

Evaluation of olive oil quality grade using a portable battery operated sensor system

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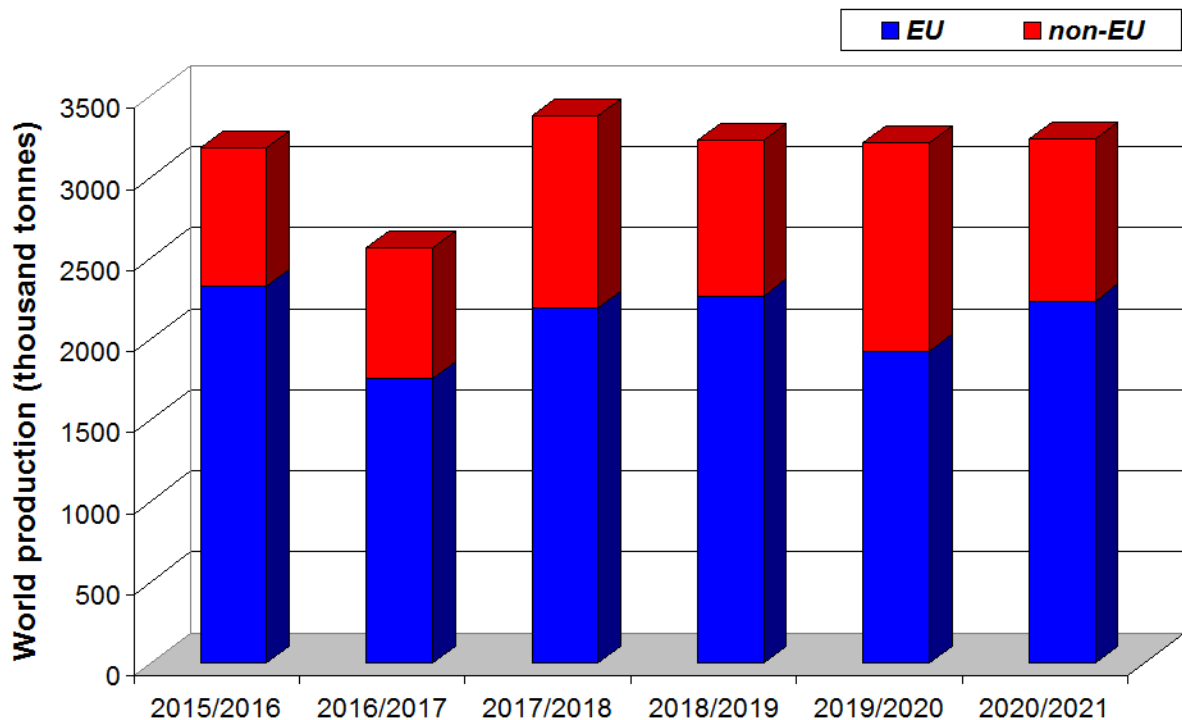
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Olive oil health benefits

EVOO is responsible for many health benefits associated to Mediterranean diet as it is a fundamental ingredient of this diet.

- Reduction of microbial activity
- Anti-tumor properties
- Benefits for blood pressure
- Prevent diabetes
- Prevent osteoporosis
- Prevent neurodegenerative diseases
- Anti-inflammatory properties
- Benefits for the digestive system
- Prevent oxidative stress

