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Article in Food Analytical Methods · August 2015

DOI: 10.1007/s12161-015-0255-y

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FTIR Spectroscopy and PLS-DA Classification and Prediction of Four Commercial Grade Virgin Olive Oils from Morocco

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Received: 13 April 2015 / Accepted: 9 July 2015
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Abstract Fourier transform infrared (FTIR) coupled to chemometrics was shown to be a useful method to classify and predict the quality of four commercial grade virgin olive oils (VOO). FTIR and physicochemical data were collected using a set of 70 samples representing extra virgin (EV), virgin (V), ordinary virgin (OV), and lampante (L) commercial grade olive oils collected in Beni Mellal region (central Morocco). Two partial least squares discriminant analysis (PLS-DA) models using physicochemical data and FTIR data were established and compared. The PLS-DA model using only physicochemical data was not accurate enough to distinguish satisfactorily among OV, V, and EV olive oil grades. On the contrary, the PLS-DA model on FTIR data was better in the calibration, able to describe 98 % of the spectral information and predicting 93 % of the VOO grades. In the external validation, this PLS-DA model accurately classified VOO commercial grades with prediction accuracy of 100 %. The proposed procedure is fast, nondestructive, simple, and easy to operate, and it is recommended for the quick monitoring of olive oil's quality.

Keywords Virgin olive oils · Commercial quality grades · FTIR · PLS-DA · Chemometrics

Introduction

Virgin olive oil (VOO) is the oil obtained from fresh olive fruits using only mechanical and physical processes (olive milling, olive paste mixing and centrifugation, and olive oil settling). Olive oil has high commercial interest since it is widely known for its delicious taste and aroma and highly prized for its contribution to the basic Mediterranean diet (Escuderos et al. 2007; Harwood and Aparicio 2000).

VOO is a fine product with high nutritional value and significant health benefits (Owen et al. 2000). The International Olive Council (IOC 2013) defines four commercial graded categories based on their acidity quality for VOO—extra virgin (EV), virgin (V), ordinary virgin (OV), and lampante (L). This acidity is influenced by a combination of factors such as variety, method of harvesting, extraction process, and storage (Pinatel et al. 2004; Tsimidou et al. 2005).

The standard analytical methods, described by Regulation COI/T.15/NC No. 3/Rev. 7 of the IOC, include several physicochemical parameters such as acidity, phenols, peroxide value, K232, K270, and others in order to qualify olive oils. Several other analytical techniques have been developed for detection and quantification of adulteration and authentication of olive oil, such as mass spectrometry direct analysis in real time (Vaclavik et al. 2009), nuclear magnetic resonance (NMR) spectroscopy (Jafari et al. 2009), infrared spectroscopy (Gurdeniz and Ozen 2009), Raman spectroscopy (Heise et al. 2005), fluorescence (Poulli et al. 2007), gas chromatography (Jafari et al. 2009), high-performance liquid chromatography (Flores et al. 2006), and differential scanning calorimetry (Chiavaro et al. 2009).

In general, the main disadvantages of all these methods are that they are time-consuming, expensive, generally destructive of the sample material, and require a high degree of technical knowledge when interpreting the data.

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In the last few years, Fourier transform infrared (FTIR) spectroscopy has been used for the study of edible oils and fats (Machado et al. 2014; Rohman and Che Man 2011). FTIR methods have demonstrated to be rapid and nondestructive powerful analytical tools, and in most cases, they require minimal or no sample preparation. FTIR is also an excellent tool for quantitative analysis, since the intensities of the spectral bands are proportional to concentration. Several applications have been performed using this analytical approach together with chemometric methods: to detect olive oil adulteration (De la Mata et al. 2012; Lerma-García et al. 2011; Maggio et al. 2010; Ozen and Mauer 2002), to evaluate olive oil freshness (Sinelli et al. 2007), to assess oil oxidation (Guillén and Cabo 2002; Muik et al. 2007; Vlachos et al. 2006), and to study thermal stress. Recently, infrared spectroscopy coupled with multivariate methods has been shown to be useful to classify different Moroccan olive oils by their geographical origin (De Luca et al. 2011).

In this context, a first goal of this work was to continue the study about the quality of Moroccan Picholine virgin olive oil, collected from the Beni Mellal geographical area. In order to do this, we conducted first a chemometric analysis of 70 VOO samples from four commercial grades with their physicochemical analyses. Second, the same 70 VOO samples were analyzed with FTIR coupled to partial least squares discriminant analysis (PLS-DA) chemometric method to model and predict their commercial grade quality.

