

Proceeding Paper

Electrochemical Measurement System for Chlorides in Drinking and Wastewater [†]

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Abstract: This paper presents a system for the measurement of chlorides in drinking and wastewater, based on an electrochemical process using a selective electrode as a transducer, which was developed by this group. The measurement for the concentration is carried out by introducing the implemented electrode (considered as reference) in the sample that will be analyzed; then a current is passed producing a potential difference in the system. Different aqueous solutions of sodium chloride (NaCl) were used, ranging between 35 and 3546 µg of chloride ions (Cl[−]). As a data acquisition and monitoring system for the analysis, an ATmega 328P microcontroller was used as the main capture element for subsequent interpretation through graphics. The experimental results show that it was possible to detect a potential difference in the electrochemical measurement system that corresponded to 35 µg of chloride ions (Cl[−]), making clear the detection process and the selectivity of chloride ions. It is important to mention that with this measurement system and the applied methodology, results are obtained in real time using a small sample volume and without generating extra liquid waste, compared to the application of the traditional analytical titrimetric method. Finally, this chloride measurement system is inexpensive and can be used in drinking and wastewater measurements.

Keywords: measurement system; data acquisition; electrodes; electrochemical process; ion selectivity; chloride ions



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1. Introduction

Measurement by electrometric methods continues to be useful in the analytical identification processes of ion-selective electrodes (ISEs) of potentiometric sensors [1,2] because only small dimensions are involved and measurements can be made requiring little sample volume with respect to the activity of the ions in solution [3,4]. With the increasing demand for environmentally friendly technologies and in situ measurements, these designs facilitate quick readings and detection of low concentrations [1,2], as observed when obtaining measurements of concentrations of 35 µg/L in NaCl solutions [5].

Due to the diverse range of applications and reduced operating times, there is a need for measurement electrodes that are selective and able to detect a specific ion of a species that interacts with it using potential difference [4,6]. Several electrodes have been developed for selective ion determination which involve use of an ionophore to generate exchange in a solution enabling determination of the influence of the exchange ion percentage [7–10].

In this study, a chloride measurement system for drinking and wastewater is proposed based on an electrochemical process using a selective electrode as a transducer which was

developed by this group. The ionophore that is proposed is an AgNO_3 solution with an extra modification that relates to the use of a metal that interacts with a natural organic membrane, modifying the attraction of the ion, which enhances the selectivity to the desired ion (Cl^-) [3,11], in addition to the copper reference electrode [9].

2. Materials and Methods

The experimental arrangement of the electrochemical measurement system, shown in Figure 1, is made up of two essential blocks: the electrochemical half-cell and the data acquisition system.

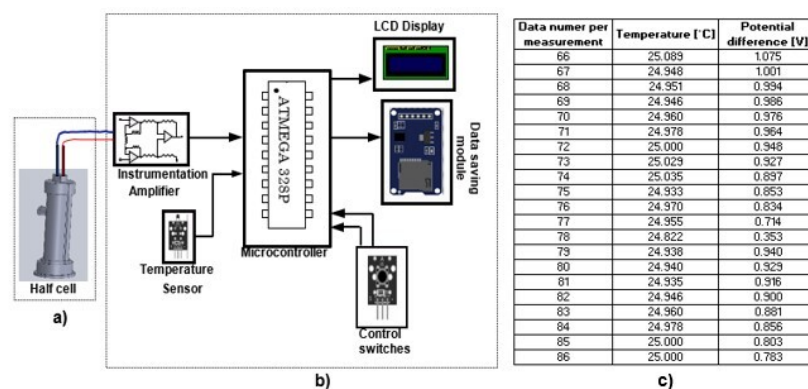


Figure 1. Experimental arrangement of the electrochemical measurement system. (a) Electrochemical half-cell; (b) Data acquisition system; (c) Temperature and potential difference data obtained directly from the measuring device.

For the half-cell (Figure 1a), a 3D design was produced and printed to ensure the electrode separation was constant and to reduce movements in the experimental arrangement. The electrochemical half-cell was constructed with an active noble metal electrode (X) and a copper reference electrode, which are submerged in different solutions, such as AgNO_3 and NaCl , respectively, according to Creus (2011) [12] and previous research by Toriz, Loredó and Marcial [13].

