Review Article

Rapid and innovative instrumental approaches for quality and authenticity of olive oils[†]

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Abbreviations: ANN, Artificial Neural Networks**, CA,** Cluster Analysis**, CART,** Classification And Regression Trees**, CE,** Counter Electrode**, CM,** Classification Map**, CV,** cyclic voltammetry, **CVA,** Canonical Variate Analysis**, DA,** Discriminant Analysis**, DF,** Discriminant Functions**, DFA,** Discriminate Factorial Analysis**, DN-PLS,** Discriminant Multi-Way Partial Least Squares Regression**, EIS,** Electrical Impedance Spectroscopy**, FAME**, Fatty Acid Methyl Esters, **FAEE**, Fatty Acid Ethyl Esters, **FGC-E-nose**, Flash Gas Chromatography E-nose, **Fisher's LDA,** Fisher's Linear Discriminant Analysis**, FSMLR,** Forward Stepwise Multiple Linear Regression**, FT-IR,** Fourier Transform Infrared Spectroscopy**, GA,** Genetic Algorithms**, IOC,** International Olive Council**, k-NN,** k-Nearest Neighbor**, LASSO,** Least Absolute Shrinkage**, LR,** Logistic Regression**, LSV,** linear sweep voltammetry, **MLR,** Multiple Linear Regression**, MLR-SA,** Multiple Linear Regression Meta-Heuristic Simulated Annealing Algorithm, **NIR**, Near InfraRed spectroscopy, **MIR,** Middle InfraRed spectroscopy, **NMF,** Non-Negative Matrix Factorization**, NPLS,** N-Way Partial Least Squares Regression, **PARAFAC,** Parallel Factor Analysis, **PCR,** Principal Component Regression, **PLS-DA,** Partial Least Squares Discriminant Analysis**, PLS-FDA,** Partial Least Squares Factorial Discriminant Analysis**, PTR-MS,** Proton Transfer Reaction-Mass Spectrometry**, QDA,** Quadratic Discriminant Analysis, **RE**, Reference Electrode, **SCV,** staircase voltammetry, **SFAM,** Simplified fuzzy Adaptive Resonance Theory Mapping, **SIMCA,** Soft Independent Modelling of Class Analogy**, SLDA,** Stepwise Linear Discriminant Analysis**, SOM,** Self-Organizing Maps, **SPA,** Successive Projection Algorithm**, SUT,** Sample Under Test**, SVM,** Support Vector Machines**, SWV,** square wave voltammetry, **UNEQ-QDA,** Unequal Quadratic Discriminant Analysis**, TDR**, Time Domain Reflectometry, **UV-Vis**, UV-visible, **WE**, Working Electrode

Abstract

The quality of virgin olive oils is assessed through the determination of several analytical parameters, whose values must be within the ranges established by the different institutions involved. In addition to official methods, there is a strong need for simple, rapid, and environmentally friendly techniques for the quality control of virgin olive oils and for addressing the challenging task of determining geographical origin and detecting adulterants. Towards this purpose, some of the most interesting applications based on optical spectroscopic techniques, on the measurement of electrical characteristics and on the use of instruments equipped with electronic chemical sensors, including also other promising techniques are herein discussed. These techniques, adequately coupled to an appropriate statistical approach, appear to be promising for assessment of several quality-related parameters. The prediction of sensory attributes and of the oxidative status of virgin olive oils have also been reviewed by adopting these selected techniques, which are also considered to be potentially appropriate solutions for identification of the geographical origin of virgin olive oils and to assess their adulteration with cheaper oils. Overall, the techniques discussed are promising and cutting-edge approaches for the establishment of useful portable instruments for in-situ monitoring of the quality of virgin olive oils.

Practical Applications

The simple, rapid, and environmentally friendly analytical approaches discussed herein represent promising analytical tools for assuring the authenticity and monitoring the quality of virgin olive oils. Such innovative techniques and tools need to be ring-tested and validated. Some innovative reviewed approaches will permit to develop useful portable instruments able to perform in-situ appropriate controls also by small laboratories or olive oil mills with limited technical facilities. These equipments will be potentially usable also by trained "non-professional analytical skilled" people. Some other approaches, rapid but more expensive, will be applicable mainly by quality

control labs and will increase the number of samples analyzed per day, thus fostering laboratory proficiency and an effective fighting against olive oil fraud.

1. Introduction

Virgin olive oils are "*oils obtained from the fruit of the olive tree solely by mechanical or other physical means under conditions that do not lead to alteration in the oil, which have not undergone any treatment other than washing, decantation, centrifugation or filtration, to the exclusion of oils obtained using solvents or using adjuvants having a chemical or biochemical action, or by re-esterification process and any mixture with oils of other kinds*" [1]. According to the quality degree, virgin olive oils can be classified in different commercial categories: in particular, the European Union Commission [2] recognizes only three classes, namely extra virgin, virgin, and lampante, whereas the International Olive Council (IOC) [3] and the Codex Alimentarius standards [4] also include the "ordinary" grade before the last lampante category. Belonging to the above mentioned categories depends on several physicochemical phenomena that act "from farm to fork", such as the hydrolytic and oxidative processes taking place in olives before extraction, during technological procedures for producing oils, and method of preservation [5]. Each category of virgin olive oils shows a different quality level, which also corresponds to a different value and, subsequently, price; in general, extra virgin olive oil is characterized by one of the highest economical values among all vegetable oils [6]. Therefore, a temptation for fraudulent actions has always been present in the olive oil sector, such as mixing virgin olive oil with cheaper or inferior quality products [5]. In fact, olive oil, milk, honey, and saffron are the most common targets for adulteration reported in scholarly journals [7]. For assuring correct categorization of each of the commercial classes, most of the analytical methods for assessing quality and genuineness of olive oils are based on the determination of specific chemical and sensory parameters, whose values must be within the ranges established by the different international institutions. Nowadays, the European Union Commission [2], the IOC [3] and the Codex Alimentarius [4] provide similar, but not equal, legal limits for

almost all analytical parameters related to quality of olive oils. In this regard, it is important to underline that even if the olive oil sector is highly regulated, "*current legislation is still fragile and not always reliable, and therefore there is a need for improvements on the ground*" [8]. In particular, there is a strong and growing demand for global analytical procedures that can substantially reduce the number of current official methods, especially in the development of rapid and environmentally friendly approaches. Most of the official methods to evaluate the quality of virgin olive oils consist of time-consuming and complex procedures that require several preparative steps of samples before analysis, often with the use of toxicchemicals and solvents for human health and the environment. Moreover, not all laboratories, especially those from developing countries or those located in small olive oil mills and packaging centers, have the technicalcapability to perform such analyses in an appropriate way. Often, the need to ship oil samples to a laboratory for analysis results in high costs and delays; all these long procedures are overwhelming for recognized analytical laboratories. Therefore, simple, rapid and environmentally-friendly techniques, suitable for on-site quality control even for new clients, who are "non-professional analytical skilled" end users, are desirable. Moreover, despite the recently developed and advanced instrumental techniques, some analytical tasks still remain very difficult to be completely addressed, such as the identification of the geographical origin of virgin olive oils [9, 10]. This latter represents an important issue, considering the obligation to indicate the geographical origin in the label of virgin olive oils sold in the European Union [11].

Considering this fragmented scenario and these urgent needs, the European Commission launched a project call within the Horizon 2020 framework to better guarantee olive oil quality and authenticity by empowering the detection and fostering the prevention of frauds. In this context, OLEUM project has been recently financed and will run from 2016 to 2020; the OLEUM Consortium is coordinated by the University of Bologna and formed by 20 partners covering 13 European countries and 3 associated countries (Swiss, Turkey, Israel), including different organizations, such

as universities and other public/private research centers, SMEs, large food industries, and non-profit organizations.