To summarize, the goal of this study was to investigate the potential use of PLS-DA coupled to FTIR spectroscopy, as an alternative approach to standard analytical methods for non-destructive and fast quality analysis of four commercial grade virgin olive oils.

Material and Methods

Sampling

After a thorough survey about the quality of virgin olive oils among different commercial producers from Beni Mellal region (central Morocco), a set of 70 samples from four commercial VOO grades was selected between October 2012 and February 2014. VOO was extracted from these olives by standard mechanical press methods. Physicochemical analysis of six quality parameters of VOO samples is given in Table 1.

Physicochemical Analysis

All 70 virgin olive oil samples were assayed for six physicochemical parameters following the standard analytical methods described by Regulation COI/T.15/NC No. 3/Rev. 7 of the International Olive Council. Free acidity was given as percentage of oleic acid and determined by titration with

0.1 N KOH of an oil solution in a previously neutralized solvent (ethanol/ethyl ether, 1:1) and using phenolphthalein as indicator. Peroxide value was expressed as milliequivalents of active oxygen per kilogram of oil (meq O₂/kg) and determined by a mixture of oil, chloroform, and acetic acid left to react with potassium iodide in darkness. Free iodine was then titrated with a 0.01 N sodium thiosulfate solution. The specific extinction coefficients, K232 and K270, were measured from the absorption in cyclohexane solution at 232 and 270 nm, respectively, with 1-cm path length using UV/VIS spectrophotometer, 2100 series (J.P SELECTA s. a, Spain). The Folin–Ciocalteu method (Singleton et al. 1999) was used to determine total polyphenolic content.

Based on the preliminary information about the origin of collected samples, together with the results of Table 1 and according to the quality criteria of The International Olive Council implemented in COI/T.15/NC No. 3/Rev. 7, to all samples have been assigned a corresponding class: extra virgin olive oil (EV), virgin olive oil, (V), ordinary virgin olive oil (OV), and lampante virgin olive oil (LV).

Reagents

HPLC gradient chloroform, cyclohexane, ethanol, and diethyl ether were purchased from Sigma-Aldrich. Analytical grade KOH, phenolphthalein, potassium iodide, sodium thiosulfate, and acetic acid were purchased also from Sigma-Aldrich.

Mid-Infrared Spectral Analysis

FTIR spectra were obtained using a Vector 22 Bruker FTIR spectrophotometer (Bruker Optik GmbH, Germany) equipped with an attenuated total reflectance accessory (ATR single-reflexion, Diamond, incident angle 45°), DTGS detector, Globar (MIR) source and KBr germanium separator, with a resolution of 4 cm⁻¹ at 98 scans. Spectra were scanned in the absorbance mode from 4000 to 600 cm⁻¹, and the data were handled with OPUS 5.5 software (Bruker Optik GmbH, Germany). Analyses were carried out at room temperature. The background spectrum was collected before each sample was measured.

Partial Least Squares Discriminate

Before the chemometric analyses (PLS-DA), the data were pretreated by taking first derivative of the absorbance spectra for the baseline removal, using the Savitzky–Golay method (Massart et al. 1998), with a second-order polynomial and three smoothing points. The partial least squares discriminate analysis method was successfully applied in previous studies to discriminate among different lubricants and milks (Elbassbasi et al. 2010; Hirri et al. 2013). In these works, PLS-DA was applied to find what were the variables which

Table 1 Physicochemical quality parameters of 70 VOO samples from Beni Mellal area, Morocco

Grades/samples	Physicochemical parameters					ΔK
	Acidity in %	Polyphenols (g/L)	Peroxide index (meq O ₂ /kg)	K232	K270	
Extra virgin olive oils, 14 samples						
Min	0.54	7.68	0.00	0.528	0.082	-0.005
Max	0.92	9.35	8.24	0.591	0.194	0.007
Mean	0.72	8.67	4.34	0.559	0.150	0.002
STD	0.12	0.54	2.03	0.017	0.031	0.003
Virgin olive oil, 20 samples						
Min	1.11	4.99	1.79	0.506	0.111	0.000
Max	1.88	8.76	12.71	0.564	0.193	0.006
Mean	1.36	7.33	7.83	0.536	0.138	0.003
STD	0.19	0.79	3.76	0.016	0.019	0.001
Ordinary virgin olive oils, 21 samples						
Min	2.02	3.34	8.45	0.501	0.110	−0.002
Max	3.28	6.31	14.16	0.556	0.197	0.014
Mean	2.49	4.96	11.16	0.528	0.164	0.003
STD	0.28	0.82	1.28	0.015	0.019	0.003
Lampante virgin olive oils, 15 samples						
Min	3.97	1.18	18.39	0.584	0.178	−0.0004
Max	5.72	2.45	24.83	0.651	0.311	0.052
Mean	4.77	2.03	22.17	0.617	0.254	0.009
STD	0.53	0.38	1.92	0.022	0.036	0.013

