

Review

Recent advances in spectroscopic approaches for assessing the stability of bioactive compounds and quality indices of olive oil during deep-frying: Current knowledge, challenges, and implications

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ABSTRACT

Foods fried in olive oil received great attention due to its bioactive profile, antioxidants, high stability, and health benefits. However, several chemical alterations contribute to olive oil degradation during deep-frying (D–F), and negatively modify its safety and quality. Therefore, measuring the quality indices of olive oil is a vital topic. The classical chemical approaches are destructive and use toxic chemicals, thus, a harmless and real-time analytical technique has become increasingly critical. This review highlights the recent advances of spectroscopic technologies (STs) stand-alone or integrated with chemometrics to provide reliable, rapid, low-cost, sustainable, multi-parametric, and eco-friendly method for monitoring the quality and safety of olive oil during thermal processing, moreover, the limitations of STs are included. The present review offers fundamental insights regarding the degradation of deep-fried olive oil and provides recent evidence in spectroscopy that can be used as consistent method, providing more benefits for the consumers and food industry.

1. Introduction

Vegetable oils/fats are a vital food component and commonly utilized as lipid sources for human diet which contribute to color, flavor, and texture of the foodstuffs and also provide essential fat-soluble vitamins, bioactive compounds, and pigments (Aryee et al., 2022). Amongst the vegetable oils, olive oil is of the main healthy oils used for its nutritional qualities. In addition, extra virgin olive oil (EVOO) is a high-grade olive oil with exceptional health benefits due to its unique bioactive content (Fig. 1) (El Sohaimy et al., 2016; Jimenez-Lopez et al., 2020; Wang et al., 2023; Yubero-Serrano et al., 2019). However, temperature, O₂, and light exposures endorse the oxidation/rancidity process and degrade the oil (Ruiz-Méndez et al., 2021). Therefore, thermal stability is the most vital issue to be considered in food quality and safety sectors (Ansar et al., 2023; Rotich et al., 2020). Deep-frying (D–F) in vegetable oils at a high temperature of 180 °C is one of the oldest and most common food manufacturing and preparation (Xu et al., 2022). D–F causes complex physicochemical variations which convey desired flavor to fried food and improve customer gratification (Erickson et al., 2022; Gabrielle Alves et al., 2022). However, D–F produces unwanted flavor compounds in the oils and changes their stability and quality by

hydrolysis, oxidation, and polymerization. In the primary rancidity stage, polyunsaturated fatty acids (PUFAs) form unstable intermediates lipid peroxidation by-products such as hydroperoxides as well conjugated dienes which afterward undergo react to form secondary oxidation compounds (Carrapiso et al., 2022). Hence, vital amino acids (AAs), tocopherols, and fatty acids (FAs) in foodstuffs are deteriorated throughout D–F (Fig. 2). The reactions in D–F depend mainly on numerous features e.g., renewal of fresh oil, frying conditions, primary oil quality, type of fryer, food ingredients, O₂ concentration, and antioxidants (Ambra et al., 2022; Mittu et al., 2023). Moreover, D–F harmfully alters the oil characteristics and is associated with a reduction in nutritional values, quality, as well as a potential source for numerous diseases (Dangal et al., 2024; Liu et al., 2023).

Numerous chemical approaches including physicochemical parameters determination e.g., peroxide value (PV), acidity, and UV–Vis spectrophotometry are used for the measurement of oxidation products in deep-fried olive oils, nevertheless these approaches require more time for analysis, high cost, use of risky chemicals, and multifaceted samples preparation. To overcome these limitations related with conventional chemical approaches, the recent development in spectroscopic analytical methods in food analyses sector aimed to the intensive

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characterization of foods to define its physicochemical, compositional, and sensory properties and to ensure their safety and quality, without negative impact on functional aspects, nutritional profile, and organoleptic properties and according to consumers desirability and regulation, with more efficient, sensitive, cost-effective, and robust analytical procedures should be further developed concerning olive oil quality control (Dymińska et al., 2022; Li et al., 2021; Liu et al., 2020; Pizarro et al., 2013; Poiana et al., 2013; Talpur et al., 2015; Meenu et al., 2021).

The analytical methods e.g., high performance liquid chromatography–mass spectrometry (HPLC–MS) (Di Stefano et al., 2012), gas chromatography–mass spectrometry (GC–MS) (Mota et al., 2021), are able to characterize the molecular profile of oil components efficiently including major compounds such as fatty acids, as well minor compounds e.g., polyphenols, tocopherols, volatile compounds, squalene, and sterols. However, modern spectroscopic procedures achieved a great and successful finding as a promising metabolomic approach providing mechanistic insights on pathological and physiological activities in distinct situations (Vazquez-Aguilar et al., 2023). Moreover, food metabolomics which mainly assesses food constituents, food processing, and food quality and safety from farm to table, has been applied in several food science sectors such as lipids showing promise in maintaining their safety and quality (Wen et al., 2023; Zhang et al., 2023). Recently, several strategies based on advanced omics technologies are integrated in order to study the vegetable oils characteristics and to monitor their quality and safety particularly during D–F (Gallo & Ferranti, 2016; Qiao et al., 2024). For instance, the chemical alteration in frying oils under D–F conditions have been studied using vibrational spectroscopic techniques (i.e. Raman spectroscopy (RS), fourier transform infrared (FT-IR), and near-infrared (NIR) to assess the quality of numerous frying oils i.e., olive oil (Meenu et al., 2021). Vibrational spectroscopic procedures e.g., infra-red (IR) and Raman allied with

chemometric tools has been utilized widely for determining the quality of many edible oils and to monitor the thermal oxidation during frying conditions (Alvarenga et al., 2018; Carmona et al., 2014; Selaimia et al., 2017; Zaroual et al., 2024; Zribi et al., 2016). Moreover, fluorescence spectroscopy (FS) (Songohoutou et al., 2023), and ^1H nuclear magnetic resonance (^1H NMR) analyses have been applied in several edible oils (Córdoba et al., 2023; Lucas-Torres et al., 2014; Wann et al., 2021) in the investigation of frying, cooking, adulteration, safety, and quality control.

Indeed, the thermo-oxidation stability of olive oil is one of the most crucial indicators for preserving its safety and quality. To the best of our knowledge, there are no review articles regarding application of spectroscopic technologies focusing on olive oil during deep-frying. Therefore, the present research highpoints recent advances in spectroscopic approaches to control and/or minimize rancidity/oxidation of numerous olive oil types, as well as to monitor their quality indicators during thermal processing in order to maintain their functionalities, minor bioactive compounds, and enhancing nutritional value, aiming to provide a reference for the food industry, consumers, and government, of olive oil highly in natural antioxidants to maximize their shelf life and safety.

2. Materials and methods

In this study, a search in Scopus data base has been conducted for articles published by different credible publishing agencies e.g., (Elsevier, Science Direct, Springer, Wiley, American Chemical Society, Taylor & Francis, and Royal Society of Chemistry) for most related investigations of the current research topic. Keywords search enquiry used in Scopus: (Olive oil, and Spectroscopy), The documents gotten are 1765 papers from 2004 to 2024 in English only (Fig. 3A) which marked as

