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Infrared spectroscopy and chemometrics for predicting commercial categories of virgin olive oils and supporting the panel test

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ABSTRACT

The aim of this study was to create rapid and sustainable instrumental methods for screening virgin olive oils (VOOs) to support the Panel test. The Panel test is the official sensory method used in EU regulations to determine the commercial category of VOOs. The Panel test is based on a time-consuming and expensive approach, so reducing the number of samples to be analysed is crucial. Spectroscopy offers a potential solution for quickly determining VOOs composition and predicting their quality grade. In this context, three spectroscopic techniques were explored: Near-Infrared (NIR), Fourier-Transform Infrared (FT-IR), and Raman spectroscopy. A dataset of 100 VOOs samples, categorized into the three official grades (extra virgin, EVOO, virgin, VOO and lampante, LOO) established in EU, based on the Panel test results, was analysed. An initial analysis of all spectra revealed typical for triacylglycerols molecular vibrations and not good variability between types of samples, indicating low specificity. However, FT-IR data paired with two different Partial Least Squares-Discriminant Analysis (PLS-DA) models – one differentiating LOO from non-LOO (VOO and EVOO) and another distinguishing LOO from VOO – yielded promising results. Cross-validation indicated successful sample classification with percentages ranging from 81% to 96%, in which LOO vs. no-LOO model showed the highest performance. These findings suggest that FT-IR coupled with chemometric analysis holds promise, particularly for discriminating LOO (inedible) from the higher-quality grade VOO and EVOO categories. Further research efforts are needed to possibly make the herein developed models more robust and potentially extend their application to differentiate all three VOO quality grades.

1. Introduction

Nowadays, the reduction of chemicals or solvents and the overall environmental footprint represent crucial aspects to be considered in food quality control, where the need to speed-up the time of analysis is also relevant to improve the number of samples checked daily. Regarding virgin olive oils (VOOs), the quality is defined by a combination of chemical, physical, and sensory properties that allow their classification into three commercial categories (EVOO, VOO, LOO) as reported in the EU Regulation (Regulation, 2022/2104). Several research efforts are aimed to better assess the purity and the quality of this product (Gagour et al., 2024), and recently, they have focused on

the development of rapid screening instrumental methods for supporting the official methods used in the commercial category determination. These methods could potentially be applied to broaden the screening of the samples requiring control, with the aim to restrict numbers needed to be further investigated by the official targeted and validated procedures. The latter are often time-consuming, or complex, such as the sensory assessment or the full chemical and compositional analysis. For instance, a rapid screening method based on volatile fingerprinting as a tool to support the Panel test has previously been proposed (Barbieri et al., 2020; Quintanilla-Casas et al., 2020).

In addition, among all the methods that could be applied to achieve this purpose: optical techniques, such as ultraviolet–visible (UV–Vis),

Fourier transform infrared (FT-IR), near-infrared (NIR), mid-infrared (MIR), Raman, and fluorescence spectroscopy, the measurement of electrical characteristics (such as electrical impedance spectroscopy, amperometry, and cyclic voltammetry), and the use of instruments equipped with electronic chemical sensors (e.g., electronic noses and tongues) can be adopted (Valli et al., 2020). NIR, MIR, Raman and FT-IR spectroscopic methods can be applied as analytical techniques for the rapid determination of VOOs alongside the official methods. These analytical approaches are based on the study of vibrational transitions occurring in the ground electronic state of the molecules after interaction with incident radiation at a particular frequency. While the spectral information and reliability of such techniques vary according to the specific analytical purpose, all the tools listed have been extensively studied for both quantitative and qualitative assessments of vegetable oils and, in particular, VOOs (Valli et al., 2020, Abbass, Dardenne, & Baeten, 2012). Many studies have been conducted to classify different types of vegetable oils (Osorio, Haughey, Elliott, & Koidis, 2015; Jiménez-Carvelo, Osorio, Koidis, González-Casado, & Cuadros-Rodrí- guez, 2017; Georgouli, Martinez Del Rincon, & Koidis, 2017; McDowell, Osorio, Elliott, & Koidis, 2018) to detect adulterations (Baeten et al., 2005; Vali Zade, Forooghi, Jannat, Hashempour-Baltork, & Abdollahi, 2023; Maggio, Cerretani, Chiavaro, Kaufman, & Bendini, 2010; De la Mata et al., 2012; Ordoudi, Strani, & Cocchi, 2023; Sohng et al., 2020; Melendreras et al., 2023) and to determine the geographical origin of VOOs (Bertran et al., 2000; Bendini et al., 2007; Galtier, Dupuy, Le Dréau, & Ollivier, 2007; Woodcock, Downey, & O'Donnell, 2008; Bra- golusi, Massaro, Zacometti, Tata, & Piro, 2021). However, to the au- thors' knowledge, there are no studies in the existing literature where NIR, Raman, and FT-IR methods have been applied to the same set of samples for a comparative analysis of classification, in terms of VOO commercial category determination. Considering the characteristics of FT-IR, NIR and Raman, the combination of these techniques allows for a more comprehensive analysis, as they each capture different aspects of the sample's molecular characteristics.

