

Review Article

Application of Infrared Spectroscopy for Functional Compounds Evaluation in Olive Oil: A Current Snapshot

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Olive oil is a liquid fat obtained from the fruit of *Olea europaea*, a plant belonging to the *Oleaceae* family, which is widely cultivated and diffused in the Mediterranean area. It is largely produced and used since antiquity. It is mainly used and consumed as food but also as key ingredient in a wide variety of cosmetic products, e.g., to moisturize and nourish dry skin. In the last few decades, olive oil has received much attention as compared to the other seed-obtained oils as well as to the animal fats due to many functional compounds with positive effects on health. To maintain the genuine picture of olive oil, it is essential to assure its authenticity and quality. The presence of bioactive compounds, which characterize the olive oil owing to their antioxidant properties, can be assessed by spectroscopic and chromatographic methods. Currently, spectroscopic techniques combined with chemometric data analysis represent one of the most promising detection methods in the food sector. They offer rapid, versatile, and inexpensive data collection and analyses. The main advantages include the limited and simple sample preparation and the possibility to get spectra directly from the production line. Infrared spectroscopy (mid- and near-infrared) coupled to chemometrics is considered as powerful, fast, accurate, and nondestructive analytical tool for rapid and precise determination of the bioactive compounds content, as well of their bioactivities, i.e., antioxidant properties. These techniques represent a valid alternative to the existing conventional methods of analysis, e.g., based on chromatography and mass spectrometry. Indeed, the present review focuses on the application of infrared spectroscopy for functional compounds evaluation in olive oil.

1. Introduction

Olive oil is a high-quality natural product, typical from the Mediterranean area, where it has been produced for millennia, and it is obtained from the fruits of *Olea europaea* L, [1–4]. The quality of the starting matrix, i.e., the olives, is a crucial parameter to obtain a high-quality product [5]. The quality can be affected, for example, by fungal occurrence and mycotoxin contamination. In particular, the contamination with microfungi capable of producing secondary metabolites (mycotoxins) that potentially affect health is a growing source of concern [6–12]. Consequently, considerable research interest towards more environmentally compatible,

field-deployable, and sustainable fungi control systems was prompted over the last couple of years [13–15].

The process of extracting the oil from the seeds is a crucial step as well. There are various methods for this purpose and they can give different yield and quality grades [16]. As an example, extra-virgin olive oil (EVOO) is obtained using mechanical pressure devices. The lower-grade products are typically obtained from a variety of extraction methods including high-pressure extraction, solvent extraction, heat treatment, esterification, and refining. The lower-grade olive oils (e.g., lampante olive oil, pomace oil, refined pomace oil, and refined olive oil) are often characterized by a comparatively high acidity. For instance,

according to the current regulations, the acidity of extra-virgin olive oil must not exceed 0.8%, while olive oil and lampante olive oil contain 2% and >2%, respectively. Refining processes lower the acidity to about 0.3%. In blends of virgin and refined olive oils the free acidity is typically about 1%. Olive pomace oil obtained by extraction with a solvent also has acidity around 1%, while the refined olive pomace oil can have an acidity of only 0.3%.

EEC Regulation 29/2012 determines the compulsory and optional information to include on olive oil labels, supplementing the general rules relating to foodstuffs and their marketing in EEC Regulation 2000/2013. The chemical composition of olive oil is characterized mainly by triacylglycerols, monoacylglycerols, diacylglycerols, and free fatty acids [17, 18], as well as fatty acid derivatives (i.e., phospholipids and waxes) [19, 20]. Moreover, there is a diverse group of compounds such as sterols, aliphatic alcohols, chlorophylls, carotenoids, and hydrocarbons [21–23]. The bioactive compounds in olive oil play an imperative role in the authentication and genuineness, quality and purity, traceability, and more importantly to the health point of view [24–33].

