

Comparing the potential of IR-spectroscopic techniques to gas chromatography coupled to ion mobility spectrometry for classifying virgin olive oil categories

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ABSTRACT

Virgin olive oil (OO) can be classified into three different categories: extra virgin, virgin and lampante. The official method for this classification, based on physicochemical analysis and sensory tasting, is considered useful and effective, although it is a costly and time-consuming process. The aim of this study was to assess the potential of some analytical techniques for classifying and predicting different OO categories to support official methods and to provide olive oil companies with a rapid tool to assess product quality. Thus, mid and near infrared spectroscopies (MIR and NIR) have been compared by using different instruments and with head-space gas chromatography coupled to an ion mobility spectrometer (HS-GC-IMS). High classification success rates in validation models were obtained using IR spectrometers (>70% and > 80% in average for ternary and binary classifications, respectively), although HS-GC-IMS showed greater classification potential (>85% and > 90%).

1. Introduction

Virgin olive oil producers, stakeholders and consumers need a proper and complete characterisation of the OOs that are produced, marketed, and consumed in order to guarantee the quality and authenticity of the product and to avoid possible mislabelling and frauds or adulteration (Moore, Spink & Lipp, 2012). According to international and European legislation (Commission Implementing Regulation (EU) 2019/1604, 2019; IOC, 2018), virgin olive oils are classified into extra virgin (EVOO), virgin (VOO) and lampante (LOO), EVOO being the most appreciated category, while LOO cannot be sold or consumed (Fernandes, Ellis, Gámbaro & Barrera-Arellano, 2018). Nowadays, the quality and the classification of virgin olive oils are based on the analysis of some combining physicochemical parameters and on a further sensory evaluation according to positive or negative attributes carried out by a “panel test” of experts (IOC, 2018). Although the panel tests are made up of well-trained professionals and this methodology is considered as the reference, it depends on human perceptions, is destructive and time-consuming. Furthermore, only a few samples per day can be

tested. Therefore, rapid and cost-efficient analytical methodologies based on instrumental techniques are necessary in order to complement and support the panel tests work.

In recent years, several techniques have been explored in order to study their capability to determine the quality of virgin olive oils (Zaroual, Chénè, El Hadrami & Karoui, 2021). Some of the best analytical techniques to classify virgin olive oils categories have turned out to be headspace gas-chromatography coupled to mass spectrometry (HS-GC-MS) or to ion mobility spectrometry (HS-GC-IMS), which are based on the analysis of volatile organic compounds (VOCs), molecules closely related to the organoleptic characteristics that the panel test evaluates. These techniques have been successfully employed to authenticate the quality of virgin olive oils classified as EVOO, VOO or LOO (Arroyo-Manzanares, Gabriel, Carpio, & Arce, 2019; Contreras, Arroyo-Manzanares, Arce & Arce, 2019; Contreras, Jurado-Campos, & Arce, 2019; García-Nicolás, Arroyo-Manzanares, Arce, Hernández-Córdoba, & Viñas, 2020; Garrido-Delgado, Arce, & Valcárcel, 2015; Gerhardt, Schwolow, Rohn, Pérez-Cacho, Galán-Solvedilla, Arce & Weller, 2019; Valli et al., 2020). Although HS-GC-IMS is still less

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common for analysing agri-food complex matrices in laboratories in comparison with GC-flame ionisation detector or GC-MS, both techniques seem to provide comparable virgin olive oil classification percentages (Contreras, Arroyo-Manzanares, et al., 2019; Jurado-Campos, Rodríguez-Gómez, Arroyo-Manzanares & Arce, 2021). In this article, HS-GC-IMS has been selected since it is a promising virgin olive oil classification technique, which combines high selectivity and identification power together with high robustness and cost-efficiency. However, this technique generates highly complex multidimensional data which also need chemometric methods to interpret them (Schwelow, Gerhardt, Rohn & Weller, 2019). Thus, other works have been focused on the exploration of different data processing strategies to improve the classification results (Contreras, Arroyo-Manzanares, et al., 2019; Gerhardt et al., 2019). Moreover, the high volume of samples to classify into quality categories requires the development of other rapid methods that provide instant results even at screening level. For these reasons, the study of other OO classification methods using some alternative analytical techniques, such as infrared spectroscopy (IRs), is addressed in the current work. IRs, coupled to chemometric techniques, conforms a fast, reliable, and cost-efficient method, also having some disadvantages and drawbacks. Thus, it should be noted that IRs techniques generally measure global fingerprints, with information about the functional groups but no specific information about the composition of VOCs. Therefore, it will be necessary to evaluate whether that analytical limitation translates into worse classification results compared to chromatographic techniques.

The most used wavelengths in IR spectroscopic analysis are near-infrared (NIR), which are considered from 14000 cm^{-1} up to 4000 cm^{-1} (700–2500 nm); and mid-infrared (MIR) analysis, whose values range from 4000 cm^{-1} to 400 cm^{-1} . Several methods based on NIR technology have been carried out to authenticate OOs according to their variety or geographical origin (Laroussi-Mezghani et al., 2015; Peršurić, Saftić, Masek, & Kraljević Pavelić, 2018) or their purity due to adulterations (Azizian, Mossoba, Fardin-Kia, Delmonte, Karunathilaka & Kramer, 2015; Mossoba, Azizian, Fardin-Kia, Karunathilaka & Kramer, 2017). Likewise, NIR spectroscopy has been used for the non-destructive assessment of physicochemical quality parameters in OO samples (Cayuela, 2017; Garrido-Varo, Sánchez, De la Haba, Torres, & Pérez-Marín, 2017). Some other studies have focused on the assessment of sensorial profile of OOs related to volatile organic compounds and/or phenolic compounds, which directly affect the quality grade, using NIR and/or MIR (Martínez Gila, Cano Marchal, Gómez Ortega, & Gámez García, 2018). A good approximation was carried out by Sinelli, Cerretani, Egidio, Bendini & Casiraghi (2010), by establishing a classification of OOs according to olfactory attributes (European Commission Regulation 640/2008, 2008) using MIR and NIR, treating the spectral data both by linear discriminant analysis (LDA) and soft independent modelling of class analogy (SIMCA). The results showed a prediction range between 71.6% and 100% as average value. Abu-Khalaf & Hmidat (Abu-Khalaf & Hmidat, 2020) were able to distinguish between four different quality groups -extra virgin, virgin, ordinary virgin and lampante- of local OOs using visible-NIR spectroscopy and also found a high correlation with acidity and peroxide indexes using partial least squares (PLS). Hirri, Bassbasi, Platikanov, Tauler & Oussama (2016) analysed a total of 70 OOs from four quality categories using Fourier Transform (FT)-MIR, also considering their physicochemical data and organoleptic information related to polyphenols content. A first partial least squares discriminant analysis supervised chemometric model (PLS-DA) over physicochemical data was not able to distinguish among EVOO, VOO, and ordinary VOO. However, the PLS-DA model based on FT-MIR data provided a 93% success rate in calibration while the external validation was 100% for binary classifications for the four categories.

