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Determination of acidity and electrical characterization of olive oils via electrochemical impedance spectroscopy

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SUMMARY: Olive oil is highly valued for its nutritional and antioxidant properties. International regulations establish acidity as a key quality parameter, differentiating high-quality oils from lower grades. The acidity measurement typically involves manual titration. This study explored Electrochemical Impedance Spectroscopy (EIS) as a rapid, non-destructive alternative for determining acidity in olive oils. Emulsions were prepared using a hydro-alcoholic solution, and the standard addition method with oleic acid was employed for calibration. Electrical conductivity was derived from impedance measurements across a frequency range of 0.4 Hz to 400 KHz. Through a non-linear fit of conductivity versus oleic acid percentage, acidities of 0.30% for extra virgin olive oil and 0.19% for refined olive oil were determined. All measurements have been carried out in triplicate and both mean value and standard deviation have been calculated. Equivalent electrical circuit accurately modeled the experimental data, revealing that adsorption effects are dominant at low frequencies.

KEY-WORDS: *Electrical conductivity; Electrochemical impedance spectroscopy; Emulsions; Oleic acid; Olive oil acidity.*

RESUMEN: ***Determinación de la acidez y caracterización eléctrica de aceites de oliva mediante espectroscopía de impedancia electroquímica.*** El aceite de oliva es muy valorado por sus propiedades nutricionales y antioxidantes. Las normativas internacionales establecen la acidez como un parámetro de calidad esencial, que tradicionalmente se mide mediante titulación. Este estudio propone la Espectroscopía de Impedancia Electroquímica (EIS) como una alternativa rápida y no destructiva para determinar la acidez en aceites de oliva. Se prepararon emulsiones usando una solución hidroalcohólica y se empleó el método de adición estándar añadiendo ácido oleico. La conductividad eléctrica se obtuvo a partir medidas de impedancia en un rango de frecuencias de 0.4 Hz a 400 KHz. Mediante un ajuste no lineal de conductividad versus porcentaje de ácido oleico se determinaron acideces de 0,30% para aceite de oliva virgen extra y 0,19% para aceite de oliva refinado. Todas las mediciones se han realizado por triplicado. además, un circuito eléctrico equivalente modeló los datos, mostrando que los efectos de adsorción dominan a bajas frecuencias.

PALABRAS CLAVE: *Acidez del aceite de oliva; Ácido oleico; Conductividad eléctrica; Electroquímica; Emulsiones; Espectroscopía de impedancia.*

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1. INTRODUCTION

Olive oil, extracted from the fruit of *Olea Europaea* (belonging to the Oleaceae family), is a prominent vegetable oil primarily used in culinary applications. It holds significant dietary importance and is highly regarded for its beneficial effects on human health, largely attributable to its high content of oleic acid and polyphenols (Tulipani *et al*., 2012). Approximately 90% of global olive oil production originates from the Mediterranean basin, with European countries accounting for 82% of this output (Carbonari *et al*., 2013).

Evidence shows that consuming between 8 and 40 g of EVOO daily has protective effects on cardiovascular disease, can prevent the onset of type 2 diabetes, and can increase HDL cholesterol levels. Regarding cancer, the effects evaluated include those found from the phenolic compounds hydroxytyrosol (HT) and oleocanthal, which have demonstrated a protective effect in some types of cancer, such as skin and breast cancer. In neurodegenerative diseases, it was observed that a daily consumption of 50 g of EVOO has an inhibitory effect on neuronal degeneration, attributed to its phenolic compounds, such as oleuropein and HT (Beatriz *et al*., 2023).

Acidity is a critical parameter in assessing olive oil quality, expressed as the concentration of free fatty acids (unesterified to triglyceride molecules), measured in grams of oleic acid per 100 g of oil. This parameter is directly influenced by the quality and freshness of the olives used. Extra virgin olive oil (EVOO) represents the highest quality grade, characterized by an acidity level below 0.8%. Virgin olive oil typically exhibits an acidity between 0.8 and 2%, while lampante olive oil has an acidity exceeding 2% (European Commission, 1991).

Prior research has explored various techniques for olive oil characterization. One study characterized ten different vegetable oils in the frequency range of 100 Hz to 1 MHz by determining the dielectric constant, e_r. This e_r value is influenced by the fatty acid composition and moisture content of the oil, remaining relatively constant between 100 Hz and 500 kHz, but decreasing with frequency from 500 kHz to 1 MHz (Lizhi, *et al*., 2007).

Near-Infrared (NIR) spectroscopy has been employed to estimate acidity and peroxide value through the analysis of transmission spectra in the wavenumber range of 4541 to 11726 cm^{-1}. NIR spectroscopy has also proven effective in detecting the adulteration of extra virgin olive oil with lower-quality products (Ozdemir *et al*., 2007).

Spectral nephelometry, combining absorption spectroscopy and nephelometry, can generate "fingerprints" of olive oil, enabling the distinction of products from different geographical origins (Mignani *et al*., 2003).

Microwave dielectric spectroscopy is proposed as a technique for the characterization of vegetable oils. For monitoring the quality of vegetable oils, four types of olive oil (various seed oils, extra virgin, lampante, and refined) with different acidity levels (0.3, 1.2, 1.6, and 4.0%, respectively) were included. By measuring the relaxation frequency, it could be possible to discriminate between different types of oil. The optimal frequency range for minimization in the case of the oils was 0–1 GHz; this range adequately includes the main dielectric response of the oils. (Cataldo *et al*., 2009).

