XVIII IMEKO WORLD CONGRESS
Metrology for a Sustainable Development
September, 17 – 22, 2006, Rio de Janeiro, Brazil

DEVELOPMENT AND CHARACTERIZATION OF A CONDUCTIVITY CELL FOR WATER QUALITY MONITORING

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Abstract: The measurement of electrolytic conductivity is widely applied as a control parameter and its relevance is continuously increasing, not only in industrial applications but also in the environmental monitoring domain.
In this work the attention is focused on the electrical behavior of low cost in-situ four electrode conductivity cells for water quality monitoring in estuaries and oceans. The design of each cell, the choice of the cell constant suitable for the range of conductivities to be measured, the modeling of the current density distribution using a finite element method are described in detail. The experimental characterization of the cell versus frequency, temperature and salt concentration is also carried out. A frequency range where parasitic effects are minimized is identified.

Keywords: conductivity cell, electrolytic conductance, salinity.

1. INTRODUCTION

The measurement of electrolytic conductivity is widely applied in several application domains and the increase of its relevance has boosted research in the area.

In order to obtain absolute methods, this measurement has recently undergone a critical revision [1], systems for the traceable measurement are being developed [2] and the search for the best conductivity measurement cell is always a goal for scientist and experimentalists [3, 4].

In this paper the attention is focused on the electrical behavior of low cost in-situ four electrode conductivity cells for water quality monitoring in estuaries and oceans.

Environment has turned into a major issue during the last decade. The increasing levels of pollution all over the world, alerted not only rulers but also the population, particularly in developed or under development countries, to the importance of preserving and improving the environment. It is generally accepted nowadays that quality of life depends on many aspects, including environment, and that growth must take them into consideration (sustainable development). The impact of these concerns in metrology has been great. The need of measuring systems both for soil, water and air monitoring developed the demand of better sensors.

Conductivity is an intrinsic property of seawater from which salinity and density may be derived. Although water itself is a very poor conductor of electricity, the presence of ionic species in solution increases the conductance considerably. The conductance of such electrolytic solutions depends on the concentration and nature of the ions present. Conductivity is calculated from the conductance, defined as the reciprocal of the resistance, measured by a sensor.

2. THEORY

Electrical conductivity is the ability of a material to carry electrical current. In water, electrical current is carried by ions and it is named electrolytic conductance. It depends on the concentration of the ions on the nature of the ions present (their charges and nobilities) and also on temperature.

There are two major types of measurement principles to access electrolytic conductivity: inductive [5] and resistive [6].

The electrode method, assembled with two, three or four electrodes, is based on metallic electrodes with direct contact with the electrolyte. The measurement principle used derives from Ohm's law and thus the current, I, passing through a given body of solution is proportional to the applied potential difference V. Theoretical results of conductivity, σ, are determined from the conductance, $1/R$, measured by the sensor using a geometric coefficient or "cell constant", K_C, which depends on the cell shape:

$$\sigma = K_C \frac{1}{R} \qquad (1)$$

A conductivity measurement using a two-electrode flow through type cell (or, a three-electrode used as a two-terminal device) is disturbed by several electrochemical processes such as double-layer capacitance, electrolysis and concentration polarization that are sources of considerable errors. To minimize these effects, the measurements are performed with alternating current (AC) but it is still very difficult to build a two-electrode cell with a stable cell constant.

This paper presents a four-electrode cell in two possible configurations. It is formed by a plastic tube, with two ring-shaped electrodes inside, and two metallic tips to measure the output voltage. In one configuration the tube is open on the two ends, and in the other configuration metallic grids were placed on those ends.