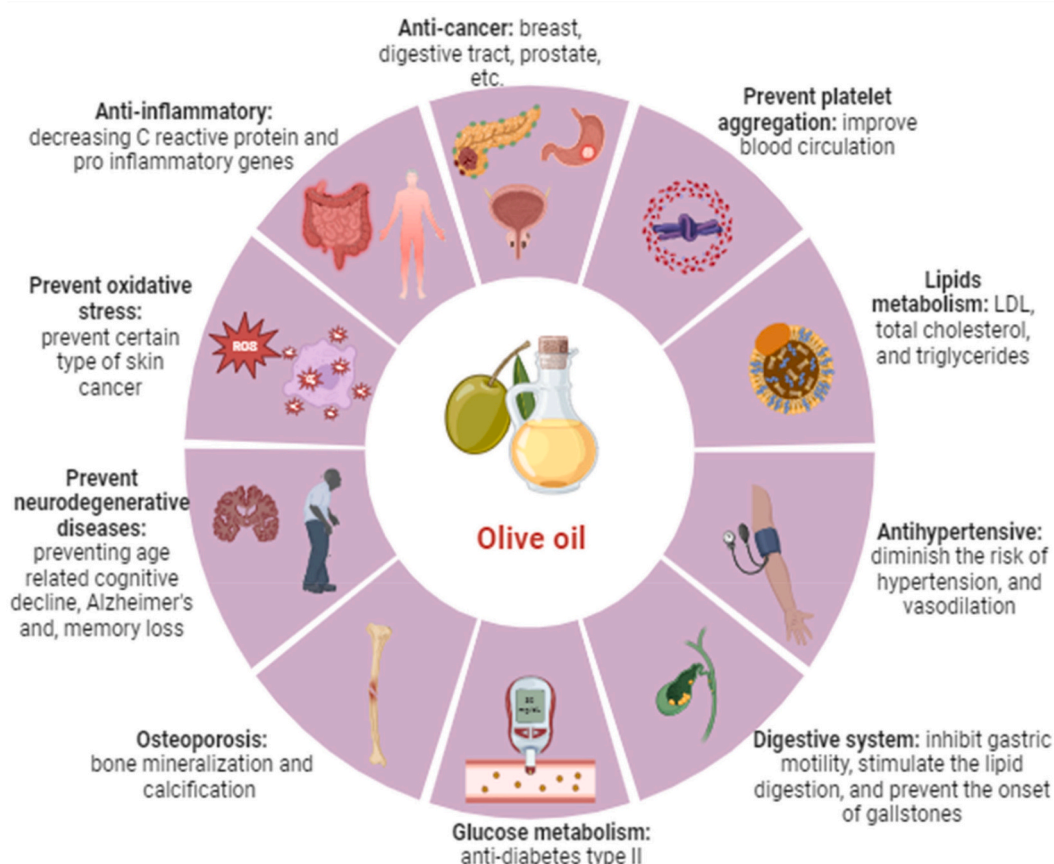


Fig. 1. Health benefits and biological indicators of olive oil.

et al., 2007). Therefore, astaxanthin could be utilized as a substitute to β -carotene in edible oils supplementation as well as a natural food colorant.

Total polar phenol compounds (TPPCs), and the antioxidant capacity through the radical scavenging activity (RSA) toward 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) of VOO and ROO were determined during the thermal process (180 °C/10 h) to monitor the oxidation progress. Furthermore, the findings showed that VOO was stable fried oil compared to ROO, and this may be attributed to the high phenolic compounds content in VOO, while refining process decreases this content substantially in resulted ROO. Moreover, RSA and polyphenols of VOO deep-fried for 2.5 h reduced approximately up to (70 % and 78 %), respectively, however, maintained its thermal stability for long time. The findings reveal that VOO has notable thermal stability (Kalantzakis et al., 2006).

The thermal stability and organoleptic attributes of flavored EVOO have been investigated (Issaoui et al., 2019). This work compared the organoleptic characteristics, and the thermo-oxidative stability of flavored extra virgin olive oil (FEVOO) made through adding various herbs (i.e., garlic, onions, and paprikas) to EVOO. Oils were exposed to several thermal temperatures (i.e., 60 °C, 100 °C, and 200 °C up to 8 h), it was found that there was no significant impact after mixing the herbs on the stability of olive oil (treated at 60 °C), on the other hand, mixing herbs (especially onions and garlic) significantly improved the stability of olive oil fried at 200 °C (Issaoui et al., 2019).

Recently, the stability of bioactive compounds in olive pomace oil (OPO) e.g., tocopherols, squalene, sterols, triterpenic acids e.g., oleanolic and maslinic acids, triterpenic alcohols such as erythrodiol and uvaol, and aliphatic alcohols which found in meaningfully larger quantities in OPO than in other olive oil types (such as hexacosanol, octacosanol, tetracosanol, and docosanol) was studied under D–F and thermo-oxidation (Ruiz-Méndez et al., 2021). The findings acquired under thermo-oxidation and D–F conditions of OPO indicated that high stability of minor bioactive substances such as triterpenic alcohols (i.e., erythrodiol and uvaol), aliphatic alcohols, and oleanolic acid were observed. Moreover, the frying process of foods with OPO showed a high nutritional profile of these foods thanks to the content of oleic acid, aliphatic alcohols, squalene, and triterpenic acids, and alcohols (Ruiz-Méndez et al., 2021). Table 1 shows the stability of minor bioactive

compounds of EVOO under different D–F conditions based on recent literature.

4. Recent updates of spectroscopic approaches used to assess the stability of bioactive compounds and to determine the quality of olive oil during deep-frying

In this section, the recent techniques i.e., vibrational spectroscopic approaches e.g., RS, NMR, FT–IR spectroscopy, mid infra–red (MIR), NIR spectroscopy as well as FS used during analyses and quality control of deep-fried various olive oils have been narrated. Table 2. illustrates the main spectroscopic approaches used to monitor the safety and quality of olive oil after D–F process.

4.1. Florescence spectroscopy

The theory of FS is based on a light-emitting procedure that is triggered by the absorption of the excited radiation of an applicable wavelength that is one of the most competent connections linking light and material (Kohli & Mittal, 2019). FS is utilized with substances able of exciting whilst subjected to fluorescence. Testimony of the creation of the inclusion complex is the amend in fluorescence of the compound (Bulani et al., 2016).

FS has been proposed as an alternative technique to analyze and monitor the quality parameters of EVOO. Fluorescence spectra of EVOO samples offer useful information about fluorophores e.g., polyphenols, chlorophylls, and tocopherols that are significant for maintaining EVOO quality. FS has advantages over the other conventional methods of its speed, and non-destructive analysis and the minimum sample preparation with the absence of toxic solvents and reagents. Moreover, FS combined with unfolded partial least squares (U-PLS) to generate a regression model and for quality parameters quantification (i.e., peroxide value, K_{232} , and the oxidative stability index) is reliable modern approach (R^2 ranged from 0.90 to 0.94 for cross-validation and validation) to assess the safety and quality indicators of EVOO, avoiding the classical methods such as sensory evaluation to decrease the time and man power, and physicochemical analysis that requires harmful chemicals (Martín-Tornero et al., 2022). In addition, the fluorescence attributes of VOO are used to authenticate and monitor oils quality.

Table 1
Stability of minor bioactive compounds of various olive oil categories under different frying conditions.

| Olive oil type | Bioactive compounds | Biological effect | Frying parameters | Main insights | Reference |
|----------------|---|--|--|--|----------------------------|
| EVOO | α -tocopherol and phenolic compounds. | Protect from cardiac hypertrophy and to exert antiatherogenic, anti-inflammatory, anti-hypertensive, and neuroprotective effects. | Heating at 180 °C/36 h. | -High degradation rate of tocopherols and polyphenols after the frying process. -The sterols, squalene, and triterpenic alcohols were quite stable, presenting a high stability toward degradation. -The content of flavones, hydroxytyrosol and its derivatives were decreased. | (Allouche et al., 2007) |
| EVOO | Carotenoid and Chlorophyll. | These pigments offer the colors of the oil, have antioxidant potential and inhibit the free radicals and thus increase the shelf life stability of the oil. | Short-time pan frying, 150 °C/ 5 min. | Moderately stable, carotenoid reduced from 1.88 to 1.41 (mg lutein/Kg oil) after frying process, while chlorophyll decreased from 1.68 to 1.43 (mg pheophytin a/Kg oil). | (Rodilla et al., 2023) |
| VOO | Carotenoids (β -carotene and astaxanthin). | β -carotene is an antioxidant that protects the body from the free radicals, while, astaxanthin had a notable role in the immune system. | 110 °C/1–14 h. | β -carotene degradation was much faster than that of astaxanthin. | (Luaces et al., 2007) |
| VOO | Total polar phenols. | Induce a wide positive biological effect i.e., anti-oxidative stress, anti-inflammation, anti-diabetes, anti-cancers, anti-neurodegenerative disorders, anti-cardiac disorders, etc. | 180 °C/10 h. | Total polar phenols were decreased from 162 to 72 (mg caffeic acid/kg oil) at 0 and 2.5 h from frying process respectively, the fried virgin olive oil presented stability against thermal stress. | (Kalantzakis et al., 2006) |
| OPO | Sterols. | Anti-inflammation properties and prompt positive impact on cardiovascular health. | The oil was treated at 175 °C/ 5 min, and then the foodstuffs were placed in the oil for 10 min and 2 h intervals. | The total content of sterols was lower in the fried foodstuffs lipids than in the initial food products due to the effect of the frying process. Moreover, significant decreases of tocopherols content in foodstuff after the 4th deep-frying operation. | (Ruiz-Méndez et al., 2021) |

Table 2

The main spectroscopic approaches used to monitor the safety and quality indices of several olive oil categories during deep-frying process.