Baldo *et al*. (2019) presented a rapid method for detecting acidity in extra virgin olive oil which combines voltametric measurements (using a platinum microelectrode and an ionic liquid) with multivariate Partial Least Squares (PLS) regression. The model, developed and validated with oils of known acidity, predicts free acidity within 5% of official titration methods, demonstrating its accuracy and practical potential for quality control.

Electrochemical sensors, sensor arrays, and biosensors, combined with chemometric tools, have made significant advancements recently and are widely used for the qualitative and quantitative analysis of olive oil. Olive oil is an important natural product rich in bioactive compounds with nutritional and therapeutic benefits, making its quality essential for both consumers and distributors. This study examines recent progress in using electrochemical (bio)sensor-based devices to evaluate these bioactive compounds in olive oil. It discusses the main advantages and limitations regarding sensor construction, targeted compounds, calculation models, and results, aiming to guide future development of a portable, practical, and rapid device for assessing virgin olive oil quality throughout the manufacturing process (Bounegru *et al*., 2021).

Electrochemical Impedance Spectroscopy (EIS) is a valuable technique for measuring sample impedance and determining electrical conductivity. Impedance spectra can provide essential physicochemical parameters for characterizing and classifying food products according to health authority quality standards. EIS offers advantages of speed, cost-effectiveness, and immediate results. Virgin olive oil contains a limited quantity

(1-2%) of minor polar components, including free fatty acids, monoacylglycerols, diacylglycerols, di- and triterpene aliphatic alcohols, sterols, and hydrophilic antioxidants. These components are soluble in a hydrophilic solution. Consequently, olive oil emulsions with a hydro-alcoholic solution have been utilized in experimental setups.

A recent study evaluated the application of electrochemical impedance spectroscopy to identify the adulteration of extra virgin olive oil with canola and sunflower oils. The results demonstrated that the approach could successfully classify the non-adulterated samples in a separate cluster in relation to the adulterated samples. An empirical equivalent electrical circuit parameter has suggested that the method is able to identify adulteration with 2% of the adopted edible oils and to provide a clear distinction between the two adulterants (De Magalhaes *et al*., 2024).

Previous studies have indicated that extra virgin olive oils can be identified by establishing a conductance threshold σ_m < 2,75 µS/cm, corresponding to an acidity below 0.8%. Conversely, samples σ_m > 3.25 µS/cm are characterized by acidity exceeding 0.8%, while samples within the conductivity range of 2.75-3.25 µS/cm have acidity values close to 0.8% (0.68 to 0.85%) (Grossi *et al*., 2014).

Grossi *et al*. (2014) introduced a novel technique for the rapid measurement of acidity in olive oil based on electrical conductance. They compared two different olive oil emulsions for these measurements: one based on a hydro-alcoholic solution (60% ethanol, 40% distilled water) and another with distilled water. Their findings demonstrated a strong correlation between the electrical conductance of the hydro-alcoholic emulsion and olive oil acidity, allowing for accurate estimations.

In another work, (Grossi *et al*., 2022) presented an alternative technique for fast and accurate acidity determination by automatically measuring the electrical conductance of a hydro-alcoholic emulsion of the olive oil sample. They developed a portable, battery-operated sensor system capable of measuring acidity in approximately 30 seconds.

The EIS presents significant advantages over traditional analytical methods such as Gas Chromatography (GC), Liquid Chromatography (LC), and advanced techniques like Nuclear Magnetic Resonance (NMR) and infrared-related methods (FTIR/NIR), especially in terms of efficiency, cost, and the nature of the assay.

Although chromatographic methods can detect trace components (down to parts per trillion), they are generally costly, require prior sample preparation, and involve longer processing times to obtain results. Similarly, methods such as magnetic resonance imaging or Near-Infrared Spectroscopy (NIR, related to FTIR) are known for their high precision, but their main drawback is that they require expensive instrumentation. EIS has a wide range of applications in the food industry. It is used to prevent unfair competition and false labeling, and is useful for characterizing and classifying foods according to quality standards. EIS is used for the rapid and accurate measurement of olive oil acidity, which is important because traditional laboratory methods cannot be used at production sites. In addition, it offers a rapid method for the detection, identification, quantification, and monitoring of bacterial content in the food industry. (Caicedo *et al*., 2020). EIS stands out as a detection technology that offers fast and economical results through a non-invasive and non-destructive process.

In this study, we employed the standard addition method to determine the acidity of two olive oil samples. This involved preparing standard emulsions of olive oil with a hydro-alcoholic solution and adding known percentages of oleic acid. Additionally, we identified the equivalent electrical circuit that best models the experimental data across the entire frequency range investigated.

2. MATERIALS AND METHODS

2.1. Materials

Electrical characterization was performed using a CORRTEST CS350M potentiostat/galvanostat. A sinusoidal signal with an amplitude of 100 mV was applied, with logarithmically spaced frequencies ranging from 0.4 Hz to 400 KHz. A two-electrode configuration was employed: the working electrode (WE) was connected to one plate of the cell acting as the anode, while the counter electrode (CE) and reference electrode (RE) were connected to the other cell plate, acting as the cathode. Conductivity calculations were performed

using Equation (2). A computer equipped with analysis software displayed the impedance modulus and phase in real-time as a function of frequency. The measurement cell consisted of a rectangular Teflon block with a cooling system. Inside were two flat, parallel stainless-steel plates, each measuring 5.2 cm x 10.5 cm, separated by 0.55 cm. The cell had a volume of 35 ml and a capacitance of 8.8 pF.