2.1. Cell Design

Two cells with the geometry represented in Fig. 1 have been implemented. They are formed by a plastic tube, with two ring-shaped electrodes inside, and two metallic tips to measure the output voltage. In one configuration the tube is opened on the two ends, and in the other configuration metallic grids placed on those ends were added. To achieve field confinement in the cell, the metallic nets are connected to the current electrodes as depicted in Fig. 1. The electric field becomes fully internal and proximity effect is eliminated. The physical dimensions are:

$$d = 45\text{mm};\ \varnothing_{\text{int}} = 16\text{mm};\ \varnothing_{ext} = 20\text{mm};\ l = 180\text{mm} \qquad (2)$$

where d represents the distance between the rings, l the cell length and $\varnothing_{int}$ and $\varnothing_{ext}$ the internal and external diameter of the glass tube.

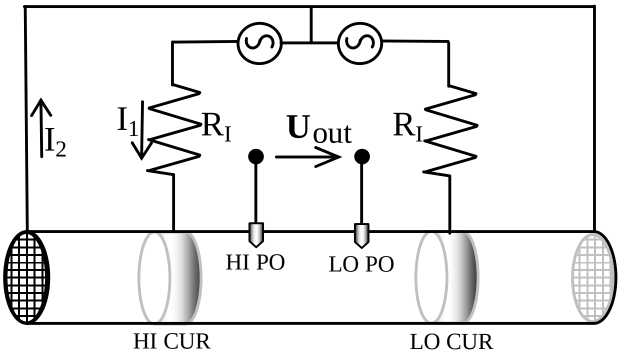

Fig. 1. Block diagram of a four electrode cell. R_I is a fixed resistor to measure the injected current.

In Fig. 2 a photo of the four electrode cell without the metallic grids on the tops, is presented.

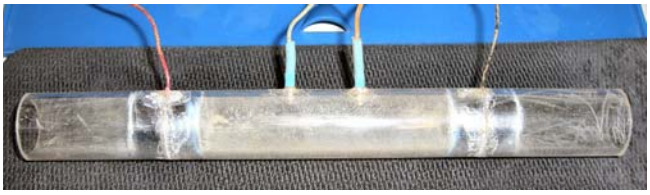

Fig. 2. Photo of the implemented four electrode conductivity sensor.

The resistance range chosen to be measured with the cells (resistance between the voltage electrodes) was from $10\,\text{k}\Omega$ to $10\,\Omega$ in order to minimize measurement errors. For electrolytic conductivities varying from 0.005 S/m, that corresponds to the typical value for tap water, to 5 S/m, the conductivity of the sea water, theses resistance values imply for the cell constant, a value around $K_C = 50\,\text{m}^{-1}$. This value results from the fact that the current flowing in the water cylinder confined by the tube and the voltage electrodes is half the current measured in the current electrodes.

2.2. Sensor Modeling

The finite element method was used to estimate the configuration of the field inside the cells and to preview the values of the resistances and of the cell constant. The application developed besides the geometric parameters of the sensing unit requires its material properties, namely conductivity, permittivity, and permeability and a variable finite element number, dependent on the required approximation degree of electromagnetic field solution, boundary and excitation conditions.

For the cell without the metallic grids the current lines are not disturbed by the presence of the voltage electrodes and the effect of deposits on electrode surface is reduced as current is applied. The simulated results obtained with the finite element method for this configuration are presented in Fig. 3. The calculated cell geometry factor is:

$$K_C = R_{\text{sensing terminals}} \times \sigma = 52.466\,\text{m}^{-1} \qquad (3)$$

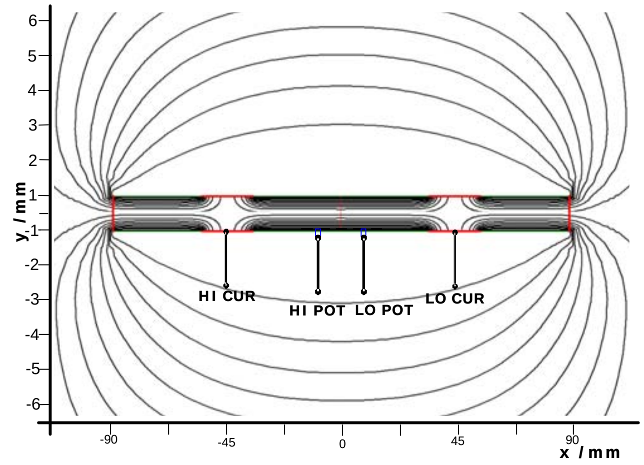

Fig. 3. Current lines in the cell without top grids

Fig. 4 shows the full internal field for the conductivity cell with metallic grids on the top ends, being anti-symmetric the voltages applied to the current electrodes and the top grids. This geometry assures that the current inside the cell (in the region between the two electrodes) equals the current that flows from the current electrodes to the metallic grids on the top ends of the cell. That leads to $K_C = 50\,\text{m}^{-1}$.