In the last decades, the use of chemometrics in food analysis has steadily grown, since the output from most analytical methods is that of multivariate data matrices (spectroscopic, chromatographic/mass spectrometry data, isotopic, sensorial, etc.), which cannot be manually (or univariately) analysed and therefore demand appropriate chemo- metric analysis to process and capture the most important and relevant information (Lohumi et al., 2015). It is clear that chemometric model- ling can be easily applicable for differentiating similar samples in different classes according to the authentication requirements under investigation such as quality or origin (Ghidini et al., 2019). In fact, the spectral information described by any vibrational spectroscopy could be used as a fingerprint. The way that multivariate statistical methods work is through pattern recognition modelling, which can transform the spectral information containing molecular structures into new variables or class responses according to the similarities of the samples. Among these methods, those mostly used for exploratory analysis and classifi- cation purposes are principal component analysis (PCA), cluster analysis and any type of discriminant analysis (linear, quadratic, or partial least squares, PLS, among others) (Gómez-Caravaca, Maggio, & Cerretani, 2016). Spectroscopic methods have been extensively studied for both quantitative and qualitative assessments of VOOs (Abbass et al., 2012), mostly for the detection of adulterations and for geographical origin determination (Valli et al., 2016). However, the spectral information could also be used as a fingerprint for the discrimination of VOOs based on their quality grade.

In the area of EVOO analysis where sensory analysis is involved (Panel test), these approaches can be used as screening methods, to support the conventional targeted analytical methods, that are often more laborious, time-consuming to conduct, expensive, and require skilled technicians. Such a spectroscopy based screening tool could reduce the number of samples to be analysed by Panel test, or at least aid to "prioritize" them by selecting those for which sensory analysis is more

urgent and thereby, simplify the quality control procedures in labora- tories and companies that operate in the olive oil sector.

Hence, the aim of this study was to investigate spectroscopic methods (FT-IR, NIR, Raman), combined with PLS-DA models to predict one of the three VOO commercial categories, namely, extra virgin (EVOO), virgin (VOO), and lampante (LOO), with respect to the com- mercial category previously determined by sensory analysis (Panel test).

2. Materials and methods

2.1. Samples and sensory analysis

The sample set was composed of 100 commercial VOOs. All the samples were sensory evaluated and classified into one of the three commercial categories (EVOO, VOO, LOO) through the Panel test method, according to regulations of the European Union (Regulation, 2022/2104) and IOC (IOC/T.20 Doc. No. 15/Rev. 10/2018), carried out by the University of Bologna professional committee of virgin olive oil panel tasters. Only the sensory analysis was performed while the phys- icochemical parameters to assess the quality and purity of virgin olive oils established by Regulation, 2022/2104 and IOC (IOC/T.15/NC No. 3/ Rev.19/2022) were not investigated and were not part of the objec- tive of the study. The oils were stored at −18 °C until analysis, thawed for an adequate time at room temperature and shaken before use.

2.2. Spectra acquisition

FT-IR analysis was performed with the use of Nicolet iS50 (Thermo Fisher Scientific, Waltham, Massachusetts, USA) FT-IR module, equip- ped with a DTGS detector and KBr beam splitter. Spectra were obtained in the range of 4000–550 cm^{-1} with a resolution of 2 cm^{-1} using a monolithic diamond attenuated total reflectance (ATR iD7) accessory. All the spectra were recorded at room temperature with 32 scans.

NIR spectra were acquired using Nicolet iS50 (Thermo Fisher Sci- entific, Waltham, Massachusetts, USA) FT-NIR diffuse reflectance module, equipped with Ge coated KBr beamsplitter (beam splitter), and InGaAs (Indium Gallium Arsenide) detector. The oil samples were placed on a 4.78 mm low OH quartz window sample ring cup combined with a Spectralon white diffuse reflectance standard. All the spectra, in the wavenumber range of 4000–10,000 cm^{-1} for each measurement with a resolution of 4 cm^{-1}, were recorded at room temperature with 32 scans.

FT-Raman measurements were all conducted using a DXR2 Raman Microscope (Thermo Fisher Scientific, Waltham, Massachusetts, USA) operated with an excitation laser light of 785 nm, laser power of 25 mW, integration time of 5 s with 10 accumulations, 10× objective lens, and the wavenumber range of 300–3300 cm^{-1} (Thermo Fisher Scientific, UK). The laser was focused on the samples contained in Greiner poly- styrene 96 well plates.

In all cases, each sample was analysed in triplicate. The acquired spectra were processed using the Omnic spectroscopic analysis software (Thermo Fisher Scientific, Madison, Wisconsin, USA).

2.3. Data analysis

The total number of variables (wavelengths) were 1868, 3112, 3528 for FT-IR, NIR, and Raman respectively. Concerning the FT-IR spectra, the region between 2750 and 1850 cm^{-1} was deleted as it contained no useful information, but only instrumental noise. Subsequently, spectra were smoothed (Savitzky-Golay method, 15 points) to reduce noise. The absorbance data were normalized by using the Standard Normal Variate (SNV) and pre-treated by first or second derivative (Savitzky-Golay method, 15 points).