2.2. Methods

According to Ohm's law, complex impedance of any material being stimulated by an alternating potential $V_{(t)} = V_0 exp(j\omega t)$ is expressed as:

$$Z^* = \frac{V_{(t)}}{I_{(t)}} = \frac{V_0 e^{-j\omega t}}{I_0 e^{-j(\omega t+\phi)}} = |Z|e^{j\phi} = |Z|(\cos\phi + j\sin\phi) = Z' + jZ'' \quad (1)$$

Where $\omega = 2pf$, Φ the phase angle between current and voltage and $j = \sqrt{-1}$; Z' and Z'' are the real and imaginary parts of impedance.

The complex conductivity is related to the complex permittivity, and the latter to the impedance, according to the following equations.

$$\sigma' = \frac{\varepsilon_0 z'}{|z|^2 C_0} \quad (2)$$

In equation (2), (Kremer and Schonhals., 2003) C_0 is the geometric capacitance of the capacitive sensor, ε_0 is the vacuum permittivity, σ' is the real part of conductivity.

EIS has been established as a simple and effective technique in the study of the electrical properties of materials (Grossi et al., 2021). It consists of applying an external alternate voltage $V = V_0 e^{(j\omega t)}$ to a test sample, thus generating a current that is captured by a sensor. With both quantities, complex impedance (Z^*) is determined (Lvovich., 2012), In turn, the permittivity and conductivity of the samples can be obtained (Jorge *et al*., 2018).

The electrical conductivity of the emulsion is primarily attributed to H+ ions resulting from the ionization of free fatty acids (RCOOH) present in 100 g of oil, as these ions exhibit significantly higher mobility compared to the RCOO- group. Considering c as the percentage of olive oil acidity, expressed as the number of RCOOH molecules in 100 g of oil, the electrical conductivity model of the emulsion as a function of olive oil acidity can be approximated as:

$$\sigma_m = \Delta\sigma_{mo} + \sigma_{m,RCOOH} = k_1 + k_2\sqrt{c} - K_3\sqrt[4]{c^3} \quad (3)$$

where

$\Delta\sigma_{mo}$ represents the variation in electrical conductance due to oil compounds other than free fatty acids (Grossi *et al*., 2014)

To establish the functional relationship between olive oil acidity and the electrical conductance of the emulsion, Equation (3), a calibration curve was developed using reference standards. Pure oleic acid was selected as the primary chemical standard, as it is the main free fatty acid present in olive oil that contributes to acidity. A series of standard emulsions with known concentrations of oleic acid were prepared, covering the expected acidity range in extra virgin olive oil (EVOO). Electrical conductance was measured for each standard. These experimental data were used as the basis for model fitting. The calibration procedure consisted of performing the nonlinear fitting of Equation (3) to the experimental data of the standard oleic acid emulsions, using the least squares method. The estimated acidity percentage is then determined by solving the non-linear equation, substituting the conductivity value of the emulsions without added oleic acid. All conductance measurements were performed in triplicate (n=3) for each sample. The results are reported as the mean value with the standard deviation as the measure of precision.

2.3. Preparation of olive oil and hydro-alcoholic emulsions

Two commercial olive oil samples with unknown acidity percentages were used: one extra virgin olive oil and one refined olive oil. To investigate the correlation between acidity and electrical conductivity, emulsions were prepared using these oils and a hydro-alcoholic solution (60% ethanol and 40% distilled water). Artificially varied olive oil samples, differing only in acidity, were created by adding known concentrations of oleic acid to both types of olive oil.

A 17.6 g sample of olive oil was initially prepared, to which 2.4 g of oleic acid were added, resulting in a 12% added-acidity concentration in 20 g of sample. Subsequent samples were prepared by dilution using the mass conservation equation: $C_1 m_1 = C_2 m_2$, where C_1, m_1 represent initial concentration and mass, and C_2 and m_2 represent final concentration and mass. Each new sample served as the "mother" sample for the subsequent dilution. This process yielded samples with added oleic acid concentrations of 10, 8, 6, 4, 2, 1, 0.50, and 0.35% for the extra virgin olive oil, and 10, 8, 6, 4, 2, 1, 0.50, and 0.25% for the refined olive oil.

Emulsions were created using a ratio of 15 ml of hydro-alcoholic solution to 1 ml of the olive oil sample with the added oleic acid percentage. Given the 35 ml cell volume, each emulsion was specifically prepared with 32.5 ml of hydro-alcoholic solution and 2.5 ml of olive oil. The samples were agitated for 1 minute to form the emulsion and their electrical characteristics were immediately measured as a function of frequency.

3. RESULTS AND DISCUSSION

3.1. Bode diagram and conductivity at different frequencies

The analysis of the phase angle (ϕ) as function of frequency provides critical insights into the dielectric and conductive properties of the investigated samples.

