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Technical note

Design of an electrochemical prototype to determine relative NaCl content and its application in fresh cheeses

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Abstract:

An electrochemical prototype (ECP) was developmed and evaluated to determine NaCl electrical variables [volt (V), ampere (A), resistance (*R*) and power (*P*)] and its use in fresh cheeses. The ECP circuit consisted of two electrodes, an aluminum (anode) and a copper (cathode). The experimental parameters established in the ECP were distance between electrodes and the presence of a resistor. Seven treatment solutions were examined at 0, 2, 4, 6, 8, 10 and 12 g of NaCl/100 mL of water. Cheeses evaluated were a commercial cheese (Control) and a commercial light cheese. Treatment influenced (P<0.05) the electrical variables in NaCl solutions and cheeses. Regression analysis showed that the best fit was a quadratic model for the ECP. Prototype results showed that at higher NaCl concentrations, voltage and resistance decreased, while amperage and power increased.

Key words: Adulteration, Cheese, Electrical potential, NaCl content, Quality assurance.

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Today, inappropriate eating habits have serious impacts on human health. Food intake with high levels of simple sugars, fats and mineral components such as NaCl present problems associated with obesity, hypertension, and chronic degenerative diseases. In the dairy industry, milk adulteration presents significant problems such as economic loss, deterioration of product quality, and threats to consumer health(1). Therefore, the dairy industry employs several often expensive and time consuming chemical and physical tests to determine fat and total solids content(1). Thus, technological alternatives based on electrical circuits have been used to assess the quality of milk(2,3), conductance effects of milk components(4), the presence of adulterants(1), and to evaluate fat content(5). Electrical circuit technology also has been applied to cheese to study dielectric properties for thermodynamic analysis of salt(6), and fractal and dynamic analysis of water(7).

Electrical conduction properties of a material represent its ability to interact in an electric current(4,8). Electrical properties of meat, milk, fruits and derivatives are dependent on the chemical composition, measurement parameters of the current, and the experimental conditions(1). Foods containing positively or negatively charged electrolytes, charged molecules, or charged macromolecules are capable of transmitting an electric current(9). In the case of foods, it is necessary to have mobile “carriers” for the cations and anions, being influenced by salinity, formulation, aggregation state, molar mass, link type, charge and the number of charged carriers(9,10).

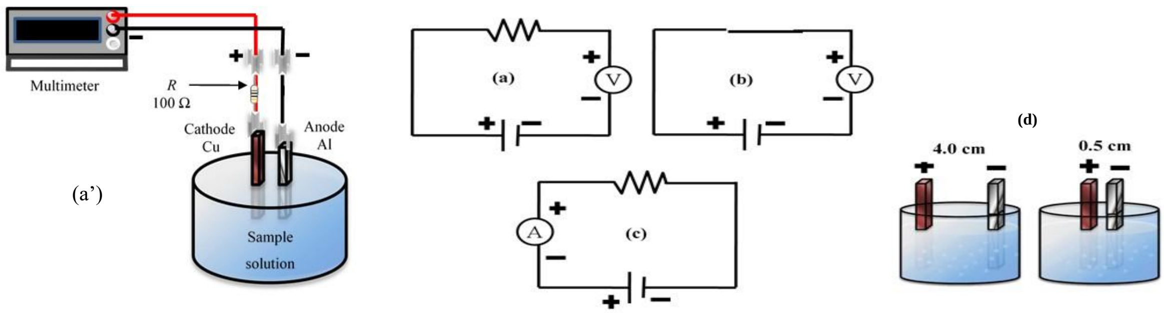
According to Figura and Teixeira(9), an electric current (I) will flow through a food sample containing ions as part of an electrical circuit. The strength of the electric current will be determined by the electrical resistance [R; 1 volt (V) * ampere (A^{-1}) = 1 Ohm (Ω)] of the food sample, where R limits the flow of electric current through the sample. Therefore, a linear relationship exists between voltage [V represented as U], current, A, and electrical resistance, R, within an electrical circuit, which is known as Ohm's Law [$I = (1/R)*U$; o $I = G * U$]. In order to be independent of sample and circuit geometry in performing certain types of calculations, it is necessary to introduce material properties, specific electrical resistivity (ρ; in Ω*m), and specific conductivity (κ; in $S*m^{-1}$); where κ depends only phase state, moisture content, and chemical composition, and not sample size, expressed as $R = \rho * (l/A)$ or $\kappa = 1/\rho$, where l is length in m, and A is current area in m^2[9,11].