From a preliminary analysis of the obtained spectra, NIR and Raman fingerprints appeared non-selective. Therefore, classification models by NIR and FT-Raman were not developed due to the low specificity of the

spectra, and FT-IR data elaboration only was conducted to classify the samples.

For the determination of quality grades, partial least squares discriminant analysis (PLS-DA) was used when building 4 binary classification models: (i) EVOO vs. noEVOO, (ii) VOO vs. LOO, (iii) LOO vs. noLOO, (iiii) EVOO vs. VOO. All the models were validated by Venetian Blinds Cross-Validation (10 segments).

The robustness and significance of all PLS-DA models, as a function of the LV number, were verified through permutation testing using PLS Toolbox for MATLAB (MathWorks Inc., Natick, MA, USA) R2022b software. This procedure allows to identify overfitting and provides the probability that the given model is significantly different (Pairwise signed rank test) from the one built under the same conditions but using random data. All the models were trained and validated using PLS Toolbox for MATLAB (MathWorks Inc., Natick, MA, USA) R2022b software.

3. Results and discussion

3.1. Sensory results

Based on the sensory assessment, 35 samples were classified as EVOO, 49 as VOO, and 16 as LOO.

Fig. 1 illustrates the main perceived defects, the median of intensity of which determine the classification of VOOs into the VOO ($\leq$3.5) and LOO (>3.5) commercial categories (Regulation, 2022/2104). Each segment represents a specific defect, with its corresponding frequency percentage, as occurrence among the samples. The chart provides a clear visual representation of the dominant defects, in which 47 % of the samples showed as main perceived defect "fusty/muddy sediments", 22 % of the samples were characterized by "frostbitten olives" defect, 17 % by rancid, 10 % by winey-vinegary, and finally, the 4 % of the samples showed "musty-humid-earthy" as the main perceived defect.

3.2. Spectral results

FT-IR, NIR, and Raman spectra of all virgin olive oils here analysed are reported in Fig. 2, where the FT-IR spectra (a) can be interpreted according to Liu et al., 2020. The major bands observed can be attributed to the following vibrations: 723 cm^{-1}, related to the overlapping of the CH$_2$ rocking vibration and the out-of-plane vibration if *cis*-disubstituted olefins, 1163 cm^{-1}, attributed to the stretching vibration of the

C—O ester groups, 1238 cm^{-1}, that represents the stretching vibration of the C—O ester groups, 1377 cm^{-1}, related to the bending vibrations of CH$_2$ groups, 1418 cm^{-1}, the rocking vibrations of CH bonds of *cis*-disubstituted olefins, 1654 cm^{-1}, representing the C=C stretching vibration of *cis*-olefins, 1700 cm^{-1}, the free fatty acids shoulder, and, finally, 1746 cm^{-1}, related to the ester carbonyl functional group of the triglycerides, C=O. NIR spectra (b) interpretation has been described by various authors (Cayuela-Sánchez et al., 2013; García-González, Baeten, Fernández Pierna, & Tena, 2013; Garrido-Varo, Sánchez, De la Haba, Torres, & Pérez-Marín, 2017; García Martín, 2022). As triolein is the main triglyceride and, thus, the major component, the highest absorption band in the NIR spectrum of olive oil is the same as that of the triolein spectrum, which is observed at 1725 nm.

Another relevant region is attributed to the absorption band near 1720 nm, which is related to the first overtone of the C—H vibration of several chemical groups such as —CH$_3$, —CH$_2$ and =CH$_2$, and the other is the absorption peaks at 1660 and 2145 nm, which are related to the C—H vibration of *cis*-unsaturation. When the degree of *cis*-unsaturation increases, the absorption peak at 1725 nm (*cis*-C18:l) shifts to lower wavelengths, i.e., to 1717 nm and 1712 nm for *cis*-C18:2 and *cis*-C18:3, respectively. The high adsorption band at 2145 nm renders the main peaks related to saturated and trans fatty acids, usually observed at 2128 and 2131 nm, respectively, hardly noticeable in the olive oil spectrum. In addition, wavelengths close to 1800 nm have also been related to the saturated fatty acids. Finally, a wide absorbance band can be observed at 1210 nm related to second overtones of C—H and CH=CH— stretching vibrations (García Martín, 2022).

Raman spectroscopy is considered a complementary technique to infrared spectroscopy methods. Indeed, both analytical tools are characterized by the exploration of molecular vibration properties. However, they present different selection rules, such as change of dipole moment for infrared and polarizability for Raman spectroscopy. This latter property is advantageous when covalent bonds in non-polar groups would be detected, as for unsaturated fatty acids in the olive oil component showing intense Raman bands (Gouvinhas et al., 2015).