All the aforementioned indicates that, on the one hand, chemometric data treatment are needed to obtain satisfactory results by IRs techniques; and, on the other hand, that there is still a lack of knowledge

about the potential of these techniques for classifying virgin olive oil categories, since the studies that address this subject are still scarce, considering very few samples from very specific or local origins, often from the same category, and whose quality had not been corroborated by at least two independent tasting panels. Thus, the analytical methods can be calibrated and validated with samples tested and labelled by at least two panels whose results match to avoid transferring the panel error to the instrumental method (Jurado-Campos, Rodríguez-Gómez, Arroyo-Manzanares & Arce, 2021). In addition, the effect of using different instrumental devices within the same analytical technique has not been explored.

In this context, the first aim of this study was to assess and compare, for the first time, the potential of NIR and MIR spectroscopies for performing a rapid screening that enables the classification of different OO categories using a ternary (EVOO, VOO and LOO) and a binary (EVOO / Non-EVOO and LOO / Non-LOO) approach, with the final purpose of supporting the current official methods and, ultimately, giving a rapid tool to olive oil companies for evaluating the quality of their own products. Another novel aspect of the work was that different IR spectrometers were also considered and compared, since each instrument can be equipped with different analytical devices and, subsequently, offer specific spectral information which might lead to different classification results. In addition, IR classification results were compared with those obtained by HS-GC-IMS, as a separation technique, to discuss and evaluate their advantages and disadvantages; and to offer a quick tool for decision-making to OO companies, entities and researchers.

2. Materials and methods

2.1. Selected samples

A set of 135 Spanish virgin olive oils coming from the harvest 2019–2020 were collected between July 2020 and April 2021. The samples were stored in a freezer at $-4\text{ }^{\circ}\text{C}$ and evaluated by two tasting panels: Panel 1 (Córdoba, Spain) and Panel 2 (Seville, Spain), which is accredited in standard 17,025 and works in accordance with EC standard no. 796/2002 and COI T20/Doc. No. 5 Rev.1 of 1996. The result of the tasting showed 23 samples (17% from the total) that did not match between the two panels and 112 samples classified into the same category by both (83 % from the total): 50 EVOO, 41 VOO, and 21 LOO. The 23 samples that did not match between the two panels could correspond to olive oil samples located at the interface of two categories, EVOO/VOO or VOO/LOO, which are difficult to label due to very similar chemical characteristics. Although all the 135 samples were analysed, only the 112 matching samples were used for chemometric model calibration and validation to avoid transferring the panel error to the instrumental method (Table I, Supplementary Material). Most of the samples were obtained by mixing several olive varieties, only including some monovarietal samples. The total amount of samples seemed to be enough for the intended purposes considering several previous works categorising and classifying OOs with IRs (Abu-Khalaf & Hmidat, 2020; Hirri et al., 2016; Sinelli et al., 2010), and the proportion of the three categories was well-balanced.

2.2. Mid-Infrared spectral analysis

To explore different MIR spectroscopic instruments and to be able to establish which factors can offer better results to characterise OO samples, MIR spectra were obtained by two different spectrometers. First, samples were analysed by using a Tensor 27 Bruker FT-MIR Hyperion 2000 spectrophotometer (Bruker Optik GmbH, Germany), equipped with an attenuated total reflectance accessory (ATR) of single reflection, incident angle 45° , DTGS detector, Globar (MIR) source and KBr germanium separator, with a resolution of 4 cm^{-1} at 100 scans, called MIR1 henceforth. Analyses of the 112 samples were carried out by pipetting $80\text{ }\mu\text{L}$ of the sample into the ATR, which was cleaned with

soapy water between one sample and the next. Secondly, the MIR analyses were also carried out using a Vertex70 Bruker spectrophotometer (Bruker Optik GmbH, Germany), with a multiple reflection - ZnSe separator 6-bounce ATR, and a resolution of 4 cm^{-1} at 50 scans, called MIR2 henceforth. In this case, analyses were carried out by pipetting around 0.7 mL of sample into the ATR. The ATR cleaning between duplicates was done just with absorbent paper, while hexane and ethanol were applied between consecutive samples, using a soft sponge for a final drying.

For both instruments, samples were analysed at room temperature and in duplicate, spectra were obtained in the absorbance mode from 4000 to 600 cm^{-1} and the data were handled with OPUS 6.5 software (Bruker Optik GmbH, Germany). The background spectrum (blank) was collected before each sample measurement.

2.3. Near-Infrared spectral analysis

All samples were analysed in duplicate by NIR spectroscopy (NIRs) using three different spectrometers. First, NIR spectra were obtained using a Bruker NIR spectrometer (Bruker Optik GmbH, Germany), equipped with a multiparameter analyser MPA II (Bruker Optik GmbH, Germany), and with a resolution of 4 cm^{-1} at 32 scans – called NIR1 henceforth. Data were handled with OPUS 6.5 software (Bruker Optik GmbH, Germany). Analyses of the samples were carried out by pipetting about 0.7 mL in a thin transparent glass vial that was later inserted in the convenient MPA port, where each sample was preheated for 15 s at $50\text{ }^{\circ}\text{C}$, to homogenise its physical state (e.g. temperature and viscosity). The background or reference spectrum (blank) was taken before the analysis of each sample.

As done for MIR, another NIR spectrometer was tested in order to compare their capability for characterising OO samples. The second analytical instrument used was a NIR FOSS DS2500L (called NIR2 henceforth), equipped with a 0.1 mm optical pitch gold slurry cup, in double transmission. The resolution was 0.5 nm, and each analysis was made at 5 scans and the software controlling the analyses was “Local Configurator (DS2500)”. Approximately 0.7 mL of the sample was used for each analysis, placing the olive oil directly on the slurry cup and taking care not to leave any air bubbles within the oil slide. Each sample was analysed in duplicate, obtaining a total of 224 spectra. Each blank was performed automatically and serially with each measurement by the instrument.

