Article

A Portable Battery-Operated Sensor System for Simple and Rapid Assessment of Virgin Olive Oil Quality Grade [†]

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Abstract: Virgin olive oil quality is assessed by chemical as well as sensory analysis. Two of the most important parameters that define the quality of virgin olive oils are the free acidity and the peroxide index. These chemical parameters are usually determined by manual titration procedures that must be carried out in a laboratory by trained personnel. In this paper, a portable sensor system to support the quality grade assessment of virgin olive oil is presented. The system is battery operated and characterized by small dimensions, light weight and quick measurement response (about 30 s). The working principle is based on the measurement of the electrical conductance of an emulsion between a chemical reagent and the olive oil sample. Two different chemical reagents have been investigated: (1) a hydro-alcoholic solution (HAS), made of 60% ethanol and 40% distilled water; (2) 100% distilled water (DW). Tests have been carried out on a set of 40 olive oil samples. The results have shown how, for most of the fresh virgin olive oil samples (31 samples out of 40), the free acidity can be estimated with good accuracy from the electrical conductance of the emulsion using HAS as the reagent. In the case of the full set of samples, the emulsion electrical conductance, using HAS as the reagent, is a function of both the sample free acidity as well as the compounds produced by oil oxidation, and a compensation method based on the measured electrical conductance, using DW as the reagent, has been introduced to improve the accuracy in the estimated free acidity. Tests have also been carried out on the full set of samples, using a k-nearest neighbors algorithm, to demonstrate the feasibility of olive oil classification according to the quality grade. The results have shown how measurements carried out using only the HAS reagent provide better classification accuracy than measurements carried out using both the HAS and DW reagents. The proposed system can be a low-cost alternative to standard laboratory analyses to evaluate the quality grade of virgin olive oil.

Keywords: olive oil; free acidity; peroxide index; electrochemical sensors; portable systems; electrical conductance; in-situ measurements

1. Introduction

Olive oil is a vegetable lipid, highly appreciated for its beneficial effects on human health [1], mainly due to the presence of a high content of oleic acid and polyphenols [2]. Studies from the literature have shown how mortality from breast and colorectal cancer [3], as well as from coronary heart diseases [4], is lower in countries with high olive oil consumption.

Virgin olive oil quality is normally assessed by chemical as well as sensory analysis. Two of the most important parameters that define the quality of virgin olive oils are free acidity, defined as the amount of fatty acids no longer linked to their parent triglyceride

molecules, and the peroxide index, quantified as milliequivalents of active oxygen for a kg of oil [5]. Free acidity is mainly affected by the quality of the olives used to produce the oil, as well as the production process, while it is only marginally affected by the storage conditions. Peroxide index, on the other hand, is an indicator of the primary oxidation of the oil and it is strongly affected by the storage conditions. For example, if the oil is exposed to light and/or the storage temperature is not adequate, the oxidation process takes place and the peroxide index increases up to a maximum, then tends to decrease. The official techniques for measuring these two chemical parameters are manual titration procedures that must be carried out in an equipped laboratory by trained personnel [6].

Virgin olive oils are defined as the oils obtained from the fruit of the olive tree (*Olea europaea* L.), solely by mechanical or other physical means, under conditions, particularly thermal conditions, that do not lead to alterations in the oil, and which have not undergone any treatment other than washing, decantation, centrifugation and filtration [7]. In the European Union, virgin olive oils can be classified into three different quality categories, according to their chemical parameters and sensory characteristics. The top class category is Extra Virgin Olive Oil (EVOO) that must feature, among other compositional characteristics, a free acidity not higher than 0.8%, a peroxide index lower than 20 meq O_2/kg, fruitiness, and not present any organoleptic defects. Virgin Olive Oil (VOO) must feature a free acidity not higher than 2%, a peroxide index lower than 20 meq O_2/kg and can have organoleptic defects, only at a low level. Lampante olive oil (LOO) is characterized by a free acidity higher than 2% and/or a peroxide index higher than 20 meq O_2/kg, with substantial organoleptic defects and/or no fruitiness.

The reference titration procedures to measure free acidity and peroxide index in olive oil use toxic chemicals that must be disposed of according to regulations at the end of the measurement. Thus, in the case of small industrial environments, such as olive oil mills and small packaging centers, which cannot afford an internal laboratory for quality analysis, the olive oil samples to be tested must be shipped to an external laboratory, and this results in costs for the analysis and long response times. Thus, the development of simple, rapid and sustainable techniques for the analysis of quality grade of virgin olive oil is important to allow in-situ measurements directly in the agro-industrial environment.

Substantial research has been carried out in recent years towards the development of novel techniques for the analysis of vegetable oils that can be implemented, in the form of portable sensor systems, for in-the-field quality measurements.

Many proposed techniques are based on optical spectroscopy, where the sample optical absorbance is measured in a selected wavelength range and the measured optical spectrum is processed by chemometric analysis to estimate the parameters of interest. Abu-Khalaf and Hmidat, in 2020, presented a study where olive oil samples were investigated by Vis/NIR spectroscopy in the wavelength range 400–1100 nm, using a USB2000 + XR1-ES (Ocean Optics, Orlando, FL, USA) spectrometer and the measured data processed by Principal Component Analysis (PCA) and Partial Least Square (PLS) regression, to evaluate the oil quality grade [8]. Giussani et al., in 2021, investigated the feasibility of olive oil category classification, using two different portable NIR spectrometers, working in the wavelength range 740–1070 nm and 1350–2558 nm, respectively [9]. Zhang et al., in 2022, presented a method based on fluorescence spectroscopy to detect the adulteration of extra virgin olive oil with oils of lower quality (peanut and soybean oil) [10]. The oil sample was irradiated with an LED (peak wavelength 372 nm) and the fluorescence spectrum measured using an FX2000 (IdeaOptics, Shanghai, China) spectrometer. Measured data were processed by PCA and PLS to detect the oil adulteration. Techniques based on optical spectroscopy have the advantage of quick analysis, without the need of sample pre-treatment, but the optical spectrometer is an expensive instrument and there is the need of frequent re-calibration for different oil varieties. Thus, an alternative optical approach is to measure the optical properties only for a single or a low number of wavelengths. Grossi et al., in 2020 and 2022, proposed a novel technique to estimate the solid fat content in vegetable oils and fats that can be easily implemented in the form of a portable embedded system for in-the-field

analysis [11,12]. The sample under test is irradiated with an LED and the transmitted radiation is collected by a photodiode, during a thermal cycle. Results have shown how the proposed technique can estimate the oil solid fat content with good accuracy.

Another sensing approach is based on the measurement of the electrical characteristics of the sample under test. An example is represented by the quality evaluation of frying oil. Fendri et al., in 2019, presented an interdigital capacitive sensor for frying oil quality assessment and the results have shown a very good correlation ($R^2 = 0.97$) with reference methods [13]. A similar approach was used by Liu et al., in 2019, who developed a portable sensor system based on an STM32 microcontroller (ST Microelectronics) for frying oil quality measurement [14]. Electrochemical sensing can also be implemented by means of biosensors, where a bio-receptor is immobilized on the electrode to allow specific detection. Zappi et al., in 2020, proposed an electrochemical method for the classification of extra virgin olive oils in terms of the corresponding cultivar [15]. The system uses screen-printed disposable electrodes, functionalized with multi-walled carbon nanotubes and titanium oxide nanoparticles, to measure the oil electrical properties, using cyclic voltammetry. Radovanovic et al., in 2021, presented a micro-fluidic platform to detect olive oil in oil blends [16]. The sensor, based on a filter paper modified with multi-walled carbon nanotubes, detects the percentage of olive oil in oil blends by measuring the resistance in the frequency range 20 Hz–200 kHz. A prototype of the portable sensor system implementing this technique was also built.

