

New primary setup for conductivity sensor calibration in pure water between $5.5 \mu\text{S m}^{-1}$ and 15mS m^{-1}

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Abstract

We present measurement results of a novel calibration setup for conductivity sensors that are designed for purity control of pure water. Stable conductivity results of purified water in a closed loop, mixed with KCl at a trace level, have been measured for the first time in the range between $5.5 \mu\text{S m}^{-1}$ (ultra pure water) and 15mS m^{-1} . This enables calibration in the concentration range and in the matrix the sensors are designed for, which was not possible before due to a lack of adequate aqueous reference solutions.

Key words: conductivity sensors, pure water, calibration setup, closed loop, ionic contamination

Introduction

Conductivity sensors for application in pure water are used in many fields, e.g. in the pharmaceutical or semiconductor industry, mostly to measure ionic impurities. The cell constant of such a sensor is typically determined in a so called secondary calibration procedure, by measuring the resistance R_{ref} of the cell, filled with an aqueous KCl reference solution. The reference solution has an assigned conductivity value κ_{ref} . Then the cell constant is calculated as

$$K_{\text{cell}} = \kappa_{\text{ref}} \cdot R_{\text{ref}} \quad (1)$$

Determined in this way K_{cell} can vary (despite its name) with the matrix and salt concentration of the reference solution, since it depends on the cell design and on the evaluation of the measurement signal. Thus sensors should be calibrated with a solution that has a matrix and concentration similar to the solution under investigation in order to avoid erroneous results. Due to the varying influence of dissociated CO_2 , which contributes about $100 \mu\text{S m}^{-1}$ to the conductivity of aqueous solutions, no stable aqueous reference solution exists for the low conductivity range of pure water. Sensors are therefore usually calibrated in closed loop circuits of pure water by comparing their measurement results with those of a reference sensor. The cell constant of the latter, however, is typically calibrated with KCl reference solutions in a conductivity range

that is up to three orders in magnitude larger than the actual application range [1].

To overcome this shortcoming the Physikalisch-Technische Bundesanstalt has developed a new calibration setup that allows a determination of the cell constant in aqueous solutions at conductivities reaching from ultra pure water (about $5.5 \mu\text{S m}^{-1}$) up to that of the lowest, stable KCl reference solution (about 15mS m^{-1}). To this end the conductivity of ultra pure water, circulating in a closed loop, can be increased to a target value by injecting trace amounts of KCl. A cylindrical conductivity cell of coaxial-symmetric geometry is directly integrated into the loop. Its cell constant is determined by dimensional measurements. The resistance of the solution in the cell is determined by impedance spectroscopy, based on an equivalent circuit that has been adapted to the low conductivity region. In this way the conductivity of the water in the loop can be measured independently from the salt concentration. The cell constant of a conductivity cell, additionally integrated into the loop, can then be determined at an adequate conductivity level.

In this paper we outline the measurement setup and the determination of the reference conductivity value. We show the results of conductivity measurements at the ultra pure water level and at the level of pure water contaminated with KCl to a conductivity of around $200 \mu\text{S m}^{-1}$ ($2 \mu\text{S cm}^{-1}$).

Calibration setup

Figure 1 shows a simplified sketch of the measurement setup. A water purification system (Millipore MilliQ A10, pre purification by an Elix System) feeds a degassing unit (not shown) with ultra pure water (UPW). Then the UPW is led into a contamination vessel (volume 5 L). From there it is pumped with a gear pump through the conductivity measurement cell back into the contamination vessel. Vessels and tubes are flushed with argon 6.0 before filling to avoid contact of the purified water with atmospheric CO₂. The vessel is made of Duran glass and the tubes of LDPE. All parts of the gear pump in contact with UPW are made of PTFE, PEEK and stainless steel. Contamination vessel, pump, conductivity measuring cell and the connecting tubes form the closed conductivity measurement loop. A circuit parallel to the measurement loop enables to feed back a part of the water into the purification system in order to clean the loop. Degassing is necessary to avoid gas bubble formation in the loop. In order to avoid CO₂ penetration into the loop, it is completely situated in a closed box, which is continuously flooded with argon 5.6. The box also contains a temperature controlled, air ventilated heat exchanger to set and stabilize the temperature in the box and the loop.