better discriminate between different groups of samples from their FTIR spectra (X block) according to their maximum covariance with a target class defined in a class pertinence variable (y data block). PLS-DA attempts to describe whether a spectrum of a sample belongs or not to a particular class, consisting of zeros and ones. According to the number of simultaneously regressed y vectors, two different PLS-DA approaches are possible. In case of only one class is modeled at a time, the method is the ordinary PLS1-DA. When several classes are simultaneously modeled at the same time, the PLS2-DA-modified method can be used (Massart et al. 1998).

The selection of optimal number of components in PCA and of latent variables in PLSR (below) was done from the lowest prediction error in cross-validation (leaving-out-one sample at a time) related to the value of PRESS_k, the sum of squares prediction error for the model when *k* factors (components) are included, and from the number of components which give an optimal prediction for the external validation samples not included in the calibration step. The model giving the lowest relative prediction errors in external validation is finally chosen.

In the classification study of this work, PLS2-DA was preferred. All data (physicochemical analysis and FTIR spectra) were processed for the purposes of PLS2-DA by The Unscrambler software, version X (Camo, Norway).

Results and Discussions

Physicochemical Data Analysis of VOO

Table 1 presents the results from the physicochemical analysis of six parameters for all 70 virgin olive oil samples. Fourteen EV samples were characterized by high amounts of total polyphenols on average 8.7 g/L (± 0.5) and by low levels of acidity 0.7 % (± 0.1) and with a peroxide index value equal to 4.3 meq O₂/kg (± 2). Twenty VO samples presented the second best quality grade. Polyphenols in VO grade were also rather high on average with a value of 7.3 g/L (± 0.8), while the acidity (1.4 %, ± 0.2), and peroxide index (7.8 meq O₂/kg, ± 3.8), increased compared to the EV grade. Twenty-one OV samples were the third best quality grade. These samples presented low amounts of total polyphenols (5 g/L, ± 0.8), relatively high acidities (2.5 %, ± 0.3), and high peroxide index (11.2 meq O₂/kg, ± 1.3) in comparison to EV and V olive oil samples. The lowest quality commercial grade samples were from lampante grade, LV. On average, this LV presented the lowest amount of total polyphenols (2 g/L, ± 0.4) and the highest acidity (4.8 %, ± 0.5) and peroxide index (22.2 meq O₂/kg, ± 1.9).

The measured extinction coefficients, K270 and K232 and ΔK , did not show any systematic tendency in accordance with the assigned quality grades to the samples.

FTIR Spectra of Virgin Olive Oil

FTIR spectra were obtained for the 70 samples of virgin olive oil, and they were preliminarily examined by visual inspection.

The entire spectral range $4000\text{--}600\text{ cm}^{-1}$ was used as a starting point for the investigation. According to the literature (Terouzi et al. 2011), the region between 2400 and 2300 cm^{-1} was discarded before chemometric analysis because of the low signal/noise ratio of this region. The region between 4000 and 3100 cm^{-1} is also removed because it coincides with the strong water absorption band which needs to be subtracted (Dupuy et al. 2010).

Figure 1 shows the MIR spectra of VOO at the frequency region of $4000\text{--}600\text{ cm}^{-1}$. Assignment of functional groups responsible for IR absorption is as follows: 3006 cm^{-1} (trans =C–H stretch), 2920 and 2852 cm^{-1} (symmetrical and asymmetrical stretching of $-\text{CH}_2$), 1743 cm^{-1} ($-\text{C}=\text{O}$ stretch), 1463 cm^{-1} ($-\text{CH}_2$ bending), 1377 cm^{-1} ($-\text{CH}_3$ bending), 1237 cm^{-1} ($-\text{C}-\text{O}$ stretch), 1161 cm^{-1} ($-\text{C}-\text{O}$ stretch; $-\text{CH}_2$ bending), 1118 cm^{-1} ($-\text{C}-\text{O}$ stretch), 1096 cm^{-1} ($-\text{C}-\text{O}$ stretch), and 722 cm^{-1} (cis-CH=CH– bending out of plane) (Guillen and Cabo 1997; Lerma-Garcia et al. 2010).