Computer vision techniques have also been widely investigated in the field of vegetable oils analysis. Song et al., in 2020, presented a system based on the smartphone integrated camera to detect the adulteration of extra virgin olive oils with lower quality oils [17]. The system irradiates the oil sample with lights of different colours and records the video using the smartphone camera. The results have shown how the proposed technique achieves comparable accuracy to optical spectroscopy. Soto et al., in 2018, proposed a computer vision technique to evaluate the characteristics of olive fruit [18]. Prediction models were developed based on PLS and the results have shown how the features extracted from the olive images can be used to evaluate the quality parameters of the produced oil. Gila et al., in 2020, presented a computer vision system to estimate the moisture and insoluble impurities content in virgin olive oils [19]. The system is composed of a chamber, equipped with controlled lighting and a camera that takes pictures at a resolution of 800×600. The parameters of interest were estimated from the colour quantification of the samples. Results have shown a very good correlation ($R^2 = 0.996$) with the reference methods.

Furthermore, the application of electronic noses is extremely promising, i.e., devices composed of an array of sensors that can distinguish between different gases and odours, for the evaluation of the quality of vegetable oils. Abu-Khalaf, in 2021, presented an electronic nose to evaluate the quality category of virgin olive oils [20]. The system consists of eight different MOS sensors, sensitive to different types of gas. Measured data have been processed by PLS and the results have shown good correlation with chemical analysis. A similar system was proposed by Veloso et al., in 2021 [21]. In this case, nine different MOS sensors were used and the measured data were processed using principal component analysis (PCA) and linear discriminant analysis (LDA) to evaluate the perceived fruitiness intensity of extra virgin olive oils. Conrado et al., in 2021, presented an optoelectronic nose, realized in the form of a QR-code, for the identification of olive oil odour [22]. Measured data have been processed by chemometric analysis to provide a method to classify the olive oil category, with a response time of about 20 min.

In this paper, a battery-operated portable sensor system for supporting the quality analysis of olive oil is presented. The system uses non-toxic reagents for easy disposal at the end of the measurement and provides a response in about 30 s. It is designed with low-cost electronics and the cost of the system is estimated to be lower than USD 200. The power consumption during the measurement phase is about 60 mW and, considering an average of ten measurements every day, the three AAA 850 mAh batteries can provide more than 1.5 years of lifetime. The working principle is based on the measurement of

the electrical characteristics of an emulsion between a suitable reagent and the olive oil sample. The work represents a continuation of the research line presented in [23], where the battery-operated portable sensor system was presented for the first time and its ability to estimate the free acidity was validated on a set of 30 fresh olive oil samples. In the current work, tests have been carried out on a set of 40 virgin olive oils, composed of both fresh and oxidized samples. The results have shown that, in the case of oxidized samples, the accuracy in the estimated free acidity is reduced, due to the presence of oxidation compounds, and a compensation procedure has been proposed to improve the estimation accuracy. The results have also shown how the system can be used to classify the quality grade of virgin olive oils, based on the measurement of free acidity and peroxide index and, thus, represents a low-cost and accurate alternative to standard laboratory analysis, for in-situ olive oil quality assessment, in a real production environment.

2. Materials and Methods

2.1. Olive Oil Samples and Basic Quality Analytical Determinations

A total of 40 virgin olive oil samples of different geographical origins have been tested using the proposed portable electronic sensor system. The set is composed of 23 EVOO samples (57.5%), 5 VOO samples (12.5%) and 12 LOO samples (30%). The free acidity of the investigated samples ranges from 0.19% to 3.72%, while the peroxide index ranges from 5.81 meq O_2/kg to 96.05 meq O_2/kg. Overall, 31 olive oil samples (77.5%) are characterized by a peroxide index < 20 meq O_2/kg, while 9 olive oil samples (22.5%) are characterized by a peroxide index > 20 meq O_2/kg.

Each olive oil sample has been tested using the portable sensor system and the reference values for free acidity and peroxide index have been determined using the standard titration procedures presented in [6].

2.2. Portable Sensor System

A portable sensor system to evaluate the quality grade of olive oil samples has been designed and built. The system, shown in Figure 1a, is characterized by small size (11 cm × 15 cm × 5 cm), light weight (350 g), quick measurement response (30 s) and can be powered by a USB port or batteries (3 AAA alkaline batteries).

(a)   (b)
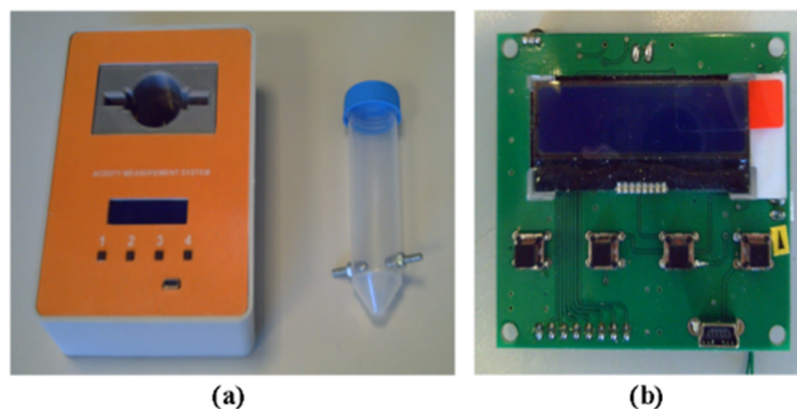
Figure 1. Photograph of the portable sensor system for olive oil quality grade detection (**a**) and designed electronic board (**b**).

The system measurement working principle is based on electrical impedance spectroscopy (EIS) [24], a popular technique used in different fields of application, such as bacterial concentration detection [25,26], food quality screening [27,28], human body analysis [29,30], detection of chemical compounds [31–33] and measurement of the corrosion rate of metallic structures in direct contact with acid electrolytes [34,35].

In voltammetric 2-electrode EIS measurements (i.e., the technique used in the proposed system), a sinewave test signal $V_{IN}(t)$ is applied to the electrodes in direct contact with the sample under test (SUT) and the current through the SUT $I_{OUT}(t)$ is measured:

$$V_{IN}(t) = V_{M,IN} \times \sin(\omega t) \tag{1}$$

$$I_{OUT}(t) = I_{M,OUT} \times \sin(\omega t + \varphi) \tag{2}$$

where $V_{M,IN}$ and $I_{M,OUT}$ are the amplitudes of the voltage test signal and the resulting current, respectively; ω is the test signal angular frequency ($\omega = 2\pi f$ with f the test signal frequency); φ is the phase shift between $V_{IN}(t)$ and $I_{OUT}(t)$. The SUT complex impedance $Z(j\omega)$ can be calculated as:

$$Z(j\omega) = \frac{V_{M,IN}}{I_{M,OUT}} \times e^{-j\varphi} = \frac{V_{M,IN}}{I_{M,OUT}} \times \cos(\varphi) - j \times \frac{V_{M,IN}}{I_{M,OUT}} \times \sin(\varphi) \tag{3}$$

The SUT complex impedance is measured on a range of frequencies and the corresponding impedance spectrum is fitted to an equivalent electrical circuit, whose parameters are used to estimate the characteristics of the investigated SUT.

In the case of our investigation, the SUT is represented by an emulsion between a reagent and the oil sample under test, placed inside a 50 mL Falcon vial modified with two cap-shaped stainless-steel electrodes (6 mm in diameter, spaced by 12 mm one from the other) that is also shown in Figure 1a (hereafter the sensor). Two different reagents have been investigated: (1) a hydro-alcoholic solution (HAS) (60% ethanol, 40% distilled water); (2) 100% distilled water (DW).