Milk is an electrolyte characterized by ionic conductivity due to its high water content and minerals content[5], as determined by: 1) Current measurements including voltage, frequency, pulse shape and type of electric current (direct, variable, alternating); 2) Chemical composition of fresh material [water content and ion (Ca, Na, K, Mg, Cl) concentrations and components of dry matter such as fats, proteins and sugars]; 3) The experimental conditions, especially temperature. Meanwhile, cheese is a colloidal system consisting of protein, fat and an aqueous phase in electrical balance where salt is a common component used in the dairy industry to preserve cheese quality[6].

In this study, an electrochemical prototype (ECP) was developed and evaluated to measure NaCl concentration as alternative to evaluate the NaCl fastly. The ECP consists of an experimental galvanic cell to generate electricity through a spontaneous redox reaction[12], and includes two electrodes and an ionic conductor, which may be a liquid or a solid[13]. The objective of this study was to develop and evaluate the ECP consisting of a copper cathode and an aluminum anode, and an ionic conductor (NaCl solutions and fresh commercial cheeses) to measure voltage, electric current, resistance and power as reflections of NaCl content.

The research was conducted at the Laboratory of Environmental Remediation and Soils Analysis, Water and Plant of the Facultad de Agronomía, Universidad Autónoma de Nuevo León, General Escobedo City, Nuevo León, México. General Escobedo is located at 26°49' N, -100°19' W and altitude of 500 m[14]. The ECP system consisted of two electrodes, an aluminum anode and a copper cathode, with electrode dimensions of 4.5 cm long x 4.5 cm high x 0.15 cm wide. A multimeter (Model 2700/Switch System Keithley, Ohio, USA) was used to measure variables V and A throughout the experiment. A resistor (Φ; 100 Ω tolerance $\pm$ 5%) was used to complete the electrical circuit (Figure 1a').

Figure 1: Circuit design of the electrochemical prototype (a'), and circuits to determinate Volt (a, b), Ampere (c) and distance (d) between electrodes (4.0 and 0.5 cm)



Experimental conditions for evaluation of the ECP were separation distance (δ) between the electrodes (0.5 and 4.0 cm) and resistor presence (with or without the resistor), during measurement of electrical variables. Variation of distance and presence of the resistor in the circuit were used to define how ECP measurements varied under these conditions in order to obtain the optimum configuration of ECP design. The experiment consisted of seven treatment solutions (T_i), based on NaCl concentrations of 0, 2, 4, 6, 8, 10, 12 g of NaCl/100 mL of water. Deionized water (CTR Scientific, Monterrey, N.L., México) at room temperature (24 °C) was used to prepare the solutions. The electrodes were inserted 2.0 cm into each solution, separating them by distances of 0.5 and 4.0 cm (Figure 1d), and with the presence or absence of the resistor (Figure 1a-b) in the circuit (δ with Φ and δ without Φ; Figure 1a-d). These conditions were established to measure variable V. To determine amperage (Figure 1c), it was necessary to place a resistor in the electrical circuit. Variables V and A were used to estimate the *R*, based on Ohm's Law[15]. Power (*P*) in watts was determined with the following equation: $P = V\ I$[15]. The experiment was replicated twice, and measurements were performed in duplicate.

The ECP was evaluated in 400 g each of two fresh commercial cheeses: a standard (Control) cheese and a light cheese (Light) low in calcium, sodium and fat (Table 1). The cheeses dimensions were 12 cm in diameter and 4 cm high. The electrical variables V, A, *R* and *P* in cheese were determined according to conditions determined in the ECP evaluation (Figure 1). Electrodes were introduced 1.5 cm into cheeses, and electrodes were placed at distances of 0.5 and 4.0 cm. Varying the distance between electrodes was done in order to validate the optimum distance between electrodes and whether a resistor in the circuit was required when amperage was measured, and to determine the optimum conditions for measuring the electrical variables and their variation in cheese. The measurements were conducted in two replicates per type of cheese and each variable was measured in triplicate. A 10-g sample of each cheese in triplicate was homogenized in 90 mL of distilled water, and pH was determined with a potentiometer (Mettler Toledo, Probiotek; Columbus, OH, USA).