Olive oil is a highly interesting product from the nutraceutical perspective [34–42]. It exhibits sensory properties due to the presence of substances with functional activity, such as carotenoids, chlorophylls, tocopherols, and phenolic compounds. These substances are often missing in other common seed-based oils [43]. Moreover, olive oil is characterized by high levels of natural antioxidants, which are associated to potential beneficial properties to humans [44–49]. Phenolic compounds are the main bioactive compounds in olive oil and can be divided into lipophilic and hydrophilic phenols. As reported by El Riachy et al. [50], lipophilic phenols such as tocopherols [51] can be commonly found in other vegetable oils. On the contrary, most hydrophilic phenols found in olive oil are exclusive and/or characteristic of the *Olea europaea* species giving rise to a chemotaxonomic peculiarity [52].

A recent work by Garcia and co-workers [53] divided the phenolic compounds with biological activity into four groups: simple phenols, secoiridoid derivatives, lignans, and flavones. Oleuropein, hydroxytyrosol, tyrosol, and ligstroside are examples of specific phenols, which are usually present in olive oil. In addition, caffeic acid, vanillic acid, and syringic acid are characteristic components of olive oil [54, 55]. The phenolic composition and its total concentration in olive oil have an impact on the characteristic taste, which is bitter and pungent. It depends on different factors, mainly on the degree of ripening of the fruit, the cultivar, the geographic origin [56–61], and the processing [62, 63]. Phenolic compounds are important antioxidants and act as radical scavengers in biological systems, consequently diminishing the lipid oxidation rate [64]. Phenolic compounds are also responsible for the olive oil stability during storage because of their antioxidant activity. With reference to the tocopherols in olive oil, α -tocopherol is the major constituent while β - and γ -tocopherols are present in minor quantities [65, 66]. Figure 1 shows the chemical structure of α -tocopherol.

The greenish color of virgin olive oil is due to the presence of chlorophyll pigments. Amongst the chlorophyll

compounds, pheophytin A is found in high amounts in olive oils. On the contrary, lutein and β -carotene are the major “yellow” coloring pigments responsible for the yellowish color of virgin olive oil. Due to the antioxidant nature and pro-oxidant activity of carotenoids and chlorophylls, respectively, they both play a crucial role in the oxidative stability during storage [67]. Moreover, phenols and tocopherols, together with carotenoids, provide excellent oxidative stability to olive oils and have a synergic anti-carcinogenic and antioxidant activity.

The main lipid components of olive oil are unsaturated fatty acids such as mono-(oleic) and di-glycerides (linoleic acid). Both are bioactive compounds and play a major role in human health [68]. Besides this, triterpene squalene is also considered as a functional compound in the unsaponifiable fraction of olive oil. The content of such functional compounds is contributing to or even determining the quality and positive sensory properties especially in extra-virgin olive oil.

Many instrumental analytical methods have been developed for the determination of functional compounds in olive oil, mainly using mass spectrometry and chromatography. However, most of these methods are expensive, time-consuming, nonenvironmentally friendly and also may require highly qualified staff for the instrumental analyses. On the contrary, spectroscopic methods such as ultraviolet, visible, near-infrared, and mid-infrared spectroscopy have been successfully employed as rapid, nondestructive, real-time techniques capable of on/offline monitoring of various quality parameters of olive oil. Their benefits include minimum sample preparation and good measurement accuracy with less or no waste generation. This review article presents an updated overview of the infrared spectroscopic methods in combination with chemometric data analysis to determine the functional compounds in olive oil.

2. Basics of Infrared Spectroscopy (Theory and Instrumentation)

2.1. Theoretical Principles. Infrared (IR) and near-infrared (NIR) spectroscopy are based on the absorption of photons by molecules. Absorption can take place when the energy of the photon to be absorbed matches the energy difference between two molecular rotovibrational energy levels. The mid-infrared spectral range is normally specified as 2.5–50 μm (200–4000 cm^{-1}), where the fundamental vibrational modes are located. On the contrary, the near-infrared covers the range 0.75–2.5 μm (4000 to 13333 cm^{-1}) containing overtone and combination bands. A general requirement for allowing the absorption of a photon is that an oscillating dipole moment be produced during the vibrational motion of the molecule. This prerequisite can be expressed mathematically by the following equation:

$$\left(\frac{\partial\mu}{\partial q}\right) \neq 0, \quad (1)$$

where μ is the dipole moment and q is the normal coordinate. When this equation is fulfilled, the molecule or a specific vibrational mode is called IR-active.