Preliminary measurements have been carried out using an experimental setup with benchtop instrumentation: thermal chamber Binder APT KB 53 to set the SUT temperature to a constant value of 23.5 °C and an impedance meter Agilent E4980A to characterize the SUT electrical properties in the frequency range 20 Hz–2 MHz. The results have shown how the emulsion can be modeled, from an electrical point of view, as the parallel of an electrical conductance G_m and an electrical capacitance C_m. The electrical capacitance C_m dominates the complex impedance at high frequency (>100 kHz) and is a function of the dielectric properties of the oil, not giving any information on the oil quality parameters (free acidity and peroxide index). The electrical conductance G_m, on the other hand, dominates the complex impedance at low frequency (<10 kHz) and can be effectively used to evaluate the olive oil quality parameters. In presence of the HAS as reagent, the free fatty acid molecule (which belongs to carboxylic acid group) dissociates and generates ions, producing an increase in the emulsion electrical conductance G_m that can be used to estimate the oil free acidity. However, when olive oil is oxidized, volatile and non-volatile compounds (such as aldehydes, ketones and hydrocarbons) are generated and the latter contributes to the increase in the emulsion electrical conductance G_m. In presence of DW as reagent, the emulsion electrical conductance is no more affected by the oil free acidity but it is still a function of the concentration of non-volatile compounds generated by secondary oxidation.

In the case of a portable sensor system for in-the-field measurements, the operative temperature cannot be considered constant, thus a compensation algorithm has been developed to calculate the emulsion electrical conductance at the target temperature of 23.5 °C ($G_{m,23.5°C}$) from the emulsion electrical conductance at the environmental temperature ($G_{m,T}$) and the value of the environmental temperature (T). The calculation of $G_{m,23.5°C}$ can be made with the following equation [23]:

$$G_{m,23.5°C} = \frac{G_{m,T} + 0.0026 \times (T - 23.5)}{1 + 0.0219 \times (T - 23.5)} \tag{4}$$

The portable sensor system has been designed to allow quick and easy evaluation of the olive oil quality grade in the field. All electrical measurements, data processing and data filing are carried out using the electronic board that is shown in Figure 1b. The

electronic board integrates an LCD screen to display the measurement results, four buttons for user interaction and a USB port that can be used to power the sensor system as well as to transfer the measured data to a PC for further data analysis. The core device of the electronic board is a microcontroller produced by ST Microelectronics (STM32L152RCT6A) which is responsible for the generation of the test signal, the acquisition and processing of all signals, and the control of all the electronic components of the board. Different commercial electronic devices are integrated on the electronic board to design the analogue circuits for the measurement of the emulsion electrical conductance. A schematic diagram of the measurement circuit is shown in Figure 2. The sinewave test signal $V_{IN}(t)$ is generated with the 12-bit DAC integrated in the microcontroller and applied to the sensor vial electrodes. The current through the electrodes $I_{OUT}(t)$ is converted to a voltage signal $V_{OUT}(t)$ using a trans-impedance amplifier with a feedback impedance composed of the parallel of a 470 kΩ resistor and a 120 pF capacitor. The sinewave voltage signals $V_{IN}(t)$ and $V_{OUT}(t)$ are acquired with the 12-bit ADC integrated in the microcontroller, processed to calculate the sinewave parameters and the emulsion electrical conductance. A temperature sensor (MCP9700A) is integrated in the electronic board to make measurements of environmental temperature to compensate variations in the emulsion electrical conductance with temperature.
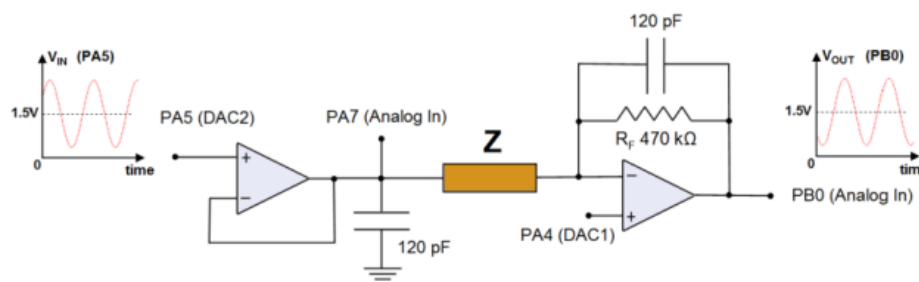
Figure 2. Schematic of the circuit for the measurement of the emulsion electrical conductance. Reprinted with permission from Ref. [23]. 2022 Elsevier.

The system's primary function is the measurement of the olive oil free acidity in fresh samples (i.e., samples with low oxidation, peroxide index < 20 meq O_2/kg). In this case the HAS is used as reagent. The measurement is carried out in the following steps:

- The HAS reagent (15 mL) is added to the sensor vial.
- The reagent electrical conductance is measured to check if the HAS is suitable for the measurement (i.e., it is not degraded).
- The olive oil under test (1 mL) is added to the sensor vial.
- The sensor vial is vigorously stirred for about 15 s to create the emulsion.
- The emulsion electrical conductance $G_{m,T}$ and the environmental temperature T are measured using the portable sensor system.
- The compensation model defined by Equation (4), implemented in the microcontroller, calculates the emulsion electrical conductance at 23.5 °C ($G_{m,23.5°C}$) from the measured values of $G_{m,T}$ and T.
- The olive oil free acidity is estimated from the calculated $G_{m,23.5°C}$ using a calibration curve equation stored in the microcontroller memory.

Before each measurement, the sensor vial and the electrodes were washed using distilled water and dried before performing the measurement. At the end of the measurement the emulsion was disposed of and the washing and drying procedure repeated. At regular times the sensor was tested with the reagent (of known conductivity) and no presence of electrode degradation was found. Each measurement, consisting of reagent test and emulsion electrical conductance determination (and not considering the reagent preparation), was carried out in about 30 s.

In the current investigation, 40 olive oil samples have been tested with the portable sensor system and, for each sample, the emulsion electrical conductance at 23.5 °C ($G_{m,23.5°C}$)

has been calculated using both HAS and DW as reagent. The calculated values of emulsion electrical conductance have been used to estimate the olive oil free acidity and to classify the oil samples according to the quality grade.

2.3. Statistical Analysis

The measured data have been processed using XLSTAT 2016 (Addinsoft, Paris, France), a statistical add-on package of Microsoft Excel. In particular, the parameters of the calibration curve used to estimate the free acidity have been calculated using non-linear regression analysis with 200 iterations and convergence 0.00001. The accuracy in the estimated free acidity has been evaluated by using the mean square error (MSE), which gives information on the mean quadratic discrepancy between the target values and the predicted ones. MSE can be defined by the following equation:

$$\text{MSE} = \frac{1}{N} \times \sum_{i=1}^{N} (Y_i - X_i)^2 \tag{5}$$

where N is the number of tested samples, Y_i is the estimated free acidity for sample i and X_i is the real free acidity (determined with the reference titration procedure) for sample i.