| Spectroscopy technique | Treatment/olive oil type | Spectral range | Physicochemical qualities | Preprocessing | Chemometric tools | The main findings | Reference |
|--|---|---|---|--|---|---|----------------------------|
| FT-IR | Continuous heating OO at 190 °C and the foodstuffs changed every 45 min. | IFS 66 v/S FT-IR spectrometer with ATR, from 950 to 4000, and 4 cm ⁻¹ . | Polymerized triglycerides (PTGs). | First derivative, and Mean centering. | Interval PLS (Ipls), Uninformative variable elimination-partial least square regression (UVE-PLS), expert knowledge (Matlab). | All the variable provided an effective PLS models to predict of PTGs. | (Kuligowski et al., 2011) |
| | Heating EVOO at (0, 60 and 90 °C) up to 35 days. | Bruker Vertex 70 spectrophotometer, 4000–400 cm ⁻¹ , 2 cm ⁻¹ . | Mode of action of oil degradation. | – | – | Increase in the hydroperoxide ratios and subsequently alcohols formation. | (Navarra et al., 2011) |
| | Frying VOO from 100 °C until the polymerization of the oil sample. | FT-IR spectrometer, Vector 22, 4000–650 cm ⁻¹ , 4 cm ⁻¹ . | Fatty acids, saturated fatty acids, polyunsaturated fatty acids, monounsaturated fatty acids. | Rutherford baseline correction. | Principal component analysis (PCA), and linear discriminant analysis (LDA) (IBM SPSS statistics version 19). | <i>Cis/trans</i> isomers exhibited an efficient tool for olive oil variety classification based on frying process. | (Román Falcó et al., 2012) |
| | Frying OO at 200 °C/8 and 16 h. | FT-IR-8400S FT-IR spectrophotometer, from 600 to 4000 cm ⁻¹ , and 4 cm ⁻¹ . | Measuring the quality changes in response to frying process. | – | LDA (Origin Ver. 6.0). | Spectral changes at 3050–2800 as well as 1745 cm ⁻¹ distinct thermal degradation. | (Poiana et al., 2013) |
| | Frying VOO at 190 °C/94 h for 8 h cycles/day. | Bruker 55 Equinox S FT-IR spectrometer, from 400 to 4000 cm ⁻¹ , and 4 cm ⁻¹ . | Total polar compounds, fatty acids and phenolic content. | – | – | Individual FT-IR analysis of polar and non-polar compounds showed better interpretation of thermo-oxidized OO samples. | (Tena et al., 2013) |
| Frying EVOO at 185 °C/4–8 h. | FT-IR-8400S from Shimadzu, from 400 to 4000 cm ⁻¹ , and 4 cm ⁻¹ . | Structural changes in deep-fried OO. | – | LDA (Origin 6.0 software). | Changes at spectra (722; 885; 967; 987; 1743) cm ⁻¹ showed thermal degradation of the oil samples. | (Poiana et al., 2015) | |
| NIR | Frying OO at 190 °C by adding and/or without adding of foodstuffs. | Bruker Multipurpose Analyzer (MPA) FT-NIR spectrometer, 15,000–3800 cm ⁻¹ , 8 cm ⁻¹ . | PTGs. | First derivatives. | PLS (iPLS and UVE-PLS) (Matlab7.7.0), | Global PLS model is recommended to determine of PTG. | (Kuligowski et al., 2012) |
| NMR | Frying EVOO at 180 °C. | ¹ H NMR spectra were registered at 500 MHz (Agilent DDR-1 NMR spectrometer). | Oleocanthal and Oleacein. | – | Cluster analysis and Pearson's test (Statgraphics Centurion SOFTWARE). | Clear variations in the polyphenols profile between unfried and fried OO. | (Córdoba et al., 2023) |
| Raman | Frying and cooking EVOO at 140–150 °C. | Raman spectra were registered via excitation laser at 785 nm in the range between 540 and 1800 cm ⁻¹ . | Molecular composition e.g., oleic acid, tocopherol, and triacyl glycerides (TAGs). | Smoothing, baseline correction (BC) and vector normalization (VN). | PCA. | PCA and Raman spectrums at 1267 cm ⁻¹ and 1302 cm ⁻¹ discriminated OO samples in the function of heating. | (Ahmad et al., 2017) |
| Excitation-emission fluorescence spectroscopy (EEFS) | Frying VOO at 190 °C/ 94 h. | The wavelength ranged from 300 to 700 nm. | Total polar compounds, tocopherols, chlorophyll, phenolics, and oxidized products. | PARAFAC algorithm. | Multiway model PARAFAC and multiple linear regression analysis (MLRA). | Spectral bands obtained permitted an individualized study of oxidation products, bio-phenols, and tocopherols. | (Tena et al., 2012) |

Oxidized compounds of VOO gave specific fluorescence bands ranging from 400 to 460 nm (Guzmán et al., 2015).

The common methods to assess thermal stability of EVOO including active oxygen assay (AOA), oil stability index (OSI), Rancimat, Schaal oven test (SOT), and differential scanning calorimetry method (DSCM), which are very complex and require high skill to use. Therefore, the

thermal treatment for 4 EVOO samples originated from several areas in Italy was conducted by FS as an alternative and sustainable approach at 120 °C at various time intervals (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 120, 150, 180 min) (Rotich et al., 2020). The fluorescence aspects of the studied oils within heating exposure were determined by front-face fluorescence and transmittance spectroscopy to evaluate the alteration

that arises owing to thermal process. Fluorescence peaks were detected at the following wavelengths 435 nm, 465 nm, and 570 nm, which are supposed to be oxidation/rancidity and hydrolysis matrices. Moreover, EVOO variety with a higher polyphenols content illustrated superior resistance for oxidation, and thus, presented a greater thermal stability. On the other hand, to build a more robust system it is highly recommended to increase the sample numbers when FS is employed to develop a better model.

Front-face fluorescence spectroscopy (FFFS) is an instrumental procedure whose theory and methodology has been extensively utilized to characterize molecular structure and function. FFFS showed considerable promise owing to no pretreatments of the sample are needed, and it evades the inner filter influences of highly concentrated samples such as EVOO. Such a front-face method has been used with synchronous spectra capture to reduce the number of variables (Al Riza et al., 2021). Furthermore, 3D front-face FS is also utilized to differentiate the quality indices between OO and EVOO based on their fluorescent composites (Lleó et al., 2016). In addition, FFFS allied with chemometrics was employed to study the degradation status of VOO induced to heating for 30, 60, 120 and 180 min at 140, 160 and 180 °C, for each frying time respectively (Mbesse Kongbonga et al., 2015). Principal component analysis (PCA) revealed the mode of action of all oxidation process stages, and FS peaks at 489 nm, which results directly from the degradation of primary oxidized molecules (hydroperoxides) into secondary oxidation products (Fig. S5). This information proposes that FSFS is a very easy and inexpensive approach, could be a useful tool to monitor the safety, quality, and the degradation level of fried VOO.

Furthermore, the spectra of synchronous fluorescence spectroscopy (SFS) allied with chemometric tools i.e., PCA has been an effective strategy used to measure thermal degradation of several olive oil types exposed to UV-irradiation (80 °C). Spectra at 300–500 nm after 12 h showed rapid oxidation proven by PCA. Oxidative values of the fried olive oil samples increased up to 10, 19 and 38-fold for EVOO, OO and OPO, respectively (Poulli et al., 2009). In another research by Ali et al. (2020), the biochemical profile and thermal stability characterization of EVOO during D–F have been studied. Seventeen monovarietal EVOOs were fried up to 170 °C/15 min in order to measure thermal stability, and further were analyzed by synchronous fluorescence spectroscopy. The results showed that SFS spectra discriminated oil samples based on polyphenolic substances that are affected negatively at a higher thermal treatment, moreover, the percentage of chlorophyll also decreased at high thermal grade. The peak at 351 nm may correspond to vanillic acid (VA), 391–471 nm is related to other phenolic compounds, while 672 and 723 nm for chlorophyll and grouped via hierarchical clustering analyses (HCA). Almost of the EVOO samples were stable thermally when fried at 150 °C, however, they degraded at 170 °C, in addition, only Arbequina variety have a sensible fluorescence emission from VA and other phenolic compounds that are support the oxidative stability of the fried oil at above of 170 °C. Furthermore, polyphenols concentration variation of Arbequina was detected with various ripening periods and the initial ripened olives formed more stable oil under deep-frying conditions comparing with oil produced from the late ripening stage of olives (Ali et al., 2020). Additionally, fried VOOs diluted in 1 % n-hexane were analyzed to explore the fluorescence characteristics. The fluorescence spectra of the collected oil samples observed at 350 nm as well from 390 to 630 nm explained the high formation of polar compounds after frying process ($R^2 > 0.997$) (Tena, Aparicio, & Garcia-Gonzalez, 2009).