Raman spectra of the virgin olive oils here analysed (c) are in agreement with what has been suggested by Li et al., 2018 and Cayuela-Sánchez, Palarea-Albaladejo, García-Martín, & Del Carmen Pérez-Camino, 2019. The spectral peak at 1746 cm^{-1} is the stretching vibration peak of ester bond carbonyl and the peaks at 1655 cm^{-1} and 1270 cm^{-1} are vibration peaks of *cis* C=C and *cis* C—H of unsaturated fatty acid. The peak at 1441 cm^{-1} is related to the scissoring vibration of
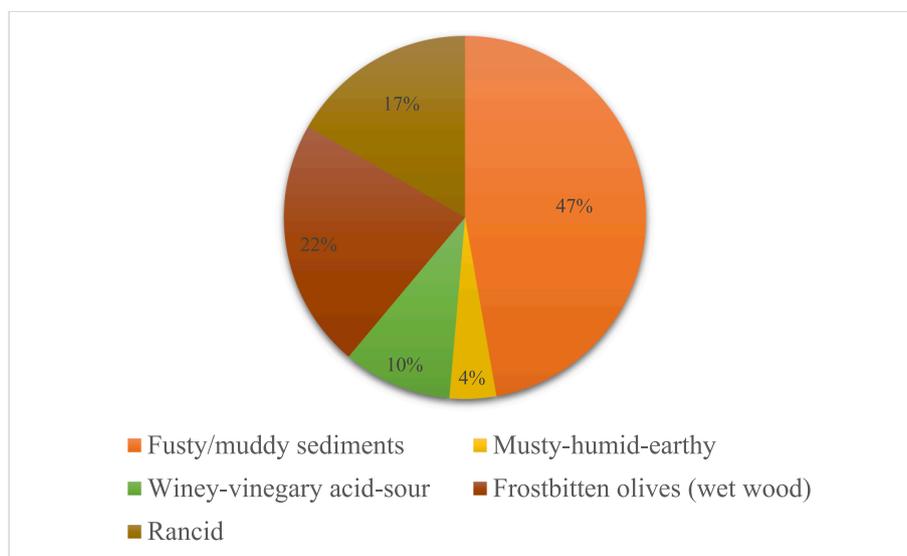

Fig. 1. Main perceived defects (fusty/muddy sediments, winey-vinegary acid-sour, frostbitten olives (wet wood), rancid, and musty-humid-earthy) in the samples, reported as frequency.
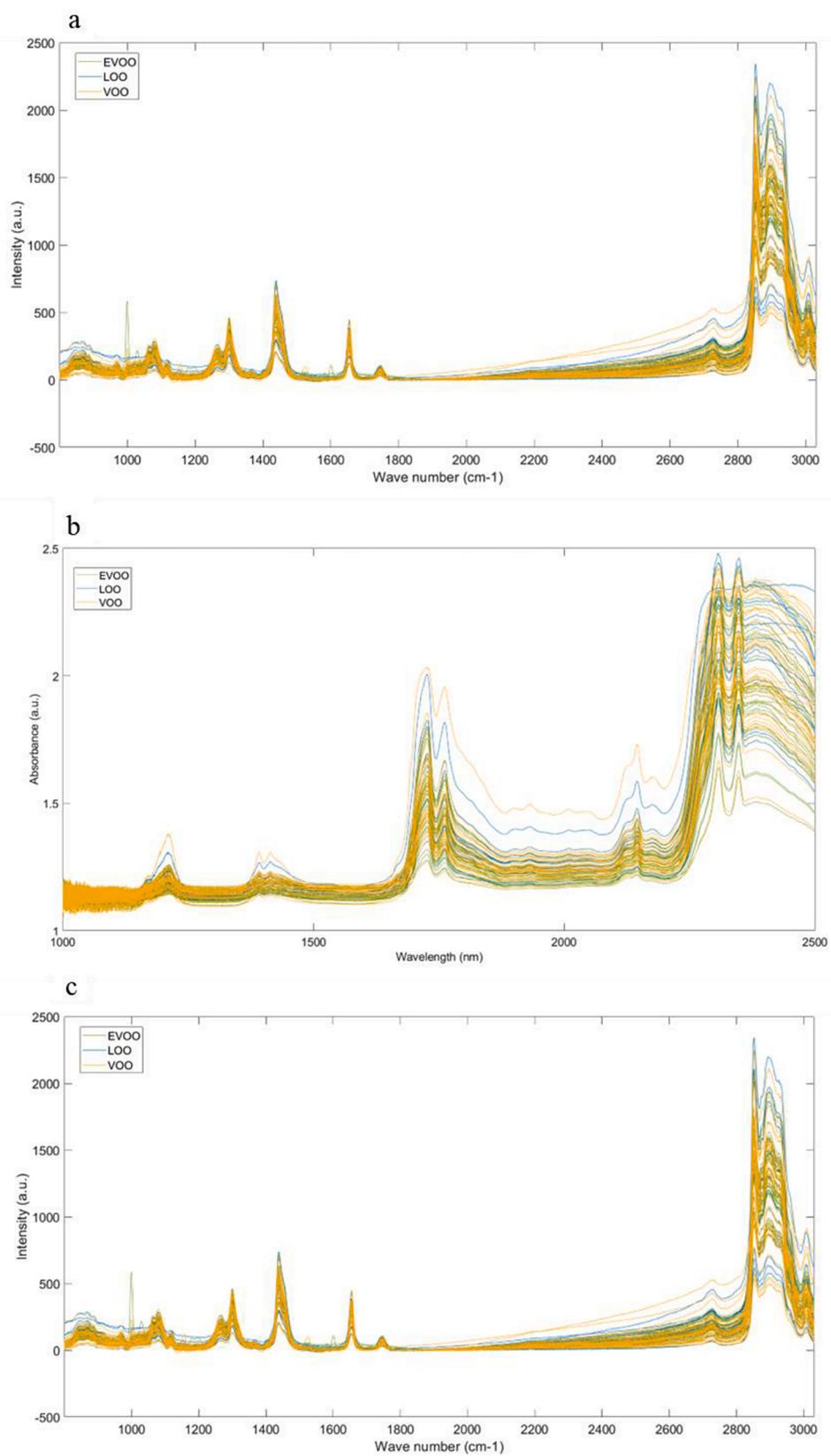
Fig. 2. (a) FT-IR, (b) NIR and (c) Raman raw spectra. Spectra of EVOO samples are reported in green, VOO samples in yellow, and loo samples in blue (n = 100).