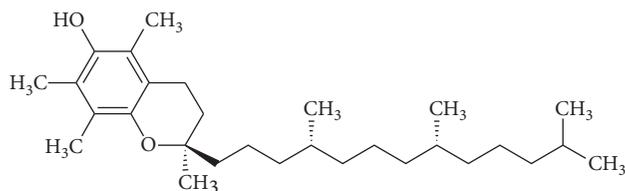


FIGURE 1: The structure of α -tocopherol.

The observed absorbance A , i.e., negative logarithmic transmission (intensity I of the light transmitted divided by the incident intensity I_0) of a sample of thickness d is given by the Beer–Lambert law:

$$A = -\log\left(\frac{I}{I_0}\right) = \varepsilon_\lambda cd, \quad (2)$$

with the extinction coefficient ε , which depends on the wavelength λ , and the concentration c of absorbing molecules. The IR spectrum eventually comprises the individual contributions from all the different vibrations originating from all the molecules in the sample. Consequently, it represents a true molecular fingerprint [69–71].

2.2. Instrumentation. As mentioned above, IR and NIR spectroscopy are absorption-based methods and hence the radiation needs to match the energy difference of the molecular transitions of interest. In other words, sources and detectors in the mid- and near-infrared are required. In the near-IR, Xenon and tungsten lamps are typically used as light sources and the detectors are commonly based on indium gallium arsenide (InGaAs) semiconductor materials. This allows us to perform spectroscopic analysis at wavelengths up to about $2.5 \mu\text{m}$. The common silicon-based detectors that can be found in digital cameras are not suitable at wavelengths longer than $1.1 \mu\text{m}$. Typical sources of mid-infrared radiation are glowing black-body radiators. Thermal detectors as well as semiconductors based on MCT and LiTaO_3 are suitable for detecting the radiation.

Spectral dispersion of the signal is normally achieved by an interferometric analysis employing a Michelson interferometer. The obtained interferogram is then Fourier transformed to yield the spectrum in the frequency domain giving rise to the common name Fourier-transform infrared (FTIR) spectroscopy. Most commercial instruments are FTIR spectrometers.

There is a variety of approaches to achieve an interaction between the radiation and the sample. The most common method is the transmission measurement. The sample is placed in-between two transmissive plates, and the transmitted intensity in the infrared region is recorded as a function of wavelength. Choosing the appropriate sample thickness, however, is crucial in this approach. A very thick sample will result in strong lines being saturated since almost all the photons around the peak center wavelength are absorbed. Such peaks manifest as broadened bands without

the typical Gaussian or Lorentzian shape. This may affect the data evaluation. For liquids, typical sample thicknesses lie in the range $25\text{--}500 \mu\text{m}$. Therefore, it is needless to say that the preparation of the sample is crucial as even dust particles may have significant influence. Common window materials include KBr, CaF_2 , ZnSe, and NaCl, which are transmissive for the IR radiation. Conventional borosilicate or fused silica quartz glasses cannot be employed.

The method referred to as attenuated total reflection (ATR) FTIR spectroscopy is easier to use. In such an experiment, the IR radiation is propagating in a transmissive high-refractive-index material (often ZnSe or a diamond crystal), called the internal reflection element (IRE). The sample has a lower refractive index and is in contact with the surface of the crystal. The radiation undergoes total internal reflection at the angle α at this surface, so that the evanescent field can interact with the sample. As a consequence, the reflected beam is attenuated and carries the spectroscopic information.

Both approaches are illustrated schematically in Figure 2. An advantage of the transmission arrangement lays in the well-defined sample thickness, which is given simply by the distance between the plates where the sample is placed. On the opposite, in ATR experiments, the effective path length depends on the penetration depth, d_p , of the evanescent wave. This is a complex function of the wavelength and must be taken into account when ATR FTIR spectra are interpreted quantitatively [72]. The penetration depth is approximately $1/5$ of the wavelength and thus consists on order of a few micrometers in the mid-infrared wavelength spectrum. The resulting effective path length, d_{eff} , is usually the actual parameter of interest. It represents the corresponding sample thickness that would lead to the same absorption in a transmission experiment [73]. It is not a physical quantity and therefore it cannot be determined in a straightforward manner [72–74].