The classification according to the quality grade has been carried out using a k nearest neighbors (KNN) algorithm using the measured electrical conductance as input and the sample quality grade determined with the manual reference titration techniques as supervised output. Tests have been performed in two different cases: two classes quality grade classification (i.e., discrimination between EVOO and non-EVOO classes) and three classes quality grade classification (i.e., discrimination among EVOO, VOO and LOO classes). For each case, KNN algorithm has been run using either the HAS emulsion electrical conductance as input either the HAS and DW emulsion electrical conductance as inputs. The accuracy in quality grade classification has been evaluated using the following parameters:

$$\text{Accuracy} = \frac{\sum_{j=1}^{k} M_{jj}}{N} \tag{6}$$

$$\text{Precision}_i = \frac{M_{ii}}{\sum_{j=1}^{k} M_{ji}} \tag{7}$$

$$\text{Recall}_i = \frac{M_{ii}}{\sum_{j=1}^{k} M_{ij}} \tag{8}$$

where N is the number of tested samples (40 in our case), k is the number of classification classes (2 in the case of discrimination between EVOO and non-EVOO; 3 in the case of discrimination among EVOO, VOO and LOO), and M_{ij} represents the number of samples that belongs to the class i and are classified to the class j. In practice, the accuracy represents the fraction of tested samples that are correctly classified. The precision for class i represents the fraction of samples correctly classified to the class i out of all samples classified to the class i. The recall for class i represents the fraction of samples correctly classified to the class i out of all samples belonging to the class i.

3. Results and Discussion

The portable sensor system was used to evaluate the quality grade of a set of 40 virgin olive oil samples (of which 31 were characterized by a peroxide index < 20 and 9 oxidized olive oil samples characterized by a peroxide index > 20). All samples were tested with the portable sensor system, and the quality parameters (free acidity and peroxide index) were determined using the reference manual titration techniques; the oil quality category (EVOO, VOO or LOO) was defined based on the results of these two parameters. This is a simplification, since the quality grade of a virgin olive oil sold in the EU can be established by considering all the parameters as reported by the EU Reg. 2019-1604 [36].

### 3.1. Analysis of Free Acidity for Fresh Olive Oil Samples

The subset of 31 olive oil samples, characterized by a peroxide index < 20, was tested with the portable sensor system, using HAS as reagent. In Figure 3, the emulsion electrical conductance at 23.5 °C ($G_{m,23.5°C}$) is plotted vs. the free acidity determined by the reference titration technique. A correlation exists between $G_{m,23.5°C}$ and the olive oil free acidity. The best-fit curve that correlates the two parameters is defined by the following equation:

$$FA = \left(\frac{G_{m,23.5°C} - 0.2858}{2.9583} \right)^2 \tag{9}$$
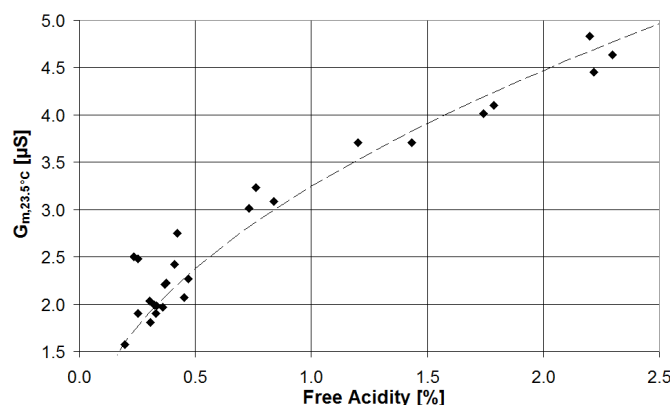
Figure 3. Scatter plot of the emulsion electrical conductance measured at 23.5 °C using the HAS reagent vs. free acidity for the subset of olive oil samples featuring a peroxide index < 20 meq O_2/kg oil.

Equation (9) was used to estimate the free acidity for all the tested olive oil samples. A scatter plot, with the estimated free acidity on the *y*-axis and the free acidity determined with the reference manual titration on the *x*-axis, is presented in Figure 4. The coefficient of determination for the corresponding linear regression equation is $R^2 = 0.9559$. The values of the estimated free acidity, as well as the free acidity determined with the reference titration technique, are reported in Table 1, for all the tested samples. As can be seen, the free acidity estimated with the portable sensor system is very close to the value obtained with the reference titration technique, and the error in the estimated free acidity is never higher than 0.32%. The calculated MSE is 0.01192.
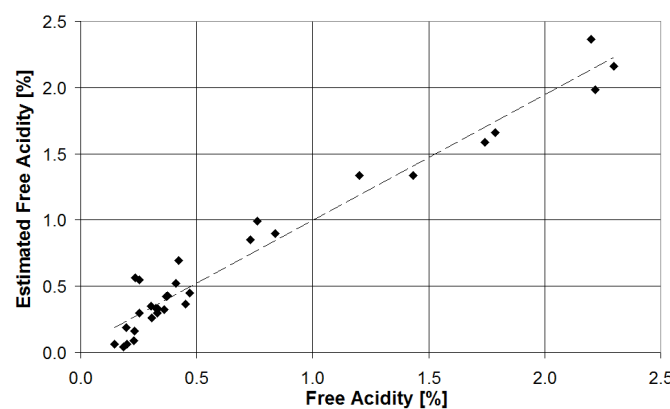
Figure 4. Scatter plot of the free acidity estimated with the portable sensor system vs. the free acidity obtained with the reference manual titration for the subset of olive oil samples featuring a peroxide index < 20 meq O_2/kg oil.

Table 1. Estimated values of the free acidity for the subset of olive oil samples featuring a peroxide index < 20 meq O_2/kg oil.

Sample Number	Free Acidity (%)	Estimated Free Acidity (%)
1	0.253	0.298
2	0.307	0.263
3	0.409	0.520
4	0.376	0.430
5	0.760	0.989
6	1.202	1.335
7	2.200	2.364
8	0.236	0.562
9	1.741	1.588
10	1.432	1.336
11	2.217	1.983
12	0.838	0.896
13	0.732	0.852
14	0.228	0.086
15	0.231	0.162
16	0.451	0.364
17	0.252	0.548
18	0.196	0.190
19	0.422	0.692
20	0.368	0.423
21	0.198	0.065
22	0.184	0.041
23	0.145	0.065
24	0.471	0.449
25	2.298	2.160
26	1.787	1.661
27	0.334	0.328
28	0.324	0.332
29	0.304	0.350
30	0.360	0.325
31	0.329	0.300

*3.2. Analysis of Free Acidity for the Full Set of Olive Oil Samples*

The full set of 40 virgin olive oil samples (classified as 23 EVOOs, 5 VOOs and 12 LOOs, based on the results of free acidity and peroxide index) was tested with the portable sensor system. In the case of oxidized samples, characterized by a peroxide index > 20, the presence of non-volatile compounds contributes to the increase in the emulsion electrical conductance. This was verified by performing the following experiment: a sample, with a free acidity of 0.42% and peroxide index of 11.07 meq O_2/kg of oil, was subjected to UV radiation for a total time of 3 weeks, and the HAS emulsion electrical conductance at 23.5 °C was measured at time intervals of 1 week. The results, presented in Table 2, confirm that even after 1 week, there was a substantial increase in the emulsion electrical conductance due to the products of oil oxidation.