methylene and the peak at 1303 cm^{-1} represents the twisting vibration of methylene. Peaks at 1083 cm^{-1} and 868 cm^{-1} are stretching vibrations of the methylene chain skeleton. The peak at 970 cm^{-1} is related to bending vibrations of *trans* C=C (Cayuela-Sánchez et al., 2019). These 9 characteristic peaks are almost common in Raman spectra of all edible vegetable oils. Raman spectra of different fats only show slight differences of relative peak intensity at 1655 cm^{-1}, 1270 cm^{-1} and 970 cm^{-1}. All three of these characteristic peaks are related to C=C in unsaturated fatty acid. Therefore, variations in Raman spectra of different fats are mainly caused by unsaturated fatty acid.

3.3. Spectral data elaboration

Firstly, a preliminary classification was performed using FT-IR, NIR, and Raman spectroscopic data analyses, applying 3-class PLS-DA model, based on the three VOO commercial categories assessed by sensory analysis (EVOO, VOO, LOO), but it was not selected since it was not significant, showing a p-value > 0.05 (Pairwise signed rank test).

The FT-IR fingerprint of VOOs showed quite strong molecular vibrations and good variability between samples, meanwhile the NIR and Raman fingerprints appeared non-selective. Therefore, classification models in NIR and Raman were not developed due to the low specificity of the spectra. As reported below, all the models developed using NIR or Raman data were not significant, although some of those showed satisfactory levels of classification. This was confirmed by the VIP (Variable Importance in Projection) analysis, in which the regions characterized by VIP > 1 were completely random. This result is in line with studies found in the literature, as reported by Zaroual, Chénè, El Hadrami, and Karoui (2022), in which NIR and Raman techniques were used mostly for the analysis of olive oil in the detection of adulterations with different vegetable oils (Jiménez-Carvelo et al., 2017; Sohng et al., 2020; Christy, Kasensumran, Du, & Uzaki, 2004; Zou et al., 2009) or in the determination of geographical origin of olive oils (Bragolusi et al., 2021; Lin, Chen, & He, 2012; Korifi, Le Dréau, Molinet, Artaud, & Dupuy, 2011; Sánchez-López et al., 2016).

FT-IR raw spectra were previously smoothed, normalized and pretreated by first or second derivative, as reported in Fig. 3, to extract accurate information in data analysis, and to enhance subtle differences between samples.

To conduct the necessary classification analysis, the FT-IR data were elaborated applying 4 PLS-DA models, one for each comparison: "EVOO vs. noEVOO" followed by "VOO vs. LOO", and "LOO vs. noLOO" followed by "EVOO vs. VOO".

A preliminary analysis was conducted to determine which models were significant. Only two of the total 4 binary models (LOO vs. noLOO and LOO vs. VOO) were found to be significant after the permutation test. Particularly, the permutation test provides the probability that the given model is significantly different from the one built under the same conditions but on random data. Repeatedly and randomly reordering of

the y-block (shuffling the class assignments on each sample, assigning samples to the "wrong" classes), rebuilding the model with the current modelling settings after each reordering, was considered. In this specific case, the class assignment was permuted 50 times. The results in terms of the correlation coefficient between the original and permuted class vectors versus the standardized sums-of-squares (SSQ) are shown in Fig. 4. In general, the cross-validated and self-prediction (calibration) values should be relatively close to each other but should be less than the results for the non-permuted y-block (right side of the plot), independently of their correlation with the real class values. The further away the un-permuted results are from the mean, the more unlikely it is the original model is overfit. Consequently, the higher the y-value, the more likely it is that the original model is significant. Only for the LOO vs. noLOO and LOO vs. VOO models, the y-values (un-permuted) were higher than 2, suggesting good model significance. Furthermore, the p-values obtained by three different probability tests (Pairwise Wilcoxon signed rank test, Pairwise signed rank test and Randomization *t*-test), confirm the robustness of these models (Table 1). For this reason, although acceptable percentages of correctly classified samples were reached applying EVOO vs. noEVOO and EVOO vs. VOO models, ranging from 62 % to 71 %, these were determined as not significant, and thus they were not selected as reliable to classify VOO samples.

Subsequently, for the classification of the samples using FT-IR data, LOO vs. noLOO and LOO vs. VOO binary models were applied. Regarding the PLS-DA results, the values of the predicted Y variable (commercial category) obtained by the model in cross validation are shown in Fig. 5 (a, b). The dotted line identifies the threshold value used to define the categorization of samples. For each class, the correctly classified samples are those located above the line. From the elaboration of these results (Fig. 5), the number of correctly classified samples was obtained (see Table 2).