In the analysis of food and food products like olive oil, the ATR approach is highly beneficial since it does not require sample preparation and hence the measurements can be performed very quickly. The measurement time per sample is typically significantly below one minute. The data analysis depends on the information desired. Chemometric approaches are the methods of choice when the aim is to quantify constituents such as unsaturated fatty acids or other bioactive compounds. Cross-correlation techniques can be applied to compare the recorded spectrum with a library in order to find out whether or not the sample is genuine. This is often sufficient in order to identify adulterated and counterfeit products. Example applications will be discussed in more detail in the following. In order to give an impression, the FTIR spectra of 17 different olive oil samples from a local supermarket in Bremen, Germany, are displayed in Figure 3. The individual spectra are very similar to each other. This highlights the potential of FTIR spectroscopy for the authentication of olive oils. The most prominent signature at 1745 cm^{-1} is the characteristic $\text{C}=\text{O}$ stretching vibration, which can be assigned to the fatty acids and ester groups.

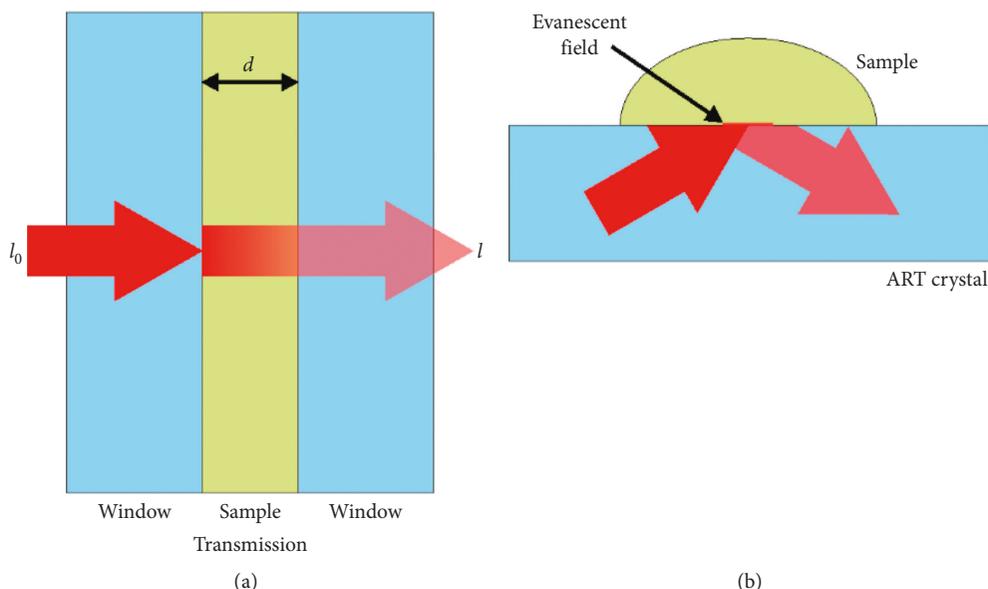


FIGURE 2: Schematic concepts of transmission and ATR spectroscopy. (a) Transmission. (b) ATR.

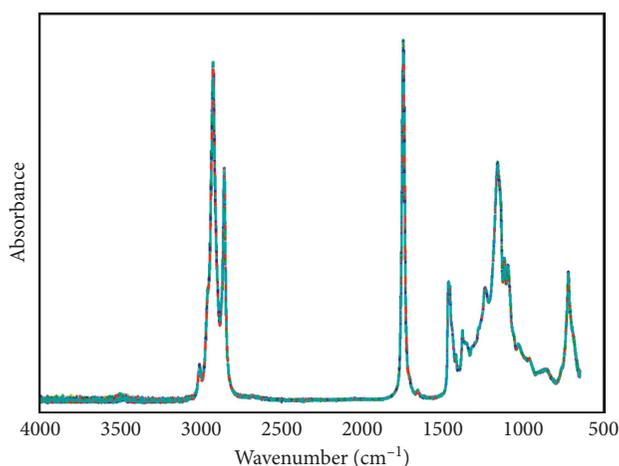


FIGURE 3: FTIR spectra of 17 different olive oil samples.