Finally, another NIR FOSS DS2500L spectrometer (called NIR3 henceforth) was used to perform the measurements but, in this case, the analytical instrument was equipped with a different sample loading accessory, specific for oil samples. This loading device allowed sample preheating ($50\text{ }^{\circ}\text{C}$) and acquiring good spectral information in the range of 400–635 nm, which was masked by the absorbance belonging to the yellow color of the gold slurry cup when using the previous instrument. 1 mL disposable vial with a diameter of 8 mm was used for each sample analysis, which was also made in duplicate using a resolution of 0.5 nm at 32 scans. The control and analysis software was FOSS Manager and ISIScan Nova, respectively. At 420 nm, the signal intensity was automatically corrected with an inner filter of the instrument. No blank between samples was needed.

The scanning was made in the absorbance mode from 800 to 2500 nm (NIR1) or from 400 to 2500 nm (NIR2 and NIR3).

2.4. Gas chromatography coupled to ion mobility spectrometry analysis

The OO samples were analysed by HS-GC-IMS using an Agilent 7497A headspace autosampler connected by a transfer line to an Agilent 8860 GC system (Agilent, Santa Clara, CA, USA) and coupled to an ion mobility spectrometer (G.A.S. Gesellschaft für analytische Sensorsysteme mbH, Dortmund, Germany) equipped with a tritium (^3H) ionisation source and a 10 cm drift tube. Sample measurements were made following a previous optimised and validated method (Contreras,

Arroyo-Manzanares, et al., 2019). Hence, for each sample, 1 g of OO was weighed and added into a 20 mL headspace glass vial, sealed with a capsule fitted with a PTFE/silicone septum (Supelco) before analysing. The incubation took place for 5 min at $80\text{ }^{\circ}\text{C}$.

Once the VOCs were extracted, 1 mL from the headspace of the vial was collected through the 1 mL sample loop (at $100\text{ }^{\circ}\text{C}$) and injected in split mode 1:4 into the GC injection port (at $200\text{ }^{\circ}\text{C}$) by a transfer line (at $110\text{ }^{\circ}\text{C}$). Then the samples were transferred into a HP-5 (5%-phenyl)-methylpolysiloxane non-polar column, with 60 m, 0.25 mm inner diameter and 1 μm thick coating (Agilent, Santa Clara, CA, USA). Helium was used as carrier gas at a constant flow rate of 3.2 mL/min. The GC oven was programmed as follows: held at $40\text{ }^{\circ}\text{C}$ for 3 min, then ramped at $15\text{ }^{\circ}\text{C}/\text{min}$ to $120\text{ }^{\circ}\text{C}$ and held at $120\text{ }^{\circ}\text{C}$ for 21.47 min. After separation, analytes were placed in the detector. Drift tube and transfer line were set at 55 and $150\text{ }^{\circ}\text{C}$, respectively. The drift gas, nitrogen, was set at 150 mL/min. The detector worked at positive polarity. IMS parameters were: 150 μs of injection pulse width, signal averaging each 24 spectra, repetition rate of 20 ms; and drift, blocking and injection voltages of 242 V, 20 V and 2500 V, respectively. HS-GC-IMS data were extracted with VOCal 1.0.0. software (G.A.S. Gesellschaft für analytische Sensorsysteme mbH, Dortmund, Germany), acquiring the corresponding spectral fingerprints for building the data matrices in last term.

2.5. Chemometrics

Spectroscopic data were preprocessed before modelling by looking at the best procedure in terms of classification results. For MIR data, after removing the uninformative and with high noise regions (explained in the following section), Standard Normal Variate (SNV) was the method selected and applied to the spectra for scattering removal (Barnes et al., 1989). SNV attempts to make all spectra comparable in terms of intensities (or absorbance level). It can be useful to correct spectra for changes in optical path length and light scattering. For NIR, after removing some uninformative or noisy regions (explained in the following section), the most adequate preprocess was found to be SNV together with Baseline removal (Barnes, Dhanoa & Lister, 1989; Cen & He, 2007; Massart, Vandeginste, Buydens, De Jong, Lewi & Smeyers-Verbeke, 1997). Baseline removal aims at resetting all spectra on a common baseline, although in some cases it can distort the real proportions between absorbance peaks and, therefore, caution should be used when interpreting the results. MIR and NIR spectra were then mean centred prior to modelling.

In the case of HS-GC-IMS, the analyses worked on the topographic map or IMS spectrum, thus considering the whole spectral fingerprint of each sample, although data were previously simplified by cropping the maps by removing the non-informative regions (e.g., those before the RIP region). Data treatment included a pre-processed consisting in peak alignment, RIP normalisation, baseline and noise removal, data reduction, unfolding of the 3D matrix, and mean-centring. All the steps of the modelling followed were described in previous papers (Contreras, Jurado-Campos, et al., 2019).

After removing the different noisy and uninformative regions from IR spectra (explained in the following section), and preprocessing the data, principal component analysis (PCA) was used to both study the best preprocessing methods applied to IRs data and to explore the datasets. Moreover, for classification modelling, partial least squares discriminant analysis (PLS-DA) was applied to each dataset formed by the preprocessed spectra without the removed regions (explained in the following section). Selection of optimal number of latent variables (LVs) was done from the lowest prediction error in cross-validation. The classification success, expressed as True Positive Rate (TPR%), was achieved for a ternary (EVOO, VOO and LOO) and binary approaches (EVOO / Non-EVOO and LOO / Non-LOO).

For calibrating and testing the PLS-DA models, the set of 112 samples (in duplicate) was randomly divided into two subsets by using the Onion algorithm (Gallagher & O'sullivan, 2020). The first subset (train set) was

composed of 90 samples (in duplicate) to calibrate the model, which was validated by internal full venetian blinds cross-validation (CV) for finding the optimum latent variables; whereas the external model validation was performed using a second subset of 22 samples in duplicate, not used for the calibration model, including 10 EVOO, 7 VOO and 5 LOO. The same samples in the calibration and validation sets were considered, both for the different techniques and for the design of ternary and binary classification models.