The phase behaves similarly for the emulsions created with the two olive oils. In the low-frequency range (0.4 to 40 Hz), the phase angle exhibits significant deviation from ideal capacitive behavior, starting at approximately -20° and moving toward 0°. This behavior signifies a regime dominated by capacitive and interfacial phenomena occurring at the electrode-emulsion interface, typically attributed to adsorption processes. Due to this non-ideal response, the system is better modeled by a Constant Phase Element (CPE) rather than a pure capacitor. In the Mid-Frequency Region (40 Hz to 1 KHz) the phase angle remains essentially constant and very close to 0°, this is the signature of a purely resisant element. This response is dominated by the bulk solution resistance of the hydro-alcoholic emulsions. Above 1 KHz, the phase angle rapidly transitions toward more negative values, peaking at around -60°. The strong negative shift in phase is characteristic of the capacitive behavior of the electrochemical double layer Cdl. At these high frequencies, the double layer impedance becomes the dominant factor, reflecting the rapid charge/discharge cycles at the electrode surface.

Figures 1a and 1b illustrate that the impedance modulus decreases as the oleic acid concentration increases in both the extra virgin and refined olive oil emulsion. This is attributed to the release of a greater number of H+ ions from the oleic acid molecules at higher concentrations, with the 12 and 10% emulsions exhibiting the lowest impedance modulus at low frequencies. For high frequencies, the impedance modulus decreases with increasing frequency. All measurements have been carried out in triplicate and both mean value and standard deviation have been calculated.

The electrical conductivity plots shown in Figures 2 and 3 were derived from the complex impedance measurements as a function of frequency, utilizing Equation (2). Figure 2a presents the conductivity as a function of frequency for the hydro-alcoholic solution and distilled water, showing that the hydro-alcoholic solution possesses lower conductivity than distilled water due to the low conductivity of ethanol. Figure 2b illustrates the conductivity of the emulsions prepared with the two olive oils (without added oleic acid) and the hydro-alcoholic solution, where the extra virgin olive oil emulsion exhibits the highest conductivity.

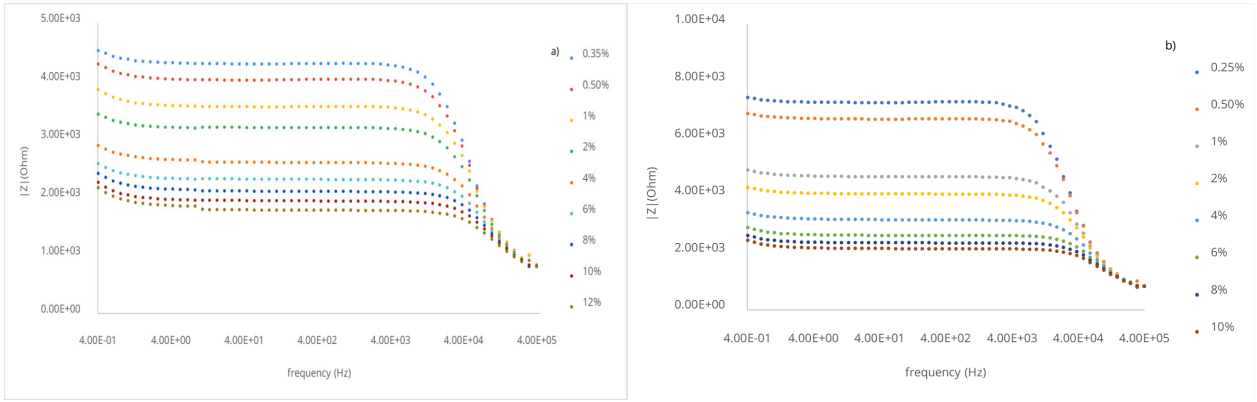

Figure 1. a): Impedance modulus as a function of frequency of extra virgin olive oil emulsions for all percentages of added oleic acid. b): Impedance modulus as a function of frequency of refined olive oil emulsions for all percentages of added oleic acid b)

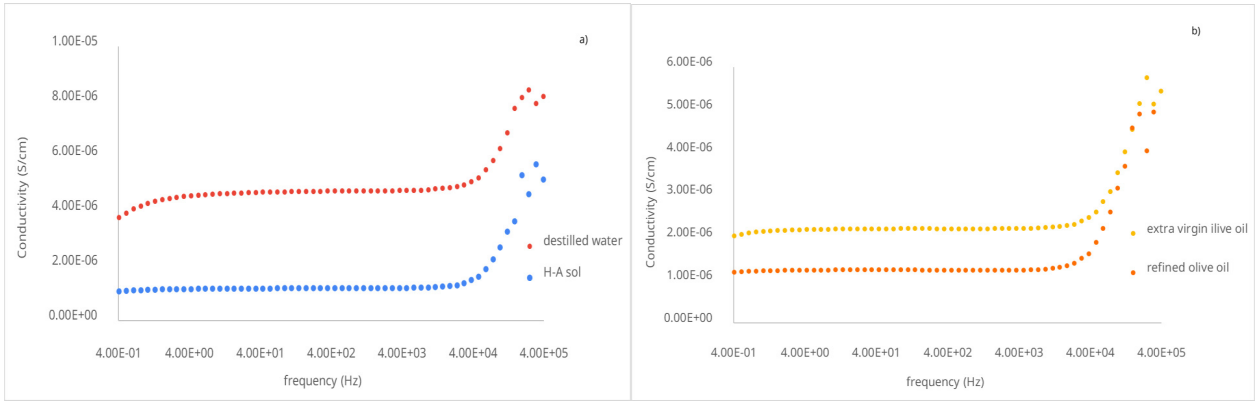

Figure 2. a): Conductivity as a function of the frequency of the hydro-alcoholic solution and distilled water. b): Conductivity as a function of the frequency of extra virgin olive oil and refined olive oil without oleic acid concentration added and the hydro-alcoholic solution.