According to the European Regulation and its amendments (European Union, 2013) the quality assessment of EVOO is completed by a series of conventional chemical analysis and through sensory evaluation by certified and/or experienced panelists. These analyses are time-consuming, expensive, and are not easily accessible for many producers. Instead of the conventional chemical analysis, FS which has the advantages of being rapid, cost-efficient, and at the same time sensitive technique was widely employed (El Orche et al., 2020). Furthermore, FS

has been demonstrated to be a promising method that can be used effectively to evaluate the freshness of EVOO and the quality of EVOO, VOO, and OO due to the natural occurrence of fluorophores in these olive oil categories, the strongest of which is chlorophyll (Al Riza et al., 2021). Additionally, FS has the capability to monitor the effect of oxidation and assess the quality of deep-fried EVOO (Venturini et al., 2024), and are relatively cheap to implement, and are easy to use comparing with the classical chemical approaches e.g., chromatographic and physicochemical analyses (Al Riza et al., 2021).

In sum, the biggest advantage of FS technique is its high sensitivity. Moreover, other benefits of FS as rapid analytical technique and low-cost technology for olive oil quality control is proposed. Also, FS can be employed for determining the quality parameters of various olive oil types with a spectrum at a single excitation wavelength without the need to scan the full spectrum at many excitations wavelength, thus saving considerable time. Furthermore, the reviewed reports therefore offer promising results by providing useful information about FS that can be used as a rapid and easy for monitoring the quality control during D–F of various olive oil types. Moreover, FS considers reliable technique owing to its spectral fingerprints can be measured promptly and easily, without the need for any pretreatment of the olive oil samples and could probably be employed to classify deep-fired olive oil types. Likewise, FS could provide an interesting complement to other spectroscopic techniques, such as the NIR and FT-IR spectroscopies used broadly in the olive oil industry. Nevertheless, one of the main limitations of FS is that it can't build robust models based on low sample numbers, therefore, to build a stronger system it is highly recommended to increase the sample numbers when FS is employed to develop a better model.

4.2. Raman spectroscopy

RS is one of vibrational spectroscopic types, and mainly used for identification the frequency of scattered light from samples after incident photons of light collide with a molecule (Moon et al., 2023). For oil adulteration investigations, RS was applied to observe the unsaturation degree of high-quality olive oils adulterated with poor quality and low-price edible oils (Jiménez-Sanchidrián & Ruiz, 2016).

RS is specialized in evaluating the oxidation status of VOO in terms of primary and secondary oxidation parameters under accelerated storage at room temperature (Guzmán et al., 2011), as well to assess the thermal degradation of OO under deep-frying (Meenu et al., 2021). In another study, the thermo-oxidative stability of EVOO and ROO fried from 25 to 205 °C were assessed by RS integrated with chemometric tools including spectral pre-processing e.g., baseline correction and Savitzky-Golay convolutional smoothing, Pearson's correlation coefficient, and quantitative evaluation models such as partial least squares (PLS) and least square support vector machine (LSSVM) methods (Alvarenga et al., 2018). Indeed, the thermal stability of olive oil exhibited a high connection with the smoke point. Therefore, spectral changes were detected in the oil sample that show lower smoke point i.e., EVOO. The data obtained in this investigation showed that Raman spectroscopy combined with chemometrics is a rapid and precise approach compared to conventional chemical methods to assess the oxidative stability of deep-fried olive oils and could be used to check the safety and quality of olive oils utilized in restaurants for frying purposes, and should be used as a promising method in food companies and small food shops.

Likewise, Ahmad et al. (2017) optimized the frying temperature range for frying and cooking with EVOO via RS combined with PCA. Clear changes of the oxidized products are presented in the bands from 540 cm^{-1} –770 cm^{-1} , and from 790 cm^{-1} –1170 cm^{-1} (Fig. 4). Additionally, 1267 cm^{-1} and 1302 cm^{-1} spectra are considered fingerprints to discriminate EVOO, the authors concluded that the temperature range from 140 to 150 °C is suitable and safe for frying and/or cooking purposes with EVOO.

In another investigation by Carmona et al. (2014), RS analysis of different olive oil types i.e., extra virgin, pomace, and refined olive oils

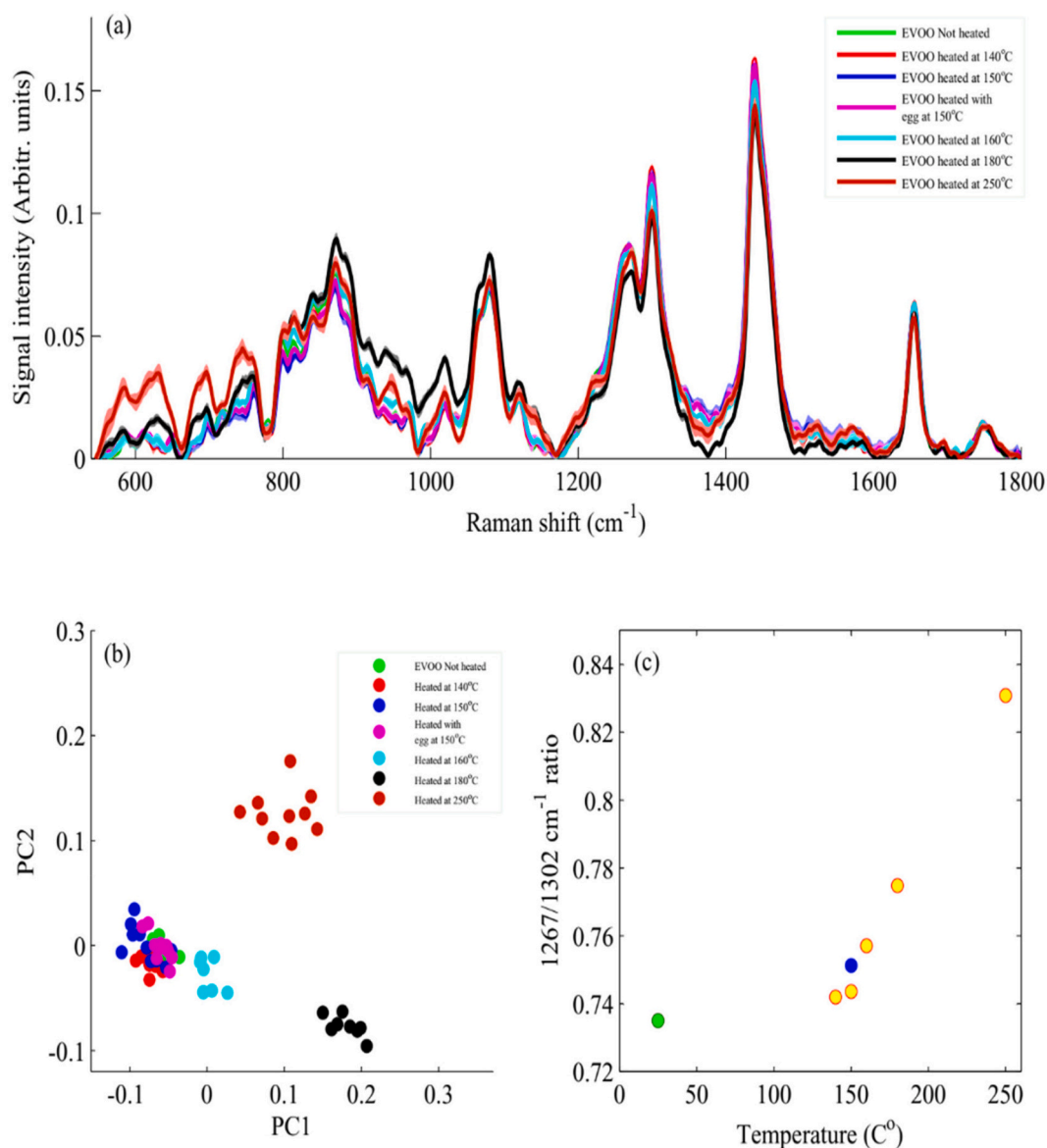


Fig. 4. (a) Raman bands of un-heated EVOO (green) and EVOO heated at 140 °C (red), 150 °C (blue), 150 °C with egg for frying (pink), 160 °C (cyan), 180 °C (black), and 250 °C (dark brown). (b) PCA scatter plot between PC1 and PC2 to illustrate classification of EVOOs according to their spectral variations shown in (a) because of heating at several temperatures. (c) The band ratio 1267/1302 cm^{-1} of un-heated and heated EVOOs at various temperatures. The green ring presents the band ratio of un-heated EVOO and yellow rings are categorized for heated oils. The blue ring presents the band ratio of the EVOO treated with an egg to get it fried, which is little bit higher. Figure adopted from [Ahmad et al. \(2017\)](#) with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fried at high temperature (190 °C/ 2 h) was carried out, the spectra were acquired and reported that, EVOO was the stable type comparing with other olive oil kinds owing to its lowest value in the intensity at 3008 cm^{-1} . Thus, the oxidative stability of the EVOO could be related to the tocopherol content.