This review does not have the ambition to be a systematic collection of all the different approaches used for monitoring the quality of oils obtained by olives. For this purpose, several interesting reviews and book chapters have already been published in recent years [5, 6, 9, 10, 12, 13, 14, 15, 16, 17]. The aim of this review is to present the most interesting, promising and innovative approaches found in the scientific literature with a potential and realistic application for the development and establishment of rapid, easy-to-use, environmentally-friendly portable instruments to be used in monitoring the quality of virgin olive oils (**Table 1** and **Table 2**). For this reason, investigations based on: i) the adoption of optical techniques, such as UV-Vis, NIR, MIR, RAMAN, and fluorescence spectroscopy; ii) the measurement of electrical characteristics, such as electrical impedance spectroscopy, amperometry, and cyclic voltammetry; and iii) the use of instruments equipped with electronic chemical sensors (e.g. electronic noses and tongues), including also other promising techniques such as flash gas chromatography electronic nose and PTR-MS, are herein proposed and reviewed. In particular, the discussion is focused on the application of such techniques for assessment of several quality-related parameters of virgin olive oils, such as free acidity, peroxide numbers, extinction coefficients, fatty acids, and fatty acid alkyl esters, but also to estimate phenolic compounds, tocopherols, and moisture content. The evaluation of sensory attributes (both positive and negative) and oxidative status of virgin olive oils have also been reviewed by adopting these selected approaches, which may also be considered as a potential solution for identification of the geographical origin of virgin olive oils and to detect fraudulent adulterations with cheaper edible oils.

2. Optical Techniques

Among non-destructive techniques, UV-Vis, NIR, MIR, RAMAN, and fluorescence spectroscopy can be considered the most explored rapid tools in the food panorama and, given the considerable

literature dedicated to this topic, also in the olive oil sector. The spectral information and power of the techniques vary according to the specific analytical purpose, but all the tools listed have been extensively studied for both quantitative and qualitative assessments of virgin olive oil samples.

2.1 UV-Vis spectroscopy

Due to the simplicity of use, handling and low cost, UV-Vis spectroscopy is particularly used in the food sector for rapid screening of some related compositional properties. Recently, the combination with powerful chemometric tools have undoubtedly enhanced the potentiality of the technique. Information contained in UV-Vis spectra, originating from electronic transition from a lower energy to a higher energy molecular orbital, and elaborated by multivariate data analysis, has been proven to be suitable for the identification of possible adulterations of virgin olive oils samples or to classify them according to their geographical origin [6]. Acquisitions conducted in the 190-900 nm spectral range and analyzed with a self-organized map based on chaotic parameters appeared to be well suited to monitor adulterated samples of extra virgin olive oils (added with low cost olive oils, such as refined olive oils or refined olive pomace oils) with a misclassification rate of less than 1.3% according to the concentration of the adulterant agent [18]. The same spectral range was also explored with multivariate regression tools to estimate extra virgin olive oil adulterations (%) and R^2 values up to 0.966 for radial basis ANNs were observed [19]. Data fusion strategies were also proposed in combination with discriminant analysis (LDA, PLS-DA, and SIMCA) for extra virgin olive oils classification purposes according to their geographical origin. In particular, several combined approaches were used: UV-Vis spectra and physical-chemical parameters were evaluated for samples produced from different Spanish regions [20]; different Ligurian production areas were assessed by combining UV-Vis spectra and headspace mass results [21], or by UV-Vis spectra, NIR and headspace mass data [22]. Moreover, a simple and low-cost technique, exploiting optical measurements at a single wavelength, was introduced in 2015 by Grossi et al. [23] for determination of peroxide value (569 nm) and total phenolic content (835 nm) in olive oils (**Figure**

1). A fully working portable electronic system (costing about $ 300) was built that is suitable for in-situ measurements in olive-oil mills and oil packaging centers since it tests the sample without lengthy preparation or extraction procedures. The system is based on the measure of optical absorbance of an emulsion of an aqueous chemical reagent and the olive oil under consideration. The chemical reagents, different for the case of peroxide value and phenol content, are: 1) 8 ml of ferrous ion oxidation xylenol orange (FOX) mixed with 7 ml of distilled water for peroxide value determination; 2) 13 ml of distilled water mixed with 1 ml of Folin-Ciocalteu reagent and 1 ml of sodium carbonate (Na_2CO_3) 15% for total phenol content. The sensor, described in **Figure 1**, has been tested with a set of 25 olive oil samples and the results have shown good correlation between the estimated quality parameter and the value measured with the reference technique ($R^2 = 0.883$ for peroxide value and $R^2 = 0.895$ for total phenolic content).

2.2 NIR, MIR, and RAMAN spectroscopy

NIR, MIR, and RAMAN spectroscopic methods are considered powerful analytical techniques for rapid determination of food chemical composition and molecular structure. They are based on the study of vibrational transitions occurring in the ground electronic state of the molecules after the interaction with the incident radiation at a particular frequency [24].

The potentiality of near infrared spectroscopy covering the 750-2500 nm spectral range, was tested by following different measurement modes for the simultaneous estimation of several olive oil components. The NIR spectral information, containing overtones and combination of the fundamental vibrations of C–H, N–H, O–H and S-H chemical bonds [25], has been proven to be suitable for quantitative and qualitative assessments of olive oil samples [26]. Both main and minor virgin olive oil components have been estimated through a chemometric analysis of NIR spectra. Accuracy of the predictive models appeared to be affected by differences in samples characterising the data set and by operative and statistical procedures. In particular, the percentages of fatty acids and the free fatty acid contents were the main predicted parameters. Investigations conducted with

virgin olive oils showed predictive models of the major fatty acid content, in percentage, characterised by R^2 up to 0.970 (16:0; 18:2 $n-6$) [27] and r values up to 0.960 (PUFA) [28] using PLS regression analysis. Appreciable PLS results were also shown by Armenta et al. [29] in terms of oleic acid percentage prediction (R^2 up to 0.999 for olive oil samples) and by Mailer [30] (R^2 of 0.99) for olive oil samples. NIR methods were also established for estimation of the polyphenol content (ppm) with R^2 values up to 0.94 for extra virgin olive oils; significantly lower accuracies emerged for samples characterised by an increment in turbidity [31]. Triacylglycerol content [27], moisture [32], peroxide index [29], extinction coefficients K_{232} and K_{270} [33], and volatiles and sensory attributes [28] are the most widely explored qualitative parameters. NIR spectra and several multivariate approaches models were also investigated to detect adulterations in olive oil samples. Methods able to predict the level of adulterants were established for virgin and extra virgin olive oils adulterated with corn oil, sunflower oil, and raw olive residue [34, 35], for extra virgin olive oils adulterated with olive pomace [36], and for olive oils adulterated with walnut and hazelnut oils [36, 38]. Among qualitative experimental research, a large number of studies have been dedicated to the classification of olive oil samples according to their geographical origin. For example, a discrimination analysis of two very similar and geographically close denominations of origin, ("Siurana" and "Les Garrigues") virgin olive oils was carried out by Bertran et al. [39]. Olive oil samples from Spain, Turkey and Italy were assessed by Lin et al. [40], while European olive oil samples were classified according to their origin by Woodcock al. [41]; Tunisian virgin olive oils where distinguished from Maghrebian and French virgin olive oils [42]. A geographical classification method based on NIR spectra of extra virgin olive oils from the eastern Mediterranean [43] and from three Italian regions (Lombardy, Tuscany and Calabria) [44] has also been proposed. Besides geographical discrimination, multivariate tools have been combined with NIR spectral information to classify Italian extra virgin olive oils on the basis of the cultivar ("Casaliva", "Leccino" and "Frantoio") [45] and to distinguish extra virgin olive oils from different European and non-European countries on the basis of the fruit aroma intensity perceived by assessors [46]. By

using LDA and SIMCA statistical methods, these experiences showed classification ability up to 90.5 % (as average value) for the varietal origin and up to 100 % for the three fruity classes considered (low, medium, and high).