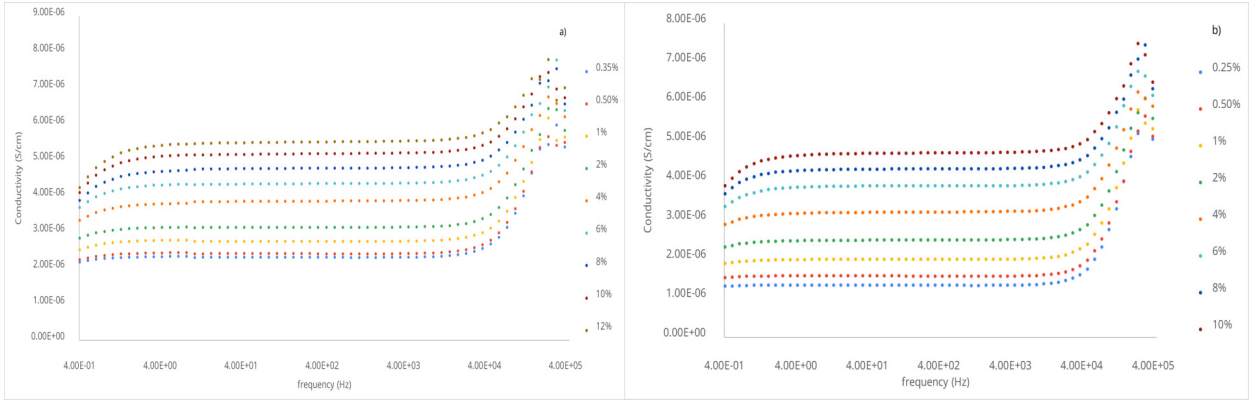

Figure 3. a): Conductivity as a function of frequency of extra virgin olive oil for all added-oleic acid concentrations. b): Conductivity as a function of frequency of refined olive oil for all added-oleic acid concentrations.

Figures 3a and 3b display the conductivity as a function of frequency for the extra virgin and refined olive oil emulsions, respectively. It is evident that conductivity increases with increasing oleic acid concentration in the emulsions. This phenomenon is attributed to oleic acid, a long-chain carboxylic acid, which donates a proton to water via its carboxyl group, thereby contributing to the electrical conductivity of the emulsions. Higher oleic acid concentrations result in a greater quantity of H+ ions donated to the aqueous solution, thus enhancing emulsion conductivity. The electrical conductivity of the samples remains nearly constant over

a broad frequency range from 1 Hz to approximately 20 kHz. At high frequencies, electrical conductivity increases with increasing frequency.

3.2. Determination of olive oil acidity

The model describes the electrical conductance s of the emulsion as a function of olive oil acidity c. It is built upon the dissociation of free fatty acids (RCOOH), which are classified as weak Brønsted-Lowry electrolytes. The resulting conductivity is primarily attributed to the high mobility of H+ ions. To accurately model this relationship, the conductance's proportionality to acidity and molar conductivity is refined using Ostwald's Dilution Law to determine the degree of dissociation. Furthermore, Kohlrausch's Law is applied as a first approximation to model the concentration's effect on ionic mobility. The final total electrical conductance is expressed in Equation (3) as a function of acidity c.

To determine the unknown acidity of the extra virgin and refined olive oils, the standard addition method was employed. The electrical conductivity values for the emulsions, measured at a fixed frequency of 1 KHz for each oleic acid concentration, were plotted as shown in Figures 4a and 4b. All measurements have been carried out in triplicate and both mean value and standard deviation have been calculated. The conductivity of the emulsion prepared without added oleic acid was 2.24 µS/cm for the extra virgin olive oil emulsion and 1.25 µS/cm for the refined olive oil emulsion at 1 KHz, consistent with Figure 2b.

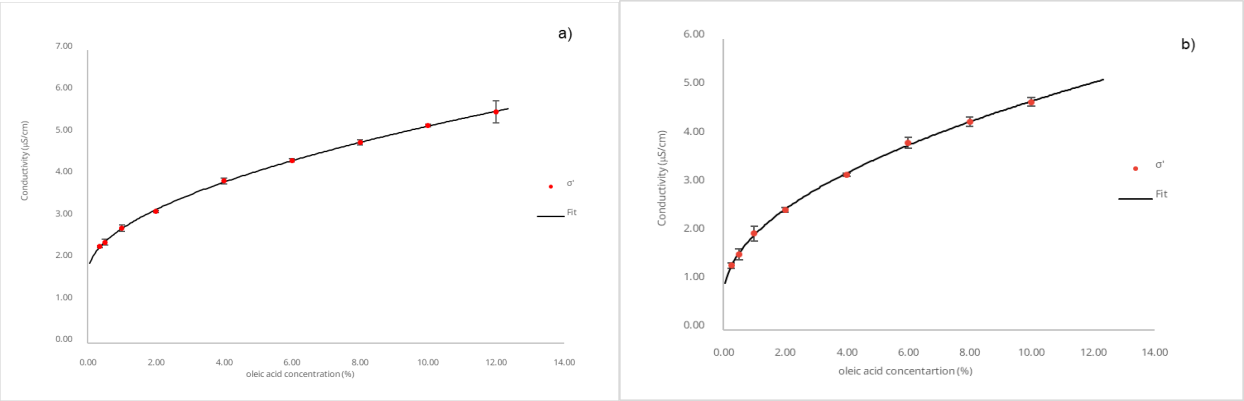

Figure 4. a): Conductivity adjustment curve as a function of oleic acid concentration for extra virgin olive oil. b): Conductivity adjustment curve as a function of oleic acid concentration for refined olive oil.