Olive oil market in the world

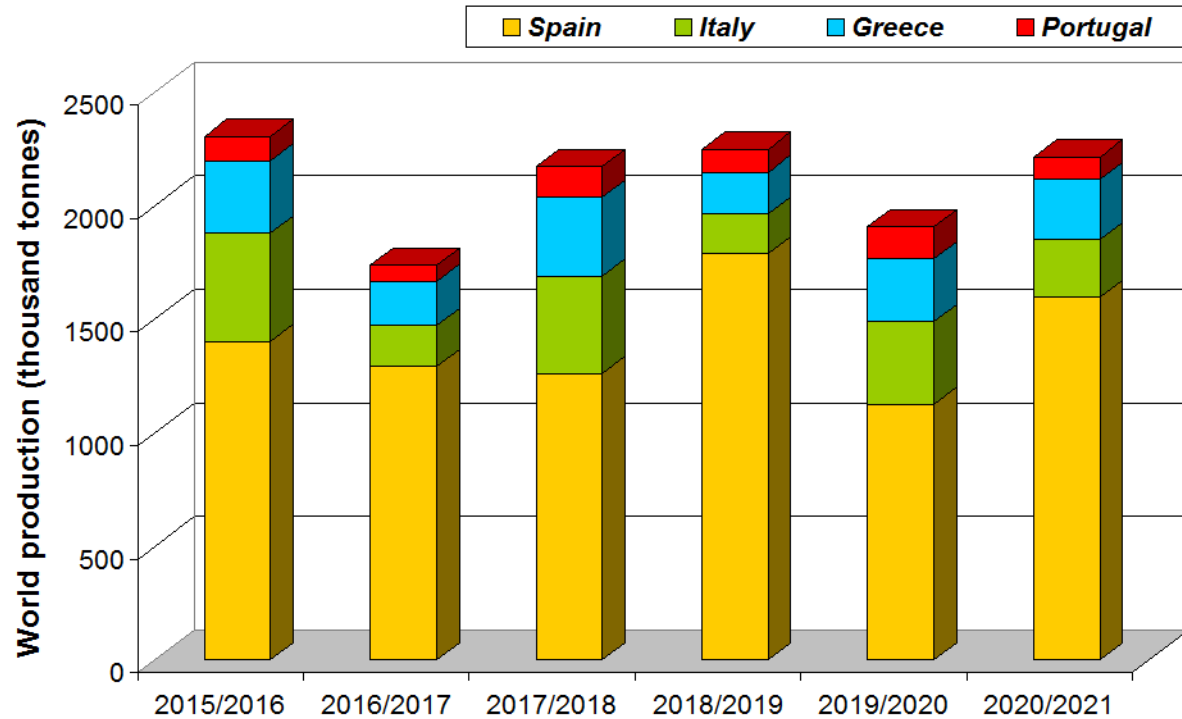


European Union (EU) is the largest olive oil producer in the world (about 66% of the world production).

EU is also the biggest olive oil consumer (1.5 million tonnes) and exporter (570000 tonnes).

Source: *International Olive Council*

Olive oil market in the European Union



Spain is the biggest olive oil producer in EU and Italy is the second biggest producer.

Spain: 66%
Italy: 15%
Greece: 13%
Portugal: 5%

Source: *International Olive Council*

Olive oil quality

Olive oil is graded to different categories according to quality parameters:

1) Physico-chemical characteristics

- **Free acidity (FA):** amount of fatty acids no longer linked to their parent triglyceride molecules. It is affected by the olive quality and production process. It does not change significantly during storage.
- **Peroxide index (PI):** indicator of the oil primary oxidation. If storage conditions are not adequate, oil oxidation takes place and degrades the product quality.

2) Organoleptic characteristics

- **Sensory analysis** to check the absence of organoleptic defects.

Olive oil quality

Based on the values of the different quality parameters, virgin olive oil can be classified into the following categories:

- **Extra Virgin Olive Oil (EVOO):** $FA < 0.8\%$, $PI < 20 \text{ meq O}_2 / \text{kg oil}$. From an organoleptic point of view, it has no defects and is fruity.
- **Virgin Olive Oil (VOO):** $FA < 2\%$, $PI < 20 \text{ meq O}_2 / \text{kg oil}$. It may have organoleptic defects at very low level.
- **Lampante Olive Oil (LOO):** $FA > 2\%$ and/or $PI > 20 \text{ meq O}_2 / \text{kg oil}$. It has no fruity characteristics and substantial organoleptic defects. Lampante olive oil is not intended to be marketed at retail stage.

Measurement of free acidity and peroxide index

The **reference techniques** to measure olive oil free acidity and peroxide index are **manual titration procedures**.

- The analysis must be carried out by trained personnel in a laboratory.
- Chemicals used in the titration must be properly disposed according to regulations.
- Small production centers, that can not afford an internal laboratory for quality analysis, must ship the samples to an external laboratory with high costs and long response time.

Objective of the research project

The objective of the research project is the development of an **electronic instrument for the evaluation of quality grade of olive oil**. The instrument must have the following characteristics.