In sum, RS has several advantages compared to other classical chemical analysis for olive oil investigation under D–F conditions, e.g., simple sample preparation, rapid analysis, sustainable, reliable, and green analytical method owing to no solvents and reagents used ([Shehnaz et al., 2024](#)). On the other hand, RS had limited applications due to its very-low efficiency of normal Raman scattering, also, RS is an expensive technique for food companies, and other limitations related to instruments. Also, limited studies are available to develop a calibration model to predict degraded products via Raman integrated with chemometric tools.

4.3. NMR

Proton nuclear magnetic resonance (hydrogen-1 NMR, proton NMR, or ^1H NMR) is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a constituent, for measuring the structural profile of its molecules ([Karunakaran et al., 2018](#)).

^1H NMR fingerprinting is used to evaluate the accelerated rancidity of EVOO stored at ambient temperature ([Almoselhy et al., 2014](#)). Minor bioactive constituents in EVOO i.e., β -sitosterol presented a vital fingerprint in defining oil authenticity and quality. Moreover, ^1H NMR was applied recently as a powerful analytical tool used for monitoring the oxidative status of the EVOO either enriched or not with lycopene during in vitro gastrointestinal digestion ([Nieva-Echevarría et al., 2020](#)).

Furthermore, three food types with different nature of fats i.e., salmon fillets, pork adipose tissue, and dough of Spanish doughnuts

were deep-fried in EVOO and then the oxidized components have been characterized by ^1H NMR spectroscopy (Martínez-Yusta & Guillén, 2014), in terms of triacyl glyceride, epoxides, aldehydes, and volatile compounds. The study confirmed that ^1H NMR spectral bands (Fig. S6) gave useful information about the thermal effect of EVOO which significantly affected not only by its content but also by the food composition.

Additionally, NMR approach has been employed for the first time to monitor the oxidized products particularly secondary aldehydic substances in the fried olive oils up to 180 °C in both continuous and discontinuous manners (Le Gresley et al., 2019). The oil oxidation products (OOPs) were further identified by ^1H NMR. The discontinuous thermal treatment of olive oil formed a high ratio of low molecular weight (LMW) oxidized compounds such as (E, E)-2,4-alkadienals, n-alkanals, and 4-oxo-n-alkanals. Indeed, the heating of olive oil can produce higher contents of OOPs compared to the continuous heating strategy. The study also indicated that discontinuous heating method comparing with continuous one had a low effect on peroxidation of oil rich in unsaturated fatty acid. Recently, OOPs including aldehydic compounds were identified by ^1H NMR in several deep-fried oils (at 180 °C) e.g., EVOO (Wann et al., 2021). The authors reported that EVOO samples were more stable under D–F and thus to the peroxidation products and aldehydes owing to their content from MUFAs than other edible oils which are rich in PUFAs. Chemometric tools and PCA offered a great pattern of aldehydic OOPs featuring LMW compounds for example n-alkanals, alka-2,4-dienals and propanal, and therefore, capable to distinguish the most stable oil to the oxidation than the low stable one.

In another investigation (Guillén & Uriarte, 2012), EVOO was treated at 190 °C/ 40 h in an industrial fryer. The evolution of oil composition was monitored by ^1H NMR after the thermal treatment. Monounsaturated fatty acids groups (oleic acid) degraded faster than polyunsaturated fats e.g., linoleic and linolenic acids. The formation of primary oxidation compounds (i.e., peroxides and hydroperoxides) was not detected with ^1H NMR, this may be attributed to these oxidized compounds are very immediately degraded at deep-frying temperatures in contrary to secondary oxidized ones. Moreover, secondary oxidation products including aldehydes were observed, amongst the aldehydes detected, alkanals and (E)-2-alkenals are present in much higher ratios than (E,E)-2,4-alkadienals and 4-oxo-alkanals. In sum, fatty acids, and secondary oxidized compounds in EVOO have been analyzed instantaneously from their ^1H NMR spectra.

In conclusion, the main advantages of using NMR during D–F of olive oil categories comparing with other conventional chemical approaches e.g., GC are reliable, rapid analysis without any preliminary treatment, also NMR has other benefits for example, sample non-destructiveness, and structure-sensitive characteristics, and the small quantity of olive oil samples required (Caligiani et al., 2016). In addition, NMR has other reported advantages such as the high stability, sensitivity of measurements and, in case of interferences, the possibility to suppress one or more signals through modern pulse sequences, thus, these benefits make ^1H NMR one of the most reliable methods in olive oil analysis during D–F, rivalling techniques like GC (Augustyn et al., 2021).

Furthermore, ^1H NMR technique can use both targeted and untargeted chemometric methods to determine the olive oil metabolomic profile and for quantification purposes as well (Maestrello et al., 2022). On the other hand, the major drawback of ^1H NMR technique is its inherent sensitivity, which is lower than the sensitivity of other conventional mass spectrometry (MS) and chromatographic methods, even if it can be enhanced via the application of more intricate apparatus e.g., cryoprobe. Lately, ^1H NMR approach was exploited by Bruker, GmbH to evaluate quality indicators of EVOO. Bruker is developing also an entirely computerized resolution for targeted and untargeted investigations to test the origin authenticity and mislabeling of olive oils. Moreover, Bruker is also evolving a technique based on an 80 MHz

benchtop scheme that could be interesting for the industry and giving the right boost to a greater use of ^1H NMR spectroscopy not only for research tenacities but also in quality control research laboratories and industry.

4.4. Infrared spectroscopy (IRS)

IRS measures the absorption of infrared radiation by chemical bonds in a material. Chemical structural fragments of molecules, known as functional groups, tend to absorb IR radiation in the same frequency range regardless of the structure of the rest of the molecule that the functional group is in. This correlation between the structure of a molecule and the frequencies at which it absorbs IR radiation was used to identify the structural formula of unknown molecules and/or monitor the chemical changes of the molecule (Stuart, 2004).

IRS (wavelengths ranging from 750 to 25.000 nm), typically involves absorption associated with the stretching of O–H and C–H bonds. For the purposes of analytical spectroscopy, the infrared spectrum can be divided into three main regions (a) NIR ranging from 750 to 2500 nm, (b) MIR ranging from 4000 to 400 cm^{-1} and (c) far-infrared (FIR) ranging from 400 to 10 cm^{-1} and the last type infrequently used in the food analysis (Johnson et al., 2023).

Several studies have been utilized IR for monitoring the quality of EVOO during deep-frying process, for example the thermal degradation of EVOO were studied by Attenuated Total Reflection Fourier-Transform Infrared (ATR-FTIR) spectroscopy (Cakmak-Arslan, 2022). The oils were deep-fried at 180 °C for one day. The bands at 722 cm^{-1} and 3007 cm^{-1} and 3007/2854 cm^{-1} ratio and 722/2854 cm^{-1} ratio were decreased after frying process, on the other hand, an increment at 987 and 965 cm^{-1} and 965/2854 cm^{-1} ratio were noticed in EVOO due to *cis-trans* isomerization as well formation of primary and/or secondary oxidized substances. Moreover, this study provided a rapid and accurate method to monitor the quality as well as the safety of deep-fried EVOO samples using ATR-FT-IR than classical chemical methodologies.

ATR approach hardly requires sampling preparation and provides a fast and accurate analysis of liquids e.g., olive oil (Mahesar et al., 2010). Moreover, FTIR allied with multivariate analyses of spectral data set, was applied to evaluate the oxidized triacyl glycerides in VOO with various oxidative grade (Lerma-García et al., 2011).