Data preprocessing and modelling for all the data sets were carried out by Matlab R2016a software (Mathworks Inc., Natick, MA, USA) with PLS Toolbox (Eigenvector Research Inc., Wenatchee, WA, USA) and some handmade scripts in the case of HS-GC-IMS.

3. Results and discussion

3.1. Olive oils predicted quality using two different MIR spectrometers

Two different MIR instruments were tested to assess their potential for OO classification. The main difference between the two spectrometers lay in the material that their ATR crystal was made of: Ge (MIR1) vs. ZnSe (MIR2). Furthermore, the former was a single bounce ATR while the second was a 6-bounce ATR. The 112 OO samples were analysed in duplicate, and a previous visual inspection was made.

At first, the entire spectral range from 4000 to 600 cm^{-1} was considered, but some bands did not seem to provide useful spectral

information, and they could lead to errors occurring in the methodology to classify the samples. Hence, in MIR1 spectra, bands around 2400 cm^{-1} , belonging to the CO_2 absorption regions (Dupuy, Galtier, Ollivier, Vanloot & Artaud, 2010; Terouzi et al., 2011), were finally discarded before modelling, because this may have led to errors due to a high variability in that spectral information, independently -e.g., non-intrinsic- of the samples according to their quality category. In addition, bands between 4000 and 3050 cm^{-1} and 1700–1500 cm^{-1} were found to show a low signal/noise ratio (S/N) in MIR1 spectra and subsequently they were also deleted. Considering MIR2 spectra, only the latest spectral bands (665–600 cm^{-1}) showed a very low S/N and were consequently discarded. Fig. 1a and b shows the raw MIR spectra for each spectrometer, with the spectral regions that were not considered for the classification models marked in red. Therefore, the MIR spectra considered for the classification approach was the whole spectra without the marked in red regions. By looking at the two different spectra, MIR1 (Fig. 1a) and MIR2 (Fig. 1b), it could be seen that the spectra obtained by MIR2, equipped with a multiple reflection - ZnSe separator 6-bounce ATR, led to obtain much more intense spectral signals, which may be the reason for the high signal/noise ratio presented and the repeatability of this device in comparison to the spectra obtained by MIR1, which used an ATR of single reflection and KBr germanium separator and showed high noise and scattering. Thus, these results were in accordance with the fact that MIR2 used a multi-bounce ATR with multiple reflection and therefore a higher effective pathlength.

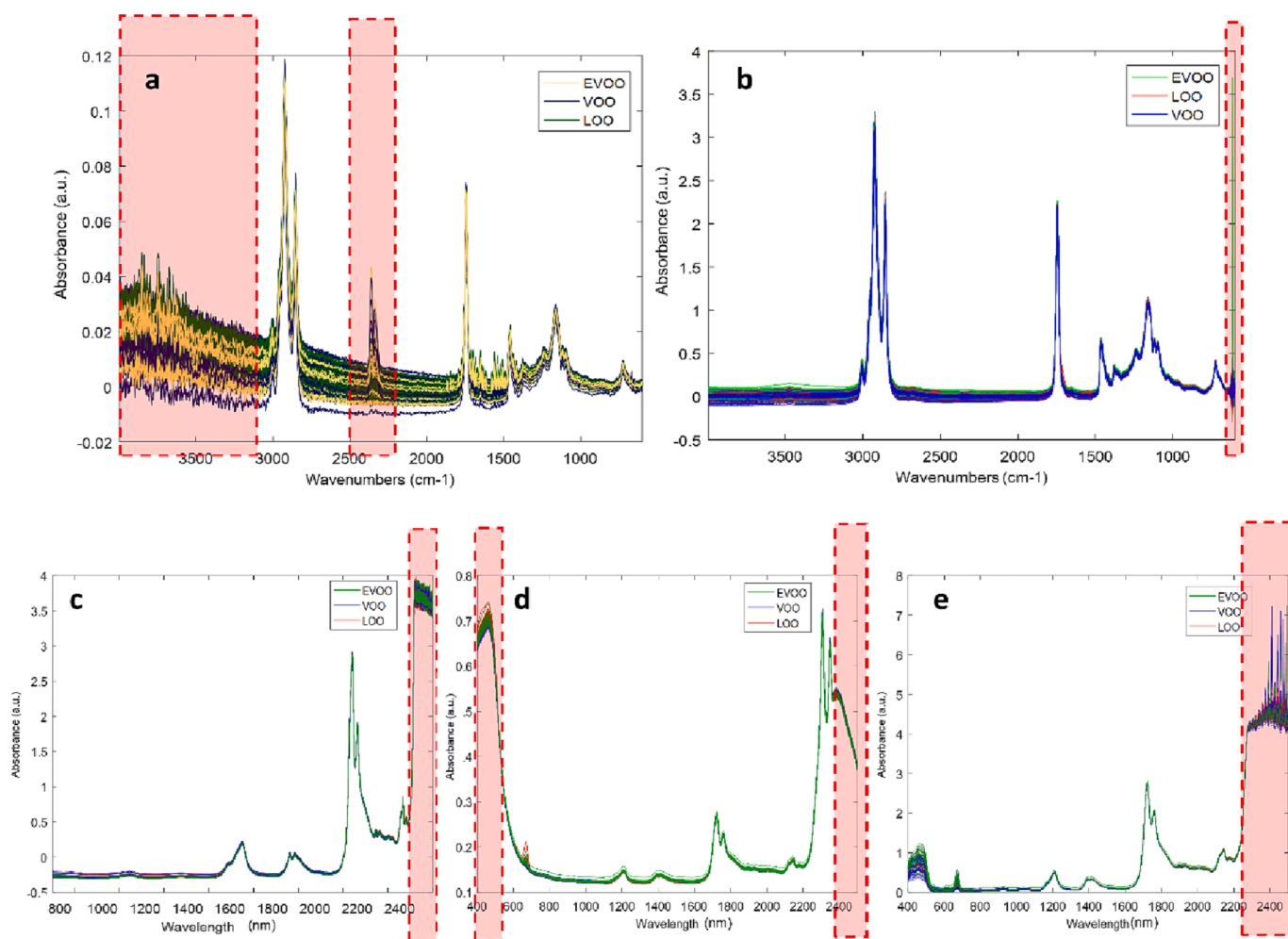


Fig. 1. Raw MIR spectra for each spectrometer, MIR1 (a) and MIR2 (b), and raw NIR spectra obtained from each device, NIR1 (c), NIR2 (d), and NIR3(e). Spectral regions marked with red squares indicates the zones removed from the classification analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

