

DEVELOPMENT OF A FLOW-THROUGH CELL FOR ACCURATE MEASUREMENTS OF LOW ELECTROLYTIC CONDUCTIVITY

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Abstract – The present paper focuses on the development of a flow-through cell and a closed circuit that permit to carry out measurements of low electrolytic conductivity of aqueous solutions under flowing condition. The traceability path has been set as follows: samples with conductivity between $200 \mu\text{S cm}^{-1}$ and $50 \mu\text{S cm}^{-1}$ have been employed for the calibration of the geometric constant of the new cell, by comparison with the primary cell of Istituto Nazionale di Ricerca Metrologica (I.N.Ri.M.). Then the flow-through cell has been used to measure values with decreasing conductivities down to $1 \mu\text{S cm}^{-1}$. The measurement system capabilities have been evaluated to be limited by contamination effects.

Keywords: pure water, low conductivity measurement, flow-through cell

1. INTRODUCTION

Pure water is extensively used in many critical applications, which include chip fabrication for semiconductors (like microelectronics rinse waters), intravenous solutions for pharmaceuticals, and high-pressure boilers for power generation [1]. Pure water has a very low, but not quite zero, electrical conductivity. Deviation from this value is a measure of trace ionic impurities. The electrolytic conductivity method is applicable for detecting trace amounts of ionic contaminants in water [2]. Accurate and reliable (hence, traceable to International System of units) measurement results are needed. Certified reference materials or calibrated sensors should be used for this purpose. Consequently, National Metrology Institutes (NMIs) dealt with the establishment of traceability for the measurement of electrolytic conductivity [3]. At the Istituto Nazionale di Ricerca Metrologica (I.N.Ri.M.) a primary measurement system for electrolytic conductivity in the range between $50 \mu\text{S cm}^{-1}$ e 2 S m^{-1} has been developed. Numerous International Comparisons have been organised by the *Comité Consultatif pour la Quantité de Matière* (CCQM) in order to check the accuracies claimed by the NMIs [4-6].

Recently several NMIs (I.N.Ri.M. among them), to answer the needs of the industrial sectors described above, engaged in the extension of traceability of electrolytic

conductivity towards pure water value (about $1 \mu\text{S cm}^{-1}$). Within this effort, a new International Comparison CCQM-P83 on low conductivity values, $5 \mu\text{S cm}^{-1}$, has been organised and it is expected in 2009.

In a measurement system intended for accurate measurements below $10 \mu\text{S cm}^{-1}$, flow-through or in-line conductivity cells should be used, in order to prevent contamination from atmosphere and by wetted surfaces. Atmospheric carbon dioxide (CO_2) can reach an equilibrium concentration in water of about 1 mg l^{-1} , and because of formation of carbonic acid can add approximately $1 \mu\text{S cm}^{-1}$ to the original sample conductivity [2].

In this work the new flow-through cell, and the closed circuit measurement system developed at I.N.Ri.M., are described. Moreover, the measurement traceability and first measurements of low conductivity are reported.

2. MEASUREMENT SYSTEM

In order to measure the conductivity of purified water and water for injection, having a conductivity below $1 \mu\text{S cm}^{-1}$, a flow-through cell has been designed at I.N.Ri.M. and constructed by “Disa Raffaele e F.lli” glass blower. The cell is shown in Fig. 1: it is made of a Pyrex® glass chamber holding two parallel and faced electrodes, positioned at a distance of 10 mm. The electrodes (thick 0.5 mm and with the diameter of 20 mm) are of smooth and pure platinum to guarantee chemical inertness and minimise impurity permeability [7]. They are connected to electrical coaxial cables with platinum wires, coated with a sheath of a boron glass with a thermal expansion coefficient matched to platinum. The platinum wires have been platinum spot-welded to the electrodes to avoid contamination of the sample. Moreover, the electrodes are removable to allow eventually a deep cleaning.

The cell chamber has a capacity of about 180 ml in order to permit a good thermal capacity. To fill and to empty the chamber an input tube has been placed between the removable electrodes, and a SVL cap avoids the solution contamination.