ATR-FT-IR was utilized effectively in order to assess the thermo-oxidative stability of oil samples such as different olive oil types and mixed frying oils according to *cis/trans* isomerization, free fatty acids, and trans fatty acids (Meenu et al., 2021). Moreover, ATR-FTIR has been employed to register the spectra of VOO samples fried up to 94 h. The wavelength 978–960 cm^{-1} represented the trans-fats and used for predicting total phenolic compounds of VOO (Tena, García-gonzález, & Aparicio, 2009).

FT-IR spectra of EVOO were obtained for the variation in wavelength from 3100 to 3600 cm^{-1} after thermal processing at several temperatures i.e., 30, 60, and 90 °C/35 days (Navarra et al., 2011). Furthermore, according to the FT-IR spectra, the hydroperoxides (ROOH), alkanals, as well secondary thermal rancidity compounds have been increased due to thermal process. All EVOO samples on FT-IR displayed an increase in their viscosity, and subsequently increase of fluorescence life-time of chlorophyll, and finally formed polar compounds with inclination to form H_2 bonds.

ATR-FT-IR has been used to evaluate the thermal deterioration of VOO samples at 100 °C till the beginning of the oil oxidation. The stretching vibration of *cis* double bonds was reallocated to fewer ranges (3006–970 cm^{-1}) allied with the bending vibration of the *trans* double bond (Román Falcó et al., 2012). Hence, the spectral signatures of EVOO blends with sunflower and palm olein oils via FTIR were studied. The obtained spectral fingerprints were firstly preprocessed with SNV and then PCA was employed, which showed clear differentiation for various frying. This report showed that FTIR could be an efficient tool for fast and non-destructive assessment of deep-fried edible oils (Ahmad et al.,

2022).

ATR–FT–IR has been employed to identify the chemical alterations stimulated in EVOO after thermal treatment at 185 °C/4 and 8 h (Poiana et al., 2015). The thermal oxidative stress decreased the absorbance at 722 and 3006 cm⁻¹, increased the absorbance at 967 and 987 cm⁻¹ (*cis-trans* isomerization), and increased the absorbance at 1743 cm⁻¹ (Fig. 5). Additionally, FT–IR was assigned to measure the spectral amendments in the polar fractions of thermo-oxidized VOO samples. The polar fractions provided excellent information about the chemical alterations occurring because of the rancidity. Furthermore, the authors reported an improvement was obtained of the OH of the spectra from 3600 to 3200 cm⁻¹ and the tertiary alcohols (~1167 cm⁻¹), including the regions related to epoxides (Tena et al., 2013). Additionally, the band at ~1746 cm⁻¹ assigned to the stretching vibration of ester linkage (C=O), this band being off-scale in all the spectra due to its robust strength. Therefore, the tendency of this band was analyzed via its first overtone (~3472 cm⁻¹). Though this overtone band impedes with the rest of absorptions in OH area (3600–3410 cm⁻¹), in the spectra of the

non-polar fractions this band is separated and can be immediately determined.

Furthermore, ATR–FTIR of fried OO allied with chemometric tools e. g., PLS regression model has been employed to analyze the formed polymerized triacyl glycerides (PTAGs) (Kuligowski et al., 2012). Several methodologies to select the spectral changes were utilized to develop PLS model as follows: (A) intervals PLS model (iPLS). (B) variables selection based on expert knowledge (EK) on the investigated system with results from iPLS and uninformative variable selection-PLS (UVE-PLS). Moreover, the three approaches provided PLS model from fried OO with exceptional implementation for the prediction of PTAGs with other statistics tools. Nevertheless, along with a high coefficient of determination ($R^2 > 0.99$) and low validation, and prediction errors of 1.14, 1.21, and 1.40 %, respectively, variables selection based on EK offered also identical low calibration (-0.0017 %) and prediction (-0.0023 %) bias (Kuligowski et al., 2012).

In another study (Tena, Aparicio, & Garcia-Gonzalez, 2009), ATR–FTIR has been applied to check the oil oxidation of fried VOO to

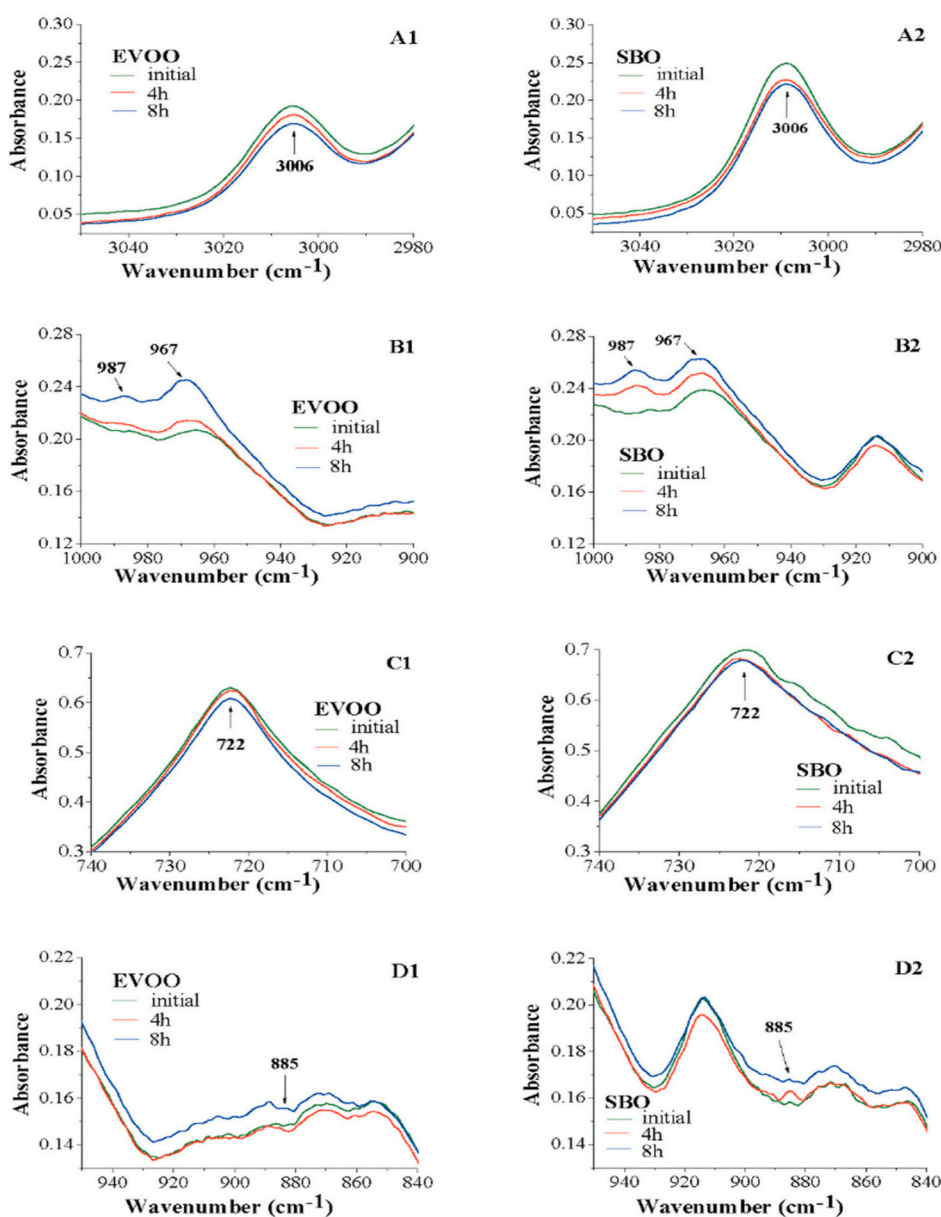


Fig. 5. The ATR- FTIR spectral variations EVOO adulterated with soybean oil (SBO) throughout heating of oil samples at 180 °C for 4–8 h, these amendments corresponding to decreases in unsaturation level (A1, A2): 3006 cm⁻¹; (B1, B2): 967, 987 cm⁻¹; (C1, C2): 722 cm⁻¹; (D1, D2): 885 cm⁻¹ (Poiana et al., 2015).

determine the total polar compounds (TPCs) as well fatty acids content. The infra-red bands allocated to isolated trans double bonds provided better relationship of the oxidation through stepwise multiple linear regression analysis (SMLRA). The bands from 978 cm^{-1} to 960 cm^{-1} were preferred to build a model for predicting TPCs especially in VOO fried up to 94 h. Promising results predicting TPCs ($R^2 > 0.997$) were effectively proven with external sample set. In addition, elaidic, linolenic, and palmitoleic acids were selected to be included in a predictor model. Moreover, after selecting the best variables, a model for frying monitoring was obtained by linear regression analysis. Fatty acid composition confirmed the excellent relationship amongst the trans ratio and TPCs content was acquired.