The experimental data were fitted using the XLSTAT statistical function in Excel, employing Equation (3) with non-linear regression, to obtain the constants k_1, k_2, and k_3. To quantify the uncertainty of the fit and the predictability of the method, the software calculated the Confidence Intervals (CI) and Prediction Intervals (PI) at 95% for each standard concentration point c, the narrow 95% Confidence Intervals (CI) confirm the statistical robustness of the non-linear fit, while the Prediction Intervals (PI) validate the high practical precision and applicability of the EIS model for predicting acidity in unknown samples. The proximity of the residuals to zero (< 0.05 mS/cm) and the fact that all measured conductance values fall within the Prediction Interval (PI) limits, demonstrate that Equation (3) is a statistically valid predictor of the conductivity across the studied acidity range and that the method offers an acceptable error level for quality discrimination in an industrial quality-control setting.

This resulted in the following equations for electrical conductivity as a function of added oleic acid concentration:

For emulsions prepared with extra virgin olive oil:

$$\sigma = 1.684 + 0.809\sqrt{\%C} + 0.070\sqrt[4]{\%C^3} \quad (4)$$

And for emulsions prepared with refined olive oil:

$$\sigma = 0.670 + 1.300\sqrt{\%C} - 0.011\sqrt[4]{\%C^3} \quad (5)$$

The absolute errors found in the fitting for the constants are less than 10%. The goodness-of-fit was evaluated using the Adjusted Coefficient of Determination R^2 and the Root Mean Square Error (RMSE). An $R^2 > 0.99$ was obtained for both curves, confirming that Equation (3) adequately models the relationship between conductance and acidity. The low RMSE value (0.024 mS/cm) confirms the minimal dispersion of the data around the fitted curve.

To determine the acidity percentage of the extra virgin and refined olive oils, the conductivity values of the emulsions without added oleic acid (2.24 µS/cm and 1.25 µS/cm, respectively) were substituted into Equations (4) and (5), solving for %C, using the Goal Seek function in Excel yielded acidity values of 0.30% for extra virgin olive oil and 0.19% for refined olive oil. These percentages showed excellent agreement with the results obtained by the titration method.

3.3. Electrical circuit model

Based on a typical electrical circuit model for conductive and ionic aqueous solutions, a fit was determined for the experimental data of both olive oil emulsions (with and without added oleic acid) using the CS Analysis software integrated into the CORRTEST CS350M potentiostat. The electrical circuit model that best fits the experimental points for high and intermediate frequencies consists of a series resistance (Rs) in parallel with an RC circuit (R_{bulk} and C_{bulk}), as shown in Figure 5. Rs represents the resistance of the emulsion at high frequencies where the system exhibits purely resistive behavior, and its value is typically low. C_{bulk} represents the system's capacitance, and R_{bulk} is the emulsion's resistance at intermediate frequencies. The sum of Rs and R_{bulk} constitutes the total impedance of the system at frequencies of around 200 Hz. The Nyquist diagram for this model presents a semicircle, as seen in Figures 6a and 6b.

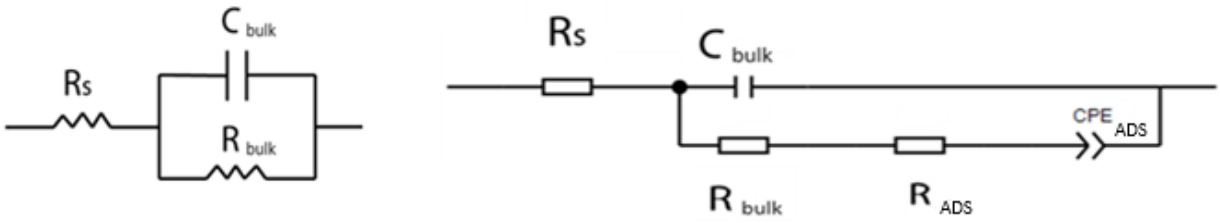

Figure 5. Circuit model for high and intermediate frequencies.

At low frequencies, adsorption processes dominate, characterized by a straight line in the Nyquist diagram, as observed in Figure 6. At these frequencies, the fit in the Nyquist diagram can be modeled by a sorption impedance dependent on the charge associated with specific adsorption and/or desorption of species at the interface, primarily in the compact portion of the double layer for low frequencies. The adsorption process results in an additional "pseudocapacitive effect" represented as $C_{ADS}^{-1} = C_{ADSOHP}^{-1} + C_{ADSIHP}^{-1}$, where C_{ADSIHP} and C_{ADSOHP} are the adsorption capacitances of the inner and outer Helmholtz layers. This low-frequency impedance can be modeled by a series combination of a current-limiting resistance R_{ADS} with a Constant Phase Element (CPE_{ADS}) (Lvovich., 2012). Figure 5 illustrates the complete circuit model for the system across the entire frequency range.

Tables 1 and 2 present the values obtained by fitting the experimental data of the prepared emulsions with both olive oils to the proposed equivalent circuits using the CS Analysis software. The adjustment program provides the percentage error in each parameter.