The cell includes two side pipelines, with Teflon taps, for the circulation of the sample flux. The sample inlet cross section is smaller than the outlet to guarantee the cell integrity caused by pressure fluctuations.

In the conjunction with the cell chamber the pipe inlet has a turn, to create a sample turbulent motion and to keep stirred the solution. A linear flux between electrodes has to be anyhow avoided because it would be confused with ion migration.

All the electrodes, the pipelines, and the tube input are vertical extended for eventually introducing the cell in a liquid thermostatic bath.



Fig. 1. I.N.Ri.M. flow-through cell

The sample flows in a closed circuit glass pipeline to prevent the CO₂ contamination, and the flux is created by a Watson-Marlow Bredel Sci-Q 323 peristaltic pump that operates with a speed of 90 rpm.

Most of the pipeline circuit is constituted of Pyrex® glass. For the cell connections and tube section within the pump, after some tests done with Teflon® and Fluorel® tubes, Tygon® pipeline has been chosen, which shows up to now the best characteristics as lowest permeability and contamination.

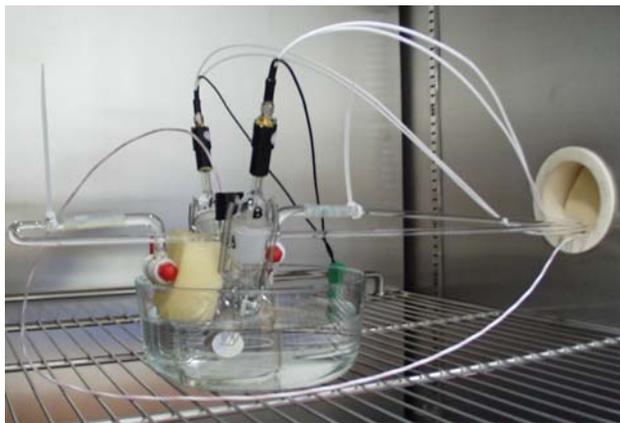


Fig. 2. Measurement system inside the air thermostatic bath

At 25 °C the conductivity temperature coefficient of pure water is about 5.4 %°C⁻¹ [1, 7]. Cell temperature is measured by a PT-100 thermoresistance (glued to outside wall) and a multimeter (Agilent Tech. mod. 3458), with an uncertainty of 0.01 °C. Temperature control is performed by

an air bath, see Fig. 2; the cell is put inside a beaker full of water for increasing the thermal capacity, hence the low-term temperature stability.

The significant heat dissipation of the peristaltic pump does not permit to place the entire closed circuit inside the air bath; the portion of the circuit with the pump has been placed outside, in a thermostated (23 ± 1 °C) laboratory. A picture of the instruments and the circuit outside the bath is shown in Fig. 3.

Cell impedance is measured in the 20 Hz – 2 MHz range with a QuadTech 7600b LCR meter. Bridge accuracy specifications is 0.07 % when measuring a conductivity of 200 μS cm⁻¹, and 0.1 % for a conductivity of 50 μS cm⁻¹. The specified accuracy has been considered insufficient, and has been improved fivefold with calibrations (before and after every measurement run) using Tinsley standard ac resistors having resistance values bracketing the resistance range of the sample. Impedance spectra are acquired and processed by purpose LabWindows/CVI and Matlab codes.



Fig. 3. Measurement system outside the air thermostatic bath

Samples having different nominal conductivity values (200, 70, 50, 20, and 1 μS cm⁻¹) have been investigated. The first four samples were solutions of KCl in ultra pure water, the last one has been prepared by leaving ultra pure water, poured into a capacious bottle, at rest without top for two days in order to reach the equilibrium with the laboratory CO₂.

In a first stage, the geometric constant of the flow-through cell has been calibrated by comparison with the I.N.Ri.M. primary cell. 200 μS cm⁻¹, 70 μS cm⁻¹, and 50 μS cm⁻¹ solutions have been used for the calibration, because the primary cell does not allow measurements with reasonable accuracy in the lower conductivity range. The cell constant has been estimated by the mean of the values obtained for each sample, as suggested in [8].

In the second stage of the experiment, the calibrated flow-through cell has been employed for measurements of 20 and 1 μS cm⁻¹ samples.