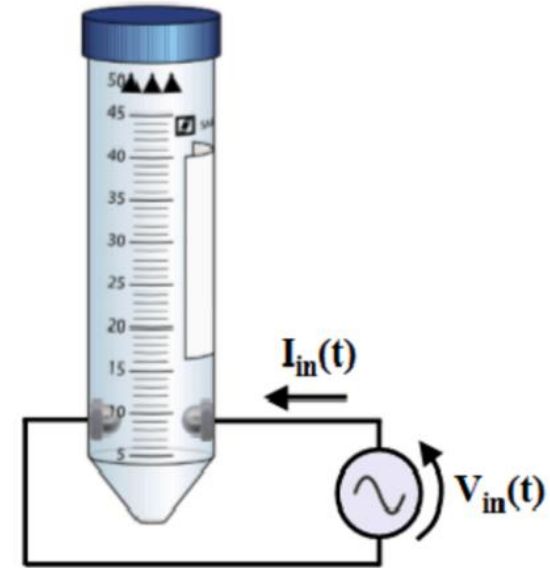
- It must be **portable** and **powered by batteries** to allow **in-situ measurements** in the production centers (oil mills and packaging centers).
- It must be **simple to use**. No particular skills for the operators.
- The measurement must be **quick**.
- **No toxic compounds** must be used.

Working principle of the proposed technique

The working principle of the proposed technique is based on the **measurement of the electrical characteristics** of an emulsion between an **hydro-alcoholic solution** (60% ethanol, 40% distilled water) and the **olive oil** under test.

The **emulsion** is prepared by mixing **15 mL** of **hydro-alcoholic solution** and **1 mL** of the **olive oil** under test.

The emulsion is stored in a **50 mL Falcon vial** modified to feature **a couple of stainless steel electrodes** (6 mm diameter, spaced by 12 mm).



Working principle of the proposed technique

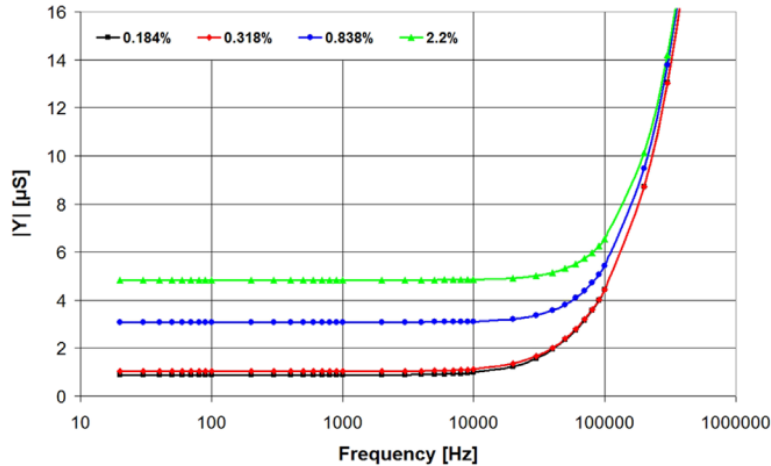
- Preliminary measurements have been carried out in a controlled laboratory environment on four olive oil samples with different levels of free acidity.
- The emulsion is stored in a thermal chamber with operative temperature 20 °C.
- The emulsion electrical characteristics have been analyzed by Electrical Impedance Spectroscopy (EIS) in the frequency range 20 Hz – 2 MHz using a commercial impedance analyzer.

Working principle of the proposed technique

- From an electrical point of view, the emulsion can be modeled as the parallel of an electrical conductance G_m and an electrical capacitance C_m .
- The sensor impedance is dominated by G_m at low frequency (< 10 kHz) and by C_m at high frequency (> 100 kHz).
- The electrical capacitance C_m is function of the oil dielectric properties and is not affected by the oil quality parameters (free acidity and peroxide index).
- The electrical conductance G_m of the emulsion is function of the oil quality characteristics.

Working principle of the proposed technique

- In the case of fresh olive oil samples, characterized by a peroxide index < 20 , the emulsion G_m is function of the olive oil free acidity.



- Samples featuring higher values of free acidity are also characterized by higher values of the emulsion G_m .
- In the case of oxidized olive oil samples, the presence of non-volatile compounds (such as aldehydes, ketones and hydrocarbons) also contributes to the increase of the emulsion G_m .