Table 1: Nutritional composition of the cheeses

Trait	Composition (g/20 g of cheese)*	
	Control	Light
Carbohydrate	0.60	0.50
Protein	3.40	4.00
Fat	5.20	2.80
Calcium	0.11	§
Sodium	0.11	0.08
Moisture and other components	10.57	12.62

*Data taken from the commercial product package.

§ = not present

The statistical evaluation of the ECP was carried through of an analysis of variance (ANOVA) with the GLM procedure of SAS(16), using the statistical model:

$$y_{ijk} = \mu + T_i + \delta_j + \Phi_k + (T\delta)_{ij} + (T\Phi)_{ik} + (\delta\Phi)_{jk} + (T\delta\Phi)_{ijk} + \mathcal{E}_{ijk};$$

Where:

$\mathbf{y}_{ijk}$ = evaluated variables *V*, A, *R* and *P*;

μ = general mean;

$\mathbf{T}_i$ = fixed effect of the *i*th treatment (NaCl solutions and cheeses);

$\boldsymbol{\delta}_j$ = fixed effect of the *j*th distance between the electrodes;

$\boldsymbol{\Phi}_k$ = fixed effect of the *k*th condition of the resistor;

$(\mathbf{T\delta})_{ij}$ = fixed effect of the interaction between treatment and distance;

$(\mathbf{T\Phi})_{ik}$ = fixed effect of the interaction between treatment and the resistor;

$(\boldsymbol{\delta\Phi})_{jk}$ = fixed effect of the interaction between distance and the resistor;

$(\mathbf{T\delta\Phi})_{ijk}$ = fixed effect of the triple interaction between treatment, distance and the resistor;

$\mathcal{E}_{ijk}$ = random error normally distributed with zero mean and variance σ^2 [$\mathcal{E}_{ijk} \sim N(0, \sigma^2)$]. The pH analysis of cheese involved a simple ANOVA. The effect of the independent variable NaCl on dependent variables V, *A*, *R* and *P* was analyzed with ANOVA, linear regression analysis and the REG procedure of SAS(16), and the following second order quadratic statistical model(17):

$$y_i = \beta_0 + \beta_1 X_1 + \beta_{11} X_1^2 + \mathcal{E}_i;$$

Where:

y_i = dependent variable *y* influenced by X (NaCl);

β_0 = intercept to the origin when X = 0;

β_1 = linear regression coefficient, which represents the change of *y* when X (NaCl) increases one unit;

X_1 = values of the *i*th solution of independent variable X_1 (NaCl);

β_{11} = regression coefficients of second order and represent the change in *y* when X_1 increases by an increment of one unit quadratically;

X_1^2 = value of the *i*th quadratic solution of independent variable X_1^2 ($NaCl^2$);

$\mathcal{E}_i$ = random error of the *i*th observation by effect of independent variable (X_1) on *y*.

A Tukey means comparison was performed by setting a 0.05 confidence level.

Table 2 presents the statistical effect (*P*-value) of factors evaluated in the ECP on the variables measured in saline solutions. Distance (δ_j) and its interaction with NaCl treatment [$(T\delta)_{ij}$] were not statistically significant (P>0.05) for the electrical variables evaluated (y_{ijk}). However, the NaCl concentration (T_i) did influence (P<0.05) the variables measured in the solutions. These results indicate that a distance of 0.5 or 4.0 cm can be used in the ECP design to measure the electrical variables in these solutions without changing the variable values. Amperage was measured only with presence of the resistor in the circuit, therefore, statistical P-value was not calculated for resistor (Φ_k) interaction with NaCl [$(T\Phi)_{ik}$], distance [$(\delta\Phi)_{jk}$] and triple interaction [$(T\delta\Phi)_{ijk}$] between treatment, distance, and resistor.

