A new primary cell for electrolytic conductivity measurements of ultrapure water

Elena Orrù , Francesca Durbiano

I.N.Ri.M. – Istituto Nazionale di Ricerca Metrologica,Strada della Cacce 91, 10135 Torino, Italy;

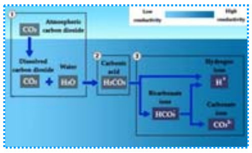
Key Points

Ultra Pure water, UPW

1. Employed in many fields of science and technology.
2. By definition only hydronium and hydroxide ions are in solution.
3. Quickly contaminated by carbon dioxide (CO_2) in the air.

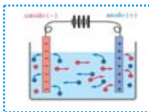
e.g. pharmaceutical, semiconductor and power plan industries, food industry, health care, envirnomental monitoring, biotechnology

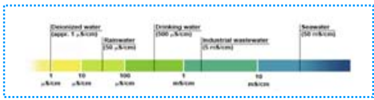
$$2H_2O \overset{K_w}{\rightleftharpoons} H_3O^+ + OH^-$$



Electrolytic conductivity, κ

1. Method to measure the amount of ions in solution.
2. Important parameter for monitoring water quality.
3. Conductivity measurements traceable to SI units required by regulatory bodies.





κ, *electrolytic conductivity*, traceable to SI units

$$\kappa = \frac{C_{cell}}{R} \qquad C_{cell} = \frac{l}{A}$$

Measured value of ***R***

C_{cell} defined through the physical dimensions of the cell geometry

Technique applied as a primary method of measurement

Aim of the work

The characterization of ultrapure water through reliable and accurate electrolytic conductivity measurements allows its use as a reference for the analysis of physical and chemical properties of solutions.

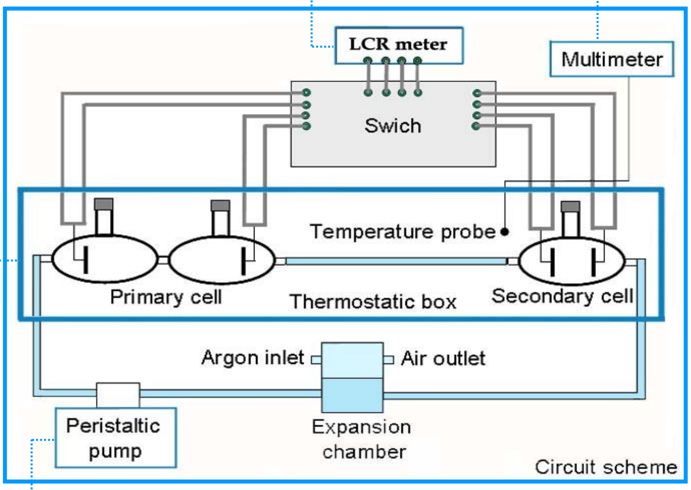
Experimental apparatus

Primary and secondary cells are included in a glass circuit for on line measurements.

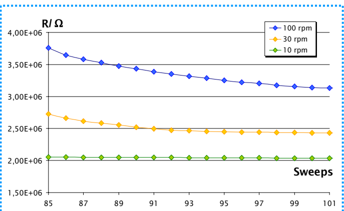
Thermostatic box – Branca Idealair
- T_{meas} = 25,000°C

LCR meter – Agilent E4980A
- 20 Hz ≤ f ≤ 2 MHz
- Level: 500 mV
- Time measurement: LONG

Multimeter – Agilent 3458A
- Pt probe Termics 002



Study of solution resistance at different flow rates



The realization of the dynamic pumping system achieves the continuous circulation of the solution under inert atmosphere (argon gas) and under accurate temperature control

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Solving issues due to contamination from the environment

Possibility to do measurements with the primary cell and *contemporaneously* calibrate the secondary cell

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Calibration of conductivity meters

Primary cell

- Two half-cells with Pt round and planar electrodes connected to current and potential terminals
- Central removable section - allowing a differential measurement of resistance and minimizing the effects due to the polarization to the interface and the electrode manufacturing defects.
- A valve pipeline placed on each half-cell permits measurements with the sample flowing.
- Geometric constant determined through dimensional measurements of the cross sectional area and the length of the central section.

$$\kappa = \frac{C_I}{R_w - R_n}$$

R is measured with, R_w, and without, R_n, the central section

Secondary cell

- Cell with Pt round, planar and faced electrodes connected to current and potential terminals
- Fixed geometry
- Two valve pipeline allow measurements with the sample flowing.
- Cell calibrated on line and contemporaneously against primary cell.

$$C_{II} = \frac{\kappa}{R_{II}}$$

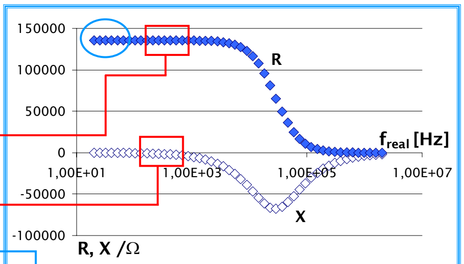
Ability to carry out measurements of solutions with very low electrolytic conductivity values

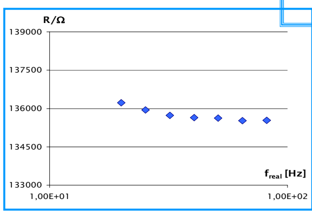
Experimental results

The impedance and temperature measurements are continuously recorded: the results are inspected in order to see temperature stabilization. In these conditions resistance sweeps are chosen.

The graph shows the real (***R***) and imaginary (***X***) components of the cell impedance versus frequency (f_{real}).

From this graph the bulk resistance value of solution is obtained in correspondence to reactance value next to zero.





Electrode polarisation takes place at the surfaces of the electrodes. A double layer, which has resistance and capacitance, occurs due to the build up of charge at the surface.

Effect: increase of resistance value as a function of frequency decrease.

Uncertainty calculation of a 50 μS/cm aqueous solution of KCl.

Measurements carried out with primary cell.

Uncertainty source X_i	Estimate x_i	Contribution to standard uncertainty $u_i(y)$	Combined Standard Uncertainty	Expanded Uncertainty (S/m)	U%
C_I	55,870 1/m	1,56 E-06	1,31 E-05	2,6 E-05	**0,46**
R_w	73248,4 W	-7,53 E-06			
T_w	24,926 °C	-1,14 E-06			
R_n	63458,2 W	-1,03 E-05			
T_n	24,881 °C	-9,91 E-07			
$k_{pol\ w}$	0 S/m	1,10 E-06			
$k_{pol\ n}$	0 S/m	9,00 E-07			
αT	0,02 %/°C	-7,10 E-07			

Future work

- To improve circuit functioning to allow electrolytic conductivity measurements of ultrapure water.
- To develop measurement system that allows impedance measurements at low frequency.
- To achieve a measurement uncertainty for ultrapure water of about 1-2%.