Design of the portable sensor system



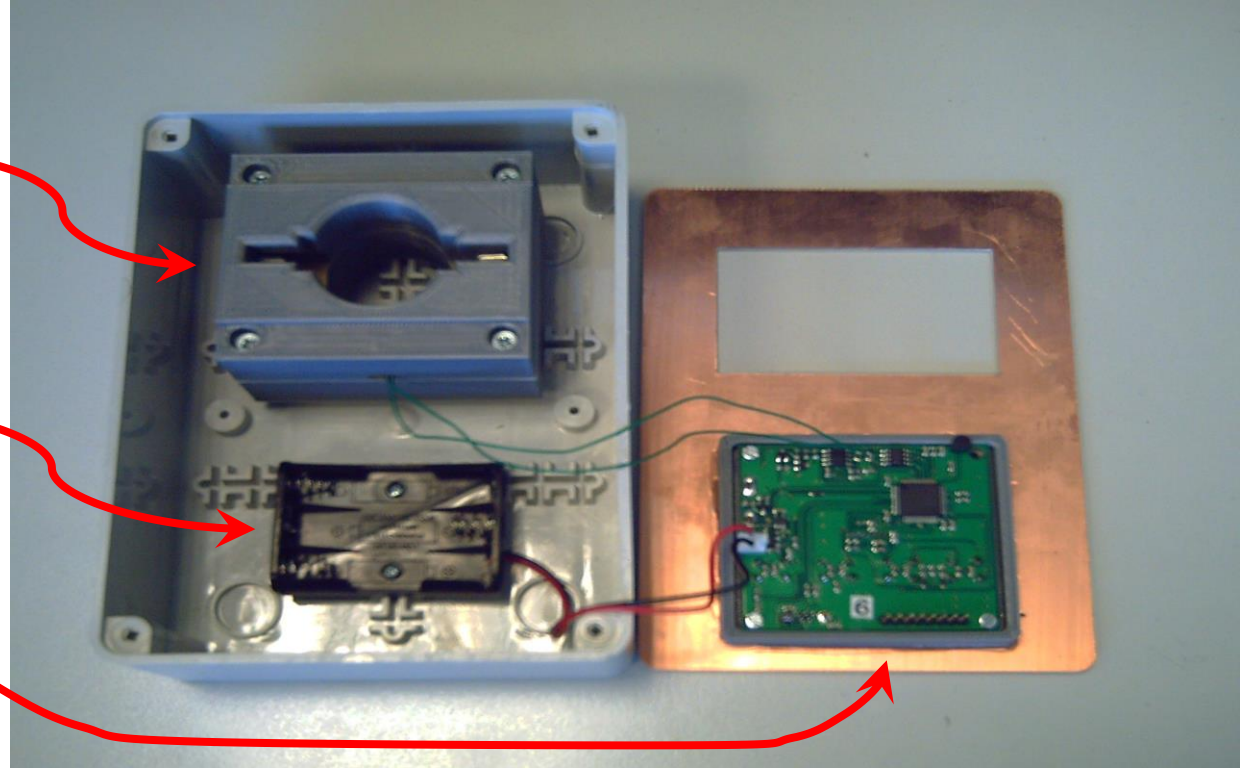
- The portable sensor system has **small size** (11 x 15 x 5 cm), **light weight** (350 g), can be powered by **USB or battery** (3 AAA alkaline batteries) and makes measurements in **about 30 seconds**.