3. Application of Infrared Spectroscopy to Olive Oil: Focus on Functional Compounds Evaluation

For many years, analytical methods such as TLC, HPLC, GC-MS, and LC-MS/MS were the gold standard to identify and quantify the bioactive compounds (phenols, squalene, tocopherol, and fatty acids) in olive oils [75, 76]. Nowadays, as pointed out previously, the evaluation of bioactive compounds should be integrated in a multidisciplinary study approach for food research. This calls for the combination of advanced and innovative analytical techniques and sophisticated statistical methods for the data analysis in food science [77–79]. NIR and MIR techniques are rapidly emerging in this field. The bioactive compounds and antioxidant properties can be predicted by the spectroscopic methods. In particular, infrared spectroscopy coupled to chemometrics is considered as a powerful, fast, accurate, and

nondestructive analytical tool for rapid and precise determination of the content of bioactive compounds as well as their bioactivities, i.e., antioxidant properties. It represents a versatile alternative to the conventional methods. Further advantages in the context of food analysis include the rapid and inexpensive acquisition of data with nil or minimal sample preparation and the possibility to record spectra at or even in the production line. Besides a lot of studies on adulteration and discrimination of olive oil as well as monitoring contaminations, process or recovery by infrared spectroscopy [80–90], the focus here is on the evaluation of functional components.

3.1. Fatty Acids. Being the main constituents of olive oils, fatty acids and their triglycerides dominate the spectra of olive oils. Mailer [91] collected 216 olive oil samples throughout the Australian olive-growing areas to develop a NIR spectroscopy calibration for a range of quality parameters including the major fatty acids in olive oil. Multiple correlation coefficients squared (R^2) for minor fatty acids such as stearic acid (0.86) and linolenic acid (0.85) were reported relatively low because of the very narrow concentration range, while the major fatty acids oleic (0.99) and linoleic (1.00) provided high levels of accuracy compared with the reproducibility of the reference method.

It has been reported that authentication of virgin olive oil is time-consuming and requires expertise in the use of sophisticated instruments. To overcome this issue, Galtier et al. [92] evaluated the chemometric treatment of NIR spectra for the assessment of fatty acids and triacylglycerols in French virgin olive oil samples ($n=125$) for their classification (PLS1-DA) into geographically closed registered designations of origin (RDOs). The chemometric treatments of NIR spectra revealed that regression vectors of each RDO were correlated to one or more specific components with similar results obtained by conventional techniques according to

their cultivar compositions. For the very first time, Maggio et al. [93] reported a rapid method to determine the fatty acid profile of olive oils using FTIR spectroscopy with the ATR sampling technique as described in Section 2. Calibration models were built using PLS regression. The fatty acid calibration models (oleic acid, linoleic acid, SFA, MUFA, and PUFA) were constructed in the spectral range from 3033 to 700 cm^{-1} using PLS. The values obtained for the correlation coefficient for all models were in the range of 0.96–0.99. The LODs of the FTIR-chemometry methods were reported for oleic acid 3.0%, linoleic acid 0.5%, saturated fatty acids 1.3%, monounsaturated fatty acids 0.3%, and polyunsaturated fatty acids 0.3%, with recovery rates in the range 98–103%. The proposed method showed results comparable to the one obtainable by using the official method, but with the advantage of being more rapid and less expensive. Another study by Gurdeniz et al. described the classification and quantification of Turkish extra-virgin olive oil on the basis of fatty acids by using mid-infrared spectroscopy in combination with chemometric methods [94]. The PCA successfully distinguished the southern olive oil samples from the northern samples, while PLS detected a correlation between the spectral data and the fatty acid profile. The values obtained for the correlation coefficient were 0.83, 0.97, 0.97, 0.83, and 0.69 for stearic, oleic, linoleic, arachidic, and linolenic acids, respectively. Dupuy et al. [95] investigated the potential use of NIR and MIR spectroscopy for the quantitative analysis of triacylglycerols and fatty acids for the identification of the RDO of extra-virgin olive oils. PLS and PLS-DA regressions were separately applied to the two spectral ranges. MIR spectroscopy was found to perform better. It was further reported that RDO identification by DA using a multiblock method showed proficiency.

