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Evaluation of Olive Oil Quality Grade using a Portable Battery Operated Sensor System †

Marco Grossi [1,*], Enrico Valli [2], Alessandra Bendini [2], Tullia Gallina Toschi [2] and Bruno Riccò [1]

[1] Department of Electrical Energy and Information Engineering “Guglielmo Marconi” (DEI), University of Bologna, 40126 Bologna, Italy; bruno.ricco@unibo.it
[2] Department of Agricultural and Food Sciences (DISTAL), University of Bologna, 47521 Cesena, Italy; enrico.valli4@unibo.it (E.V.); alessandra.bendini@unibo.it (A.B.); tullia.gallinatoschi@unibo.it (T.G.T.)
* Correspondence: marco.grossi8@unibo.it; Tel.: +39 051 2093038

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Abstract: Olive oil quality is normally assessed by chemical analysis as well as sensory analysis to detect the presence of organoleptic defects. Two of the most important parameters that define the quality of olive oil are the free acidity and the peroxide index. These chemical parameters are usually determinated by manual titration procedures that must be carried out in a laboratory by trained personnel. In this paper, a portable sensor system to evaluate the quality grade of olive oil is presented. The system is battery operated and is characterized by small dimensions, light weight and quick measurement response. The working principle is based on the measurement of the electrical conductance of an emulsion between an hydro-alcoholic solution and the olive oil sample. Tests have been carried out on a set of 17 olive oil samples. The results have shown how for fresh olive oil samples, the olive oil free acidity can be estimated from the electrical conductance of the emulsion. In the case of oxidized olive oil, the measured electrical conductance is also function of the oxidation level and a conductance threshold can be set to discriminate extra virgin olive oils from lower quality grade oils. The proposed system can be a low-cost alternative to standard laboratory analysis to evaluate the quality grade of olive oil.

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

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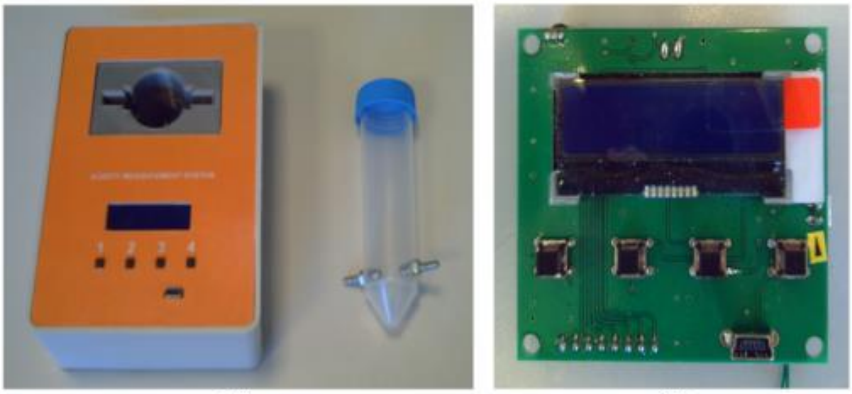
1. Introduction

Olive oil is a vegetable lipid highly appreciated for its beneficial effects on human health [1]. Olive oil quality is normally assessed by chemical analysis as well as sensory analysis to detect the presence of organoleptic defects. Two of the most important parameters that define the quality of olive oil are the free acidity, defined as the amount of fatty acids no longer linked to their parent triglyceride molecules, that is affected by the quality of the olives used to produce the oil as well as the production process, and the peroxide index,expressed as milliequivalents of active oxigen for a kg of oil, that is an indicator of the oil primary oxidation and is affected by the storage conditions [2]. The official techniques to measure these chemical parameters are manual titration procedures that must be carried out in a laboratory by trained personnel [3].

In the case of small industrial environments, such as olive oil mills and small packaging centers, that can not 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 high costs for the analysis and long response times. Thus, the development of simple and quick techniques for the analysis of quality grade of olive oil is important to allow in-situ measurements, directly in the industrial environment. A lot of research has been carried out in recent years towards the development of portable and low-cost sensor systems for the quality analysis of food products. Some examples include a portable biosensor system for bacterial concentration detection in raw milk [4], a system for the detection of chicken meat freshness [5], a low-cost handheld system for rapid non-destructive testing of fruit firmness [6], a system for the characterization of ice-cream properties with electrical impedance [7], a system for the determination of solid fat content in fats and oils [8], an optical system for the assessment of lycopene content in tomatoes [9]. Many portable sensor systems presented in literature are designed using a microcontroller as the core device of the system as well as commercial electronic chips to realize the analog measurement system and the communication system with an external PC. More recently, a lot of research has been carried out in the development of smartphone based sensor systems, since modern mobile phones integrate powerful processors for data analysis, a rich sensor set (camera, accelerometer, gyroscope, light sensor, etc.) as well as peripherals for wireless and wired communication [10].