The conductivity, k , of each sample is given by (1):

$$k = \frac{C_{cell}}{R \cdot [1 - \alpha_T (T - T_{Ref})]} \quad (1)$$

where C_{cell} is the geometric constant of the flow-through cell, defined by its calibration with the I.N.Ri.M. primary

cell, α_T is the temperature coefficient, T is the temperature, and T_{Ref} is the reference temperature (25 °C).

Many impedance sweeps (20 Hz - 2 MHz) in the RLC bridge frequency range have been performed, and the ones showing the better temperature stability have been selected. In order to reject parasitic contributions, the solution resistance and reactance versus frequency have been plotted, and the resistance at which the minimum point of reactance is verified has been extracted. The minimum of the reactance values corresponds to the plateau range of the resistance values (bulk resistance). This value of resistance is utilized for the determination of the electrolytic conductivity value of solution. So that the polarisation effects at low frequency range and capacitive effects at high frequency range are minimised. The mean value of the minimum point resistances has been evaluated, and has been taken as representative of resistance, R , of the solution. Then R , has been corrected to T_{Ref} and the conductivity value has been estimated by (1).

For 1 $\mu\text{S cm}^{-1}$ sample, in addition with measurements with the RLC bridge, further measurements have been conducted with a calibrated lock-in amplifier (EG&G 7265) to achieve an extended frequency range (0.1 - 20 Hz). The need of data in such low range is important for a better understanding of the resistance behaviour versus frequency, strongly influenced by interface contributions.

3. RESULTS

The first measurement stage, the calibration of the flow-through cell, has been carried out by repeating the measurements at least three times for each conductivity value. The calibration by comparison of the flow-through cell has been undertaken considering a static system, without the closed circuit, in order to be in the same conditions of the primary system and because the measured solutions (samples with conductivities of 201.85 $\mu\text{S cm}^{-1}$, 70.99 $\mu\text{S cm}^{-1}$, and 49.98 $\mu\text{S cm}^{-1}$) showed enough stability time. Table 1 resumes the results of each solution and their associated uncertainties.

Table 1. Cell constants and the associated standard uncertainties obtained with the three solutions.

Electrolytic conductivity ($\mu\text{S cm}^{-1}$)	Cell constant (m^{-1})	Expanded uncertainty (m^{-1})
49.98	14.721	0.096
70.99	15.032	0.092
201.85	15.008	0.089

In the third column of Table 1 the expanded uncertainties include the contributions associated to the temperature (the temperature stability was kept during the measurements within 0.01 °C), to the solutions measured with the primary system, to the measurement repeatability, and to the RLC bridge. The C_{cell} estimation has been obtained by the mean of geometric constants measured with the three solutions, and has been resulted of 14.920 m^{-1} . The

largest value among ones obtained by the measurements of the three solutions has been chosen as the uncertainty contribution associated to C_{cell} , that is of 0.096 m^{-1} .

In order to have the possibility to use the C_{cell} value for the measurements with the flow system, with the closed circuit, a measurement comparison between the static system and the flow one considering the same solution has been carried out. This comparison has been undertaken with the 70 $\mu\text{S cm}^{-1}$ and the 50 $\mu\text{S cm}^{-1}$ samples. The obtained differences were respectively of 0.01 % and of 0.02 %, which have been considered negligible with respect to the uncertainty associated to the cell constant.

The flow system used 7 hours to reach the temperature stability, so each measurement kept at least 10 hours. The maximum temperature variation considered acceptable at 25 °C was of 0.02 °C.

The solution with nominal conductivity of 20 $\mu\text{S cm}^{-1}$ has been measured, and an example of plot with the resistance and reactance as a function of frequency is shown in Fig. 4.