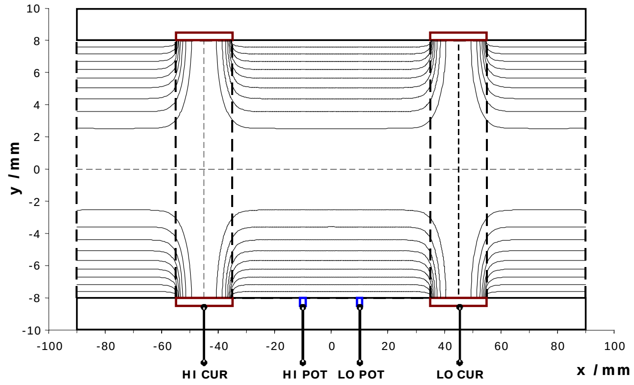

Fig. 4. Current lines in the cell with top grids.

3. EXPERIMENTAL CHARACTERIZATION

3.1. Experimental setup

The block diagram of the automated temperature controlled bath used to characterize the cells is shown in Fig. 5. The bath has a maximum capacity of 14 liters. The temperature is controlled with a heating/cooling thermoelectric pump based on Peltier modules and a PID controller implemented in LabVIEW is used. The temperature range was specified to be in the 7ºC to 32ºC interval. A full description of the testing system can be found in [7].

To measure temperature, a three terminal sensor (TMP36) whose metrological characteristics include a 10 mV/ºC scale factor, ±2ºC accuracy and a ±0.5ºC linearity error, is used. A 16-bit ADC (AD974) digitizes the output signal every 100 ms. The basic resolution is increased using dither, as for each measurement 1000 readings from the sensor are taken for averaging.

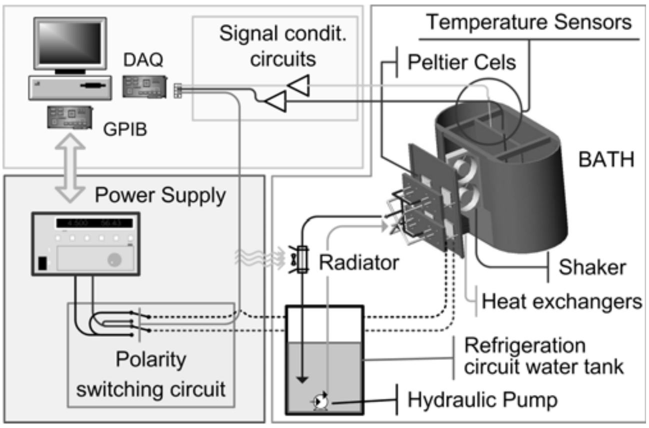

Fig. 5. Block diagram of the testing system

The impedance (admittance) measurement system, based on two simultaneously acquisition channels and sine-fitting algorithms presented in [8] is used. For its implementation a DSP based system was required. The processor chosen was a ADSP-BF533 interfaced with a AD1836 multichannel codec that includes 4 ADCs and 6 DACs. The current imposed to the two current electrodes (HI CUR and LO CUR) of the four-terminals conductivity sensor is a sine stimulus generated by one of the 24-bit resolution DAC with a 5.6 Vpp maximum amplitude range. It value is measured by sampling the voltage across a well known resistance with one of the ADCs included in the AD1836. Another ADC is used to measure the voltage at the voltage terminals (LO POT and HI POT) of the conductivity sensor (with null current). These ADCs have a 24-bit resolution, 98 KS/s maximum sampling rate and input voltage range of ±3.08 V.