The contamination vessel is connected with a vessel containing the contamination solution for injection into the loop. Defined volumes of the solutions are transferred with a dosage unit. It has a resolution of 1 µL and a total volume of 10 mL. The flow of the solutions is controlled by

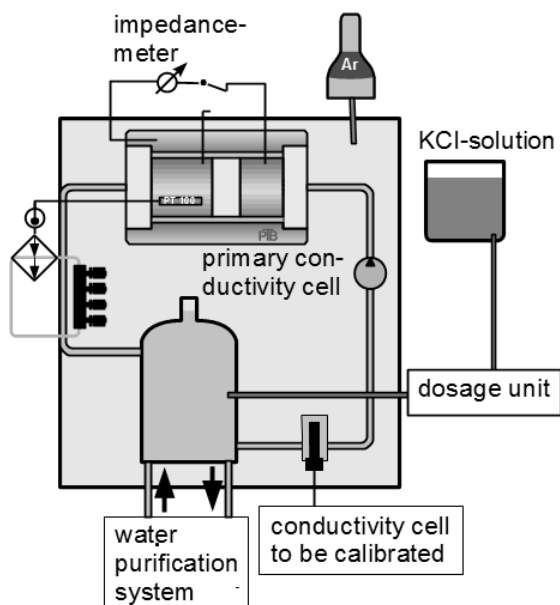


Figure 1 Simplified sketch of calibration setup

a sophisticated system of valves, which is not shown in order to keep the schematic clearer.

Figure 1 also outlines a cross section of the conductivity measuring cell. It is a cylindrical cell of two inner electrodes of different length and an outer electrode, which encompasses the inner electrodes concentrically. Such, two half cells are formed, which can both measure the resistance between the inner and the outer electrodes. The electrodes are made of cavity free, homogeneous stainless steel. They are electrically separated by PTFE. The inner electrodes are connected to the high potential/current terminals of an impedance-meter (Agilent E4980A), the outer electrode is connected to the low terminals. The dimensions of the cell have been measured in the scientific instrumentation department of the PTB with an uncertainty of a few µm. The (nominal) lengths of the inner cells are 30 mm and 45 mm, respectively. Their diameter is 45 mm. The diameter of the outer cell is 55 mm.

Determination of the conductivity reference value

The reference conductivity value of the (contaminated) pure water is determined in two main steps

- (i) Determination of the solution bulk resistance in each of the two half cells (short inner electrode/outer electrode and long inner electrode/outer electrode).
- (ii) Calculation of an effective cell constant to account for stray contributions at the electrode rims.

(i) The determination of the solution bulk resistances R_s and R_l , corresponding to the long and short half cells, is based on the measurement of impedance spectra. Note that throughout this paper the indexes s and l denote the short and long half cell, respectively. In the high frequency part of the spectrum polarisation effects can be neglected and the spectrum is dominated by the solution resistance in parallel to the geometric capacitance of the electrodes [2]. In a complex plane plot the spectrum of such circuit elements forms a semicircle, which diameter corresponds to the solution resistance. Hence, it can be determined by fitting a semicircle into the measured impedance spectrum. Figure 2 shows the measured impedance spectrum of ultra pure water in the long half cell in a complex plane plot. The solid line is a semicircle fit to the impedance spectrum (dots) R_l herein is the single fit parameter. The average relative deviation of the measured data points from the fit is less than 5×10^{-5} . It should

be noted that the bulk resistance can also be calculated directly from a (single) impedance value, assuming a parallel of the solution resistance and the electrode capacity. However, resistances calculated this way have turned out to be more sensitive to uncertainties of the measured impedances, in particular at the rims of the semicircle.