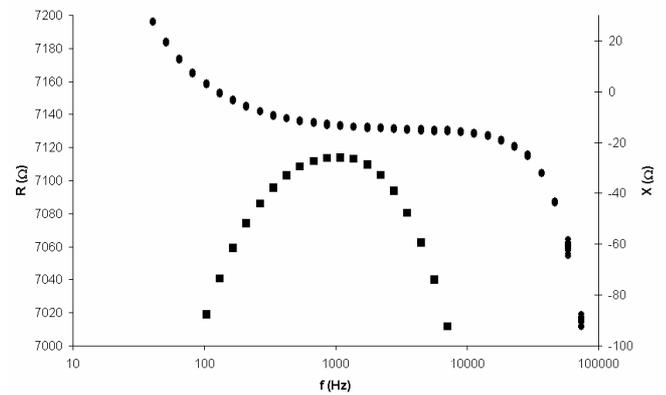


Fig. 4. Example of selected resistance (●) and reactance (■) sweeps carried out with the RLC bridge for the 20 $\mu\text{S cm}^{-1}$ solution.

In Fig. 4, the minimum point of reactance (modulus of the value) was at 1000 Hz.

During the same measurement, after the solution has reached the temperature stability, the resistance has slightly continued to decrease due to the contamination of atmosphere CO_2 and of pipeline. Taking into account the time spent to carry out a set of three measurements, the 20 $\mu\text{S cm}^{-1}$ sample has changed of 0.01 % per hour.

Table 2. Uncertainty budget for the solution with nominal conductivity of 20 $\mu\text{S cm}^{-1}$ at 25 °C.

Quantity	Estimate	Standard Uncertainty	Assumed distribution
C_{cell}	14.920	0.048	normal
R	7131.56	34.08	normal
T	0	0.007	rectangular
α_T	0.020	0.001	rectangular

The conductivity value resulted to be $20.92 \mu\text{S cm}^{-1}$, considering the model equation (1). The uncertainty contributions are summarized in Table 2. In the treatment of the uncertainty the relevant international documents [9] and [10] have been followed. The standard uncertainties have been combined by applying the uncertainty propagation law, where the input quantities are considered uncorrelated. The standard uncertainty resulted to be $1.2 \cdot 10^{-5} \text{ S m}^{-1}$ and the expanded uncertainty $2.4 \cdot 10^{-5} \text{ S m}^{-1}$ (1.2 %). The main contribution (34.08Ω) associated to R includes the uncertainties due to the RLC bridge calibration, the measurement repeatability, and the solution contamination due to CO_2 and pipeline. The contribution amount due to the RLC bridge is known, that is evaluated 5.49Ω . Most of the term is due to the repetition shortage and to the contamination which have not been distinguished.

The main problem of the measurements carried out with the $1 \mu\text{S cm}^{-1}$ sample was referred to the solution stability due to the pipeline and to the CO_2 contamination. After the solution has reached the temperature stability, the resistance value (measured with the RLC bridge) has continued to decrease during the time of the same measurement of 0.07 % per hour. Since the solution wasn't in contact with the air, that change was mostly due to the contamination of Tygon® pipeline. A set of seven repetitions with the $1 \mu\text{S cm}^{-1}$ sample have been carried out distributed on ten days. Considering also the solution storage in a capacious bottle, with air in it, the resistance has decreased of about 1 % per hour. The uncertainty contributions are summarized in Table 3.

Table 3. Uncertainty budget for the solution with nominal conductivity of $1 \mu\text{S cm}^{-1}$.

Quantity	Estimate	Standard Uncertainty	Assumed distribution
C_{cell}	14.920	0.048	normal
R	182977	8858	normal
T	0	0.008	rectangular
α_T	0.020	0.001	rectangular

The obtained conductivity value was $0.82 \mu\text{S cm}^{-1}$, the contribution associated to the RLC bridge was of 211Ω , and the expanded uncertainty $8.0 \cdot 10^{-6} \text{ S m}^{-1}$.

Another significant problem has been caused from the detection of the frequency value at which the solution resistance could be considered as representative of the bulk (no polarisation effects are included). The reactance minimum point was at 25 Hz, very close to the minimum value of the RLC bridge full scale. Consequently, another set of six measurements have been undertaken with the lock-in in the range between 0.1 Hz and 50 Hz in order to define the resistance range where the parasitic effects are minimised. Before each sample measurement at the chosen frequencies, the lock-in autophase was started with a resistor with a similar resistance. The current measurements (imaginary and real terms) have been carried out and transformed respectively in reactance and resistance values.