3.2. Experimental Characterization and Discussion

Electrolytic conductance measurements entail an understanding of the electrochemical processes involved when a current crosses a system consisting of electrolyte and electrodes. Some phenomenon like double-layer capacitance, electrolysis, polarization and ohmic resistance through the electrolyte occur. These effects with an alternating voltage applied to the electrodes reverse them selves with the period of the voltage and are thus minimized. However as their relaxation times are different, their contributions vary with frequency. For instance, as the frequency is increased polarization can be greatly reduced but, for high frequency values, the effects of stray capacitances increase.

In order to find out for which frequency these effects are minimized, tests were conducted to study the cell behavior with frequency. In Fig. 6 and in Fig. 7 the admittance amplitude and phase are shown as function of the applied sine wave frequency for solutions with different conductivity values. It is clear from these experimental results that for frequency values below 20 kHz, the stray capacitances are still very low. This agrees with the solution of Maxwell’s equations for water solutions.

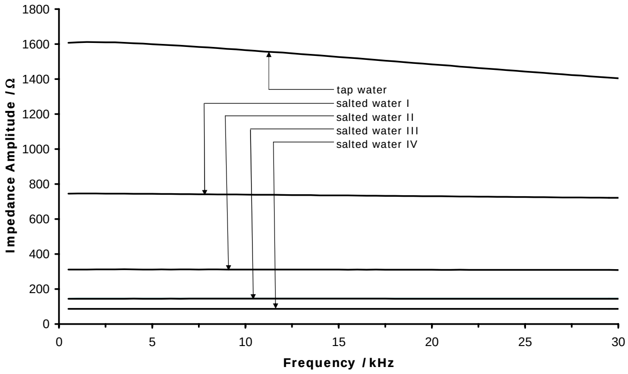

Fig. 6. Conductivity sensor impedance amplitude for different values of water conductivity as function of the sine frequency for T = 20ºC.

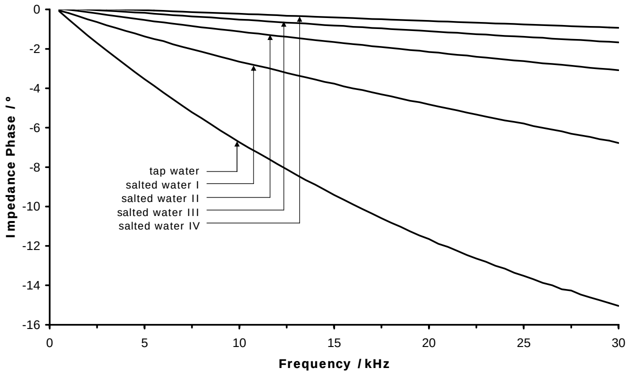

Fig. 7. Conductivity sensor impedance phase for different values of water conductivity as function of the sine frequency for T = 20ºC.

The macroscopic interactions of electromagnetic fields with materials are described by Maxwell’s equations. Solution of Maxwell’s equations requires knowledge of the properties of the material: magnetic permeability, dielectric permittivity and conductivity. For the water, the permeability is nearly that of free space. As a result the electromagnetic response is determined by its dielectric properties and the conductivity. The constitutive relation describing the response is:

$$\overline{J} = \sigma \overline{E} \tag{4}$$

$$\overline{D} = \varepsilon_r \, \varepsilon_0 \, \overline{E} \tag{5}$$

where $\overline{J}$ is the current density, $\overline{E}$ the applied electric field, $\overline{D}$ the electric displacement vector, σ the conductivity, ε_0 the permittivity of free space and ε_r the relative permeability or dielectric constant.
Considering that distilled water as a relative permittivity around 80 and that $\sigma \approx 0.005\,\text{Sm}^{-1}$ for the tap water

$$\frac{J}{\partial D / \partial t} = \frac{\sigma}{\omega\varepsilon} \gg 1 \tag{6}$$

for frequencies less that 20 kHz. In this case, even for the tap water, the electric displacement current can simply be ignored when compared with the conduction current.