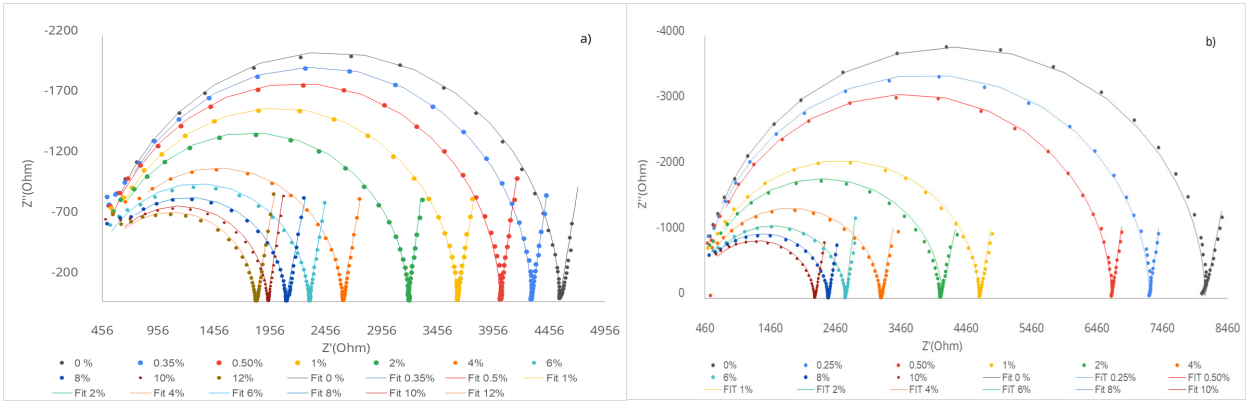

Figure 6. Nyquist diagrams of extra virgin olive oil emulsions and fitting according to the proposed circuit a) Nyquist diagrams of extra virgin olive oil emulsions and Nyquist diagrams of refined olive oil emulsions b)

TABLE 1. Element values and errors of the circuit which models the system obtained from the adjustment of the experimental data of the emulsions created with extra virgin olive oil.

Oleic acid %	R_s (Ohm)	C_{bulk} (nF)	R_{bulk} (Ohm)	R_{ADS} (Ohm)	CPE_{ADS}(mF)	CPE_α
0	419 ± 7	1.091 ± 0.007	3950 ± 9	178 ± 9	0.452 ± 0.007	0.888 ± 0.009
0.35	416 ± 4	1.122 ± 0.007	3700 ± 6	179 ± 6	0.488 ± 0.013	0.899 ± 0.013
0.5	402 ± 9	1.052 ± 0.013	3421 ± 15	191 ± 14	0.415 ± 0.024	0.907 ± 0.027
1	422 ± 5	1.112 ± 0.007	3000 ± 7	205 ± 7	0.516 ± 0.018	0.883 ± 0.016
2	396 ± 5	1.103 ± 0.007	2625 ± 7	171 ± 6	0.501 ± 0.015	0.913 ± 0.014
4	390 ± 3	1.132 ± 0.008	2000 ± 3	209 ± 3	0.517 ± 0.009	0.875 ± 0.007
6	347 ± 6	0.995 ± 0.007	1700 ± 8	252 ± 8	0.536 ± 0.023	0.885 ± 0.020
8	367 ± 3	1.113 ± 0.008	1500 ± 4	227 ± 4	0.519 ± 0.009	0.866 ± 0.008
10	354 ± 3	1.063 ± 0.009	1400 ± 4	182 ± 4	0.489 ± 0.004	0.901 ± 0.005
12	344 ± 3	1.072 ± 0.010	1300 ± 4	183 ± 4	0.498 ± 0.010	0.877 ± 0.009

The adjustment program provides the percentage error in each parameter. Here it is represented as absolute error
Rs: resistance of the emulsion at high frequencies, C_{Bulk}: system's capacitance, R_{Bulk}: emulsion's resistance at intermediate frequencies, R_{ADS}: adsorption process current-limiting resistance, CPE_{ADS}: adsorption process Constant Phase Element, CPE_α: exponent of the CPE

TABLE 2. Element values and errors of the circuit which models the system obtained from the adjustment of the experimental data of the emulsions created with refined olive oil.

Oleic acid %	R_s (Ohm)	C_{bulk} (nF)	R_{bulk} (Ohm)	R_{ADS} (Ohm)	CPE_{ADS} (mF)	CPE_α
0	443 ± 7	1.091 ± 0.005	7480 ± 16	184 ± 11	0.399 ± 0.005	0.881 ± 0.008
0.25	442 ± 8	1.113 ± 0.006	6150 ± 13	669 ± 13	0.489 ± 0.009	0.913 ± 0.011
0.5	457 ± 5	1.124 ± 0.005	5850 ± 8	372 ± 8	0.481 ± 0.005	0.913 ± 0.008
1	445 ± 5	1.132 ± 0.006	4050 ± 7	159 ± 7	0.495 ± 0.006	0.892 ± 0.007
2	433 ± 5	1.141 ± 0.008	3575 ± 6	78 ± 6	0.500 ± 0.005	0.884 ± 0.006
4	397 ± 7	1.062 ± 0.015	2618 ± 9	130 ± 9	0.492 ± 0.007	0.881 ± 0.009
6	401 ± 4	1.124 ± 0.009	2153 ± 5	54 ± 5	0.432 ± 0.004	0.922 ± 0.004
8	366 ± 5	1.061 ± 0.010	1919 ± 6	51 ± 6	0.530 ± 0.016	0.882 ± 0014
10	378 ± 4	1.091 ± 0.011	1600 ± 5	158 ± 5	0.521 ± .014	0.871 ± 0.012