The measurement of chloride ions (Cl^-) was achieved through reaction in the half-cell taking as analytes NaCl solutions at different concentrations, in which an ionic migration was generated through an organic (natural) membrane. The organic membrane and the inert metallic material (X) allow the potential difference to remain active during the measurement.

The coefficients of total ionic activity are related to the individual coefficients of ionic activity, detecting free energy in the system that connects the thermodynamics of the reaction with the values of the electromotive force (*emf*) [10] and that can only be applied in reversible reactions. This can be represented by Equation (1).

$$\mathcal{E}^\circ = \frac{-\Delta F^\circ}{nF} \quad (1)$$

where \mathcal{E}° is the potential difference, ΔF° is the total free energy of the system, n is the number of moles used in the reaction, and F = Farad (free energy value = 96,500 Joules: approximate value = 23,052 cal).

The electromotive force (*emf*) depends on the concentration of the cation according to the Nernst equation [14]. According to the literature, the relationship between the signs ΔF° and \mathcal{E}° correspond directly to a spontaneous reaction (Maron and Prutton) [9].

Referring to a standard *emf* when the activity is a unit, the fundamental equation can be related to the thermodynamic equation and the *emf* values. The values of \mathcal{E}° can be tabulated for each reaction of a half-cell and added algebraically to obtain the value of \mathcal{E}° .

To calculate the total free energy of the system, the relationship with thermodynamics is considered, calculating the *emf* from enthalpy and entropy tables for the reference half-cell [9,10], where $T = 298\text{ K}$, applying the relationship described in Equation (2):

$$\Delta F^\circ = \Delta H - T\Delta S \quad (2)$$

The calculation of the total ΔF° corresponds to the sum of the cathodes of the system; the reaction of each cell is stated as in Equation (3):

$$\Delta F^\circ = \mu_{Ag^\circ} + \mu_{Cu^\circ} + \mu_{Cl^-} - \mu_{AgCl} - \mu_{Ni} \quad (3)$$

Substituting the values for the half-cell reaction of the system (total ΔF°), Equation (4) is obtained:

$$\Delta F^\circ = 1000(0 + 23.6 + (-40.02) - (-30.36) + 7.2) - 298(17.67 - 23.6 + 13.17 - 22.9 - 7.2) \quad (4)$$

Solving Equation (4), the results presented in Equation (5) are obtained:

$$\Delta F^\circ = 21140 + 6812.28 = 27952.28 \quad (5)$$

Considering $n = 1$ and substituting the values in the equation, the standard potential of the system will be defined by Equation (6):

$$\varepsilon^\circ = \frac{27952.28}{23052} = 1.2126 \text{ volt} \quad (6)$$

The value obtained from Equation (6) represents the *emf* of the ionic activity with respect to the constant concentration of the ionic activity of the cell. It provides the voltage difference with respect to the element. This theoretical value was obtained experimentally using the measurements presented in Figure 1c. The relationship of this value and the concentration was used to establish the scale.

The data acquisition system is mainly comprised of an ATMEGA328P microcontroller that multiplexes two analog channels to store the temperature data and the potential difference of the half-cell in the microSD memory module for subsequent graphic analysis. The data from the potential difference of the electrodes are acquired through an instrumentation amplifier with unity gain to reduce the effects of electrical noise that may exist in the system (Figure 1b). The system also has an LCD module that prints the values of the analog channels sampled in the microcontroller (temperature and potential difference of the half-cell) every 5 s to verify changes in real time. When acquiring measurements with this system, the data id was saved in an Excel file where the first column shows the temperature and the second column the potential difference (Figure 1c).

3. Results and Discussion

The data stored in the microSD memory shown in Figure 1b were treated by a moving average filter with an N length window, which allows smoothing of the signal obtained from the potential difference measured in the half-cell.

The most significant data captured at different concentrations are shown in Figure 2, in which it is observed that the signals reached a stable state in the potential difference of each, which can be used for their subsequent characterization. The stabilization of the voltage occurs approximately in the same period, after the ionic migration of the oxidation-reduction reaction (transient response).