The quantification of oxidized fatty acids in virgin olive oil using mid-infrared spectroscopy coupled with multiple linear regression has been described by Lerma-García et al. [96]. For the prediction of oxidized fatty acid, the entire mid-infrared region was divided into 25 subregions. The subregions affected by oxidation were identified using multiple linear regression with a cube root data transformation that successfully predicted oxidized fatty acids. The value obtained for correlation coefficient was 0.944 with a prediction error of 17%. Uncu and Ozen [97] studied some important quality parameters (oxidative stability, color pigments, fatty acid profile, and phenolic composition) of olive oils by FTIR spectroscopy as one of the vibrational spectroscopic methods: it is possible to predict successfully the oxidative stability, the major fatty acids (palmitic (0.87), oleic (0.94), and linoleic acid (0.97), saturated (0.91), monounsaturated (0.94), and polyunsaturated fatty acids (0.97)), and the chlorophyll content and some phenolic compounds of the samples.

Casale et al. [98] authenticated the Italian protected designation of origin (PDO) extra-virgin olive oil Chianti Classico using UV-vis, NIR and MIR spectroscopy coupled with a chemometric data analysis. Unequal class models (UNEQ) and soft independent modelling of class analogy (SIMCA) along with PLS were employed individually and jointly on the fatty acid composition data. PLS successfully

predicted the oleic and linoleic acid content in the extra-virgin olive oils. Similarly, Inarejos-García et al. [99] investigated the degree of unsaturation of virgin olive oil by NIR spectroscopy. They reported an excellent performance of the multivariate algorithms in particular for the fatty acid profile (r -multiple coefficient of determination = 0.84–0.96). In a different approach, Valli et al. [100] pointed out new parameters for the detection of low quality of extra-virgin olive oil. These parameters were based on the total amount of fatty acids methyl and ethyl esters Σ (FAMEs + FAEEs) and their ratio (FAEEs/FAMEs) applying PLS to MIR spectra. The spectroscopic data showed a good agreement between predicted and actual reference values of calibration data sets. The limit of detection and quantification was reported to be 8.8 and 29.3 $\text{mg}\cdot\text{kg}^{-1}$ for Σ (FAMEs + FAEEs) with R^2 (0.98). On the contrary, the ratio of FAEEs/FAMEs showed R^2 (0.83).

Recently, the European Union regulation for olive oil set a value of fatty acids ethyl ester contents ($35\text{ mg}\cdot\text{kg}^{-1}$) in extra-virgin olive oils. To evaluate the fatty acid alkyl esters in extra-virgin olive oil, Cayuela [101] recently developed predictive models for the determination of total fatty acid alkyl esters based on NIR spectroscopy. The external validation exercise of FAAEs, FAEEs, and FAMEs using the NIR spectrometer showed SEP values of 33.6 and 54.5, 25.6, and 67.2, 18.7 with $r = 0.91$ and 0.93, 0.89, and 0.88, 0.92, respectively, for two validation sets.

3.2. Phenolic Compounds, Tocopherols, and Squalenes.

Several studies applied chemometrics to spectroscopic data in order to develop models and predict the content of minor components/functional compounds such as phenolic compounds and tocopherols in olive oils [1, 102, 103]. The recent chapter of Lagouri et al. [102] summarizes the optical UV-Vis-NIR-MIR spectroscopic tools and chemometrics used for the monitoring of olive oil functional compounds. Fatty acids, phenols, tocopherols, carotenoids, and squalene were considered with a focus on the bioactivity, chemistry, and processing. Inarejos-García et al. [99] investigated minor components, sensory characteristics, and quality of virgin olive oil by NIR spectroscopy. Their multivariate algorithms allowed reasonably accurate measurements, in particular of hydroxytyrosol derivatives (r -multiple coefficient of determination = 0.86–0.88) and C6 alcohols (r -multiple coefficient of determination = 0.69–0.80). FTIR spectroscopy, on the contrary, was used by Gouvinhas et al. [104]. They carried out a chemometric analysis of FTIR spectra from extra-virgin olive oils of three cultivars from Portugal (cultivars “Cobranco,” “Galega,” and “Picual”) at different maturation stages. To create a model for the discrimination of the olive oil samples, principal component analysis and discriminant analysis were utilised. The need for such sophisticated data analysis can also be seen in Figure 3, which shows that the spectra of olive oils are very similar. For the quantification of individual compounds, Gouvinhas et al. [104] developed regression-based calibration and validation models. This allowed the determination of the total phenolic content, *ortho*-diphenols, flavonoids, and