**Table 2.** Emulsion electrical conductance at 23.5 °C as a function of UV stress time.

UV Stress Time	$G_{m,23.5°C}$ (µS)
No UV stress	2.26
1 week UV stress	5.09
2 weeks UV stress	5.22
3 weeks UV stress	5.12

The HAS emulsion electrical conductance at 23.5 °C is presented in Figure 5, as a function of the free acidity determined by the reference manual titration for two different
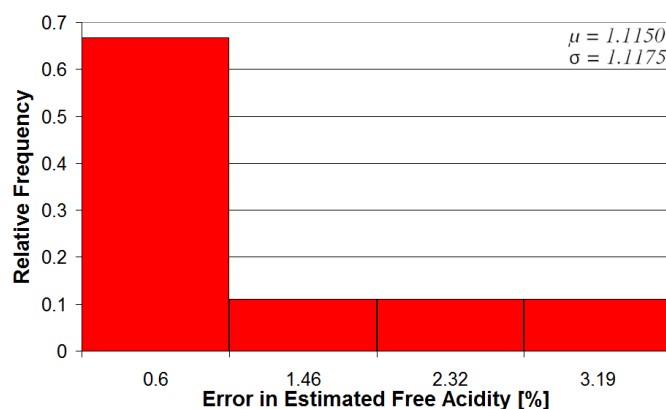
groups of the olive oil samples (fresh samples featuring a peroxide index < 20 meq O_2/kg oil and oxidized samples featuring a peroxide index > 20 meq O_2/kg). In the same figure, the calibration curve calculated for fresh samples and defined by Equation (9) is also presented. As can be seen, while in samples with low peroxide index, the free acidity can be accurately predicted by the calibration curve, the HAS emulsion electrical conductance of the oxidized samples is generally higher, which leads to a severe overestimation of the sample free acidity. This can be explained by the presence of non-volatile compounds from secondary oxidation that produce an increase in the emulsion electrical conductance. Further evidence of this effect is shown in Figures 6 and 7, where the histograms for the error in the estimated free acidity are presented for samples with low and high peroxide values, respectively. The number of bins of the histograms has been selected according to the Sturges formula $\log_2(N) + 1$, where N is the number of samples (31 for samples with lower peroxide index and 9 for samples with higher peroxide index). As can be seen, in the case of samples with peroxide index < 20 meq O_2/kg, the error for estimated free acidity is characterized by a negligible mean value (0.012) and a standard deviation of 0.142. On the other hand, in the case of oxidized samples (peroxide index > 20 meq O_2/kg), the error for estimated free acidity is characterized by a mean value significantly higher than 0 (1.115) and a standard deviation (1.117) much higher than the case of fresh samples.
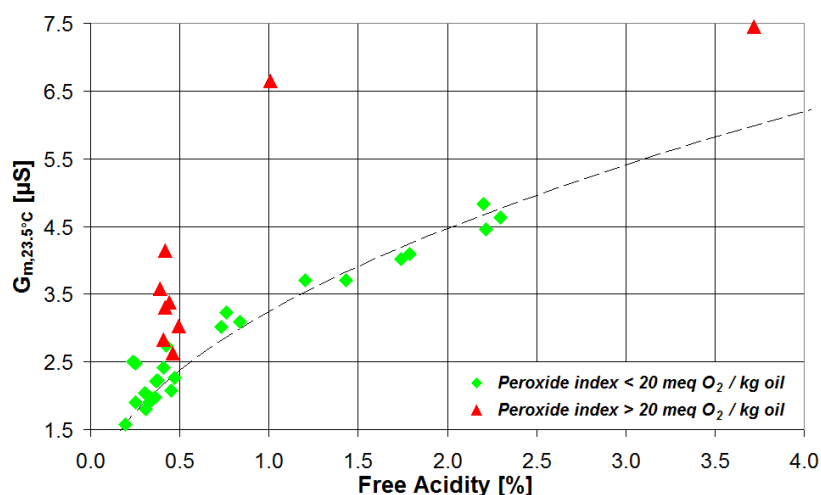
Figure 5. Scatter plot of the emulsion electrical conductance measured at 23.5 °C using the HAS reagent vs. free acidity for two different subsets of olive oil samples (fresh samples and oxidized samples).
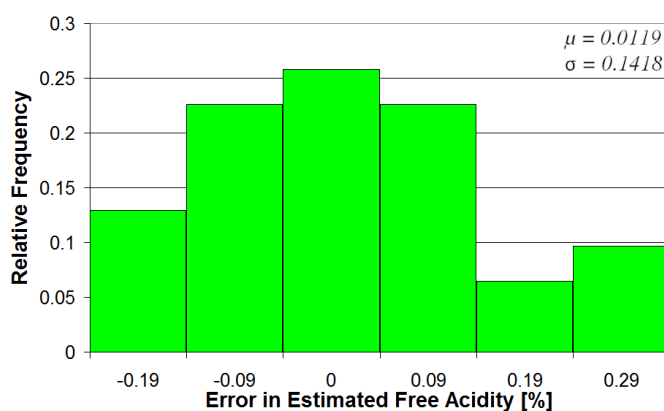

Figure 6. Histogram for the error in the estimated free acidity in the case of fresh samples (i.e., samples featuring a peroxide index < 20 meq O_2/kg).

Figure 7. Histogram for the error in the estimated free acidity in the case of oxidized samples (i.e., samples featuring a peroxide index > 20 meq O_2/kg).

Measurements have also been carried out to investigate if the emulsion electrical conductance, using DW as reagent, can be used to improve the accuracy in the free acidity estimation, in the case of oxidized virgin olive oil samples. The emulsion electrical conductance at 23.5 °C, in the case of DW reagent, is plotted vs. free acidity in Figure 8 and vs. peroxide index in Figure 9, for the full set of olive oil samples. A Pearson correlation test with a 5% significance level was carried out to evaluate the presence of correlation between the emulsion electrical conductance and the quality parameters (free acidity and peroxide index). The correlation between the electrical conductance and the free acidity is characterized by a *p*-value of 0.263 (>0.05), thus, the null hypothesis of absence of correlation cannot be rejected. The correlation between the electrical conductance and the peroxide index is characterized by a *p*-value < 0.0001, thus, the null hypothesis of absence of correlation is rejected. Thus, the emulsion electrical conductance at 23.5 °C, using DW as reagent, is uncorrelated with the sample free acidity but presents a correlation with the sample peroxide index.
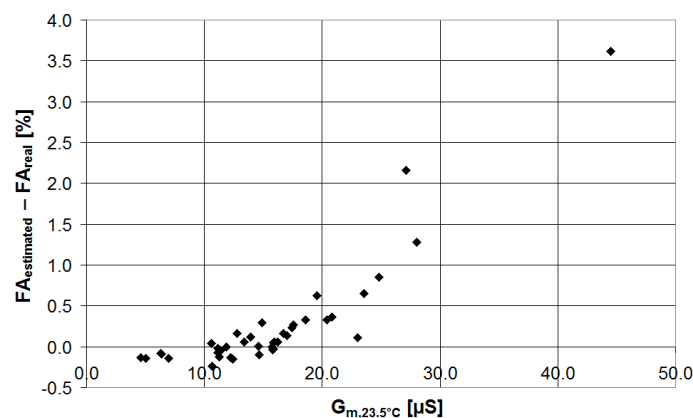
The error in the estimated free acidity (i.e., the difference between the free acidity estimated using Equation (9) and the free acidity determined with the reference titration procedure) is plotted vs. the emulsion electrical conductance at 23.5 °C, using DW as reagent, for the full set of samples and is shown in Figure 10. As can be seen, the error is relatively small for samples characterized by low values of electrical conductance in DW, while it increases significantly for samples characterized by high values of electrical conductance in DW.
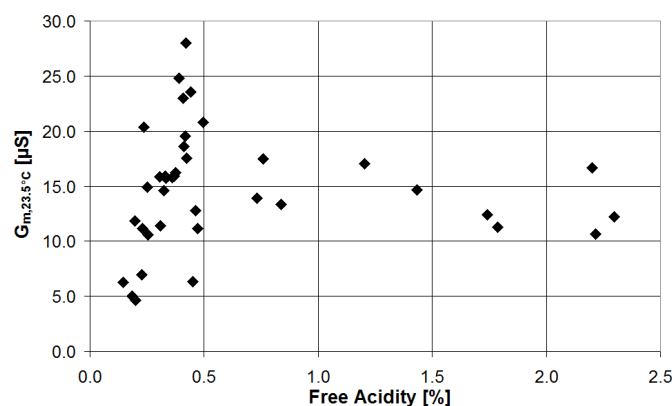
Figure 8. Emulsion electrical conductance at 23.5 °C using the DW reagent as function of free acidity for the full set of 40 olive oil samples.
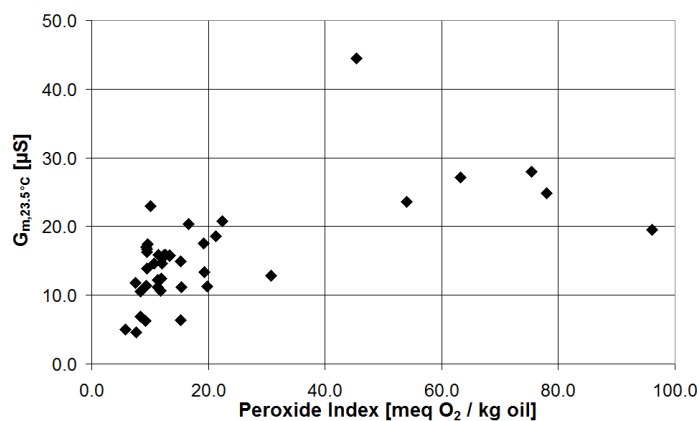
Figure 9. Emulsion electrical conductance at 23.5 °C using the DW reagent as function of peroxide index for the full set of 40 olive oil samples.