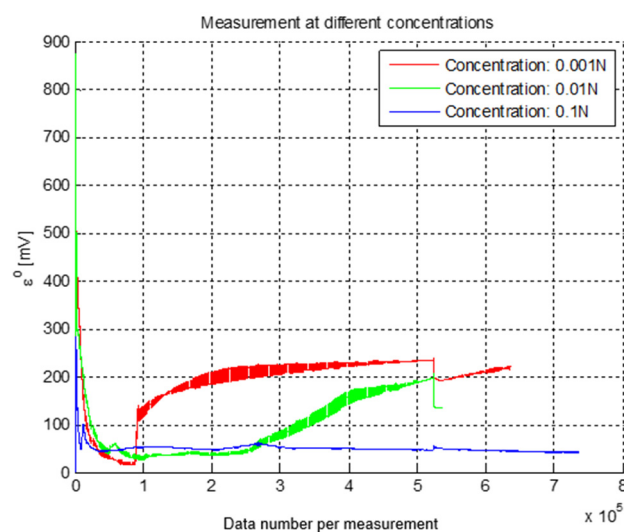


Figure 2. Graph of *emf* measurement at different concentrations of NaCl.

The data show the behavior of the concentration and the *emf* obtained for each concentration [5,15]. A scale was established to observe the change in electric potential as a function of the ionic activity in the solution [16].

Figure 3 shows that the values of the half-cell (\mathcal{E}°) are proportional to the logarithm of the ion concentration in the solution, in addition to presenting a Nernstian slope, as shown in Equation 7, which presents an r^2 coefficient of 0.9953 and a correlation of 0.99.

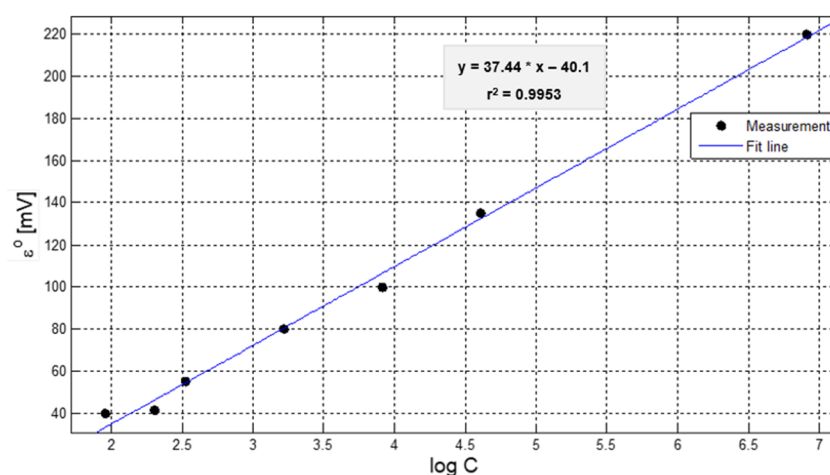


Figure 3. Graph of half-cell values (\mathcal{E}°) as a function of the logarithm of the concentration.

It is important to mention that the value of the half-cell ($\mathcal{E}^\circ = 1.2126$ V) corresponds to the standard electrode data and confirms a reversible reaction and the ion selectivity; while the value of the half-cell I ($\mathcal{E}^\circ = -40.47$) represents the value of the ion that will be detected in the analyte.

$$\mathcal{E}^\circ = -37.54 \ln(C) - 40.47 \quad (7)$$

It is of note that it was possible to optimize the resolution of the analog-digital converter of the ATMEGA 328P microcontroller so that it can detect potential differences of 1.05 mV, in addition to increasing the number of samples per second that are processed through this internal microcontroller module.

4. Conclusions

In this study, it was possible to implement a novel chloride ion measurement system using a selective membrane (natural) and a support structure to assemble a half-cell based

on a design made in a 3D printer. The half-cell obtained $\mathcal{E}^\circ = 1.2126$ V; this data corresponds to the value reported for a standard electrode, ion-selective and for a reversible reaction. The indicated value of the ion-selective in the half cell ($\mathcal{E}^\circ = -40.47$), represents chloride ions (Cl^-).

The behavior of ionic activity at different concentrations shows a logarithmic trend and a typical Nernstian response and is verified with the coefficient (r^2 of 0.9953) of the fitted curve.

Based on the measurements made, the results obtained and the functionality of the assembled device, it was determined that the electrode can be used as a potential chloride ion meter for wastewater and drinking water.

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