antioxidant activity during the ripening process. For *ortho*-diphenols and flavonoids, the slope R^2 and the RMSE were higher than 0.98 and lower than 0.03, respectively, whereas the phenolic content had the lowest multiple coefficient of determination in the calibration model ($R^2 = 0.94$). The same authors reported a slope R^2 and the RMSE of 0.93 and 0.04, respectively, for the determination of the antioxidant activity. Their quality measures became worse when data were cross validated ($R^2 = 0.86$, RMSECV = 0.05).

Mora-Ruiz et al. [105] applied NIR and MIR spectroscopy to study polar phenolic compounds of virgin olive oil and their impact on the oil quality. They obtained satisfactory multivariate test set validation algorithms for total polar phenolic (TPP) compounds (r -coefficient of determination = 0.91), hydroxytyrosol and tyrosol secoiridoid derivatives (HtyrSec, TyrSec; $r = 0.91$ and 0.92, respectively) by NIR spectroscopy. Moreover, the authors pointed out that, in contrast to the NIR data, the chemometric analysis of the MIR spectra gave no satisfactory validation models ($r = 0.43$, 0.54, and 0.66 for HtyrSec, TyrSec, and TPP). This was unexpected as the calibration algorithms for MIR actually gave an even better correlation than NIR ($r > 0.96$ for all the polar phenolics studied). On the contrary, the optimization of phenolic compounds extraction from EVOO was achieved applying a response surface methodology as proposed by Fratoddi et al. [106].

Also, very good MIR results for the quantification of virgin olive oil phenolic compounds were reported by Hirri et al. [107]. They obtained values for the correlation coefficient and the root mean square errors of prediction of 0.99 and 0.11, respectively. This study underlined also that the spectral region in the range 3050–600 cm^{-1} was useful for predicting the total polyphenol content. Bellincontro et al. [108] also focused on the total phenols. They developed a portable NIR-AOTF tool for the on-field and non-destructive measurement of specific and total phenols in olives for oil production. Models were developed for the main phenolic compounds (e.g., oleuropein, verbascoside, and 3,4-DHPEA-EDA) and total phenols by PLS. The results in terms of R^2 for the calibration, prediction, and cross validation ranged between 0.930 and 0.998, 0.874 and 0.942, and 0.837 and 0.992, respectively. A recent preliminary study of Trapani et al. [109] applied cost-saving NIR based on a discrete filter system for the rapid measurement of total phenolic content and oleuropein of olive fruits, in addition to the moisture, oil, and sugar. Although PLS models built for the latter ones were satisfactory, the instrument did not prove itself suitable for obtaining predictive models for phenolic compound contents. This is probably because the necessary wavelengths in the section of absorbance from 1100 to 1400 nm were not covered. Further studies in this direction are necessary and requested for enabling the possible application and use.

Concerning tocopherols, Cayuela and García [110] recently reported the classification of olive oils based on α -tocopherol and total tocopherol content using NIR spectroscopy. Other studies utilised pigments such as carotenoids and chlorophyll derivatives in extra-virgin olive oil as parameters/index of authenticity and quality. Pigments in oil