Figure 10. Error in the estimated free acidity plotted as a function of the emulsion electrical conductance at 23.5 °C using DW as reagent for the full set of 40 olive oil samples.

Thus, we have designed a compensation algorithm to improve the accuracy in the estimation of free acidity for the full set of samples. Data in Figure 10 have been best-fit with a polynomial function $P(G_{m,23.5\,°C,DW})$. The cases of polynomial order 1 (linear), 2 (quadratic) and 3 (cubic) have been considered and the best-fit polynomial functions are reported in Equations (10)–(12), respectively.

$$y = 0.0839 \times x - 1.0618 \tag{10}$$

$$y = 0.0025 \times x^2 - 0.0224 \times x - 0.1344 \tag{11}$$

$$y = -7 \times 10^{-5} \times x^3 + 0.0075 \times x^2 - 0.1181 \times x + 0.3629 \tag{12}$$

The compensated value of free acidity has been calculated by subtracting the polynomial function to the value estimated with Equation (9), according to the following equation:

$$FA_{estimated,comp} = FA_{estimated} - P(G_{m,23.5°C,DW}) \tag{13}$$

If the calculated value of free acidity with the compensation algorithm is lower than 0, then a free acidity of 0% is assumed. The results are shown in Figures 11–14, where the estimated value of free acidity is plotted vs. the free acidity determined with the reference titration procedure, and the linear regression line and the coefficient of determination (R^2) are calculated. In Figure 11, the free acidity is estimated without any compensation algorithm (i.e., using Equation (9)) and this results in low accuracy and a low coefficient of determination ($R^2 = 0.6647$). In Figure 12, the free acidity is estimated using the compensation algorithm of Equation (13) and the polynomial function of order 1. The free

acidity accuracy is increased and a coefficient of determination of 0.8743 is obtained. The use of a linear function to best-fit the data of Figure 10 allows us to increase the accuracy for the samples featuring high values of free acidity, but produces an accuracy decrease in the case of samples with low values of free acidity. Finally, in Figures 13 and 14, the free acidity is estimated using the compensation algorithm of Equation (13) and the polynomial function of order 2 and 3, respectively. In this case the free acidity accuracy is strongly increased for the full set of samples and coefficients of determination of 0.9497 and 0.9592 are obtained, respectively.
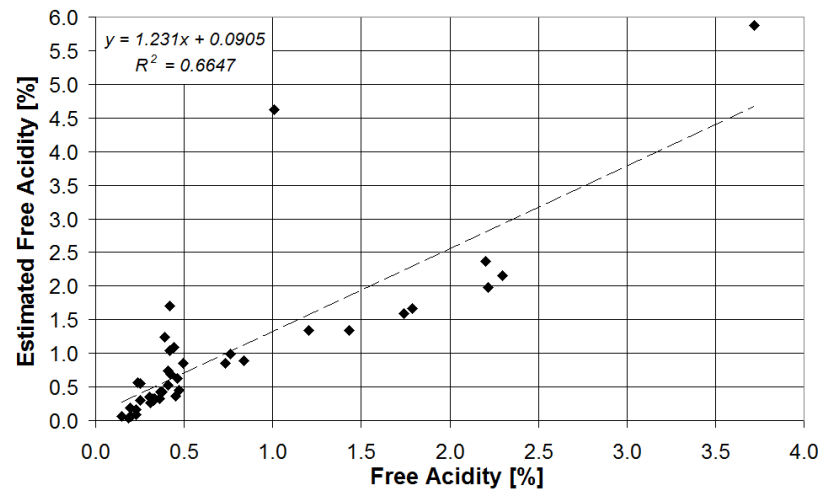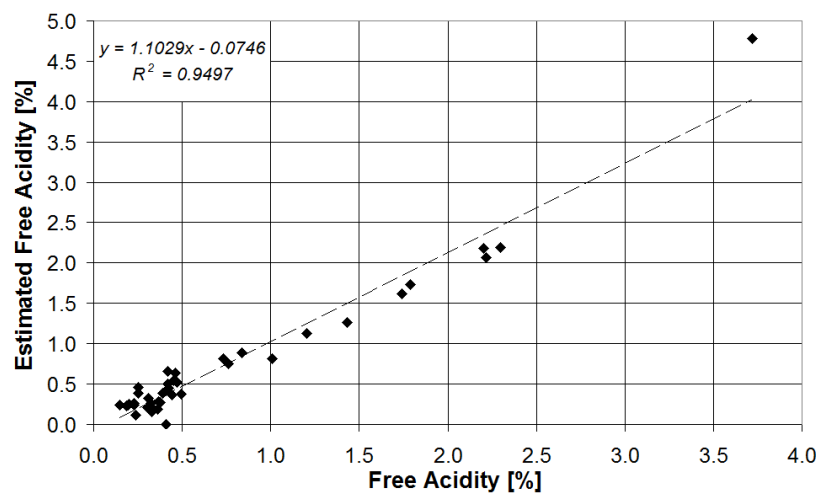