Design of the portable sensor system

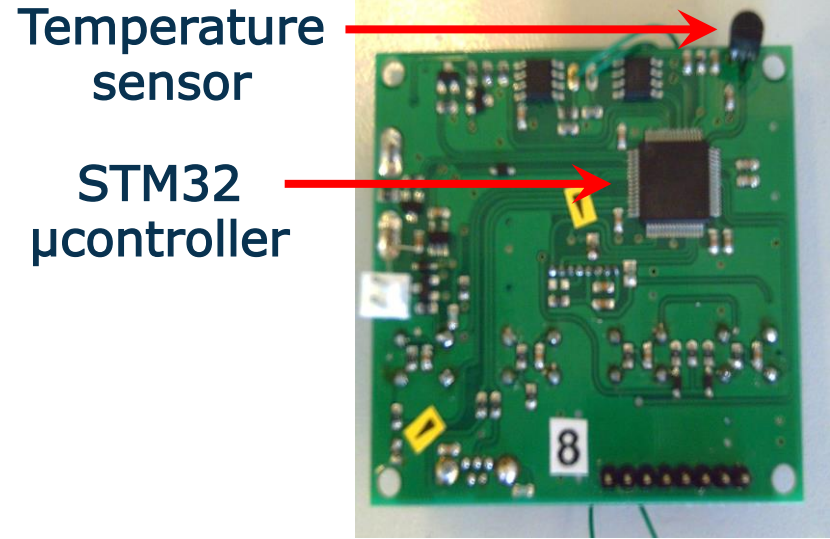
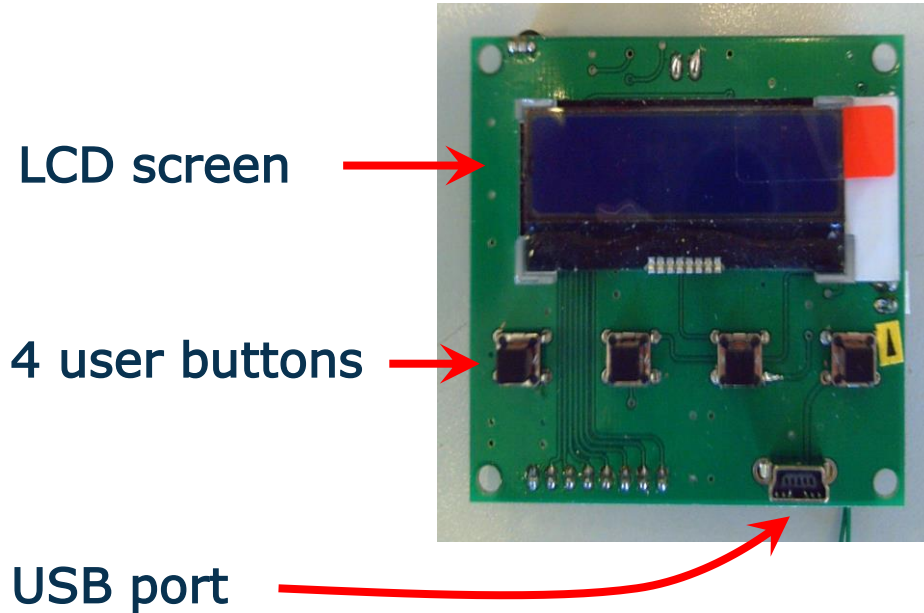
Slot to host the modified Falcon vial