In Table 1, the percentages of correctly classified samples are reported in both calibration and cross-validation comparing the classification provided by the two PLS-DA models individually and the results of sensory analysis. The reached percentages of correctly classified samples ranged from 88 % to 98 % in calibration, and from 81 % to 96 %, in cross-validation, demonstrating very good performance of the models. Comparable results were obtained between the models LOO vs. noLOO and LOO vs. VOO, in which for both cases, 96 % was the highest percentage observed. Consequently, the two models showed comparable predictive effectiveness. The misclassified samples do not have any specific characteristics in common. In both models, they were LOO and VOO samples characterized by different sensory defects at different intensity.

Considering these results, it is possible to affirm that the FT-IR technique can discriminate with a satisfactory percentage the LOO samples from both all noLOO and VOO samples. These results are in line with those reported by previous studies in which a classification of olive oil samples based on their quality grade was determined (Borràs et al.,
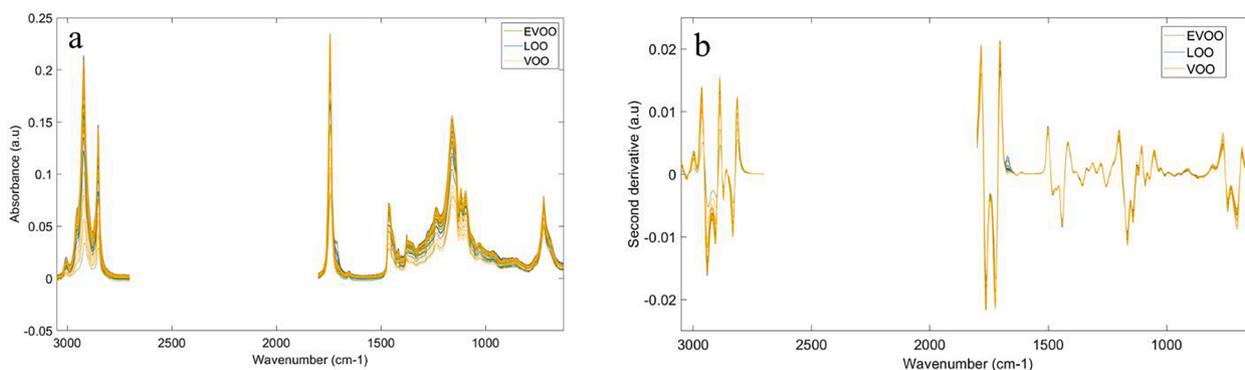

Fig. 3. FT-IR analysis spectra, pre-processed by SNV and first (a) or second derivative (b). Spectra of EVOO samples are reported in green, VOO samples in yellow, and LOO samples in blue.
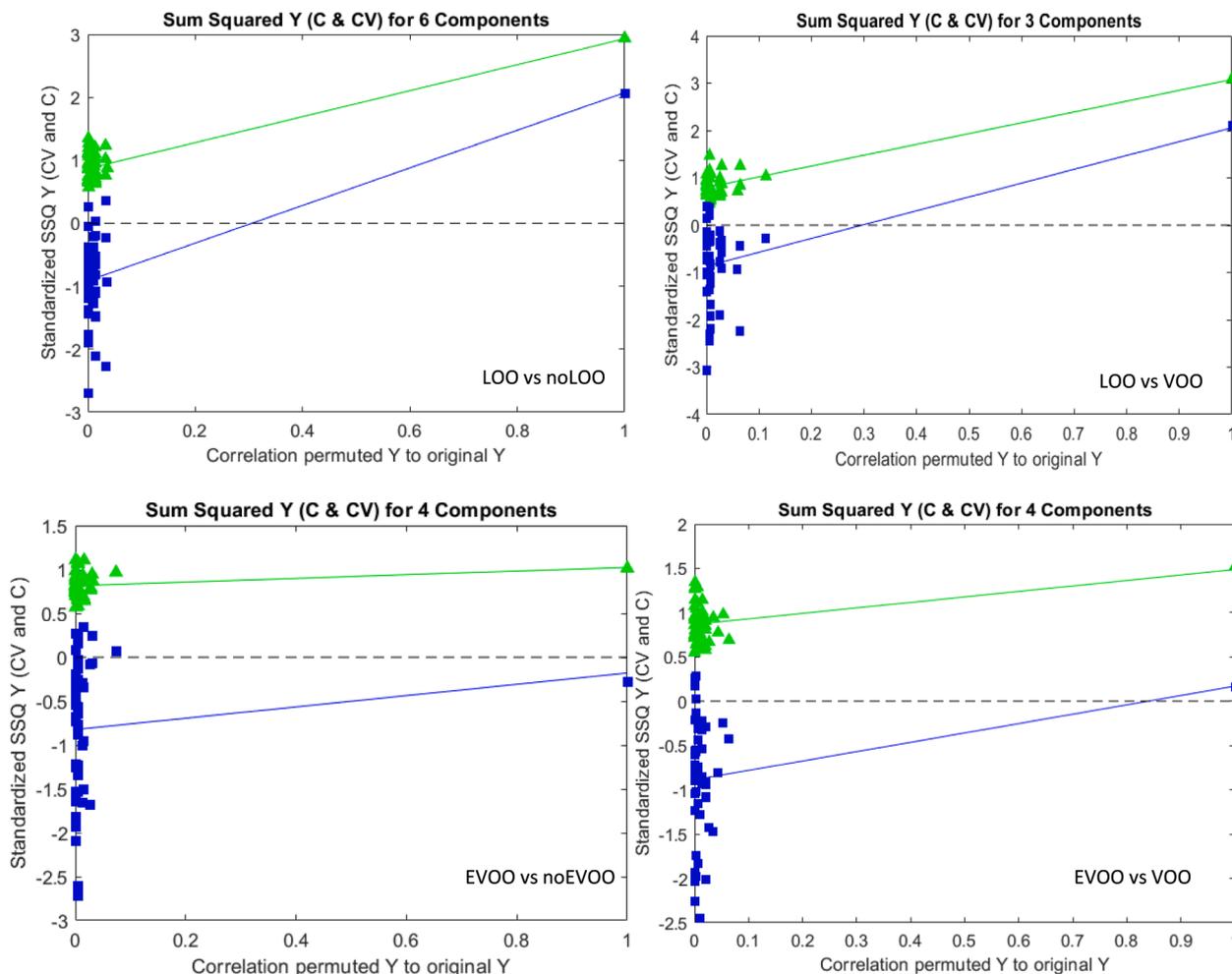
Fig. 4. Correlation coefficient between the unpermuted and permuted regression vectors versus the Standardized Sums-of-Squares (SSQ) for the 4 PLS-DA models.