Each frequency sweep has been carried out selecting two ranges: between 0.1 Hz and 1 Hz the Time Constant (TC) was 10 s and the time between two values (Δt) was 50 s; in the frequency range 1 - 50 Hz, TC was 5 s and Δt 25 s. The main instrument settings were: Input Limit $3 \mu\text{A}$ (correspondent to a gain of 0 dB); Sensitivity $1 \mu\text{A}$; Voltage 0.1 V (the saturation occurs if more than 0.1 V was set); and Signal Channel Coupling DC (for the reactance measurement).

A resistance and reactance measurement comparison of $1 \mu\text{S cm}^{-1}$ sample with the RLC bridge and with the lock-in as a function of frequency is shown in Fig. 5. It shows a good compatibility of the measurements carried out with the two instruments. The resistance seemed to be invariant to frequency down to 10 Hz. At lower frequencies interface effects occur.

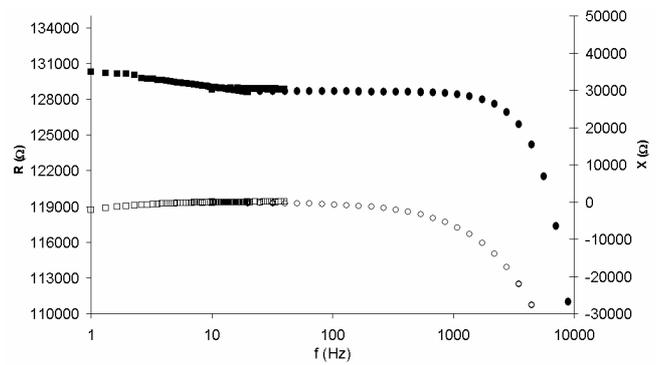


Fig. 5. Comparison between resistance and reactance sweeps undertaken with RLC bridge and lock-in with the $1 \mu\text{S cm}^{-1}$ sample (for RLC bridge: resistance (●) and reactance (○); for lock-in: resistance (■) and reactance (□)).

In this case the obtained conductivity value was of $0.77 \mu\text{S cm}^{-1}$, and the expanded uncertainty of $7.1 \cdot 10^{-6} \text{ S m}^{-1}$. The uncertainty contribution due to the lock-in was 1116Ω , whereas the one due to the repeatability and contamination was 8632Ω .

4. CONCLUSIONS

A flow-through cell and a closed circuit that permit to carry out low electrolytic conductivity measurements of aqueous solutions have been developed.

After the calibration of the geometric constant of the new cell have been performed by solutions with conductivity from $200 \mu\text{S cm}^{-1}$ to $50 \mu\text{S cm}^{-1}$, it has been employed to measure solutions with conductivity of $20 \mu\text{S cm}^{-1}$ and $1 \mu\text{S cm}^{-1}$. Since the solutions with very low conductivity show frequencies at which the resistance could be considered as representative of the solution close to the minimum value of the RLC bridge full scale (25 Hz), a lock-in amplifier has been employed. A good agreement has been obtained between the RLC bridge measurements and the lock-in ones both for the resistance and the reactance and the frequency, although the lock-in is not an accurate instrument for this kind of measurements, the low frequencies, and the applied voltage was low and the measured current high.

Moreover, some indications about uncertainty contributions of $20 \mu\text{S cm}^{-1}$ and $1 \mu\text{S cm}^{-1}$ samples have been reported.

The future activities regards the improvement of the measurement system in order to increase the time stability of the solution. For example, a study on soft plastic tubes with the most suitable technical specifications will be carried out. Moreover, a solution storing system which operates under argon gas will be developed.

Another improvement will consist in the test and study of a more specific and accurate instrumentation for the resistance and reactance at low frequencies.

In addition, the development of a measurement system directly connected to the outlet of a ultra pure water production system will be carried out in order to have the possibility to perform measurements of electrolytic conductivity around $0.05 \mu\text{S cm}^{-1}$. Concerning this value, the main aim will be to achieve a measurement uncertainty lower than 2 % as prescribed by the U.S. Pharmacopeia and enforced by the Food and Drug Administration for the manufacture and use of ultra pure water and water for injection.

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