When the MIR spectra were correctly preprocessed and regions uninformative and noisily were removed, a PLS-DA ternary model was built with a proper number of latent variables (LVs) (i.e., 12 and 13 latent variables (LV) for MIR1 and MIR2 respectively) considering the selected spectra from both MIR spectrometers as *X* variables, while the *Y* variables had the three OO quality classes. Table 1 shows the confusion matrices for the internal and external validation (CV and prediction) obtained by PLS-DA carried out with the spectral data from the two MIR spectrometers. Considering the subset with 180 spectra included in the cross-validation, coming from the 90 samples in duplicate, the results from both instruments showed high success percentages for classifying EVOO, VOO and LOO, with TPR% between 75.00 % and 86.25 %. However, for the external validation (prediction set) only EVOO samples obtained an acceptable classification success using MIR1: 14/20 samples (70.00 %). Most of VOO and LOO samples were misclassified in this ternary classification model. Likewise, MIR spectra from MIR2 enabled the correct classification of 18/20 EVOO samples (90.00 %), but only half of the VOO and LOO samples were predicted to be the correct category (57.14 % and 50.00 %, respectively). Among the few works focused on predicting OO categories applying MIRs, Hirri et al. (2016) achieved 100% of classification success considering four OO quality grades. However, the set of samples studied may not be representative of the real market, since they used olive oils from very local varieties (collected in central Morocco). Furthermore, only 70 samples in total, representing those four commercial grades, were included in the study and sample analyses did not seem to have been performed in duplicate; thus, the total amount of MIR spectra generated per each quality category considered could be somewhat low, it being possible that the prediction models obtained with those data were underfitted.

Additionally, binary classification models were also built to evaluate whether MIR spectroscopy could reach higher classification success just trying to discriminate EVOO from VOO and LOO (modeled as a single group: Non-EVOO) and then LOO from EVOO and VOO (modeled as a single group: Non-LOO). Despite the limitations found for classifying the three OO classes, MIR spectroscopy has shown to be able to distinguish quickly and objectively a given OO from the best or the worst quality category (Table 2). This could also be a great achievement, as a first screening, in order to guarantee a proper OO value/price both for producers and consumers (Tsimidou, 2006). Considering the same calibration and validation sample sets as for ternary models, the binary classification model obtained with data from MIR1 showed successful validation results only when differentiating EVOO from Non-EVOO, with an accuracy of 70.00 % in classification of EVOO samples; and Non-LOO from LOO, with 85.29 % of Non-LOO samples correctly classified. However, very low classification success was found for Non-EVOO (50.00 %) and LOO (30.00 %) samples. Spectral data from MIR2 provided higher prediction success in the binary approach than MIR1, reaching percentages of 90.00 %, 91.67 %, 70.00 % and 88.24 % for EVOO, Non-EVOO, LOO and Non-LOO, respectively.

As mentioned above, the main difference between the two analytical

instruments was the type of ATR that they were equipped with and the single and multiple reflection that it was used. As can be concluded from the above-described outcomes, the ZnSe-crystal-ATR of MIR2 spectrometer offered better OO classification results compared to Ge-crystal-ATR of MIR1, even though some bands of the IR spectrum that introduced errors in the spectral information had been removed to optimise the results given by this second spectrometer. On the one hand, as seen above by looking at the spectra (Fig. 1 a and b), Ge-crystal-ATR with single reflection provided a low spectral signal/noise (S/N) ratio and high scattering, whereas ZnSe-crystal-ATR with multiple reflection gave the opposite. This led to great differences among sample spectra and, in the case of Ge-crystal-ATR used in MIR1 device, a decrease in the spectra repeatability and, consequently, in the repeatability of the method. In fact, although an acceptable intra-day repeatability was observed when a control sample was analysed in triplicate by MIR1 a notable difference in the spectra of the replicates by day of analysis when the same control sample was analysed on different days was observed (data not shown). This suggested a great influence of that variable -day of analysis- over the technique. Finally, the control sample was analysed nine times in the same day and a mean relative standard deviation (RSD%) from the spectra absorbance intensity was calculated, with a value of 161 %. This high RSD% confirmed that the results given by the Ge-crystal-ATR MIR1 device were not repeatable and, subsequently, not reliable enough. ZnSe-crystal-ATR MIR2 device, aside from better classification results for the three OO categories, showed an RSD of 3.0 % in the spectra wavenumbers of the analysis of the control sample. All these results lead to the conclusion that ATR-MIR spectroscopy coupled with this PLS-DA chemometric method can be moderately effective to discriminate among OO categories, although the sampling device and instrument used have influence on the results.

3.2. Olive oils predicted quality using three different NIR spectrometers

The same procedure that was performed with MIRs was carried out with NIRs using three different spectrometers, named as NIR1, NIR2 and NIR3. After an initial visual checking of the spectra obtained from each device (Fig. 1 c, d and e), the spectral regions with high noise, which did not provide real spectral sample information, were removed (marked in red in Fig. 1): from 2400 to 2500 nm for the spectral data obtained by NIR1 (Fig. 1c), since it corresponded to a strong water absorption band (Tsimidou, 2006); from 400 to 635 nm due to its absorbance belonging to the yellow color from the slurry cup, and from 2369 to 2500 nm (high final noise) for NIR2 data (Fig. 1d); and, finally, from 2200 to 2500 nm (high final noise) for NIR3 data (Fig. 1e).

The same as for MIR, each PLS-DA ternary model from NIR data was built with a proper number of LVs considering the spectra without the removed regions from the three NIR spectrophotometers as *X* variables, while the *Y* variables had the three OO categories. Table 3 shows the confusion matrices containing the % of classification success both for ternary cross-validation and prediction (i.e., internal and external

Table 1

Confusion matrices using the PLS-DA ternary models for calibration (CV) and external validation (prediction) with the two different ATR-MIR spectrometers.