The adjustment program provides the percentage error in each parameter, Here it is represented as absolute error
Rs: resistance of the emulsion at high frequencies, C_{Bulk}: system's capacitance, R_{Bulk}: emulsion's resistance at intermediate frequencies, R_{ADS}: adsorption process current-limiting resistance, CPE_{ADS}: adsorption process Constant Phase Element, CPE_α: exponent of the CPE

It is observed that Rs is relatively low, ranging between 300 Ohms and 450 Ohms, showing no significant variation with increasing oleic acid concentration. Similarly, C_{bulk} exhibits values between 1.09 μF and 1.16 μF, also without significant variation with increasing oleic acid concentration, representing the emulsion's capacitance.

R_{bulk} decreases with increasing oleic acid concentration due to the higher concentration of H+ ions released from oleic acid in the emulsion, leading to increased conductivity, as demonstrated in the graphs in Figures 5a and 5b. As observed from Tables 2 and 3, CPE_{ADS} is in the range of 0.4 mF to 0.5 mF with an alpha between 0.87 and 0.91, and R_{ADS} is between 50 and 200 ohms for all prepared emulsions.

A fundamental limitation of the EIS methodology lies in data processing and interpretation, as impedance data, in theory, admit multiple alternative circuit topologies that can be fitted to the same experimental data. This mandates that the model selection must be firmly supported by the physical and electrochemical justification of the phenomena (solution resistance, bulk resistance, double-layer capacitance and adsorption). The main challenge of the technique is the interference from compounds other than free fatty acids, such as secondary oxidation compounds, polar compounds (phenolics), temperature and the oil's storage condition. It must be guaranteed that the measurements can be extrapolated to the food industry, since, under real conditions, it is difficult to control all variables of the production process, which could affect the validity of the model used.

4. CONCLUSIONS

The impedance modulus of the emulsions, hydro-alcoholic solution, and distilled water, as a function of frequency, decreases with increasing frequency in the low-frequency range. For intermediate frequencies, the impedance modulus remains constant, and at high frequencies, it decreases with increasing frequency. For the prepared olive oil emulsions, the impedance modulus decreases with increasing oleic acid concentration due to the increased quantity of H+ ions originating from the dissociation of the free fatty acid molecules present in the emulsion.

The Bode diagrams of the phase angle at low frequencies exhibit a decrease as frequency increases. At intermediate frequencies, the angle tends towards zero, indicating purely resistant behavior. At high frequencies, the phase tends towards angles between -45° and -60°. This behavior is consistently observed across all emulsions of both olive oils, the hydro-alcoholic solution, and distilled water.

Electrical conductivity demonstrated an almost constant behavior in the low and intermediate frequency ranges, and a continuous increase as frequency increased, for all emulsions of both olive oils, distilled water, and the hydro-alcoholic solution. The conductivity values for the prepared emulsions of both oils increased with increasing added-oleic acid concentration. This is attributed to the dissociation of the RCOOH molecule of oleic acid, contributing more H+ ions, and consequently leading to higher conductivity. The electrical conductivity as a function of oleic acid percentages exhibits a non-linear behavior consistent with the existing theoretical model. The experimental data were well-fitted to the model, demonstrating good agreement between experimental points and the performed fit.

By solving the non-linear mathematical expression obtained from the fit, and utilizing the electrical conductivity values for the emulsions without added oleic acid, an acidity of 0.31% (corresponding to a conductivity of 2.25 μS/cm) was determined for extra virgin olive oil, and an acidity of 0.20% (corresponding to a conductivity of 1.25 μS/cm) for refined olive oil. These obtained percentages are in agreement with those estimated by the titration method.

The experimental data from the Nyquist diagrams were fitted using the CS Analysis software of the CORRTEST equipment according to the proposed electrical model, consisting of $R_{sol}(C_{bulk}(R_{bulk}R_{ads}CPE_{ads}))$. This allowed for the determination of values for each element of the circuit for the different emulsions created. At high and intermediate frequencies, the circuit represented by the series resistance Rs in parallel with an $R_{bulk}C_{bulk}$ circuit dominates, which is observed as a semicircle in the Nyquist diagram. At low frequencies, adsorption processes at the electrode surfaces dominate, modeled by a series circuit of a current-limiting resistance Rads and a CPEads, which appears as a straight line in the Nyquist diagram.

The method provides a rapid and non-destructive alternative to conventional chemical titration for determining olive oil acidity. Unlike traditional methods that demand costly instrumentation, specialized

personnel, and extensive sample preparation, the EIS approach is inherently simple, fast, and easy to use. This makes it highly suitable for industrial quality control and for real-time monitoring applications in processing and storage plants, allowing for immediate decision-making regarding batch quality and authenticity. Due to the simplicity of the technique, it is possible to develop capacitive sensors that adapt to the particularities of industrial processes in olive oil production.

RESEARCH DATA POLICY

The data underlying this article will be shared on reasonable request to the corresponding author.

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DECLARATION OF COMPETING INTEREST

The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

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AUTHORSHIP CONTRIBUTION STATEMENT

J. Jorge: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Writing – original draft, Writing – review & editing.

J. D. Martinez: Conceptualization, Formal analysis, Investigation, Methodology, Writing – review & editing.

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