Table 2: Effects of model parameters on variables evaluated in NaCl solutions by the electrochemical prototype

Model parameters*	*P*-value			
	Volt	Ampere	Resistance	Power
Model	0.3902	0.0007	0.0007	0.0003
T_i	0.0076	< 0.0001	< 0.0001	< 0.0001
δ_j	0.3768	0.8698	0.3705	0.7297
Φ_k	0.1794	§	-	-
$(T\delta)_{ij}$	0.9202	0.7314	0.6128	0.4448
$(T\Phi)_{ik}$	0.8566	-	-	-
$(\delta\Phi)_{jk}$	0.9527	-	-	-
$(T\delta\Phi)_{ijk}$	0.9971	-	-	-
$\mu \pm \mathcal{E}_{ijk}$	0.564 ± 0.007	2.615 ± 0.097	220.333 ± 7.562	1464.686 ± 37.189

* T_i = *i*-th treatment (NaCl); δ_j = *j*-th distance; Φ_k = *j*-th resistor condition; $(T\delta)_{ij}$ = interaction between treatment and distance; $(T\Phi)_{ik}$ = interaction between treatment and resistor; $(\delta\Phi)_{jk}$ = interaction between distance and resistor; $(T\delta\Phi)_{ijk}$ = triple interaction between treatment, distance and resistor; $\mu \pm \mathcal{E}_{ijk}$ = mean ± standard error. n = 42.

§ = not detected.

The electrical conductivity measured in NaCl concentrations (T_i) by the ECP is presented in the Table 3. Concentrations 2, 4 and 6 g of NaCl/100 mL of water gave the highest voltage values, while the control at 0 g of NaCl/100 mL of water gave the lowest value (P<0.05). The higher NaCl concentrations, including 6 g of NaCl/100 mL of water, showed high ampere and power, but lower values for resistance. Muske *et al*[18] evaluated electrical variables in lemon juice while varying NaCl concentrations. The conclusions from that study were that the presence of weak acids directly influenced electron transfer and mainly affected the magnesium anode, while the addition of NaCl blocked interaction of the acid on the electrode surface, and resulted in the decrease in electric potential.

Table 3: Electrical conductivity measured in solutions of various NaCl concentrations by the electrochemical prototype

NaCl* (T_i)	Variables¶			
	Volt	Ampere	Resistance	Power
0	0.539^{b}	§	-	-
2	0.576^{a}	2.055^{b}	277.810^{a}	1,168.018^{b}
4	0.576^{a}	2.240^{b}	253.215^{ab}	1,267.343^{b}
6	0.580^{a}	2.715^{a}	212.785^{bc}	1,553.998^{a}
8	0.566^{ab}	2.663^{a}	211.610^{c}	1,499.765^{a}
10	0.553^{ab}	2.960^{a}	186.723^{c}	1,626.340^{a}
12	0.556^{ab}	3.058^{a}	179.858^{c}	1,672.655^{a}
SE	0.007	0.088	9.110	45.778

* NaCl in g/100 mL of water.

¶ Means (n = 42) with the same superscript are not significantly different. SE = standard error.

§ = not detected.

Regression analysis of the ECP validation (Table 4) showed significant effect (P<0.05) for a linear behavior, and indicated that the best fit for the electrical variables was a quadratic model. In the case of V, the ECP detected a decrease of -0003 V and R a reduction of-19 Ω for each increase in the NaCl concentration. In contrast, in A and P were detected more than 0.17 and 107 for each unit increase in sodium concentrations, respectively. The quadratic parameter (β_{11}) was found appropriate for detection of decreases in the V, A and P parameters and an increase in R with the NaCl variation.

Table 4: Regression (β) and determination (R^2) coefficients in validation of the electrochemical prototype

Dependent variable	Regression coefficients*			R^2		*P*-value
	β_0	β_1	β_{11}	Linear	Quadratic	
Volt	0.563	-0.003	- 0.0004	0.2127	0.2664	0.0387
Ampere	1.712	0.173	- 0.0051	0.7854	0.8024	< 0.0001
Resistance	314.511	-19.289	0.6733	0.7756	0.8064	< 0.0001
Power	959.196	107.242	- 4.0418	0.7384	0.7785	< 0.0001

* β_0 = intercept when $X = 0$; β_1 = change in y when X (NaCl) increases one unit; β_{11} = represent the change in y when X_1 increases one unit quadratically; R^2 = determination coefficient.