A mesh cell accessory was used with FTIR to monitor the primary (hydroperoxides) and secondary (alcohols and aldehydes) oxidation molecules in VOO samples. This method does not require high temperature unlike Rancimat used to analyze the thermal stability of olive oil (Tena et al., 2017). Thus, the present study can propose that other studies by this technique are recommended to monitor the thermal stability of olive oil during deep-frying.

In sum, FTIR is a rapid approach to evaluate the chemical amendments in the deep-fried olive oils based on the decrease or increase in the certain band's absorption. On the other hand, a few investigations have used chemometric tools to predict the thermally degraded molecules of OO samples followed by classified samples depending on the frying stress level (time/temperature).

For authenticity, and origin's discrimination of olive oil, Fourier transform mid-infrared spectroscopy (FT-MIR-ATR) has been employed to monitor autoxidation in VOO (Nenadis et al., 2013). FT-MIR-ATR has several advantages such as it requires no sample preparation, rapid technique, green apparatus, and the bands are correlated to all chemical components of the oil and are registered over a broad spectral region between 4000 and 400 cm^{-1} . Additionally, chemometric tools i.e., (PCA, multiple linear regression (MLR), principal component regression (PCR), and PLS regression) extracted useful information that could improve claims about the rancidity level of VOO samples. There are 4 common physicochemical indices i.e., acidity, PV, K_{232} , and K_{270} spectrophotometric attributes that can be measured by NIRS in order to define the quality of OO, with high accuracy (García Martín, 2022).

NIR spectroscopy has been confirmed as an advanced and efficient method used to analyze liquid foods e.g., alcoholic, and nonalcoholic beverages, dairy, and vegetable oils (Wang et al., 2017). More specifically, for D-F practices, NIR is a rapid, non-destructive technique and successful findings on the lab scale were obtained, however, NIR is not yet widely utilized in the food industry on large scale at industrial level, and on small scale at food processing units and/or restaurants in food sectors. Thus, it is highly recommended to employ NIR spectroscopy in food sectors for assessing oil quality during deep-frying (Meenu et al., 2021). In addition, MIR and NIR spectroscopy have been employed for measuring the changes after edible oil heating either through the direct observation in the infrared spectral alterations (Le Dréau et al., 2009), or by using multivariate data analysis (MVDA), chemometric tools such as PCA, multivariate pattern recognition methods (PRMs), linear discriminant analysis (LDA), and multivariate curve resolution-alternating least square (MCRLS) (Martín-Torres et al., 2022). In addition, MIR apparatus was used to evaluate the oxidation status of VOO deep-fried at $80\text{ °C}/3\text{ h}$, the findings showed that spectral bands were chosen as main powerful ones i.e., $1245\text{--}1180\text{ cm}^{-1}$ as well $1150\text{--}1030\text{ cm}^{-1}$ (Maggio et al., 2011).

Oxidative degradation of several olive oils i.e., EVOO, pomace olive oil (POO), and ROO have been analyzed using ATR-FT-MIR and FT-NIR transmittance spectroscopy coupled with chemometrics. Furthermore, PCA revealed spectral amendments due to thermal oxidation. MCR revealed 3 spectral compounds in MIR and NIR spectra, due to the oxidation/degraded molecules, saturated, and un-saturated components (Wójcicki et al., 2015).

ATR-MIR spectra of various oils including OO treated under thermal

stress with and without various foods have been used to assess polymerized triglycerides (PTGs) in the fried oils (Kuligowski et al., 2012). An improved root mean square error of prediction (RMSEP) was noticed based on the oil kind with PLS model according to the selected calibration set comparing with the pooled calibration sets. Moreover, PLS-DA provided a real classification of the oil types heated without foods, and the PTG concentration was the independent factor. On the other hand, this classification of fried oils with foods was less evident. In the study of Kuligowski et al. (2011), ATR-MIR spectral fingerprints of heated OO were studied to determine PTG content after deep-frying procedure. One-class-classifier PLS-DA and a rooted binary directed acyclic graph tree (RBDAGT) offered accurate classified fried oil. Fried oils without food were classified correctly, but the samples fried with foods were less obvious. Moreover, double-cross model validation along with permutation test were employed in order to validate PLS-DA. Root mean square error of prediction could be adjusted substantially by PLS model based on the selected calibration set via PLS-DA, varying from 1.06 % to 2.91 %.

Refined olive oil was submitted to deep-frying at 160 and 190 °C , and for pan frying of potatoes at 180 °C (Zribi et al., 2014). Various chemical indices including TPCs, dimeric and polymeric triacylglycerols (DPTG), and anisidine value (AnV) by FT-NIRS were performed after deep-frying process to assess the oxidation of the heated refined olive oils. ROO was found to be more stable than other studied refined seed oils. Also, a chemometric analysis through principal component analysis (PCA) using XLSTAT software for Windows (v.2014.1.08, Addinsoft, New York, USA) has exhibited that the lower deteriorated oil amongst all oil kinds was ROO at 160 °C .

In conclusion, compared to other conventional analytical methods, the main advantages of IR spectroscopy technique are its easy to use, the instrument relatively low price, and is typically non-destructive and non-invasive method, reduced sample preparation time, and rapid approach of measuring the chemical composition and metabolomic profile of a wide range of different olive oil types (Johnson et al., 2023; Walsh et al., 2020). Likewise, IR spectroscopy showed considerable potential for the quantification and relative prediction of the levels of bioactive components in different olive oil categories during D-F.

Furthermore, IR spectroscopy is highly sensitive, requires a small amount of samples and allows users to analyze samples from a varied variability of olive oil types, and does not produce any waste. Contrarywise, the challenges engage interpreting spectra from olive oil mixtures and the creation and maintaining robust calibration models for quantitative analysis are required (Bureau et al., 2019). Further studies on IR spectroscopy are required to build a robust model without dropping precision over time, or when applied to different olive oil varieties, and/or from different geographic localities.

5. The advantages and the technical challenges of spectroscopic approaches comparing with the conventional analytical methods

An illustration of the advantages and challenges of the conventional analytical methods and spectroscopic techniques used to identify the oxidized products of the olive oil after deep-frying is presented in Fig. 6. The current findings illustrate that several advantages of the spectroscopic approaches can be achieved as reliable, sustainable and green methods, easy to use, relatively inexpensive method and also provide rich chemical and physical information, as well as well-established techniques in analytical and bio-analytical chemistry laboratories, on the other hands, due to their prevailing disadvantages, various spectrometers are always used together to tackle the disadvantages of other spectroscopic instrument when used separately.

FS allied with chemometrics can be capably used for both quantitative and qualitative measurements as an effective analytical approach compared to the conventional techniques such as AOA, OSI, Rancimat, SOT, and DSCM. Further investigations are required to address several technical limitations of FS e.g., the method verification for definite

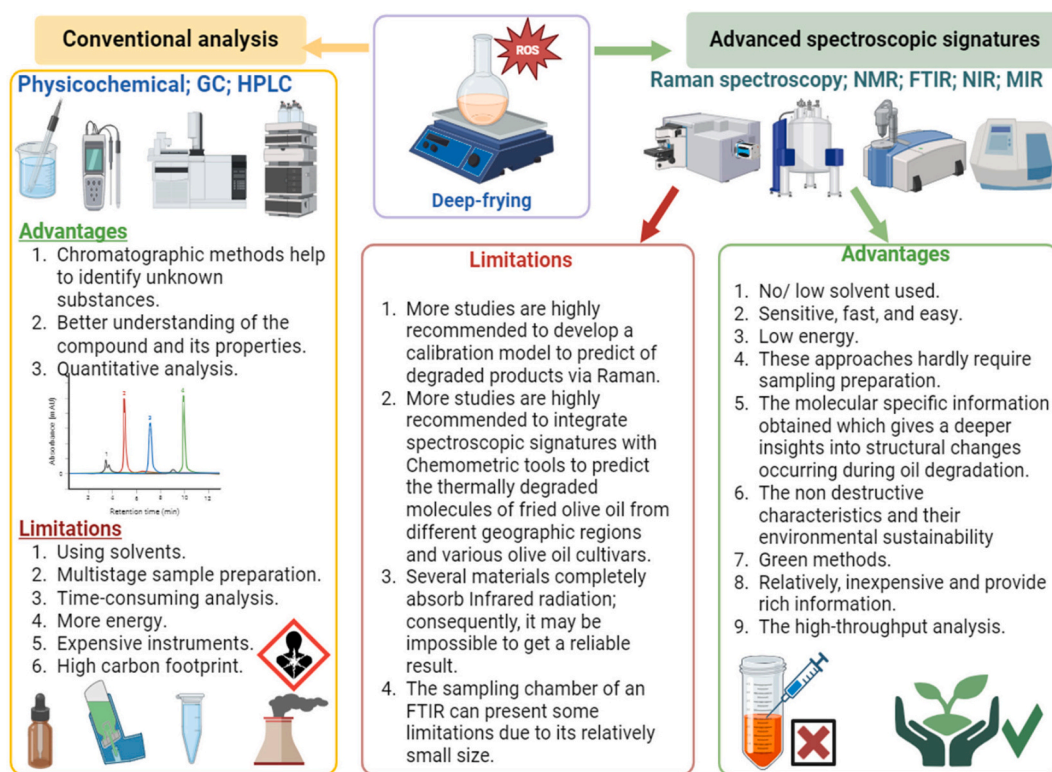


Fig. 6. A representative illustration of advantages and limitations of the instruments used for monitoring the quality changes occurring after deep frying of olive oil.