Mid-infrared (MIR) spectroscopy covers the 2500–25,000 nm spectral range. This part of the electromagnetic spectrum is characterized by bands from stretching and bending fundamental vibrations of the functional groups. The adsorption characteristics of lipids, carbohydrates, proteins, and water can be easily identified and information related to structural properties can be also extrapolated [24]. The assignment of edibles oils bands in the mid-infrared spectra can be appreciated in the work by Guillén and Cabo [47]. Mid-infrared spectroscopy was tested for quantitative determinations of saturated and unsaturated fatty acids in olive oil samples [48], fatty acids, and triacylglycerols in virgin olive oils [49], and oleic acid, linoleic acid, saturated fatty acids, mono-unsaturated fatty acids and poly-unsaturated fatty acids in virgin olive oils [50].

Apart from the fatty acid composition, the information contained in the infrared spectrum was used to estimate other qualitative parameters such as water content, total phenol amount, and antioxidant activity in virgin olive oils [51], as well as the phenolic and chlorophyll contents in olive oils [52] and the fatty acid alkyl ester amounts in extra virgin olive oils [53]. Different stages of the oxidation process of extra virgin and olive oils have been shown to involve changes in FT-IR spectrum frequency values of different bands and in ratios between absorbances of some bands [54]; these changes appear to be related to variations in peroxide and anisidine values levels occurring during the oxidation course [55]. Peroxide value has also been estimated in extra virgin olive oils [56] and the oxidized fatty acid concentration under different oxidative status was determined in virgin olive oils [57]. Mid-infrared spectroscopy techniques combined with chemometric tools have been demonstrated to be effective in the detection and estimation of adulterants in olive oil samples. Different quantitative and qualitative methods based on PLS, PCR, and PLS-DA analyses were established for extra-virgin olive oils adulterated with corn–sunflower, cottonseed, and rapeseed oils [58], with canola, hazelnut, pomace, and high linoleic/oleic sunflower

oils [59] and with palm oil [60], or with sunflower oil, soyabean oil, sesame oil, or corn oil [61]. A large number of studies have been dedicated to MIR methods that are able to discriminate olive oils samples according to their qualitative attributes and to differences with other edible oils [62, 63, 64]. In addition, discrimination and classification tools were set up from FT-IR spectra in order to confirm the geographic origin of extra virgin olive oil from Liguria [65], to classify virgin olive oils from different Morocco regions [66], to distinguish between Italian and non-Italian and between Ligurian and non-Ligurian extra virgin olive oils [67] to assess the authenticity of monovarietal and mixture of extra-virgin and olive oils [68] and to classify Italian monovarietal extra virgin olive oils and blends of different cultivars [69]. A traceability method based on a combination of both NIR and MIR spectroscopic techniques aiming at the origin verification of the Italian PDO Sabina extra virgin oils was explored by Bevilacqua et al. [70]. Discrimination and classification models were finally developed in order to distinguish between olive oil samples characterized by different sensory defects (musty, winey, fusty, and rancid) [71] between extra virgin olive oils coming from whole and stoned olive pastes [72], between virgin olive oil samples according to freshness in terms of oxidation processes [73] or between extra virgin olive oils according to fruity aroma intensity [46]. A modelling of FT-MIR virgin olive oils spectra was also carried out to identify spectral regions affected by differences in oxidative stability [74].

More innovative and emerging in the food panorama, hyperspectral imaging technique merges the potentiality of spectroscopic analysis with computer vision information. Acidity, moisture content, and peroxide index have been estimated by processing hyperspectral images acquired between 900 nm and 1700 nm on different types of olive oils samples (from extra virgin to lampante) [75]. According to different component selection algorithms, maximum regression coefficients of 0.98, 0.99, and 0.99 were, respectively, obtained for estimation of acidity, moisture, and peroxide index, respectively. Hyperspectral data (200 nm–1700 nm) were also processed in order to cluster extra virgin olive oils samples according to geographical origin [76].

Raman spectroscopy is considered to be a complementary technique to infrared methods. As described above, both analytical tools are characterized by the exploration of molecular vibration properties. However, they present different selection rules, such as change of dipole moment for infrared and polarizability for Raman spectroscopy. This latter property is advantageous when covalent bonds in non-polar groups would be detected, as for unsaturated fatty acids in the olive oil component showing intense Raman bands [77]. According to this premise, the prediction ability of the technique was explored to obtain rapid tools for estimation of fatty acid content. In detail, multivariate regression models for the prediction of free fatty acid content were set up by Raman spectroscopy in extra virgin olive oil, with R^2 values up to 0.963 [78] and to 0.994 [77], and by FT-Raman spectroscopy in olive oil and olives with r values up to 0.997 [79] depending on the selected spectral range. FT-Raman was also used recently for quantification of the fatty acid content in extra virgin olive oil samples [80]. Furthermore, in the work conducted by Gouvinhas et al. [77], PLS and PCR regression models for estimation of the peroxide value were discussed. Information contained in Raman bands has been analyzed in different studies focused on discrimination multivariate methods regarding the problem of authentication and adulteration with other edible oils. Based on the intensity ratio of Raman spectroscopy vibration bands, particularly the cis (=C-H) and cis (C=C) bonds normalized by the band at 1441 cm^{-1} (CH_2), the method proposed by Zou et al. [81], appears to distinguish olive oil samples containing 5% in volume of other edible oils (soybean oil, rapeseed oil, sunflower seed oil, or corn oil). The presence in olive oil of the hazelnut oil was also explored by Baeten et al. [82], with a limit of 8% in volume for Turkish blends, and estimated by López-Díez et al. [83] by PLS regression analysis with R^2 of 0.979. Raman spectra combined with PLS-discriminant analysis also appeared able to correctly classify French virgin olive oils (92.3%) and 100% of protected designation label samples made with only one principal cultivar [84].

2.3 Fluorescence spectroscopy

Similar to the above described optical techniques, fluorescence spectroscopy can also be considered a well known and extensively used method for a rapid and reliable assessment of qualitative and

quantitative properties of olive oil samples. Methods and applications of the technique were reviewed in detail by Sikorska et al. [85], together with main potentialities related to the multi-way analysis of excitation and emission spectra characterizing the fluorescence properties of olive oil. It is known that vitamin E, chlorophylls, and phenolic compounds are the main olive oil components influencing the fluorescence properties that have been extensively explored in order to discriminate between different grades of olive oils from extra virgin to olive pomace oils [86, 87, 88]. Fluorescence discrimination appears to be related to the free acidity of the olive oil [89]. Different fluorescence methods have also been used to classify virgin olive oils according to geographical origin [90] and to identify possible adulterations [91, 92]. With respect to experiences carried out to qualitatively assess olive oil samples, the prediction power of fluorescence spectra of the main compounds of olive oil are scarce in the literature. Methods to evaluate the concentration of different fluorescent molecules (phenols, α-tocopherol, and chlorophyll) of extra virgin olive oils by using a front-face (FF) fluorescence technique were proposed by Zandomeneghi et al. [93]. Sikorska et al. [94], and Díaz et al. [95] explored methods for the assessments of tocopherol content, while Papoti and Tsimidou [96] have investigated phenolic content determination. Prediction models of the peroxide value, K_{232}, K_{270} and acidity were reported by Guzmán et al. [97] from fluorescence spectra acquired on virgin olive oil samples in their natural and oxidized state between 300 and 800 nm using a 300-400 nm excitation wavelength. In external validation, R^2 values of 0.902, 0.907, 0.924, and 0.679 were reported, respectively, for peroxide value, K_{232}, K_{270}, and free acidity.