Figure 11. Estimated value of free acidity without any compensation algorithm (i.e., using Equation (9)) plotted vs. the free acidity determined with the reference procedure.
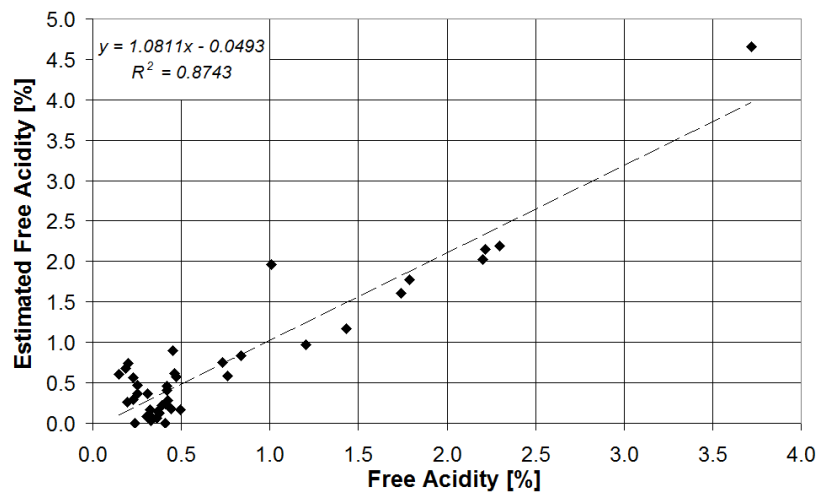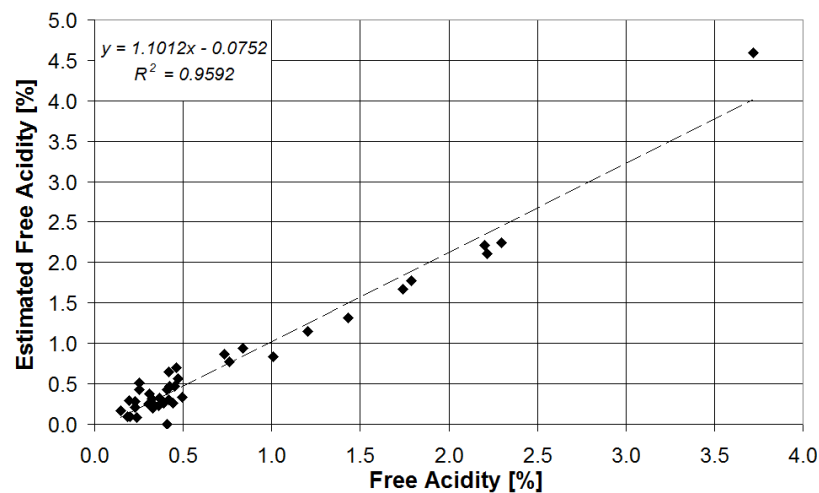

Figure 12. Estimated value of free acidity using the compensation algorithm of Equation (13) and the polynomial function of order 1 plotted vs. the free acidity determined with the reference procedure.

Figure 13. Estimated value of free acidity using the compensation algorithm of Equation (13) and the polynomial function of order 2 plotted vs. the free acidity determined with the reference procedure.


Figure 14. Estimated value of free acidity using the compensation algorithm of Equation (13) and the polynomial function of order 3 plotted vs. the free acidity determined with the reference procedure.

3.3. Estimation of Quality Grade for the Full Set of Olive Oil Samples

The full set of 40 virgin olive oil samples (classified as 23 EVOOs, 5 VOOs and 12 LOOs) has been tested to check if the sample quality grade can be assessed with good accuracy from the measured value of electrical conductance. As a first step, we have tested the feasibility of quality grade estimation, using the measured value of the emulsion electrical conductance at 23.5 °C, using HAS as reagent.

In Figure 15, the correlation between the olive oil quality parameters (free acidity and peroxide index) and the HAS emulsion electrical conductance at 23.5 °C is evaluated, where each sample is represented by a circle of different colours, depending on the quality grade established according to free acidity and peroxide value (EVOO, VOO and LOO), while the circle diameter represents the emulsion electrical conductance at 23.5 °C. In general, samples of lower-quality grades are characterized by higher values in the circle diameter (thus, higher emulsion electrical conductance).
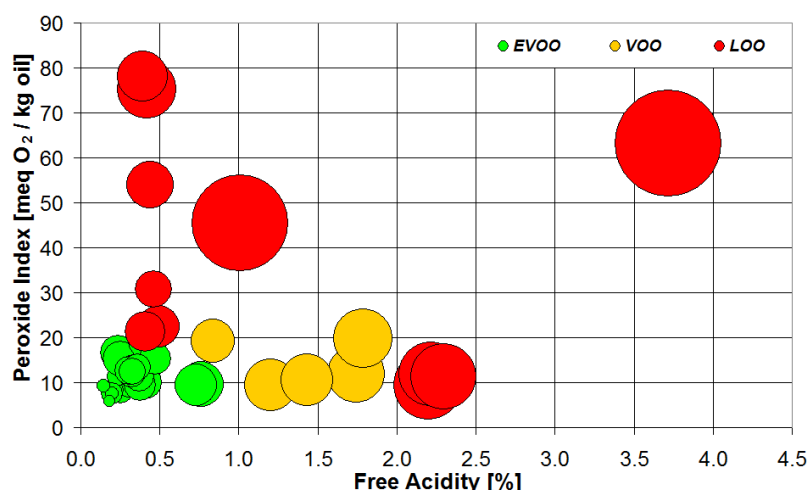
Figure 15. Emulsion electrical conductance at 23.5 °C using the HAS reagent as function of free acidity and peroxide index for the full set of olive oil samples.

To investigate if the HAS emulsion electrical conductance at 23.5 °C is capable of discriminating different quality grades, a KNN test has been carried out, according to what was reported in Section 2.3. In Table 3, the results of the KNN test are presented in the case of two different quality grades: EVOO and non-EVOO (VOO + LOO). In the columns, the number of samples classified as EVOO and non-EVOO from the values of free acidity and peroxide index, measured with the reference titration procedures, is presented. In the rows, the number of EVOO and non-EVOO samples estimated with the emulsion electrical conductance, using HAS as reagent, is presented. The results show that 37 out of 40 samples are correctly classified, a single non-EVOO sample (a LOO with free acidity 0.46% and peroxide index 30.78 meq O_2/kg) is misclassified as EVOO, while two EVOO samples (featuring a free acidity of 0.76% and 0.73% and peroxide index of 9.6 and 9.52 meq O_2/kg, respectively) are misclassified as non-EVOO. The calculated accuracy is 0.925, the precision is 0.954 and 0.888 for EVOO and non-EVOO samples, respectively, while the recall is 0.913 and 0.941 for EVOO and non-EVOO samples, respectively.

Table 3. Results of the KNN test in the case of two quality grade classes (EVOO and non-EVOO) and the HAS reagent.

	EVOO	Non-EVOO
Estimated EVOO	21	1
Estimated non-EVOO	2	16

In Table 4, the results of the KNN test are presented in the case of three different quality grades: EVOO, VOO and LOO. In the columns, the number of samples classified as EVOO, VOO and LOO from the values of free acidity and peroxide index, measured with the reference titration procedures, is presented. In the rows, the number of EVOO, VOO and LOO samples estimated with the emulsion electrical conductance, using HAS as reagent, is presented. The results show that 36 out of 40 samples are correctly classified, a LOO (with free acidity 0.46% and peroxide index 30.78 meq O_2/kg) is misclassified as EVOO, a LOO (with free acidity 0.42% and peroxide index 75.36 meq O_2/kg) is misclassified as VOO, a VOO (with free acidity 0.84% and peroxide index 19.26 meq O_2/kg) is misclassified as LOO and one EVOO (with free acidity 0.76% and peroxide index 9.6 meq O_2/kg) is misclassified as LOO. The calculated accuracy is 0.9, the precision is 0.956, 0.8 and 0.833 for EVOO, VOO and LOO samples, respectively, while the recall is 0.956, 0.8 and 0.833 for EVOO, VOO and LOO samples, respectively.

Table 4. Results of the KNN test in the case of three quality grade classes (EVOO, VOO and LOO) and the HAS reagent.