Battery container

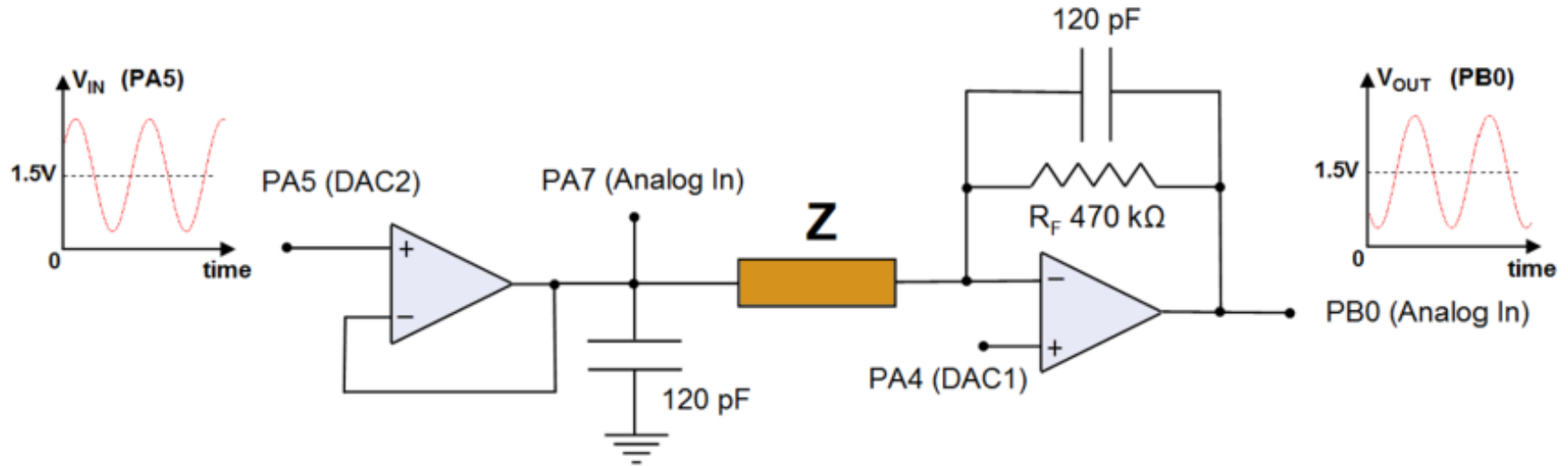
Electronic board



The electronic board of the sensor system



The electronic board of the sensor system



The electronic board of the sensor system

- The sinusoidal voltage signal $V_{IN}(t)$ (1.5 V offset, 1 V amplitude, 200 Hz) is generated using the microcontroller integrated 12-bit DAC (Digital-to-Analog converter) and applied to the sensor electrodes.
- The sensor current is converted to a voltage $V_{OUT}(t)$ with a I/V converter.
- The voltage signals $V_{IN}(t)$ and $V_{OUT}(t)$ are **acquired** with the 12-bit ADC (Analog-to-Digital converter) integrated inside the microcontroller.
- The voltage signals $V_{IN}(t)$ and $V_{OUT}(t)$ are **processed** and the sinewave parameters ($V_{M,IN}$, $V_{M,OUT}$, φ) are calculated.
- The emulsion conductance is calculated as
$$G_m = \frac{1}{R_F} \times \frac{V_{M,OUT}}{V_{M,IN}} \times \cos(\varphi)$$

Compensation of the temperature effect

- The portable sensor system has been designed for in-situ measurements in a production environment where the temperature can not be controlled.
- A compensation algorithm has been developed to estimate the emulsion conductance at 23.5 °C ($G_{m,23.5^{\circ}\text{C}}$) from the emulsion conductance at the environmental temperature ($G_{m,T}$) and the temperature value (T).
- The compensation algorithm has been implemented with the microcontroller.

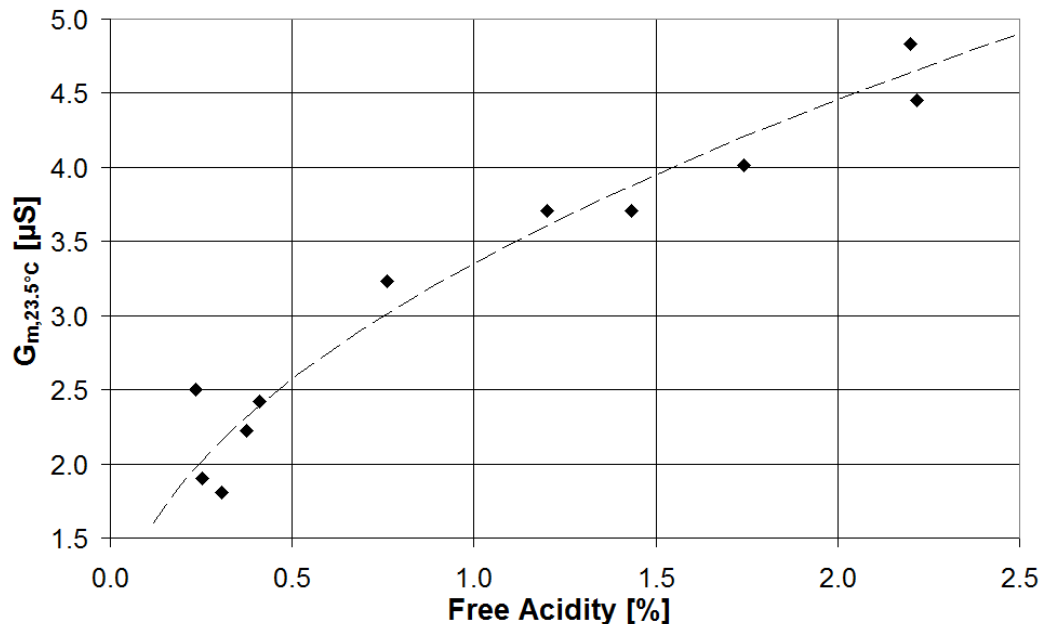
$$G_{m,23.5^{\circ}\text{C}} = \frac{G_{m,T} + 0.0026 \times (T - 23.5)}{1 + 0.0219 \times (T - 23.5)}$$

Validation of the sensor system

- Tests have been carried out on a set of 17 olive oil samples (6 EVOOs, 3 VOOs and 8 Lampante olive oils).
- A subset of 11 samples (fresh olive oils featuring a peroxide index < 20) has been tested and a correlation with the sample free acidity is found.
- In the case of full set of 17 olive oil samples, the emulsion G_m is affected by both the oil free acidity and the oxidation level, thus a threshold value for G_m can be set to discriminate EVOOs from lower grade olive oils.