3. Analysis of electrical characteristics

An alternative to the reference techniques to measure quality parameters of olive oil is Electrical Impedance Spectroscopy (EIS) [96], widely used to investigate different types and aspects of food products [99, 100, 101, 102]. In EIS, the SUT is placed in direct contact with a couple of electrodes through which a sinusoidal voltage (on a wide range of frequencies) is applied and the current

through the sample is measured (Figure 2). Then electrical parameters are extracted from the acquired data using a fitting algorithm [103].

The SUT and electrodes system is often modeled with an equivalent electrical circuit composed of resistances, capacitances, and other non-linear models, whose parameters are extracted by means of software packages. Since vegetable oils are good insulators, when EIS is applied for the analysis of raw olive oil (i.e. not mixed with any reagent) the SUT impedance is essentially capacitive. Prevc et al. [104] investigated the electrical properties of different vegetable oils in the frequency range 50 Hz–2 MHz and found that the electrical conductance at low frequency is extremely low (lower than 0.5 nS·m^{-1}). Modeling the electrodes as two parallel conducting plates of area A, separated by a distance d, the measured capacitance is given by:

$$C = \varepsilon_0 \varepsilon_r \cdot \frac{A}{d} \quad , \tag{1}$$

where ε_0 (8.85·10^{-12} C^{2}N^{-1}m^{-2}) is the vacuum dielectric constant, while ε_r is the relative one, defining the SUT dielectric properties. The measurement of ε_r has been widely used since 1981 as a quick and inexpensive method to monitor the deterioration of frying oils subjected to thermal stress cycles [103, 104]. According to Prevc et al. [104], ε_r is relatively constant for f < 500 kHz while it decreases with frequency for f > 500 kHz. Its value depends essentially on: content of free fatty acids; oxidation status; temperature (ε_r decreases linearly with increasing temperature). Lizhi et al in 2008 published a study where 10 vegetable oils (olive, sesame, soybean, safflower, corn, sunflower, canola) were electrically characterized in the frequency range 100 Hz–1 MHz [107]. The results showed that oils of the oleic acid type (characterized by high percentages of this fatty acid) are characterized by significantly lower values of ε_r than oils belonging to linoleic or low linolenic acid types. Furthermore, since the dielectric constant depends on the oil moisture content, in 2013, Ragni et al. proposed a rapid and inexpensive method to estimate the water content in extra virgin olive oil [108] based on the measurement of ε_r. As the relative dielectric constant of water is much higher than that of oil (77 vs. 3-3.2), the presence of water (even in very small concentrations)

results in an increase of ε_r that can be detected by capacitive measurements. A commercial capacitor probe for radio applications was used for measurements at six different frequencies (500 Hz, 2 kHz, 8 kHz, 32 kHz, 128 kHz, and 512 kHz). Initially, oil samples with the same composition but different water content were tested and a very good correlation ($R^2 = 0.962$) between water content and measured capacitance was found at 8 kHz. Next, a set of 17 EVOOs (featuring different composition) were tested and their water content was correlated with the measured capacitance ($R^2 = 0.818$). The reduced accuracy in the case of real EVOO samples can be explained by the variation of ε_r with the fatty acid composition of the oil [102]. The possibility to detect the adulteration of olive oil with other vegetable oils was investigated in 2010 by Lizhi et al. [109]. The oil ε_r was measured using a 16452A liquid test fixture (Agilent Technologies) in the frequency range 100 Hz–1 MHz at 25°C. Adulterated olive oil samples were artificially created by spiking the sample with different concentrations of vegetable oils of linoleic or low linolenic acid type (soy, corn, canola, sesame, perilla) as well as the oleic acid type (safflower). The measured ε_r in the frequency range 174 Hz–1 MHz (17 points) was used for Principal Component Analysis (PCA) and Partial Least Square (PLS) regression to estimate the percent of added adulterants. The results showed the possibility to detect the adulteration with linoleic or low linolenic acid oils, while the ε_r variations induced by oleic acid oils were too small for reliable discrimination. A different use of EIS to investigate quality parameters of olive oil requires mixing the oil under test with a chemical reagent to create an emulsion to be electrically characterized. This approach was used by Grossi et al. in 2014 to estimate olive oil free acidity [110] with the procedure sketched in **Figure 2 (a)**. The oil sample under test (1 ml) was mixed with 15 ml of an hydro-alcoholic reagent (60% ethanol, 40% distilled water) to create an emulsion whose electrical parameters were measured in the frequency range 20 Hz–2 MHz at constant temperature (20°C). When the fatty acid molecules (RCOOH, where R is the monovalent functional group $CH_3(CH_2)_7CH=CH(CH_2)_7$) meet the hydro-alcoholic reagent, a dissociation reaction takes place that creates H_3O^+ ions in the emulsion, thus increasing the emulsion electrical conductance, from which the sample free acidity can be calculated. From the

results obtained with 55 samples, the estimated free acidity correlated well with the value obtained with the reference method (R^2 = 0.931), while a further increase in correlation (R^2 = 0.979) can be achieved by making two measurements, one with the sample mixed with the hydro-alcoholic reagent and the other where the oil is mixed with distilled water. The technique described above has been implemented in the form of a portable embedded system for in-situ olive oil quality control [111] based on the microcontroller DSPIC33ep512 by Microchip Technologies that uses a laptop PC for data display and filing. A similar approach was used by Yu et al. to determine the free acidity of different types of vegetable oils (olive oil, palm oil, coconut oil, rapeseed oil) [112]. In this case the emulsion was created between 40 ml of potassium hydroxide (KOH) 0.04 M (the reagent) and 4 g of the oil under test. The acidity was estimated from the difference of electrical conductivity between the reagent and the emulsion, and a very good correlation was found between such a variation and the free acidity determined by the reference method. Other authors proposed a technique to measure the peroxide value in different edible vegetable oils based on changes in electrical conductance due to reaction of potassium iodide (KI) with the hydroperoxides present in the oil sample [113].

A different technique, related to EIS, is amperometry, where current is measured as function of the applied potential. A sub-class of amperometry is voltammetry where the applied potential varies with time. Different sub-classes of voltammetry exist, depending on the waveform of the applied potential such as linear sweep voltammetry (LSV), staircase voltammetry (SCV), square wave voltammetry (SWV), and cyclic voltammetry (CV). In the latter a periodic linear voltage is applied between the working electrode (WE) and the reference electrode (RE) and the current is measured at the counter electrode (CE). In the case of a supporting electrolyte with a single electrochemical reactant, a typical voltammogram (current vs. voltage) is shown in **Figure 2 (b)**, where the current maximum values (function of the voltage scan rate) and voltage values for which such maxima are achieved, which are the relevant parameters used to investigate the electrical properties of the electrochemical cell. An amperometric electrochemical sensor to measure hydroperoxide

concentrations in olive oil was presented by Adhoum and Monser in 2008 [114]. The sensor was initially characterized by cyclic voltammetry (CV) and then used with constant voltage amperometry (with an applied potential of 50 mV vs. the reference electrode RE) to measure the concentration of H_2O_2 and tert-butyl hydroperoxide as well as hydroperoxides in actual olive oil samples. An amperometric biosensor to measure the polyphenol content in olive oil was presented by Hammani et al. in 2016 [115], which uses a gold WE modified with tyrosinase on a self-assembled monolayer of ω-mercaptopropyl naphthoquinone and a working potential of -0.35 V vs Ag/AgCl RE. Measurements on polyphenols (previously extract from olive oil) resulted in very good correlation (R^2 = 0.999) in the concentration range 0–135 μM with a limit of detection of 0.019 μM.