	Actual OO commercial category	N	Ge-ATR MIR1					ZnSe-ATR MIR2				
			Predicted OO commercial category			Classification results		Predicted OO commercial category			Classification results	
			EVOO	VOO	LOO	TPR (%)	Mean TPR (%)	EVOO	VOO	LOO	TPR (%)	Mean TPR (%)
CV	EVOO	80	69	8	3	86.25	83.77	67	13	0	83.75	80.56
	VOO	68	10	57	1	83.82		12	51	5	75.00	
	LOO	32	6	0	26	81.25		2	3	27	84.38	
Prediction	EVOO	20	14	4	2	70.00	42.86	18	2	0	90.00	70.45
	VOO	14	8	4	2	28.57		3	8	3	57.14	
	LOO	10	1	6	3	30.00		0	5	5	50.00	

Notes: OO = olive oils; CV = cross-validation; EVOO = extra virgin olive oil; VOO: virgin olive oil; LOO: lampante olive oil; N: number of samples; TPR: true positive rate.

Table 2

Confusion matrices using the PLS-DA binary models for calibration (CV) and external validation (prediction) with the two different ATR-MIR spectrometers.

Actual OO commercial category		N	Ge-ATR MIR1				ZnSe-ATR MIR2			
			Predicted OO commercial category		Classification results		Predicted OO commercial category		Classification results	
			EVOO	Non-EVOO	TPR (%)	Mean TPR (%)	EVOO	Non-EVOO	TPR (%)	Mean TPR (%)
CV	EVOO	80	72	8	90.00	90.00	66	14	82.50	83.33
	Non-EVOO	100	10	90	90.00		16	84	84.00	
Prediction	EVOO	20	14	6	70.00	59.09	18	2	90.00	90.91
	Non-EVOO	24	12	12	50.00		2	22	91.67	

Actual OO commercial category		N	Predicted OO commercial category				Classification results			
			Predicted OO commercial category		Classification results		Predicted OO commercial category		Classification results	
			LOO	Non-LOO	TPR (%)	Mean TPR (%)	LOO	Non-LOO	TPR (%)	Mean TPR (%)
CV	LOO	32	27	5	84.38	95.00	28	4	87.50	93.33
	Non-LOO	148	4	144	97.30		8	140	94.60	
Prediction	LOO	10	3	7	30.00	72.72	7	3	70.00	84.09
	Non-LOO	34	5	29	85.29		4	30	88.24	

Notes: OO = olive oils; CV = cross-validation; EVOO = extra virgin olive oil; VOO: virgin olive oil; LOO: lampante olive oil; N: number of samples; TPR: true positive rate.

Table 3

Confusion matrix using the PLS-DA ternary models for cross-validation (CV) and external validation (prediction) with NIR.

Instrument	Model	Actual OO commercial category	N	Predicted OO commercial category			Classification results	
				EVOO	VOO	LOO	TPR (%)	Mean TPR (%)
NIR1	CV	EVOO	78	66	11	1	84.62	78.65
		VOO	68	19	45	4	66.18	
		LOO	32	1	2	29	90.63	
	Prediction	EVOO	20	16	4	0	80.00	69.05
		VOO	14	4	9	1	64.29	
		LOO	8	1	3	4	50.00	
NIR2	CV	EVOO	80	66	14	0	82.50	78.89
		VOO	68	14	50	4	73.53	
		LOO	32	0	6	26	81.25	
	Prediction	EVOO	20	18	2	0	90.00	72.73
		VOO	14	2	9	3	64.29	
		LOO	10	3	2	5	50.00	
NIR3	CV	EVOO	80	68	11	1	85.00	76.67
		VOO	68	11	47	10	69.12	
		LOO	32	3	6	23	71.88	
	Prediction	EVOO	20	16	4	0	80.00	72.73
		VOO	14	2	8	4	57.14	
		LOO	10	0	2	8	80.00	

Notes: OO = olive oils; CV = cross-validation; EVOO = extra virgin olive oil; VOO: virgin olive oil; LOO: lampante olive oil; N: number of samples; TPR: true positive rate.

validation, respectively). EVOO, VOO and LOO samples were correctly classified in CV for each NIR device with mean classification percentages between 76 and 79 %. For the prediction results, EVOO samples were classified with a high success (i.e., TPR%) using the three devices: 80.00 % (12 LV), 90.00 % (12 LV) and 80.00 % (18 LV) for NIR1, NIR2 and NIR3 spectral data, respectively. However, external validation results for defective samples (VOO and LOO) did not surpass 64.29 % except for classifying LOO using NIR3 (TPR% = 80.00%). NIRs did not therefore seem to be a reliable and efficient technique in general terms to distinguish between defective OO in a ternary model. Nevertheless, it must be

considered that the number of LOO samples considered for the prediction model was relatively low in all this study, which could lead to a great decrease in the classification success percentages for this category with very few LOO samples being misclassified.

Therefore, since the classification results were not completely satisfactory in ternary model, binary classification models were also built from NIR data. Classification results are shown in Table 4. The binary PLS-DA model obtained with NIR1 (8 LVs), was promising for distinguishing defective (non-EVOO) from non-defective samples (EVOO), with an accuracy of 80.00 %TPR in the external validation (prediction)

Table 4

Confusion matrix using the PLS-DA binary models for cross-validation (CV) and external validation (prediction) with the three NIR spectrometers.

Actual OO commercial category		NIR1				NIR2				NIR3			
		Predicted OO commercial category		Classification results		Predicted OO commercial category		Classification results		Predicted OO commercial category		Classification results	
		EVOO	Non-EVOO	TPR (%)	Mean TPR (%)	EVOO	Non-EVOO	TPR (%)	Mean TPR (%)	EVOO	Non-EVOO	TPR (%)	Mean TPR (%)
CV	EVOO	68	10	87.18	87.64	70	10	87.50	85.56	69	11	86.25	84.44
	Non-EVOO	12	88	88.00		16	84	84.00	85.56	17	83	83.00	
Prediction	EVOO	16	4	80.00	80.95	18	2	90.00	77.27	15	5	75.00	84.09
	Non-EVOO	4	18	81.82		8	16	66.67		2	22	91.67	
		LOO	Non-LOO			LOO	Non-LOO			LOO	Non-LOO		
CV	LOO	23	9	71.88	91.01	28	4	87.50	93.33	22	10	68.75	86.67
	Non-LOO	7	139	95.21		8	140	94.60		14	134	90.54	
Prediction	LOO	4	4	50.00	85.71	8	2	80.00	84.09	8	2	80.00	84.09
	Non-LOO	2	32	94.12		5	29	85.29		5	29	85.29	