The significance level (P-values) of statistical parameters and means of cheese variables are present in Table 5. The type of cheese (T_i) statistically affected V, A, *P* and pH ($P<0.05$), while distance (δ_j) affected V ($P<0.05$). The interaction between cheese and distance [$(T\delta)_{ij}$] did not influence the variables. In other parameters involving resistance, P-values were not presented for interactions, because the resistor was included in the circuit to measure amperage only. In mean comparisons, control cheese showed the highest values for V, A and *P* but lower values for *R* and pH with respect to light cheese. Voltage at the 4-cm distance was the highest compared to V at 0.5 cm. These results may be related to the composition of control cheese, because it had a higher lipid content, and, consequently, a greater presence of fatty acids available in the system, influencing oxidation at the anode. For example, some acids such as CH_3COOH are weak electrolytes, and are not completely ionized, being a reversible reaction that gives H^+ ions in the medium, and with the presence of metals such as Zn, Mg and Fe conduct electricity[12]. Moreover, dissolved hydrogen (H^+) in solution is reduced in the absence of copper by the effect of electrode oxidation to H_2[19], affecting the electrical variables measured in cheeses. Sadat *et al*[1] indicated that dielectric properties of foods depend of their chemical compositions. The reactions determined in the current study could explain the high values found in the control cheese, with higher fat content, Ca and Na with respect to the light cheese. Hence, this prototype can be used to evaluate the fat and Na content in cheeses to evaluate its quality and levels of this variables respect to Mexican official standars.

Table 5: Effects of model parameters on variables evaluated in cheeses with the electrochemical prototype

Model parameters*	**Volt**	**Ampere**	**Resistence**	**Power**	**pH**
			P-value		
Model	0.0008	0.2118	0.2821	0.1505	§
T_i	0.0004	0.0421	0.0867	0.0312	< 0.0001
δ_j	0.0118	0.5687	0.4656	0.4322	-
Φ_k	0.0639	-	-	-	-
$(T\delta)_{ij}$	0.3775	0.9026	0.5623	0.8712	-
$(T\Phi)_{ik}$	0.2091	-	-	-	-
$(\delta\Phi)_{jk}$	0.9773	-	-	-	-
$(T\delta\Phi)_{ijk}$	0.3930	-	-	-	-
			Commercial cheeses (T_i; μ)¶		
Control	0.528[a]	1.082[a]	507.307[b]	568.701[a]	6.530[b]
Light	0.512[b]	0.982[b]	536.689[a]	505.675[b]	6.755[a]
			Distance (δ_j; cm)		
0.5	0.515[b]	1.021	525.609	527.127	-
3.0	0.526[a]	1.044	513.388	547.250	-
Resistor (Φ_k)	0.520	1.032	519.498	537.188	-
$(T\delta)_{ij}$	0.520	1.032	522.590	542.330	-
$(T\Phi)_{ik}$	-	-	-	-	-
$(\delta\Phi)_{jk}$	-	-	-	-	-
$(T\delta\Phi)_{ijk}$	-	-	-	-	-
SE	0.003	0.024	9.378	15.394	0.013

* T_i = *i*-th treatment (cheeses); δ_j = *j*-th distance; Φ_k = *j*-th resistor condition; $(T\delta)_{ij}$ = interaction between treatment and distance; $(T\Phi)_{ik}$ = interaction between treatment and resistor; $(\delta\Phi)_{jk}$ = interaction between distance and resistor; $(T\delta\Phi)_{ijk}$ = triple interaction between treatment, distance and resistor; [2] $\mu \pm \mathcal{E}_{ijk}$ = mean ± standard error (SE); n = 12.

§ = not detected.

¶ Means (n = 12) with the same superscript are not significantly different.

The voltage and resistance are variables that can measure with the electrochemical prototype due that these variables decrease at higher concentrations of NaCl, while amperage and power increased. The distances between the electrodes and presence of the resistor in the circuit had no influence on levels of the electrical variables accessed, but the resistor is necessary to determine of resistance data. The electrochemical prototype perceived differences in the electrical variables (volt, ampere, resistance, and power) of cheeses according to their chemical composition. Therefore, this prototype could be used to evaluate the minerals and quality of the cheeses with the volt, ampere, resistance and power.

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