The characterization of oil samples by EIS or voltammetric techniques is usually carried out at frequencies in the range from 1 Hz to a few MHz.

To investigate sample properties at higher frequencies (i.e. in the GHz range), different techniques must be used. Time Domain Reflectometry (TDR) was historically used in the telecom industries to identify discontinuities in cables and more recently adopted to measure the water content in soil and investigate the dielectric properties of different types of samples [116, 117]. TDR is based on the reflection of electromagnetic waves at encountered interfaces: measuring the time delay between generated and reflected waves, information on the dielectric properties of the involved materials can be obtained. A typical set-up for TDR measurement is shown in **Figure 2 (c)**. A pulse generator provides a voltage pulse that propagates to the TDR probe immersed in the sample of interest. In correspondence to the probe/sample interfaces, a reflected pulse is generated (by the impedance mismatch) that travels backward. All voltages are monitored by a high sampling rate oscilloscope and the acquired voltage waveform has the typical shape shown in **Figure 2 (c)**. Measuring the delay between t_2 (reflection from the probe end in the sample) and t_1 (reflection at the interface air/sample), the sample dielectric constant can be calculated. Ragni et al. investigated the possibility to measure the water content in extra virgin olive oil [118] using an oscilloscope equipped with a

sampling head with TDR function and a two-terminal probe made of silver-plated copper wires covered by glass pipes. The water content was initially estimated from the difference between the reflection at the oil/air interface and at the probe end, but this resulted in low accuracy (R^2 not higher than 0.305). Thus, a different approach was used: the entire acquired wave was analyzed and the time ranges affected by the sample moisture content were identified; next, the voltage wave in the selected time ranges was used as input data for a PLS analysis to build a model for the oil water content. This approach was found adequate since a strong correlation was found between the estimated water content and the value determined by reference method ($R^2 = 0.984$). This technique was also used by the same research group as a rapid screening for the content of fatty acid alkyl esters (FAAE), fatty acid methyl esters (FAME), and fatty acid ethyl esters (FAEE) [119]. The results showed good correlation for FAAE ($R^2 = 0.927$), FAME ($R^2 = 0.905$), and FAEE ($R^2 = 0.923$). Cataldo et al. investigated the use of TDR to measure the acidity of olive oil and detect its adulteration with lower quality oils (castor, corn, sunflower, peanut, soybean, and various seed oils) [120, 121].

4. Electronic noses, electronic tongues and other promising approaches

Recently, a different approach to sensing has gained a increasing interest, where arrays of sensors, and not a single sensor, are used to collect a large amount of information for specific and nonspecific molecular recognition (**Figure 3**). This approach has led to the design of devices known as electronic nose (e-nose) and electronic tongue (e-tongue): the former are used to characterize different gas mixtures, while the latter try to artificially reproduce the taste sensation [122].

Instruments characterized by arrays of electronic chemical sensors with partial specificity and capable of identifying simple or complex odors are commonly named electronic nose systems. Published literature on olive oil refers to about four gas sensors: metal oxide semiconductors, metal oxide semiconductor field effect transistors, piezoelectric crystals, and organic polymers [123]. Metal oxide semiconductors sensors combined with multivariate data analysis were extensively

used in the quality control of virgin olive oils. Some examples include: different olive oil samples were classified, with accuracy values up to 66.7% [124], and discriminate [125] on the basis of the belonging to different qualitative categories (from extra virgin to lampante); virgin olive oils were classified on the basis of five different sensory defects (fusty, mouldy, muddy, rancid, and winey, with average prediction errors below 0.90%) [126]; the oxidative status was analyzed for olive oils [127] and virgin olive oils [128]; virgin olive oils adulterated with sunflower and olive-pomace oils (from 5% to 60%) were classified (percentage of correct classification up to 100%) [127]. Another interesting application of metal oxide semiconductors and qualitative statistical tools is the possibility to identify the geographical origin of olive oils. More than 96% success rate in the recognition of 27 olive oil samples (from 5 different geographical areas of Morocco) was obtained by heating samples and transferring the generated volatile compounds to a set of 6 metal oxide semiconductors sensors using pure nitrogen as a carrier gas [130]; monovarietal and commercial extra virgin olive oils obtained from different Italian and Spanish regions were also classified by exploring, in addition to metal oxide semiconductor sensors, the potentiality of metal oxide semiconductor field effect transistors [131]. A Quartz Crystal Microbalance sensor array has been used to distinguish between edible and non-edible olive oils and a correct sample classification percentage of 91.7% was shown [132]. An example of application of a polymer-based gas sensor is the study by Guadarrama et al. [133] which aimed at discriminating samples of olives oils from different origins, varieties, and qualitative categories.

By using electronic tongues, the signals obtained from an array of sensors not necessarily specific for any particular components in the liquid are analyzed. Published works on olive oils show arrays of sensors mainly based on electrochemical principles: potentiometric through the measurement of a potential value created by the diffusion of ions across a membrane, amperometric or voltammetric [134]. The potential of the potentiometric electronic tongue combined with linear discriminant analysis and SA metaheuristic variable selection algorithm was explored in order to classify 18 different monovarietal extra virgin olive oils according to the cultivar, with a sensitivity greater

than 97%, and to discriminate Spanish olive oils from Portuguese oils [135]. Potentiometric arrays were also used to classify extra virgin olive oils on the basis of sensory intensity of fruitiness, bitterness, and pungency attributes (average correct classification of 80% in cross validation) [136] and to monitor the quality of extra virgin olive oils during storage through the estimation of peroxide values, extinction coefficients, and oxidative stabilities with R^2 values up to 0.990 in cross validation [137]. Amperometric tyrosinase or peroxidase enzyme-based sensors with different specificities towards groups of phenolics affecting bitterness and pungency of virgin olive oils were tested by Busch et al. [138] and correlations coefficients values up to 0.860 and 0.930 were, respectively, observed for tyrosinase-based (with o-diphenols) and peroxidise-based (with monophenols) sensors. Qunfeng et al. presented an e-tongue composed of 3 WEs (platinum, silver and gold) tested with CV between -2V and 2V with different scanning rates [139] that discriminated 12 different vegetable oils. Apetrei et al. presented an e-tongue where the WEs were realized with carbon paste electrodes (CPE) obtained by mixing graphite with different vegetable oils [140]. The system was characterized by CV and SWV using a supporting electrolyte of 0.1M HCl and 0.1M KCl and the grade of bitterness in samples was estimated. Arrays of voltammetric sensors were also set up to discriminate extra virgin olive oils according to their phenolic content (correlation value of 0.993 in PLS-DA validation) [141], to quantify total polyphenol content in extra virgin olive oils (correlation value of 0.988 in PLS validation [142], and to detect adulteration of extra virgin olive oils with sunflower, soybean, and corn oils (100% of correct classification with 10%, 20%, and 10 % of sunflower, soybean and corn oils, respectively) [143].