	EVOO	VOO	LOO
Estimated EVOO	22	0	1
Estimated VOO	0	4	1
Estimated LOO	1	1	10

As a second step, measurements have also been carried out on the full set of 40 olive oil samples, using both HAS and DW as reagent, calculating the emulsion electrical conductance at 23.5 °C in the case of both reagents, to investigate if two different measurements can provide higher accuracy in the classification of the sample quality grade. A scatter plot presenting the tested olive oil samples, classified with three quality grades (EVOO, VOO, LOO) as a function of the emulsion electrical conductance at 23.5 °C, using HAS and DW as reagents, is presented in Figure 16.
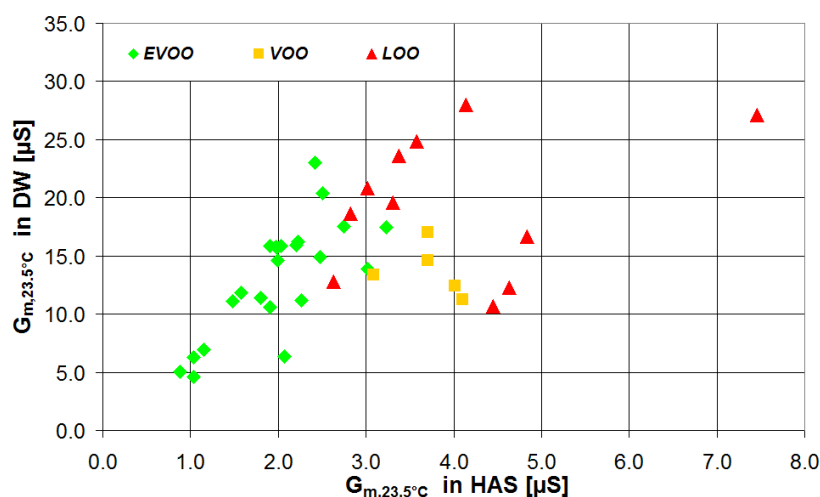
Figure 16. Scatter plot of the emulsion electrical conductance at 23.5 °C using the DW reagent (*y*-axis) vs. the emulsion electrical conductance at 23.5 °C using the HAS reagent (*x*-axis) for three different quality grades (EVOO, VOO, LOO).

A KNN test has been carried out according to what was reported in Section 2.3, using the measured values of the emulsion electrical conductance at 23.5 °C, for both HAS and DW reagents as inputs.

In Table 5, the results of the KNN test are presented using the emulsion electrical conductance for HAS and DW as inputs, in the case of two different quality grades: EVOO and non-EVOO (VOO + LOO). In the columns, the number of samples classified as EVOO and non-EVOO from the values of free acidity and peroxide index, measured with the reference titration procedures, is presented. In the rows, the number of EVOO and non-EVOO samples estimated with the emulsion electrical conductance, using HAS and DW as reagents, is presented. The results show that 34 out of 40 samples are correctly classified, three non-EVOO samples (a VOO with free acidity of 1.2% and peroxide index of 9.4 meq O_2/kg; a VOO with free acidity of 1.43% and peroxide index of 10.66 meq O_2/kg; a LOO with free acidity of 0.43% and peroxide index of 21.29 meq O_2/kg) are misclassified as EVOO, and three EVOO samples (featuring a free acidity of 0.41%, 0.24% and 0.73% and peroxide index of 10.03, 16.62 and 9.52 meq O_2/kg, respectively) are misclassified as non-EVOO. The calculated accuracy is 0.85, the precision is 0.869 and 0.823 for EVOO and non-EVOO samples, respectively, while the recall is 0.869 and 0.823 for EVOO and non-EVOO samples, respectively.

Table 5. Results of the KNN test in the case of two quality grade classes (EVOO and non-EVOO) and both the HAS and DW reagents.

	EVOO	Non-EVOO
Estimated EVOO	20	3
Estimated non-EVOO	3	14

In Table 6, the results of the KNN test are presented using the emulsion electrical conductance for HAS and DW as inputs, in the case of three different quality grades: EVOO, VOO and LOO. In the columns, the number of samples classified as EVOO, VOO and LOO from the values of free acidity and peroxide index, measured with the reference titration procedures, is presented. In the rows, the number of EVOO, VOO and LOO samples estimated with the emulsion electrical conductance, using HAS and DW as reagents, is presented. The results show that 32 out of 40 samples are correctly classified, two LOO samples (with free acidity 1.2% and 1.43%, and peroxide index 9.4 and 10.66 meq O_2/kg, respectively) are misclassified as EVOO, a LOO (with free acidity 0.41%, and peroxide index 21.29 meq O_2/kg, respectively) is misclassified as EVOO, three LOO samples (with free acidity 2.2%, 0.43% and 2.3%, and peroxide index 9.5, 30.78 and 11.3 meq O_2/kg, respectively) are misclassified as VOO and two EVOO samples (with free acidity 0.41% and 0.23%, and peroxide index 10.03 and 16.62 meq O_2/kg, respectively) are misclassified as LOO. The calculated accuracy is 0.8, the precision is 0.875, 0.5 and 0.8 for EVOO, VOO and LOO samples, respectively, while the recall is 0.913, 0.6 and 0.666 for EVOO, VOO and LOO samples, respectively.

Table 6. Results of the KNN test in the case of three quality grade classes (EVOO, VOO and LOO) and both the HAS and DW reagents.

	EVOO	VOO	LOO
Estimated EVOO	21	2	1
Estimated VOO	0	3	3
Estimated LOO	2	0	8

A comparison for the classification metrics obtained with the emulsion electrical conductance, for only the HAS reagent and both the HAS and DW reagents, is presented in Table 7, for the two classes classification (EVOO and non-EVOO), and in Table 8, for the three classes classification (EVOO, VOO and LOO). The results show how the electrical measurement, using only the HAS reagent, produces better classification accuracy than using both the HAS and DW reagents. This could be due to the fact that the emulsion electrical conductance, using DW as reagent, is strongly affected by the presence of non-volatile compounds, generated by the oil secondary oxidation, while the peroxide index represents an indicator of the primary oxidation of the oil.

Table 7. Comparison of the classification metrics in the case of two classes classification (EVOO and non-EVOO).

Reagents Used	Accuracy	Precision EVOO	Recall EVOO	Precision Non-EVOO	Recall Non-EVOO
HAS	0.925	0.954	0.913	0.888	0.941
HAS + DW	0.850	0.869	0.869	0.823	0.823

Table 8. Comparison of the classification metrics in the case of three classes classification (EVOO, VOO and LOO).

Reagents Used	Accuracy	Precision EVOO	Recall EVOO	Precision VOO	Recall VOO	Precision LOO	Recall LOO
HAS	0.900	0.956	0.956	0.800	0.800	0.833	0.833
HAS + DW	0.800	0.875	0.913	0.500	0.600	0.800	0.666

4. Conclusions

A portable, battery-operated sensor system to support the quality grade assessment of virgin olive oil has been presented. The system is characterized by small size, light weight and quick measurement response. It can be used for the in-situ evaluation of olive oil quality grade in small industrial environments that cannot afford an internal laboratory.

The system working principle is based on the measurement of the electrical conductance of an emulsion between a chemical reagent and the olive oil sample. Two different reagents have been tested: (1) a hydro-alcoholic solution (HAS), made of 60% ethanol and 40% distilled water; (2) 100% distilled water (DW). The emulsion electrical conductance, using the HAS reagent, is affected by the free acidity, as well as the oxidation level of the sample, and can be used to estimate with good accuracy the free acidity in the case of fresh samples. The emulsion electrical conductance using the DW reagent is not affected by the free acidity but is affected by the oxidation level of the oil sample and can be used to improve the accuracy of free acidity determination, in the case of oxidized olive oil samples. Tests on 40 olive oil samples have shown how EVOO samples (this category was determined considering only the free acidity and peroxide value) can be discriminated from lower quality oils (VOO and LOO) with good accuracy. The results have shown that the quality grade classification is more accurate if only the emulsion electrical conductance using the HAS reagent is used. The herein presented outcomes are promising, but they need to be confirmed by analyzing a wider number of samples, characterized by a wide range in terms of peroxide values and free acidity, as well as other compositional characteristics.

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