The evaluation of the electrolytic conductivity is generally a comparative procedure. The conductance cell is calibrated by determining the cell constant using a solution of known conductivity, usually a standard solution. For the case reported in this paper the conductivity of the solution was measured using a commercial highly resistant inductivity sensor from Hobeco (OLS 50) with a measuring range from 0.5 mSm^{-1} to 200 Sm^{-1} with a maximum value deviation of $\pm\left(1\,\text{mSm}^{-1} + 0.5\%\,\text{of measured value}\right)$.

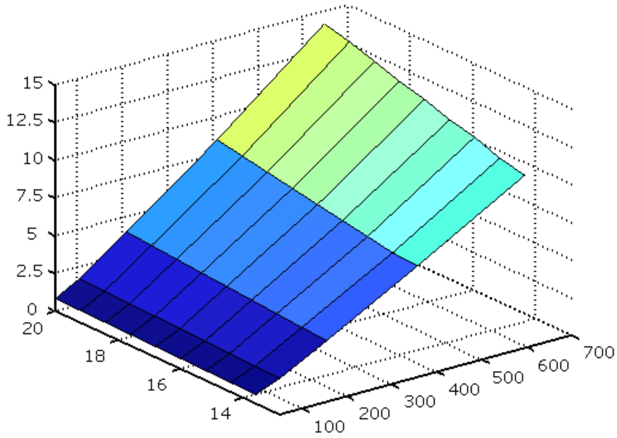

Fig. 8. Conductivity sensor admittance for different values of temperature, as a function of the solution conductivity.

Fig. 8 shows the conductivity sensor admittance for different values of temperature as a function of the electrolytic conductivity. These results were obtained at 1 kHz. For that frequency value the phase is null and the admittance amplitude is a direct reading of conductivity as it is clear from expression (1).

The same results are presented in Fig. 9. From these data it is possible to obtain by linear regression the relationship between admittance amplitude measurements and conductivity values. By averaging the values calculated in this way, the experimental value of 52.186 m^{-1} is obtained for the cell geometry factor with a standard deviation of 4.7 m^{-1}. For the sensors characterized in this paper one can conclude that this factor is almost independent of the conductivity of the liquid and also with temperature.

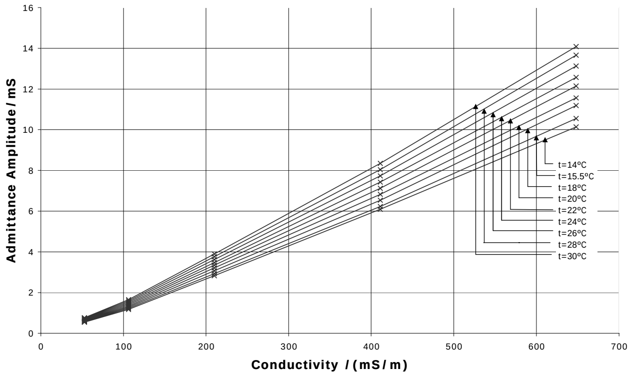

Fig. 9. Conductivity sensor admittance for different values of temperature, as a function of the solution conductivity.

The effect of temperature is also important when an electrical conductivity measurement of a solution must be done. A solution of a higher temperature will present a higher quantity of ions dissociated, therefore a higher concentration of electric charges and as consequence conductivity will raise.

The degree to which temperature affects conductivity varies from solution to solution and can be calculated from the expression:

$$\sigma_t = \sigma_{ref}\left[1 + \alpha\left(t - t_{ref}\right)\right] \tag{7}$$

where σ_t is the conductivity at any temperature t (in ºC), σ_{ref} is the conductivity at the calibration temperature t_{ref} (in ºC) and α the temperature coefficient of the solution at t_{ref}.