To increase the accuracy in the estimation of quality parameters, some authors have tried a combined approach of e-nose and e-tongue. Methods combining both e-nose and e-tongue sensors have been proposed to discriminate between extra virgin olive oils according to the degree of bitterness [144], to classify extra virgin olive oils according to storage conditions [145] or virgin olive oils from different geographical areas of Morocco [146].

Moreover, a further promising analytical approach able to obtain a chemical fingerprinting of the samples was focused on the adoption of the flash gas chromatography electronic nose (FGC E-nose) combined with chemometrics; such technique has been preliminarily adopted for performing a rapid screening of commercial extra virgin olive oils characterized by different geographical origin [147]. Another quite recent rapid application consists in a continuous air sweeping of the head-space volatiles in a thermostated bottle to the drift tube of the mass spectrometer (Proton Transfer Reaction-Mass Spectrometry, PTR-MS). Such analytical approach, followed by a PLS-DA applied on the full spectra fingerprint, permitted to classify monovarietal virgin olive oils samples into their variety [148] and to classify them also according to the geographical origin [149]. Moreover, PTR-MS combined with chemometric techniques has been also used for the classification of rancid oils against extra virgin olive oils and to predict independently their thermooxidative degrees and to estimate their peroxide numbers [150]. Finally, the potentialities of a 60 MHz ^{1}H nuclear magnetic resonance (NMR) [151] and of a fast Differential Scanning Calorimetry (DSC) [152] were tested in terms of detection of adulterations in olive oil samples.

5. Conclusions

The analytical approaches found in the recent scientific literature have demonstrated to be among the most rapid, cutting-edge, environmentally-friendly, and easy-to-use for the potential set-up of instruments to be widely adopted in the in-situ quality control of virgin olive oils. In a preliminary phase, such analytical approaches will need to be applied "in parallel" with the official method, in order to permit their calibration and subsequent validation: only in this way will it be possible to support the adoption of the most promising solutions, even without the application of the official methods. In the next future, it is desirable that such innovative approaches will be tested for the analyses of a large number of samples of virgin olive oils characterized by different quality degrees, years of harvest, cultivars and origin in order to confirm the reliability, robustness, and applicability of the analytical solutions. In fact, especially for some, the creation of reliable databanks and data-

sharing platforms with appropriate users' access rights and collecting the data acquired from a large number of samples, will be fundamental to support their adoption. Starting from the herein discussed and promising approaches, it is important to highlight that their worldwide diffusion will be possible only if adequate public/private investments and research efforts will be addressed towards this direction in the near future. Towards these aims, the Horizon 2020 project OLEUM (2016-2020) is focused on guaranteeing olive oil quality and authenticity by fostering the prevention of fraud thanks to the development of cutting-edge analytical solutions. Such a desired scenario will permit increasingly effective controls for monitoring the quality of virgin olive oils and for resolving some emergent analytical issues. For this purpose, the herein discussed spectroscopic approaches have been demonstrated to be potentially useful analytical tools for the identification of geographical origins of the product, which represents a hard and ambitious challenge for its complexity, and also for the classification on the basis of the different cultivars. These are promising techniques for estimating several quality-related parameters, such as polyphenol content and peroxide indexes, but also for assessing sensory attributes and oxidative stability; moreover, they represent a useful approach for evaluating the authenticity of virgin olive oils, in terms of detection of adulterations with cheaper edible oils. Other analytical methods, such as the measure of the electrical properties of the virgin olive oils, have been shown to be a useful approach for monitoring several quality-related parameters (free acidity, peroxide value, fatty acid alkyl esters, water content) and to guarantee the authenticity of virgin olive oils. The adoption of electronic noses and tongues showed also good possibility to be used as instruments potentially able to discriminate oils obtained by olives in different categories by predicting the presence of sensory defects, identify their geographical origin, monitor their quality during storage, and detect the presence of adulteration with cheaper oils.

The final purpose of the adoption of all these analytical efforts will be to protect consumers against fraud, making virgin olive oils among the most protected foodstuffs, thus indirectly increasing consumer trust in these valuable products.

Conflict of interest

The authors have declared no conflict of interest.

Permission statements

The manuscript does not contain experiments using animals. The manuscript does not contain human studies.

Tables

Table 1: Composition and level of adulteration in virgin olive oils by using different analytical techniques.

Technique	Statistics	Quantitative parameter	Reference
NIR	prediction (PLS)	fatty acids-triacylglycerols	[27]
UV-VIS-NIR	prediction (PLS)	fatty acids - free fatty acids - peroxide value - phenolic compounds - induction time - chlorophyll	[30]
NIR	prediction (PLS)	free acidity - peroxide value	[29]
NIR	prediction (PLS)	peroxide value - free fatty acids- K_{232} - K_{270} - fatty acids-pigments - total phenolic compounds - thiobarbituric acid reactive substances value	[33]
NIR	prediction (PLS)	peroxide value - free fatty acids - K_{232} - K_{270} - fatty acids - tocopherols - phenolic compounds - volatiles-sensory attributes (fruity, bitter, pungent and defects)	[28]
MIR	prediction (PLS)	fatty acids	[48]
MIR	prediction (PLS)	fatty acids - triacylglycerols	[49]
MIR	prediction (PLS)	fatty acids - peroxide value	[50]
MIR	prediction (PLS)	fatty acids	[63]
MIR	prediction (MLR)	oxidised fatty acids	[57]
MIR	prediction (PLS)	fatty acids - oxidative stability - colour pigments - total phenolic content	[52]
Raman	prediction (PCR-PLS)	free acidity - peroxide value	[77]
Raman	prediction (PLS)	free acidity	[81]

Raman	prediction (PLS)	free acidity	[79]
Raman	prediction (PLS)	fatty acids	[80]
Fluorescense	prediction (PLS-NPLS)	free acidity - peroxide value - K_{232} - K_{270}	[97]
Capacitance	prediction (PLS)	fatty acids	[107]
Impedance spectroscopy	correlation	free acidity	[110, 111]
Electrical conductivity	prediction (liner models)	free acidity	[112]
MIR	prediction (PLS)	peroxide value	[20]
Electrical conductivity	prediction (liner models)	peroxide value	[113]
Electrochemical sensor	prediction (liner models)	peroxide value	[114]
E-tongue (potentiometric sensors)	prediction (MLR-SA-PCR-PLS)	peroxide value - extinction coefficients - oxidative stabilities	[137]
PTR-MS	prediction (PLS)	thermooxidative degradation – peroxide index	[150]
569 nm (peroxide value) and 835 nm (total phenol content)	correlation	peroxide value - total phenolic content	[23]
NIR	prediction (PLS-FSML)	total phenolic content	[31]
Fluorescense	linear methods	phenolic compounds – α-tocopherol- chlorophill	[93]
Fluorescense	linear methods	total phenolic content	[96]
Fluorescense	prediction (PLS)	tocopherols - pheophytins	[94]
Fluorescense	prediction (PLS)	tocopherols	[95]
Electrochemical tyrosinase-based biosensor	prediction (liner models)	phenolic compounds	[115]
E-tongue (amperometric	correlation	phenolic compounds	[138]

sensors)