variety of OO as well as to quantify other fluorescent OO components. Another limitation of FS is that it can't build robust models based on low sample numbers, therefore, to build a stronger system it is highly recommended to increase the sample numbers when FS is employed to develop a better model.

As reported in the current study (Fig. 6), RS has several advantages compared to other classical chemical analyses for olive oil investigation during D—F, e.g., simple sample preparation, rapid analysis, sustainable, and green analytical method owing to no solvents and reagents used, on the other hand, it had limited applications due to its very-low efficiency of the normal Raman scattering, it is expensive for food companies, and the limitation related to instruments. Hence, other main limitations of Raman spectroscopy approach are strong fluorescence backgrounds can mask Raman bands, high laser powers can damage oil samples, and RS compared to infrared spectroscopy (IRS) is less utilized to analyze the thermal oxidation of olive oils under deep-frying. Furthermore, very few investigations have examined the effect of the frying process on olive oil quality and safety by RS. Likewise, limited studies are available to develop a calibration model to predict degraded products via Raman integrated with chemometric tools. Consequently, a big enhancement of spectrophotometers should be carried out to Raman which allows to overcome limitations fundamentally change the proficiencies of spectroscopy. Furthermore, the portable Raman could improve the in-situ analysis of degraded oils under deep-frying in the nearest future.

One of the main conventional analyses that are used to determine the fatty acids (FAs) profile of different olive oil types is GC. Though GC is a more sensitive method, NMR spectroscopy can also be utilized for this principle (Schripsema, 2019). The easy sample preparation and speed analysis are attractive and cost-effective benefits of NMR than GC technique. For NMR analysis, the sample only has to be dissolved, and the FAs are analyzed as their glycerol esters. While in GC analysis the ester bonds should be hydrolyzed and derivatized before analysis. In this process, the more unstable FAs might be lost owing to the degradation. The NMR method is also more appropriate for quantification due to the

integrated area of an ^1H NMR signal depends on the number of protons present and therefore removes the need to consider detector response factors, as is the case with chromatographic detectors (Augustyn et al., 2021; Schripsema, 2019). As shown in the present research also, NMR was less utilized in the analysis of olive oil categories during thermal process, thus, the current research recommend that additional studies should be carried out for measuring the metabolomic profiling of various olive oil types and for identification, and quantification of their compounds allied with chemometric tools i.e., targeted and untargeted methods to maximize the oxidative stability and the health benefits of deep-fried olive oil. On the other hand, the main drawback of ^1H NMR technique is its inherent sensitivity, which is lower than the sensitivity of other conventional mass spectrometry (MS) and chromatographic methods.

In the last years, mid- and near-infrared spectroscopy have achieved prominence for the measuring and quantification of changes occurring during D—F for various olive oil types through direct monitoring the infrared spectral deviations. FTIR spectroscopy for example, has promising advantages compared to conventional chemical analyses to monitor the oxidation status and the metabolomic profile of olive oil samples, on the other hand, a few investigations have used chemometric tools to predict the thermally degraded compounds of different olive oil types followed by classified samples depending on the frying stress level (time/temperature). Therefore, more studies should address these issues while studying different olive oil varieties and/or from different origins. An additional issue in IR spectroscopy approach is that the sampling chamber of an FTIR can present some limitations due to its relatively small size.

Moreover, according to the promising outcomes reported in the literature, NIR spectroscopy could be an appropriate method to monitor the oxidative stability of several olive oil categories due to its remarkable performance either in the laboratories or on large scale in predicting the oxidized products in olive oil samples. However, some compounds in different olive oil types i.e., alpha-tocopherol, K_{225} , and squalene could be predicted by NIRS, but the calculation errors are high

for practical application, thus, further studies are still required to address these limitations. Finally, NIR should offer self-learning model calibration schemes, for olive oil samples fried under different thermal stress conditions, and to be added to the calibration set to reinforce the PLS model. On the other hand, several limitations in IR spectroscopy are reported such as, materials completely absorb infrared radiation; consequently, it may be impossible to get a reliable result. Finally, more studies are highly recommended to integrate IR spectroscopic signatures with chemometric tools to predict the thermally degraded products of fried olive oil from different geographic regions and various olive oil cultivars.

6. Outlook, conclusions, and future perspectives

Recently, FS coupled with machine learning (ML) algorithms achieved accurate classification of olive oil as extra virgin or non-extra virgin (Venturini et al., 2024). Determination of specific excitation wavelengths e.g., 480 nm and 300 nm that are highly informative for assessing EVOO quality during different ageing stages, which can be used in-field by non-scientists, could provide an easily accessible assessment of the quality of EVOO. However, the main limitation is that models rely heavily on the quality and representativeness of the training data, which necessitates a diverse data set that includes different types and conditions of olive oil. Thus, the present investigation recommends that future studies should be conducted to monitor the oxidation of EVOO under deep-frying while using other spectroscopic methods coupled with ML.

Other modern techniques can be used alongside of spectroscopic methods, for example, a kinetic-thermodynamic study was conducted to investigate the impact of the olive cultivar (Arbequina and Cobrançosa) and polyphenols concentration on the oxidative stability fried up to 160 °C (Veloso et al., 2020). The authors reported that oil rancidity grade increased with the decrease of the polyphenols content. In addition, the kinetic thermodynamic aspects provide an efficient approach to classify and discriminate the olive oil based on the cultivar brand and polyphenols content. Additionally, the non-linear optical characteristics of various oils were measured i.e., EVOO using the Z-scan instrument (Marbello et al., 2020). The study showed that EVOO presented better non-linear responses at lower excitation potencies. In sum, Z-scan method was a sufficient tool to study the correlation amongst non-linear optical aspects with chemical modulations after the exposure to high thermal treatment.

In conclusion, the current review discusses various spectroscopic approaches e.g., FS, NIR, FTIR, RS, NMR spectroscopy, and amongst others used to monitor the quality and thermal stability of olive oils to minimize their degradation under deep-frying conditions. This review provides fundamental insights regarding the chemical amendments in fried OO endured to high thermal process in particular minor bioactive constituents. The current detailed opinion reports that, the spectroscopic technologies can be used as reliable, rapid techniques to reduce the time of the analyses, manpower, reagents, and high-cost instruments as well as green method, providing more benefits for the consumers and food industry. Additionally, the advantages and drawbacks of these approaches have also been highlighted.

Moreover, and based on the current research, most of the recent studies have used individual spectroscopic methods, however, combining multiple spectroscopic approaches could be useful in procedures dedicated to decision makers for quality control of deep-fried olive oils.

Further studies are highly recommended to obtain the required information on the monitoring of the thermal stability of different cultivars of olive oils based on spectroscopic approaches and to tackle their limitations for identifying differential spectroscopic fingerprints allied with improved olive oil stability to ensure its safety and quality. Finally, the current study recommend that some spectroscopic approaches could be applied on large scale, also collaboration between the academia and the industry should be conducted to tackle the limitations of each

approach, as a preliminary step to obtain formal approval of these methods from the International Olive Council as reliable and sustainable tools for monitoring the oxidation stability of various olive oils categories and to extend its health properties and unique organoleptic attributes.

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CRedit authorship contribution statement

Taha Mehany: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **José M. González-Sáiz:** Writing – review & editing, Validation, Supervision, Resources, Investigation, Data curation, Conceptualization. **Consuelo Pizarro:** Writing – review & editing, Validation, Supervision, Project administration, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interests.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2024.141624>.

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