(a) (b)

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

In this paper, a battery operated portable sensor system for quality analysis of olive oil is presented. The system working principle is based on the measurement of the electrical characteristics of an emulsion between an hydro-alcoholic solution and the olive oil sample [11]. Tests on a set of 17 olive oils have shown how the system can discriminate extra virgin olive oils (EVOOs) from lower quality grade olive oils 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

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

The system working principle is based on Electrical Impedance Spectroscopy (EIS) measurements [12] on an emulsion between an hydro-alcoholic solution and the olive oil under test. The emulsion electrical properties are measured using a 50 mL Falcon vial modified with a couple of cap-shaped stainless steel electrodes (hereafter the sensor). More in details, the following steps are carried out:

- The reagent (15 mL), an hydro-alcoholic solution of 60% ethanol and 40% distilled water, is added to the sensor vial.

- The reagent electrical conductance is measured using the portable system to check if it 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 seconds to create the emulsion.
- The emulsion electrical conductance and the environmental temperature are measured using the portable system and these values are used to estimate the olive oil quality grade.

The system primary function is the measurement of the olive oil free acidity. In fact, in presence of the hydro-alcoholic solution, the free fatty acid molecules dissociate and generate ions that contribute to the increase of the emulsion electrical conductance that, once compensated for variations of the environmental temperature, can be used to estimate the olive oil free acidity. In the case of fresh olive oil samples, characterized by low values of peroxide index, a very good correlation exists between the emulsion electrical conductance and the oil free acidity measured with the standard titration technique. However, when olive oil storage conditions are not adequate, that is the oil is exposed to heath or light, oxidation takes place and this results in the generation of non-volatile compounds (such as aldehydes, ketones and hydrocarbons) that also contribute to the increase of the emulsion electrical conductance. Thus, by setting a threshold for the emulsion electrical conductance, olive oil top quality grade (EVOO) can be discriminated from lower quality grades, virgin olive oils (VOOs) and Lampante olive oils (LOOs).

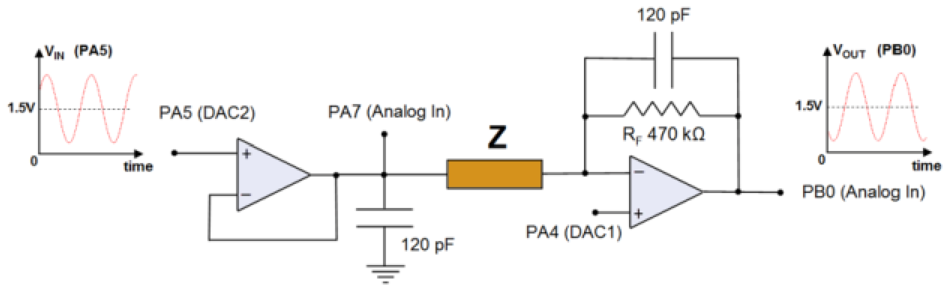


Figure 2. Schematic of the circuit for the measurement of the emulsion electrical conductance.

All electrical measurements, data processing and data filing are carried out using the electronic board that is shown in Figure 1 (b). The electronic board integrates a LCD screen to display the measurement results, four buttons for user interaction, 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 by ST Microelectronics (STM32L152RCT6A) that is responsible for the generation of the test signal, the signals acquisitions, the signals processing and the control of all the electronic components of the board. Different commercial electronic chips are integrated on the electronic board to design the analog circuits for the measurement of the emulsion electrical conductance G_m. A schematic diagram of the measurement circuit is shown in Figure 2. A 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 is converted to a voltage signal $V_{OUT}(t)$ using a trans-impedance amplifier. 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 G_m. A temperature sensor (MCP9700A) is integrated in the electronic board to make measurements of environmental temperature to compensate variations of G_m with temperature.

The estimation of the olive oil free acidity is carried out with the following steps:

- The emulsion electrical conductance at a generic temperature $G_{m,T}$ and the value of temperature T are measured.

- A compensation model, 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.

3. Results and Discussion

The portable sensor system has been used to evaluate the quality grade of a set of 17 olive oil samples (11 fresh olive oil samples characterized by a peroxide index < 20 and 6 oxidized olive oil samples characterized by a peroxide index > 20). All samples have been tested with the portable sensor system, the quality parameters (free acidity and peroxide index) determined using the reference manual titration techniques and the oil quality category defined as suggested by the EU Reg. 2019-1604.