E-tongue (voltammetric sensors)	prediction (PLS)	total phenolic content	[142]
E-tongue (voltammetric sensors)	prediction (PLS)	bitterness	[140]
E-nose + e-tongue (metal oxide semiconductors sensors + voltammetric sensors) + e-eye	prediction (PLS)	bitterness	[144]
MIR	prediction (PLS)	fatty acid alkyl esters	[53]
Time Domain Reflectometry	prediction (PLS)	fatty acid alkyl esters	[119]
MIR	prediction (PLS)	water content - total phenolic content - antioxidant activity	[51]
NIR	prediction (PLS)	moisture content - free acidity	[32]
Hyperspectral imaging	prediction (GA-MLR, SPA-MLR, LASSO)	free acidity - peroxide index - moisture content	[31]
Capacitance	prediction (linear metods)	water content	[108]
Time Domain Reflectometry	prediction (PLS)	water content	[118]
UV-VIS	prediction (MLR-ANN)	adulteration (refined olive, olive-pomace, sunflower, corn)	[19]
UV-VIS-NIR	prediction (PLS)	adulteration (sunflower)	[35]
NIR-MIR-raman	prediction (PLS)	adulteration (olive pomace)	[36]
NIR	prediction (PLS)	adulteration (soya-sunflower-corn-walnut-hazelnut)	[37]
NIR	prediction (PLS)	adulteration (soya-sunflower-corn-hazelnut)	[38]
NIR	prediction (linear models)	adulteration (corn-sunflower-refined olive residue)	[34]

MIR	prediction (PLS)	adulteration (corn–sunflower binary mixture, cottonseed, rapeseed)	[58]
MIR	prediction (PLS-PCR)	adulteration (palm)	[60]
MIR	correlation	adulteration (sunflower-soyabean-sesame-corn)	[61]
MIR	prediction (PLS)	adulteration (canola-hazelnut-pomace-high linoleic/oleic sunflower)	[59]
Raman	prediction (PLS)	adulteration (hazelnut)	[83]
E-tongue (voltammetric sensors)	prediction (PLS)	adulteration (sunflower-soybean-corn)	[143]
Fluorescense	preediction (N-PLS)	adulteration (olive pomace)	[91]
Fluorescense	prediction (PLS)	adulteration (sunflower)	[92]
Capacitance	prediciton (PLS)	adulteration (soy-corn-canola-sesame-perilla)	[109]
60 MHz ^{1}H NMR	Prediction (PLS)	adulteration (hazelnut)	[149]

Table 2: Qualitative assessments in virgin olive oils by using different analytical techniques.

Technique	Statistics	Qualitative parameter	Reference
UV-VIS	classification (LDA-PLS-DA)	geographical origin	[20]
UV-VIS	classification (LDA-SIMCA)	geographical origin	[21]
UV-VIS-NIR	classification (SIMCA-UNEQ-QDA)	geographical origin	[22]
UV-VIS-NIR	classification (PLS-FDA-k-NN)	geographical origin	[43]
NIR	classification (PLS-DA)	geographical origin	[27]
NIR	classification (ANN-LR)	geographical origin	[39]
NIR	classification (PLS-DA)	geographical origin	[41]
NIR	classification (SIMCA)	geographical origin	[42]
NIR-MIR	classification (LDA-PLS-DA-SIMCA)	geographical origin	[44]
MIR	classification (FDA-PLS-DA)	geographical origin	[65]
MIR	classification (PLS-DA)	geographical origin	[66]
MIR	classification (CART-SVM)	geographical origin	[67]
Hyperspectral imaging	discrimination (CM)	geographical origin	[76]
Raman	classification (DF)	geographical origin - harvest year -olive variety	[80]
Raman	classification (PLS-DA)	geographical origin	[84]
E-nose (metal oxide semiconductors sensors)	classification (LDA)	geographical origin	[146]
E-nose (metal oxide semiconductors sensors-metal oxide semiconductor field effect transistors)	classification (ANN)	geographical origin	[131]
E-tongue (potentiometric	classification (LDA)	geographical origin	[135]

sensors)

E-nose + e-tongue (metal oxide semiconductors sensors + voltammetric sensors)	classification (SVM)	geographical origin	[130]
MIR	classification (PLS-DA-SIMCA)	geographical origin	[70]
PTR-MS	classification (PLS-DA)	geographical origin	[149]
FGC-E-nose	classification (PLS-DA)	geographical origin	[147]
NIR-MIR	classification (LDA-SIMCA)	cultivar	[45]
MIR	classification (SIMCA)	olive variety	[68]
E-nose (polymer-based gas sensors)	discrimination (PCA)	origins, olive varieties and commercial categories	[133]
E-tongue (voltammetric sensors)	discrimination (PCA)	olive varieties	[139]
PTR-MS	classification (PLS-DA)	olive varieties	[148]
Fluorescense	discrimination (CA)	commercial categories	[87]
Fluorescense	clssification (NMF-Fisher's LDA-PARAFAC-DN-PLS)	commercial categories, adulteration (olive pomace)	[88]
MIR	classification (SIMCA)	fatty acids	[63]
NIR-MIR-Raman	classification (LDA-CVA)	botanical origin	[62]
MIR	classification (PLS-DA)	botanical origin	[64]
Fluorescense	classification (SFAM-ANN)	botanical origin	[86]
Fluorescense	discrimination (PCA-CA)	botanical origin	[88]
Capacitance	electrical properties characterisation	botanical origin	[104]
Time Domain Reflectometry	electrical properties characterisation	botanical origin	[120]
Time Domain	electrical properties	botanical origin	[121]

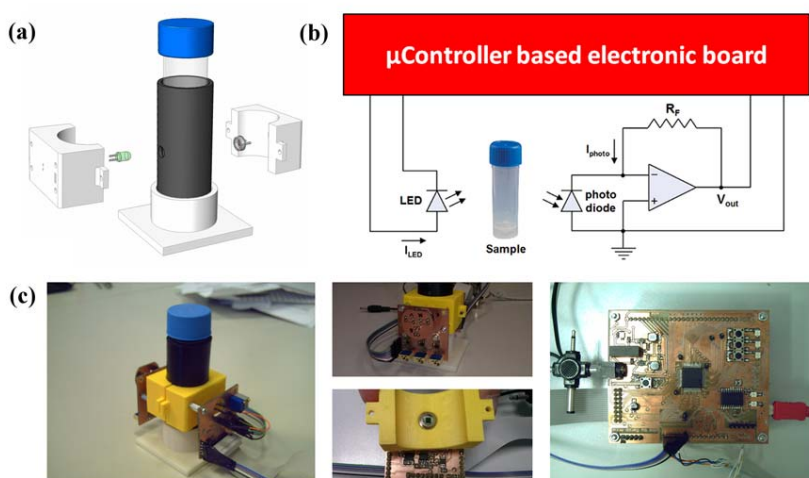|			
Reflectometry	characterisation		
E- nose (metal oxide semiconductors sensors)	classification PCA-(DFA)	commercial categories	[124]
E- nose (metal oxide semiconductors sensors)	discrimination (PCA)	commercial categories	[125]
E-nose (quartz crystal microbalance sensors)	discrimination (PCA)	botanical origin	[132]
E-nose (metal oxide semiconductors sensors)	classification (LDA)	oxidative levels	[127]
E-nose (metal oxide semiconductors sensors)	classification (LDA)	oxidative levels	[128]
E-nose + e-tongue (metal oxide semiconductors sensors + metal oxide semiconductor field effect transistors + amperometric sensors)	classification (LDA)	storage conditions	[145]
PTR-MS	classification (PLS-DA-LDA-CVA)	oxidative alteration	[150]
MIR	classification (LDA-PLS-DA-SIMCA)	freshness	[73]
NIR-MIR	classification (LDA-SIMCA)	fruity intensity	[46]
E-tongue (potentiometric sensors)	classification (LDA)	fruity intensity	[136]
E-nose (metal oxide semiconductors sensors)	classification (LDA-MLR-ANN)	sensory defects (fusty-mouldy-muddy-rancid-winey)	[126]
MIR	classification (PLS-DA)	sensory defects (musty-winey-fusty-rancid)	[71]
E-tongue (voltammetric sensors)	discrimination (PCA)	phenolic compounds	[141]
E-tongue	discrimination (PCA)	bitterness	[140]