Tests on fresh olive oil samples

- A correlation exists between $G_{m,23.5^{\circ}\text{C}}$ and the sample free acidity.

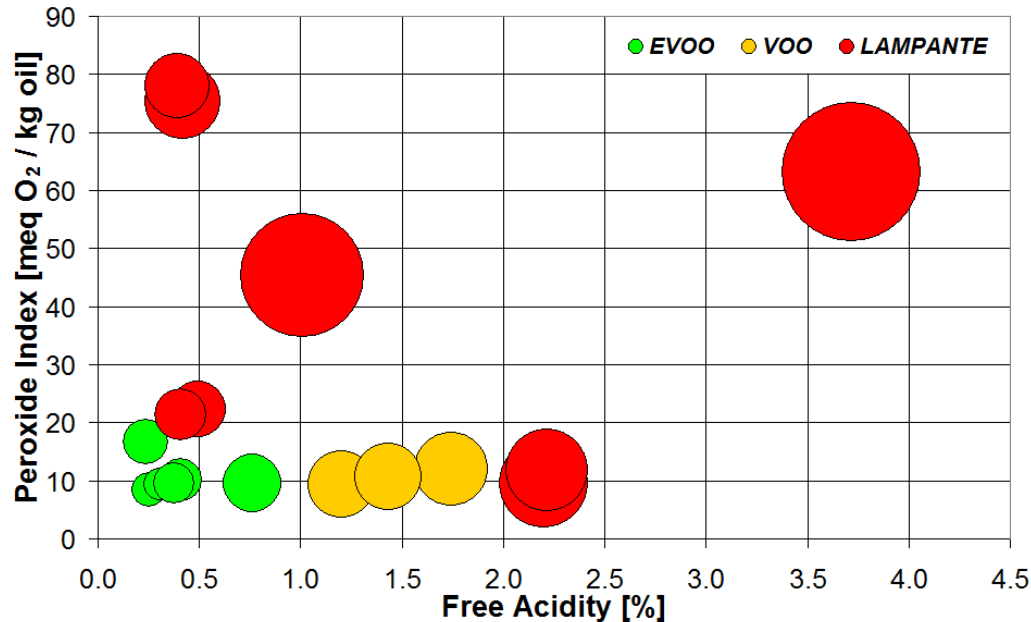


$$FA = \left(\frac{G_{m,23.5^{\circ}\text{C}} - \alpha}{\beta} \right)^2$$

$$\alpha = -0.6856 \quad \beta = 2.6662$$

Tests on the full set of olive oil samples

- The value of $G_{m,23.5^{\circ}\text{C}}$ is affected by both free acidity and oxidation level.



- The circle diameter represents $G_{m,23.5^{\circ}\text{C}}$.
- EVOO can be discriminated from lower grade oils by setting a conductance threshold $G_{m,23.5^{\circ}\text{C},\text{TH}} = 2.7 \mu\text{S}$.
- $G_{m,23.5^{\circ}\text{C}} < G_{m,23.5^{\circ}\text{C},\text{TH}} \rightarrow \text{EVOO}$

References

- Marco Grossi, Giuseppe Di Lecce, Tullia Gallina Toschi, Bruno Riccò, “Fast and accurate determination of olive oil acidity by electrochemical impedance spectroscopy”, *IEEE Sensors Journal* 14 (9), 2014, 2947-2954.
- Marco Grossi, Giuseppe Di Lecce, Tullia Gallina Toschi, Bruno Riccò, “A novel electrochemical method for olive oil acidity determination”, *Microelectronics Journal* 45 (12), 2014, 1701-1707.
- Enrico Valli, Alessandra Bendini, Annachiara Berardinelli, Luigi Ragni, Bruno Riccò, Marco Grossi, Tullia Gallina Toschi, “Rapid and innovative instrumental approaches for quality and authenticity of olive oils”, *European Journal of Lipid Science and Technology*, 118, 2016, 1601-1619.
- Marco Grossi, Rosa Palagano, Alessandra Bendini, Bruno Riccò, Maurizio Servili, Diego Luis Garcia-Gonzales, Tullia Gallina Toschi, “Design and in-house validation of a portable system for the determination of free acidity in virgin olive oil”, *Food Control*, 104, 2019, 208-216.

Thanks for your attention