Notes: OO = olive oils; CV = cross-validation; EVOO = extra virgin olive oil; VOO: virgin olive oil; LOO: lampante olive oil; TPR: true positive rate.

of EVOO samples and 81.82 %TPR in Non-EVOO. When grouping LOO and Non-LOO samples, and considering 4 LV, the model successfully predicted 32/34 Non-LOO samples (94.12 %), although only 4/8 (50.00 %) LOO samples were classified in the correct category. As discussed above, one should consider the unbalanced samples that formed this binary approach that could affect the classification results obtained. The validation results (prediction) for the corresponding binary models with NIR2 were 90.00 % and 66.67 % for EVOO / Non-EVOO (8 LVs), and 80.00 % and 85.29 % for LOO / Non-LOO (9 LVs), while with NIR3 were 75.00 % and 91.67 % for EVOO / Non-EVOO (7 LV), and 80.00 % and 85.29 % for LOO / Non-LOO (6 LV) in external validation (prediction). Although the total classification results were similar for the three NIR spectrometers in binary models, the third device (NIR3) provided a total mean TPR slightly higher (84.09 %), at the same time as being able to classify every OO category considered with a success rate above 75.00 %.

All these results could be explained by the different spectral information extracted from the NIR instruments (Fig. 1 c, d and e). Thus, NIR1 only seemed to provide useful spectral information in the absorption bands between approximately 1600 and 2450 nm (Fig. 1c). Likewise, NIR2 and NIR3 included the information of that range and, in addition, extended it by offering information belonging to the visible spectrum (400–700 nm) (Fig. 1 d and e). This indicates that the latter two instruments were able to provide broader spectral information, and this should lead to better classification results compared to NIR1, as seen above for the ternary model.

Looking at the comparison between the two NIR FOSS spectrometers, an absorption region with high signal and inter-category variability appeared in NIR3 from 400 to 550 nm (Fig. 1e), but not in NIR2 spectra since the absorption in the yellow by the gold of the slurry cup generated a band that was overlaid above the useful information of the OO samples (Fig. 1d). A classification test considering only those visible spectral bands from NIR3 data showed a high potential for distinguishing between EVOO and VOO samples (data not shown). Related to this, Abukhalafa & Hmidat (2020) obtained high classification percentages when analysing 48 local OOs, from four different categories, by Visible/NIRs considering the region from 400 to 1100 nm; which confirms the capability and usefulness of that spectral region for classifying OO samples and, subsequently, the influence of the spectral range selection on these classification results. Likewise, NIR2 provided useful spectral information in the region from 2200 to 2400 nm, whereas a high noise region was observed at those bands using NIR3. Furthermore, NIR3 showed higher signal intensity than NIR2 (Fig. 1c and d). Hence, each instrument had some useful spectral information in the above-mentioned regions of the IR absorbance spectrum, which enabled

obtaining very similar classification results, as noted above, although it should be pointed out that NIR3 provided slightly higher TPR% in the binary approach.

The repeatability of the NIRs was also tested by the visualisation of the spectra and the calculation of the RSD%. Thus, the mean RSD% calculated from all the wavenumbers from the sample spectra had a mean value of 2.43 % for the three NIR spectrometers, which indicated a high spectral homogeneity and a high repeatability of the methods.

3.3. Olive oils predicted quality using HS-GC-IMS

The 112 OO samples were finally analysed using a robust separation technique, such as HS-GC-IMS, in order to compare its classification potential with the best results obtained using MIR and NIR spectrometers (i.e., with MIR2 and NIR3). The HS-GC-IMS data was treated as a fingerprint, taking the total data contained in the samples, as explained before in Section 2.5. The comparison of the classification success rates among HS-GC-IMS, NIRs and MIRs is shown in Table 5. In contrast with IRs results, a substantial improvement in OO classification percentages for ternary model can be observed by PLS-DA with HS-GC-IMS data, since this technique not only allowed correctly classifying 90.00% of the EVOO samples, but at the same time was capable of providing 85.71% and 80.00% of classification success for VOO and LOO, respectively. The explanation for this classification upgrading may lie in the fact that, as the OO categories are established by sensory tasting and chromatographic techniques detect the VOCs that directly provide the sensory attributes to the OO, HS-GC-IMS stands out as more specific than IRs. These percentages of success in OO ternary classification, averaging a TPR % of 86.36 %, were close to those obtained in similar studies carried out with chromatographic techniques, both using GC-MS (García-Nicolás et al., 2020; Quintanilla-Casas et al., 2020; Sales, Cervera, Gil, Portolés, Pitarch & Beltrán, 2017; Sales, Portolés, Johnsen, Danielsen & Beltrán, 2019) and GC-IMS (Contreras, Arroyo-Manzanares, et al., 2019; Contreras, Jurado-Campos, et al., 2019; Garrido-Delgado et al., 2015; Gerhardt et al., 2019; Valli et al., 2020). For binary models, the chromatographic technique and method here applied also showed a greater classification potential compared to spectroscopic ones, with only one misclassified sample from 22 for EVOO / Non-EVOO model (6 LVs) and 3/22 for LOO / Non-LOO model (2 LVs) in the prediction. The TPR% stood at 90.91 %, once again in the same order than percentages success obtained in similar OO classification studies using chromatographic techniques (Cecchi et al., 2019; Dierkes, Bongartz, Guth & Hayden, 2012; Garrido-Delgado, Mercader-Trejo, Arce & Valcárcel, 2011; Purcaro, Cordero, Liberto, Bicchi & Conte, 2014). However, with only five LOO samples considered for the classification study, as was previously

Table 5

Comparison of NIRs and MIRs best OO classification results (true positive rate, TPR) with HS-GC-IMS; both in cross-validation (CV) and prediction (Pred) for ternary and binary approaches.

Model	Category	MIR2		NIR3		HS-GC-IMS	
		TPR CV (%)	TPR Pred (%)	TPR CV (%)	TPR Pred (%)	TPR CV (%)	TPR Pred (%)
Ternary	EVOO	83.75	90.00	85.00	80.00	82.50	90.00
	VOO	75.00	57.14	69.12	57.14	73.53	85.71
	LOO	84.38	50.00	71.88	80.00	75.00	80.00
Binary EVOO-NonEVOO	EVOO	82.50	90.00	86.25	75.00	85.00	90.00
	Non-EVOO	84.00	91.67	83.00	91.67	92.00	100
Binary LOO-NonLOO	LOO	87.50	70.00	68.75	80.00	100	80.00
	Non-LOO	94.60	88.24	90.54	85.29	94.60	88.24

mentioned, a single sample misclassified leads to a very high decrease in TPR% value.

