutions (normally NaCl) and the corresponding salt concentration is stated. The conductivity is converted by means of a factor, which depends on the way in which the result is to be expressed.

$$\text{TDS} = \frac{\beta}{\gamma_{\text{theo}}} \times \gamma_{\text{meas}}$$

TDS: Total dissolved solids in mg (salt)/L

β : Mass concentration of the corresponding salt concentration in mg/L

γ_{theo} : Theoretical conductivity of the corresponding salt concentration in $\mu\text{S}/\text{cm}$

γ_{meas} : Measured conductivity of the sample solution in $\mu\text{S}/\text{cm}$

If, for example, TDS is expressed as $c(\text{NaCl}) = 0.01 \text{ mol/L}$, the factor is 0.51, as quotient of the concentration of $\beta(\text{NaCl}) = 584 \text{ mg/L}$ and its theoretical conductivity of $1156 \mu\text{S}/\text{cm}$.

6. Conductometric titrations

For conductometric titrations, the cell constant does not normally need to be known. A conductivity measuring cell is used as measuring electrode. Thermostating is not required for simple titrations. Alterations in conductivity caused by temperature variations are of virtually no consequence. Room temperature is adequate as long as sample and titrant are having the same temperature.

As example the TBN titration of motor oil according to IP400 is presented here (see also AB 405).

Instruments

- 856 Conductivity Module with *tiamo*TM
- Magnetic stirrer
- 10 mL buret

Electrodes

- Conductivity measuring cell with temperature sensor

Reagents

- Toluene
- 2-propanol (IPA)
- Ultrapure water

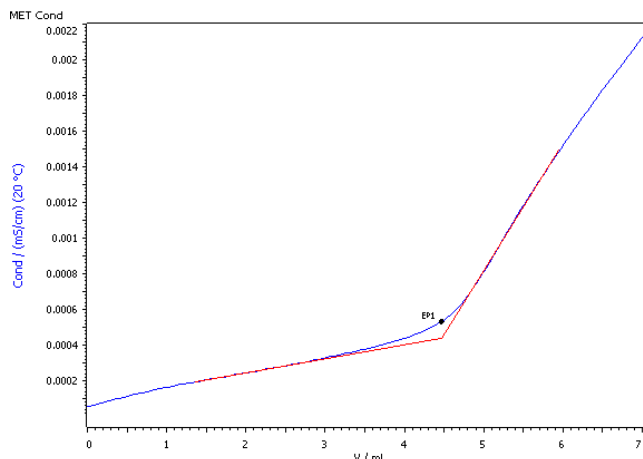
Solutions

Titrant	HCl in IPA; $c(\text{HCl}) = 0.1 \text{ mol/L}$, if possible this solution should be bought from a distributor.
Solvent	500 mL toluene + 495 mL IPA + 5 mL ultrapure water.

Procedure

- Weigh out 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 0.1 mol/L alcoholic HCl. 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 can be found in the Application Bulletin 405.)

Example determination



Conductometric determination of TBN (blue = measured curve, red = extrapolation)

Calculation

$$\text{TBN} = \frac{V_{\text{EP1}} \times c_{\text{HCl}} \times f \times M_{\text{A}}}{m_{\text{s}}}$$

TBN	Total base number in mg KOH/g sample
V_{EP1} :	Titration consumption in mL to reach the first equivalence point.
c_{HCl} :	Concentration of titrant in mol/L; here $c(\text{HCl}) = 0.1 \text{ mol/L}$
f:	Correction factor (titer) without unit
M_{A} :	Molar mass of KOH; 56.106 g/mol
m_{s} :	Sample weight in g

Comments

- Measurement according to DIN 51627-4 in ethanol is possible using the stainless steel cell.
- For samples in the pS/cm range (e.g. organic solvents) standard laboratory conductometer cannot be used. For such applications special instruments are available on the market from third party suppliers.

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