Table 1
p-Values obtained by three different probability tests to evaluate the probability of model insignificance vs. permuted samples.

PLS-DA model	Wilcoxon	Sign Test	Rand *t*-test
LOO vs noLOO	0.000	0.001	0.009
LOO vs VOO	0.000	0.000	0.020
EVOO vs noEVOO	0.074	0.129	0.212
EVOO vs VOO	0.142	0.17	0.549

2015; Hirri, Bassbasi, Platikanov, Tauler, & Oussama, 2016). In the previous study, a PLS-DA model applied on FT-IR data was able to predict 93 % of the VOO grades (EVOO, VOO, ordinary virgin olive oil, LOO), in calibration (Hirri et al., 2016). In their external validation, this PLS-DA model accurately classified VOO commercial grades, claiming perfect prediction accuracy (Hirri et al., 2016). In addition, Borràs et al., 2015 used FT-IR for the analysis of olive oils to identify the four main sensorial defects, musty, winey, fusty, and rancid. PLS-DA models were applied to classify samples of extra virgin olive oils (no defects) and
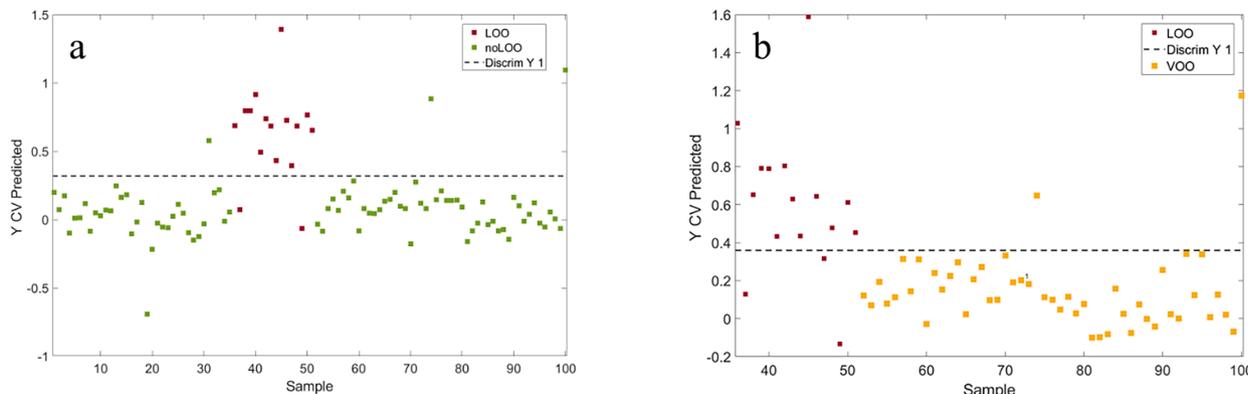

Fig. 5. Prediction performance of LOO vs. noLOO model (a) and LOO vs. VOO model (b) from FT-IR spectra. (LOO samples: red; noLOO samples: green; VOO samples: yellow).

Table 2

Correctly classified samples by the PLS–DA models for the quality grade classification of VOOs (LOO vs. noLOO; VOO vs. LOO), in calibration and cross-validation, and number of correctly classified samples in cross-validation.

PLS-DA model	Commercial category	Correctly classified samples		
		% calibration	% cross-validation (CV)	N° of correctly classified samples (CV)
LOO vs. noLOO	LOO	88	88	14/16
	noLOO	98	96	81/84
LOO vs. VOO	LOO	88	81	13/16
	VOO	96	96	47/49

lower quality olive oils (virgin and lampante, with defect). PLS-DA was able to discriminate between defective and extra virgin olive oils, with predictive abilities around 87 % for the musty defect and around 77 % for winey, fusty, and rancid defects.