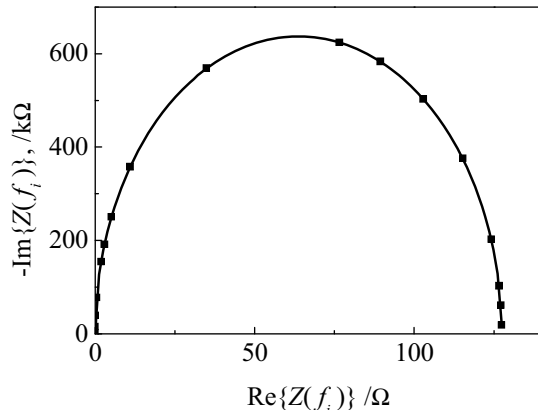


Figure 2 Complex plane plot of the impedance spectrum (dots) of ultra pure water in the long half cell. The solid line is the fitting curve of a semicircle using the solution resistance R_s as a fit parameter.

(ii) In contrast to the determination of the cell constant using a secondary measurement procedure, in a primary measurement procedure the cell constant is calculated from the measured geometric dimensions of a defined volume. The cell constant of an ideal cylindrical, coaxial cell is given by

$$K = \frac{\ln(D_o / D_i)}{2\pi b} \quad (2)$$

With D_o being the diameter of the outer electrode, D_i being the (outer) diameter of the inner electrode and b being the length of inner electrodes (with $b=l$ or $b=s$, respectively). The measured impedances Z_l and Z_s in the half cells are affected by stray capacitances and charge transport outside the region between the inner and outer electrodes. Hence, eq. (2) must consider these stray effects. Therefore the effective cell constants K_{la} and K_{sa} are defined for the long and the short half cell

$$K_{la} = \frac{\ln(D_o / D_i)}{2\pi(l+a)}, \quad K_{sa} = \frac{\ln(D_o / D_i)}{2\pi(s+a)}, \quad (3)$$

with a being the effective stray length. a is supposed to be equal for the long and the short electrode due to the symmetric cell design. Hence, assuming the conductivity being equivalent in the long and short half cell, a can be calculated from eqs. (1) and (3):

$$a = \frac{R_l l - R_s s}{R_s - R_l} \quad (4)$$

Which enables the calculation of K_{la} or K_{sa} and, with one these and eq. (1), the reference conductivity value of the water in the measurement loop.

Finally the conductivity value κ of UPW is corrected for the deviation of the measurement temperature t from the set temperature t_0 . To this end we used a parabolic correction:

$$\begin{aligned} \kappa(t_0) = \kappa(t) + 0.0048712 \frac{\mu S}{m^\circ C^2} \times (t_0^2 - t^2) \\ - 0.003595 \frac{\mu S}{m^\circ C} \times 10^{-5} \times (t_0 - t) \end{aligned} \quad (5)$$

The coefficients have been determined from a square fit to the measured UPW conductivity values at 10 °C, 15 °C, 20 °C, 25 °C and 30 °C. Currently we are not able to perform measurements of contaminated UPW at various temperatures. Therefore we estimated a linear temperature coefficient for KCl contaminated UPW from the linear temperature coefficient of UPW (5.09 %/K) and of the linear temperature coefficient of a KCl at 15 mS m⁻¹ (1.95 %/K) by linear interpolation. Due to the relatively small deviation in the order of 100 mK to 300 mK the uncertainty of this rough approximation is acceptable. The conductivity values of contaminated UPW are then linearly corrected according to

$$\kappa(t_0) = \frac{\kappa_m(t)}{1 + \frac{\alpha}{100}(t - t_0)} \quad (6)$$

In this paper all reported conductivity values are referred to a set temperature of 25 °C

Results

Figure 3 illustrates the conductivity results of a series of independent measurements of ultra pure water from a commercial purification system (Millipore MilliQ A10). The results show a good repeatability. The mean value of 5.490 μS m⁻¹ is about 0.1 % to 0.2% lower than values reported in literature [3], which is, however, well covered by the expanded (k=2) measurement uncertainty, indicated as bars. It should be noted that former publications did not report measurement uncertainties.