matrices can be identified and quantified by chromatographic techniques after a pretreatment of the samples such as extraction and/or saponification, or by spectroscopic techniques without pretreatment of the samples [111]. Another work by the same authors quantified the main pigments, i.e., β -carotene, lutein, pheophytin A, and pheophytin B, in several extra-virgin olive oils produced from a blend of three cultivars (Moraiolo, Frantoio, and Leccino) typical of Tuscany (Italy) in three different years. For this purpose, they employed a method based on the mathematical analysis of the near-ultraviolet-visible absorption spectra of the oils [112]. Besides a good prediction of fatty acid ethyl ester and wax, Uncu et al. [113] quantified lutein, pheophytin A, and their derivatives and total xanthophylls by FTIR + UV/vis with a range of R_{cv}^2 of 0.71–0.85, R_{pred}^2 of 0.70–0.84, and RPD = 1.5–2.5 values but the prediction of the rest of the pigments were poor ($R_{\text{cv}}^2 = 0.60$ –0.76, R_{pred}^2 : 0.42–0.62, and RPD = 1.2–1.5). Along the same line, Borello and Domenici [114] compared two near-UV/vis spectroscopic techniques for the determination of pigments, i.e., total carotenoids, and total chlorophyll derivatives in virgin and extra-virgin olive oils. Although UV/vis spectroscopy is very tempting for analysing the pigments, NIR and MIR spectroscopy typically gives a more specific molecular fingerprint of oil. Cayuela and García [115] developed rapid NIR techniques using PLS analysis for measuring the squalene content of olive oil. The external validation exercise for estimating squalene was performed with the squared validation regression coefficient (r^2) 0.83 and residual predictive deviation of 2.31.

3.3. Antioxidants. The assessment of interactions between natural active compounds and other food matrix components represent the bioactivity of a food. The first indicator of potential health benefits is commonly given by the antioxidant properties. The comprehension of concerted and synergistic actions, of antagonist interactions, or of no effect of biologically active compounds should be considered in this context. The same is true for the factors influencing the overall effects such as the peculiar combination of antioxidants and the structure of the food matrix [77]. Lu and Rasco [116] reviewed and summarized the recent applications of infrared spectroscopy for the development of models for the prediction of antioxidant properties in food, in addition to qualitative and quantitative analysis of antioxidant compounds. It is also worthy of mentioning the review article of Cozzolino [117], who concluded that infrared spectroscopy is a versatile analytical tool for the quantitative determination of antioxidant properties in agricultural products, foods, and plants.

Carretani et al. [118] reported the rapid FTIR determination of phenolics and antioxidant activity of olive oil, in addition to water. For total phenols, good results were obtained considering the spectrum from 3610 to 816 cm^{-1} , while the range from 3707 to 1105 cm^{-1} was most suitable for ABTS+. Satisfactory LOD values were achieved by the FTIR-chemometry approach: 12.5 (mg gallic acid/kg oil) for total phenols and 0.76 (mmol Trolox/kg oil) for ABTS+. The authors concluded that the results obtained with the

chemometric data analysis are comparable to those obtained using the official reference method. This highlights the potential of the spectroscopic technique as an alternative to the standard procedure for routine analysis or control at-line of production processes.

4. Conclusion

NIR and MIR spectroscopy coupled with chemometric data analysis has shown considerable potential for the determination of functional compounds present in olive oil. Recent applications have demonstrated to perform the assay of antioxidant activity (tocopherols, phenols, and squalene), to allow the discrimination of geographical origins, to facilitate the assessment of sensory attributes, and to determine the fatty acid profile, which is characteristic of the oil matrix. IR spectroscopic methods represent an interesting alternative to the conventional analytical methods as they do not require a pretreatment of the samples. Moreover, they offer a high sample throughput and significant time saving. In addition, these techniques are considerably more environmentally friendly since no solvents or carrier gases are used. These new approaches based on mid- and near-IR absorption spectroscopy are therefore interesting alternatives, for example, for rapid screening purposes.

In the future, IR spectroscopic methodology in combination with chemometric data evaluation will possibly overtake the conventional methodologies. In some cases, this may require the change of the regulatory frameworks, which are currently naming only conventional analytical tools for certain official purposes. However, the convincing performance of the spectroscopic approaches with respect to authentication and comprehensive quantitative analysis will certainly make a strong case in the regulatory and political processes. Without a doubt, the methods reviewed in this paper will soon be extensively used in the oil processing industries as a routine method to evaluate the characteristic parameters of olive oil.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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