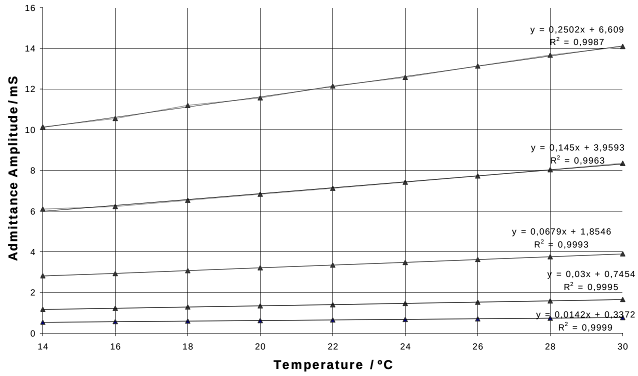

Fig. 10. Amplitude admittance of the conductivity sensor for different values of the electrolytic conductivity, as a function of temperature

In Fig. 10, dots represent the amplitude admittance measured as a function of temperature for different values of the solution conductivity. These experimental data fit the straight lines obtained by linear regression that are also presented in the figure. From the values depicted a temperature coefficient of $\simeq 2.21\%/^{\circ}\text{C}$ at 20ºC was calculated. For each conductivity value of the solution, the conductivity was measured at a range of temperatures. The slope of the graph change in conductivity versus the change of temperature divided by the conductivity value for 20ºC is α.

From an application point of view, conductivity is given at a certain temperature, which has been stated as a reference in order to get a better comparison of measurements taken at different locations and times. Typical values for the reference temperature found in the literature are 20ºC and 25ºC. As the conductivity sensor characterized in this paper is to be used to monitor estuarine waters with an average temperature value through the all year of 20ºC the chosen temperature for the present case was 20ºC.

Fig. 11 depicts the experimental results obtained for the admittance amplitude of the sensor (a direct reading of the electrolytic conductivity) for the measured value and for the compensated value.

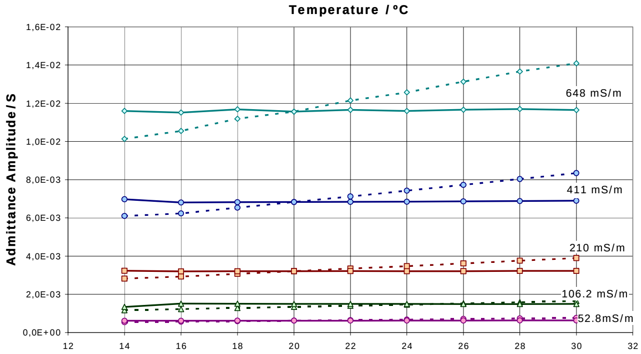

Fig. 11. Experimental results obtained for the conductivity sensor admittance: dotted lines represent measured values and full lines are the compensated value for 20ºC.

4. CONCLUSION

The conductivity sensors that were implemented and characterized have a cell constant adequate for conductivity measurements for estuarine water. Besides this geometry cell factor was found to be independent of the conductivity of the solution and the value obtained with a calibration procedure is similar to the value calculated with a finite element method. The temperature of the solution doesn't affect its value either.

The cell without top grids was completely characterized. An optimal frequency range for the alternate conductivity measurement of aqueous solutions was found experimentally. It agrees with the theory that explains the ion electric conduction in salted water.

The admittance amplitude of the sensor, which is a direct reading of the solution conductivity, varies linearly with temperature. The temperature coefficient obtained is similar to those presented in the literature for NaCl aqueous solutions. The values obtained for the conductivity referenced for 20ºC are presented.

For the cell implemented with metallic grids at the ends preliminary results show even better results. As for this geometry the electric field is internal there are no current paths spreading out of the sensor and thus, there are no perturbations caused by the proximity of external objects.

ACKNOWLEDGMENTS

This work was supported in part by Portuguese Science and Technology Foundation and project "Design, Implementation and Characterization of Stand-Alone Prototypes for Water Conductivity Assessment" reference DICSAP/WCA - IT/LA/298/2005 financed by Instituto de Telecomunicações. This support is gratefully acknowledged.

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