The calculation of the conductivity value from the actually measured quantities is quite complex. It involves in particular the fitting of the semi circles into to impedance spectra. An analytical uncertainty calculation of the

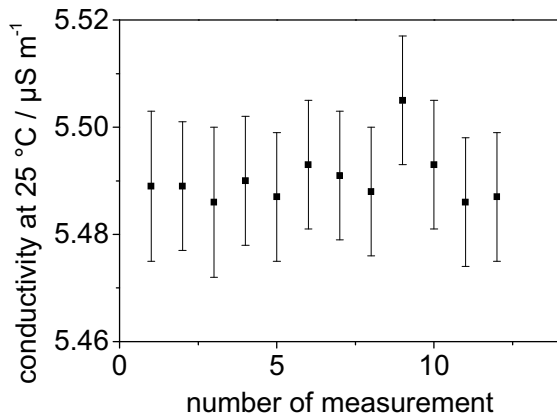


Figure 3 Conductivity measurement results of several independent conductivity measurement of ultra pure water referred to 25°C. The bars indicate the expanded ($k=2$) measurement uncertainty.

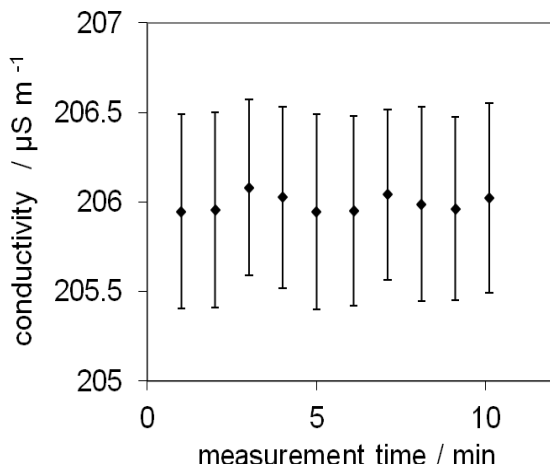


Figure 4 Exemplary conductivity measurement results of an ultra pure water contaminated with KCl (mass fraction is roughly around 1 ppm) referred to 25°C. The bars indicate the expanded ($k=2$) measurement uncertainty.

conductivity values according to GUM [4] is very difficult to realise. Therefore a Monte Carlo simulation has been used according to GUM supplement 1 [5]. A normal distribution has been assumed for random sampling of all measured input quantities, i.e. the real and imaginary parts of the impedances at each frequency, the measurement temperature and the dimensional parameters. Herein the measured values represent the mean and their measurement uncertainty the standard deviation of the correlated normal distribution. The best estimates of the conductivities shown in figure 3 have been calculated from the means of the Monte Carlo results and their expanded uncertainties from the standard

deviation of the Monte Carlo results multiplied by the coverage factor $k=2$.

Figure 4 shows, exemplarily, for the first time measured conductivity values of ultra pure water, contaminated with KCl to a level around $200 \mu\text{S m}^{-1}$. This roughly corresponds to a KCl mass fraction of 1 mg kg^{-1} . Conductivity measurements at contamination levels ranging from $10 \mu\text{S m}^{-1}$ up to 15 mS m^{-1} have also been successfully measured (not shown). The conductivity results are indicated versus measurement time, which demonstrates the stability of the measurement. This time window is appropriate for the purpose of sensor calibration. The bars again show the expanded measurement uncertainties that have been calculated in analogy to the measurements of ultra pure water.

The results have not been compared with calibration curves like given in ref [6]. Such curves are analytical functions for conductivity in terms of the KCl content in water, typically molality based. They have been established from measurements at conductivities above 15 mS m^{-1} . The mass of water in our measurement loop can only be estimated with an uncertainty in the order of several percent. Hence, a comparison of the measured results with calibration curves is not meaningful. We plan to measure the KCl mass fraction with ion chromatography, in order to verify the calibration curves in the low conductivity region. However, in contrast to former calibration procedures (like OIML recommendation 56 for instance), where a conductivity value is assigned to a defined KCl mass fraction in water, here the conductivity value of the reference solution (the water in the loop) is directly measured traceable to the SI. Consequently, the knowledge of the actual KCl content is not necessary to determine the cell constant of a conductivity sensor that has to be calibrated. Knowing the conductivity reference value κ_{ref} of the water in the loop, its cell constant can easily be determined using eq. (1), provided it is integrated into the loop (see fig. 1) and provided it measures the resistance of the same water simultaneously with the primary cell.

In the meanwhile first sensor calibrations have been successfully performed at various conductivity levels of contaminated ultra pure water. Future work will focus on different contaminants and the temperature dependence of the corresponding conductivity values.

Acknowledgments

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