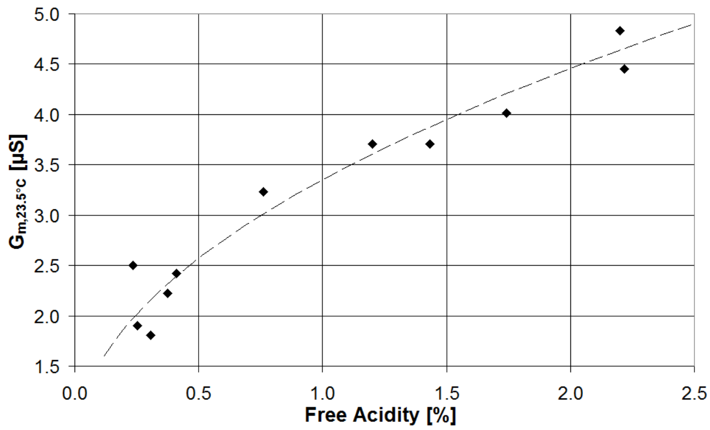


Figure 3. Scatter plot of the emulsion electrical conductance measured at 23.5 °C vs. free acidity for the subset of olive oil samples featuring a peroxide index < 20 meq O_2 / kg oil.

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	0.25	0.21
2	0.31	0.18
3	0.41	0.42
4	0.38	0.33
5	0.76	0.91
6	1.20	1.28
7	2.20	2.42
8	0.24	0.46
9	1.74	1.56
10	1.43	1.28
11	2.22	1.99

3.1. Analysis of Fresh Olive Oil Samples

The subset of 11 olive oil samples characterized by a peroxide index < 20 has been tested with the portable sensor system. In Fig. 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:

$$FA = \left(\frac{G_{m,23.5^{\circ}C} - 0.6856}{2.6662} \right)^2 \tag{1}$$

The equation (1) has been used to estimate the free acidity for all tested olive oil samples. The values of the estimated free acidity as well as the free acidity determined with the reference titration technique are reported in Table 1. As can be seen the free acidity estimated with the portable sensor system is very close with the value obtained with the reference titration technique and the error in the estimated free acidity is never higher than 0.23%.

Table 2. Emulsion electrical conductance at 23.5 °C as 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

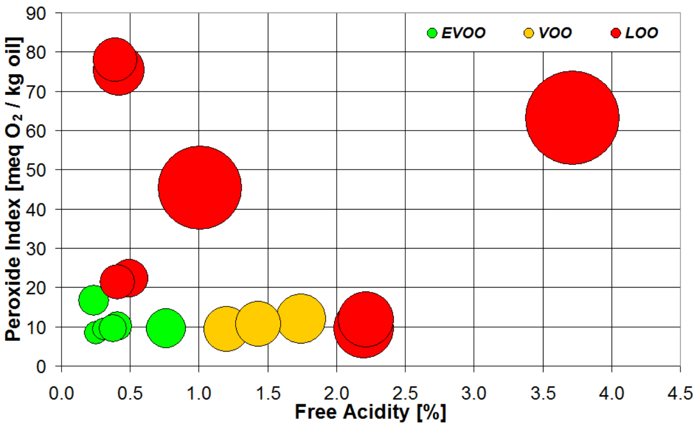


Figure 4. Emulsion electrical conductance at 23.5 °C as function of free acidity and peroxide index for the full set of olive oil samples.

3.2. Analysis of the Full Set of Olive Oil Samples

The full set of 17 olive oil samples (6 EVOOs, 3 VOOs and 8 LOOs) has been 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 of the emulsion electrical conductance. This has been verified by performing the following experiment: a sample, with free acidity 0.42% and peroxide index 11.07 meq O_2 / kg of oil, has been subjected to UV radiation for a total time of 3 weeks and the emulsion electrical conductance at 23.5°C has been measured at time intervals of 1 week. The results, presented in Table 2, confirm that even after 1 week there is a substantial increase of the emulsion electrical conductance due to the products of oil oxidation.

The results on the full set of samples is presented in Figure 4, where each sample is represented by a circle of different color depending on the quality grade (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 of the circle diameter. The results show that setting a suitable threshold value for the emulsion electrical conductance at 23.5 °C ($G_{m,23.5\,°C,TH}$ = 2.7 μS) EVOOs can be discriminated from lower quality oils (VOOs and LOOs) with good accuracy. In particular, all 11 samples of lower quality grades (3 VOOs and 8 LOOs) are correctly classified. In the case of EVOOs, 5 samples are correctly classified and the only misclassified sample features a free acidity value (0.76%) that is close to the threshold between EVOO and VOO (0.8%).

4. Conclusions

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

The system working principle is based on the measurement of the electrical conductance of an emulsion between an hydro-alcoholic solution and the olive oil sample. The emulsion electrical conductance is mainly affected by the free acidity as well as the oxidation level of the sample. Tests on a set of 17 olive oil samples have shown how EVOO samples can be discriminated from lower quality oils with good accuracy.

Author Contributions: Conceptualization, M.G.; methodology, M.G and A.B..; software, M.G.; validation, M.G. and A.B.; investigation, M.G., E.V. and A.B.; data curation, M.G. and A.B.; writing—original draft preparation, M.G.; writing—review and editing, M.G., E.V. and A.B.; supervision, T.G.T. and B.R.; project administration, T.G.T.; funding acquisition, T.G.T. All authors have read and agreed to the published version of the manuscript.

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