(voltammetric sensors)			
E-nose + e-tongue (metal oxide semiconductors sensors + voltammetric sensors)	discrimination (PCA-PLS-DA)	bitterness	[144]
MIR	classification (PLS-DA)	Different extraction procedures	[72]
UV-VIS-NIR	classification (SIMCA)	adulteration (sunflower)	[35]
MIR	classification (SIMCA-PLS-DA)	adulteration (corn sunflower binary mixture-cottonseed-rapeseed)	[58]
MIR	classification (DA-Coomans plot)	adulteration (palm)	[60]
UV-VIS	classification (SOM)	adulteration (refined olive- olive-pomace)	[18]
NIR	discrimination (PCA)	adulteration (soya-sunflower-corn-walnut-hazelnut)	[37]
Raman	discrimination (PCA)	adulteration (olive pomace-sunflower-soybean-rapeseed-corn)	[81]
MIR-Raman	classification (SLDA)	adulteration (hazelnut)	[82]
E-nose (metal oxide semiconductors sensors)	classification (LDA-QDA-ANN)	adulteration (sunflower-olive pomace)	[129]
E-tongue (voltammetric sensors)	classification (PLS-DA)	adulteration (sunflower-soybean-corn)	[143]
Fast DSC	discrimination	adulteration (sunflower)	[152]

Figures:

Figure 1: Optical measurements at a single wavelength: (a) sensor used to measure peroxide value and total phenol content in olive oil; (b) schematic of the electronics; (c) picture of the system.

Figure 2: (a) Working principle of the EIS method to measure acidity in olive oil samples; (b) voltage test signal and voltammogram for cyclic voltammetry; (c) experimental set-up and acquired voltage for Time Domain Reflectometry measurements.

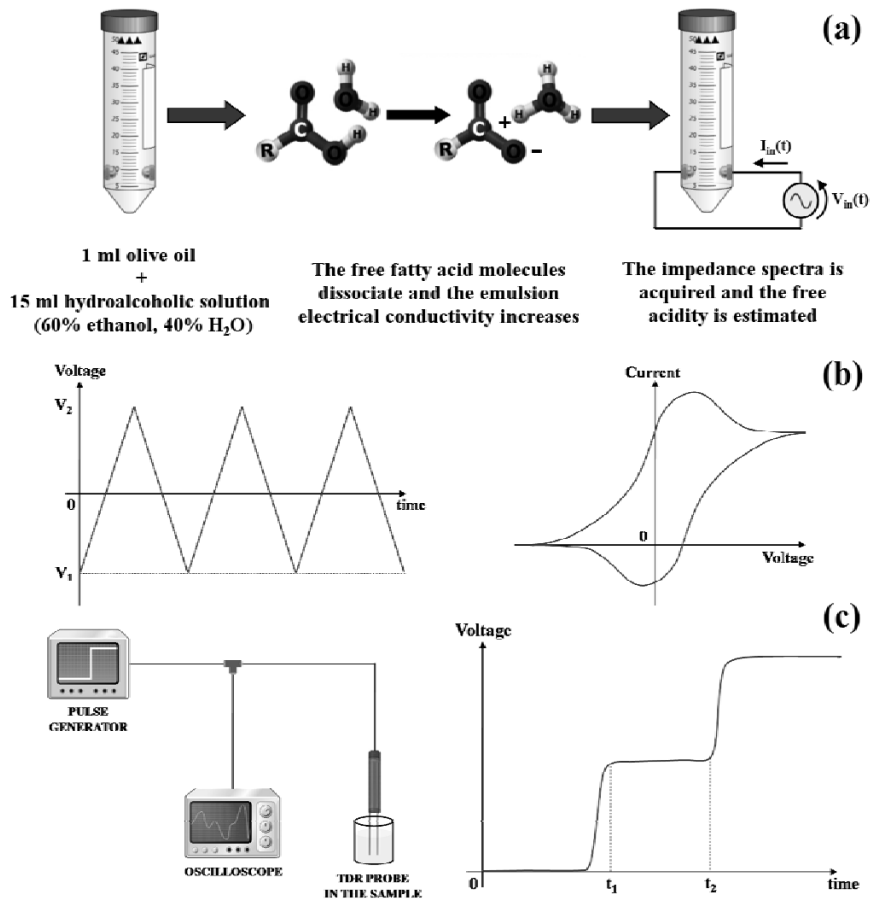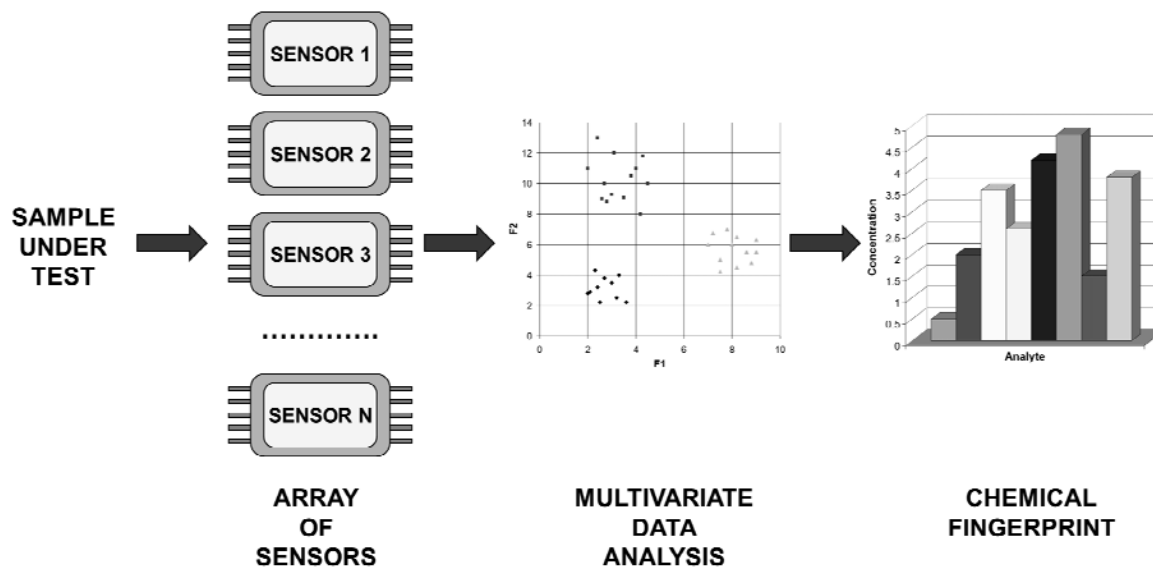**Figure 3:** Electronic tongues and electronic noses: working principle.

Figure 1

(a)

1 ml olive oil
+
15 ml hydroalcoholic solution
(60% ethanol, 40% H$_2$O)

The free fatty acid molecules
dissociate and the emulsion
electrical conductivity increases

The impedance spectra is
acquired and the free
acidity is estimated

$I_{in}(t)$

$V_{in}(t)$

(b)

Voltage

V_2

0

time

V_1

Current

0

Voltage

(c)

PULSE
GENERATOR

OSCILLOSCOPE

TDR PROBE
IN THE SAMPLE

Voltage

0

t_1

t_2

time

Figure 2

Figure 3

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