3.4. Comparison of techniques (IR vs GC-IMS). Pros and cons discussion

In the present work, three different techniques and six analytical instruments have been tested based on their potential to classify OOs by their quality categories, and copious information from each analytical technique, both from their experimental procedure and the results obtained, has been acquired. Considering all the outcomes obtained from this study, several advantages and disadvantages of each technique are going to be highlighted and discussed, with the aim of summarising some useful information about different analytical procedures for classifying OOs, so that the OO sector can have a scientific criterion to decide which technique may be more interesting for categorising OOs.

In this regard, the spectroscopic techniques (NIRs and MIRs) presented several analytical or methodological advantages compared to the fingerprint treatment of HS-GC-IMS signal, such as there being no need to weigh the samples prior to analysis or to use carrier gases (He or N₂) or separation columns for the analyses, the great speed at analysing each sample, allowing the analysis of up to 10 samples per hour, or the simplicity of the processing and treatment of the spectral data generated. Furthermore, the main advantage of NIRs over MIRs was that there is no consumption of any organic solvent other than the solvents required in some ATR-equipped MIR spectrometers to clean the accessory between loading consecutive samples. However, it would be necessary to consider that the features that IR instruments analyse from the samples are more related to the alteration degree of the samples (e.g. acidity, hydroperoxides, etc.) while HS-GC-IMS analyse the VOCs responsible for the aroma of the samples. The main methodological drawback of HS-GC-IMS with respect to IRs is the time needed to complete the analysis of each sample, around half an hour, but this disadvantage is offset by having an autosampler, which allows the analyses to be performed continuously, without depending on the presence of a technician. In addition, the use of reagents or sample dissolution or handling are not required in HS-GC-IMS analyses. However, it must also be considered that these GC instruments are significantly more expensive than spectrophotometers; therefore, in light of the results obtained here, it may be necessary to get a HS-GC-IMS if the aim is to ensure a high percentage of success in classifying an OO as EVOO, VOO or LOO. Only if the objective is to distinguish only between defective and non-defective - or edible and inedible - oils, an IR spectrometer (NIR / MIR) could also be used, in view of the results of the binary models, thus taking advantage of the benefits offered by these devices. All these technical characteristics have been collected and summarised in Table II, [Supplementary Material](#).

3.5. Misclassified samples

A final study based on the identification of the misclassified samples by each technique applied in this work, revealed that 50 % of the samples considered in the prediction models were always correctly

classified by the three techniques, so there was some agreement between analytical instruments in this regard. On the other hand, 23 % of those validation samples were incorrectly classified by a particular technique, 18 % by two of them, and only 9 % (2 from 22) were classified in a different category by the three techniques (NIR3, MIR2 and HS-GC-IMS) at the same time. These classification imprecisions by the different techniques employed in this study can be due to the technical differences between instruments and analytical methods such as signal/noise ratio, selected spectrum range in the case of IR measurement, or alignment, baseline correction or weighting in the case of the HS-GC-IMS methodology, among others.

4. Conclusions

Studies on the potential of spectroscopic techniques for the classification of different categories of virgin olive oil are very scarce and not very representative of the global oil market. With this work, the potential of different infrared spectroscopic techniques and, within them, of various analytical instruments or devices, to classify and predict OO samples quality was compared for the first time; as well as the advantages and disadvantages that the analysis of OO samples using this alternative technique can pose compared to some other more widespread techniques such as HS-GC-IMS. Moreover, it is also important to underline that the evaluation of the samples by more than one panel has been considered in this work, which is important in order to be ranked on the quality grade in a robust way.

The results obtained shown that infrared -both near and medium-spectroscopy coupled to chemometric methods, presented some potential to classify or discriminate among OO samples according to their quality category, especially when considering binary models differentiating defective and non-defective samples, or edible and non-edible OOs. In ternary models, however, IRs classification potential success was constrained to one single OO category, usually EVOO. On the other hand, the results showed that the effectiveness of the technique can strongly depend on the spectral absorption range considered, the type of instrument used for the analyses and its accessory equipment. In this way, under the experimental conditions here described, NIRs seems to be a more proper technique compared to MIRs, since slightly better EVOO classification results were achieved while the analytical methodology was simpler and required less solvent consumption. Nevertheless, neither MIRs nor NIRs reached sample classification success as high as other more specific and widespread technique, such as HS-GC-IMS, for ternary models, although the differences were smaller in a binary approach. In light of these results, it is proposed to use rapid techniques such as IRs to carry out preliminary screenings of OO categories, but techniques such as HS-GC-IMS should be in charge for confirming them, since they provide a greater reliability to distinguish between the three categories of OO here considered. Furthermore, the HS-GC-IMS analyses the volatile compounds, which are the direct responsible of the aroma.

Further studies should be carried out to confirm that this type of spectroscopic techniques could be integrated as effective methods for the discrimination of the quality of virgin olive oil by adding more

samples. Moreover, from the base of this work, those additional studies could be focused on the application of some other robust non-separation techniques on OOs, such as Raman, Electrospray-Ion Mobility Spectrometry or Fluorescence, and the OOs classification capability of those techniques, instruments and methodologies compared to IRs could also be tested. Moreover, data fusion could be another option to be tested, although the advantage or disadvantage of using two or more teams should also be assessed. Hence, a comprehensive study of the performance of these and other rapid techniques may provide the producers and other olive oil actors with the necessary information to implement new analytical strategies to support the panel test work.

Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

CRediT authorship contribution statement

Clemente Ortiz-Romero: Conceptualization, Investigation, Writing – original draft. **Rocío Ríos-Reina:** Conceptualization, Formal analysis, Writing – original draft. **Diego L. García-González:** Visualization, Writing – original draft, Supervision. **María José Cardador:** Visualization, Formal analysis, Writing – original draft. **Raquel Callejón:** Conceptualization, Validation, Visualization, Supervision, Writing – review & editing, Funding acquisition. **Lourdes Arce:** Conceptualization, Validation, Supervision, Writing – review & editing, Funding acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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