In this study, FT-IR showed better results in classifying VOOs, and especially LOO samples, compared to NIR (Near-Infrared) and Raman spectroscopy. These results can be linked to FT-IR's ability to capture specific chemical information related to the molecular composition of virgin olive oil, particularly related to specific functional groups and mainly secondary oxidation products. The differences in the classification efficiency of these spectroscopic techniques can be attributed to their varying sensitivity to different types of molecular vibrations and their interaction with a complex matrix, such as olive oil.

NIR and Raman spectroscopy, while useful in certain applications, are less effective in capturing the detailed molecular information necessary for the classification of VOOs. NIR involves the absorption of light in the near-infrared region, which primarily excites the first overtone of the C—H vibration of several chemical groups such as —CH_3, —CH_2 and =CH_2 (García Martín, 2022). These bands are generally broader and less distinct than those in the mid-infrared region used by FT-IR, making it harder to discriminate between similar chemical structures. Meanwhile, Raman spectroscopy measures the scattering of light by molecular vibrations, particularly those involving non-polar function groups, such as C=C stretch (Su & Sun, 2018).

Instead, FT-IR spectroscopy works by measuring the absorption of infrared light by molecules in the sample, leading to vibrations in specific bonds within the molecules. This technique is particularly sensitive to carbonyl (C=O), and other polar function groups commonly found in fatty acids (Liu, Chen, Shi, Yang, & Han, 2020) of the triacylglycerols, associated with the degradation of VOOs, more prevalent in LOO samples. It is well known that oxidation generates compounds in olive oil that are detectable by spectroscopic techniques, and in particular FT-IR (Guzmán et al., 2011; Tena, Aparicio, & García-González, 2017), that are directly responsible for rancid defects (Frankel, 1983). This could suggest that, comparing the sensory results determined by Panel test with those obtained by PLS-DA models applied in this study, those identified as LOO samples could be characterized by the presence of rancid defect. However, even if this association was not observed with the current experimental setup, since not all the samples were classified by the Panels as "lampante" due to presence of rancidity, it is probable that their lower quality, detected by the spectroscopic techniques, is also linked with their degree of oxidation. There were no specific characteristics in common, such as presence of rancidity, among these LOO samples. It should also be argued that although spectroscopic techniques cannot easily directly detect volatiles, specifically those related with oxidation, their signal could contain some chemical information related to the secondary and to a lesser extent, primary oxidation products. Further studies could be focused to deepen investigation of this aspect in relation to the experimental characteristics and the sensitivity of the acquisition, and to evaluate if a focus on rancidity can be useful as a prediction parameter.

4. Conclusions

Recent research has focused on developing rapid and sustainable analytical methods for predicting the commercial category of virgin olive oils (VOOs) to support the official analyses, such as the Panel test sensory analysis, which can be resource intensive and time-consuming. The novel methods are based on sample pre-screening and could potentially modernise the traditional quality control. Theoretically, spectroscopic techniques (NIR, FT-IR, and Raman), could perfectly play this role, given that they do not require sample pre-treatment. Thus, in this research work, 100 VOOs samples (35 EVOO, 49 VOO, 16 LOO), belonging to the three commercial categories based on the sensory assessment, were assessed. The need, which is also a challenge, was to classify the VOOs based on the composition of the volatile fraction, given that these molecules are strictly related with the positive or the negative direct and *retro*-olfactory notes, responsible for the Panel test sensory discrimination and classification. However, volatile compounds are minor components, accounting for even less than 0,1% of the total weight of a virgin olive oil and are mainly concentrated in the headspace, making it a challenge to detect them by Infrared or Raman spectroscopy techniques.

This study attempted to do that using a reasonable number of samples (n = 100) in the framework of companies or quality control laboratories, by initially building a reliable calibration set. NIR and Raman spectroscopy demonstrated to be less effective in capturing the specific molecular information necessary for the sensory classification of VOOs, while FT-IR, being more sensitive to carbonyl (C=O) and other polar functional groups associated with the degradation of VOOs, was quantitatively more relevant in oils of lower quality (LOO). In fact, FT-IR coupled with two PLS-DA models (LOO vs. noLOO and LOO vs. VOO), showed the most reliable results, with 81–96 % accuracy especially in identifying non-edible LOO samples.

Therefore, in addition to other rapid separative screening methods specifically focused on the headspace (e.g. Flash-GC or GC-IMS), FT-IR coupled with the PLS-DA algorithm can be useful to complement sensory quality control, providing information that allows the Panel test to be applied to a limited and targeted number of samples, identifying, within a large sampling, those outside the EVOO and VOO clusters.

CRediT authorship contribution statement

Ilaria Grigoletto: Writing – original draft, Investigation. **Chiara Cevoli:** Writing – review & editing, Supervision, Resources, Investigation. **Anastasios Koidis:** Writing – review & editing, Supervision. **Tullia Gallina Toschi:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Enrico Valli:** Writing – review & editing, Supervision, Project administration, Methodology.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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