Partial Least Squares Discriminate

The set of 70 samples were divided into two subsets randomly using the Kennard–Stone algorithm (Kennard and Stone 1969). PLS2-DA was used to build a calibration model using

the first subset of 50 samples. External model validation was performed using the second subset of 20 new olive oil samples (not used for the model calibration). In this study, two PLS2-DA models were built considering, first the physicochemical data and second the FTIR spectra as X predictor variables. While the predicted Y block of variables contained a y variable for each quality grade, with 1 or 0 depending on whether it belongs or not to the considered data group for each of the four different quality grades. These calibration models were first validated by internal full cross-validation. Comparison between different models was done considering some figures of merit such as R^2 , root mean square error of calibration (RMSEC), and root mean square error of cross-validation (RMSECV).

Figure 2 presents the obtained PLS2-DA scores and loading plots (LV1 vs LV2) in the analysis of the physicochemical parameters and of the FTIR spectral data.

The PLS2-DA model for physicochemical data needed two latent variables and explained 52 % of the variance in Y block with 82 % of the information in physicochemical parameters data (X matrix). Figure 2a shows the score distribution for the four grades of VOO. Results were satisfactory only for the lampante grade of VOO (left side of the plot with negative scores) along LV1 (factor 1), while EV, V, and O grades were distributed together on the right side of the plot with positive scores. Figure 2b presents the distribution of the six parameter loadings in the space spanned by LV1 and LV2. LV1 discriminates between the total polyphenols (positive loadings on the

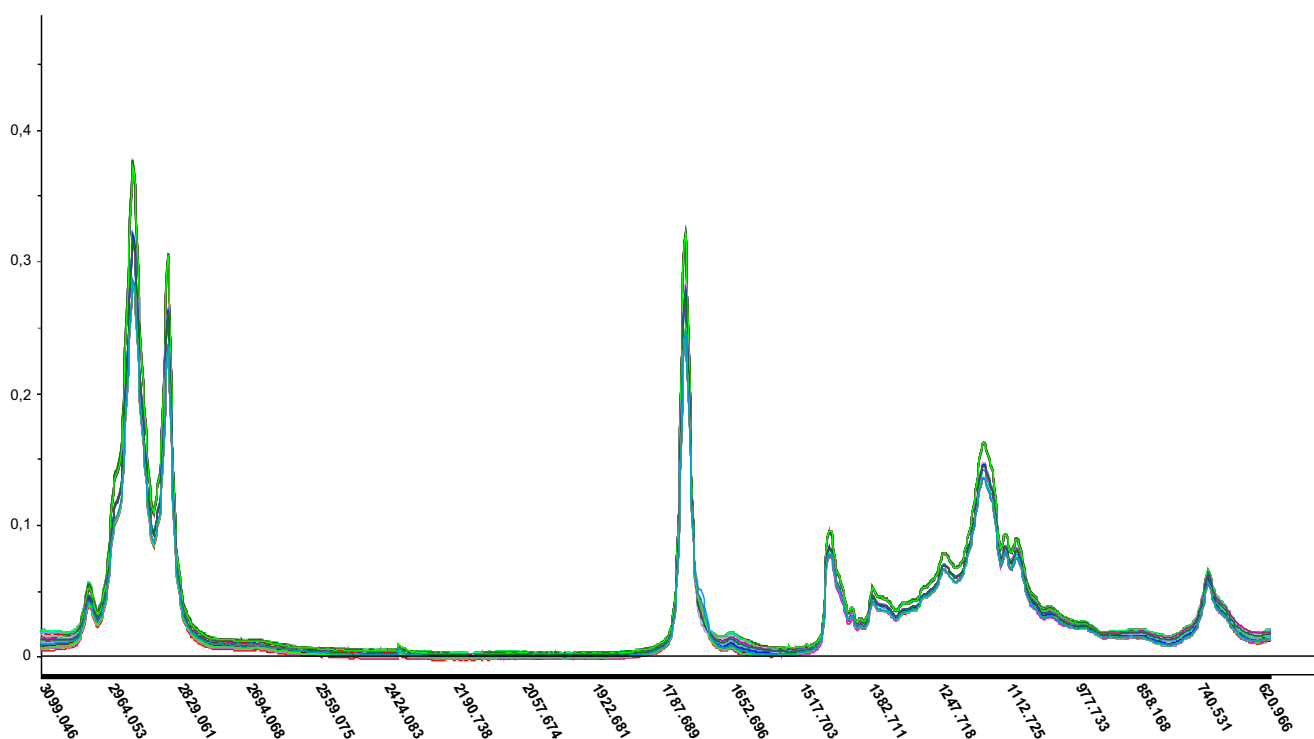


Fig. 1 ATR-MIR spectra of the virgin olive oil samples in the spectral range $4000\text{--}600\text{ cm}^{-1}$

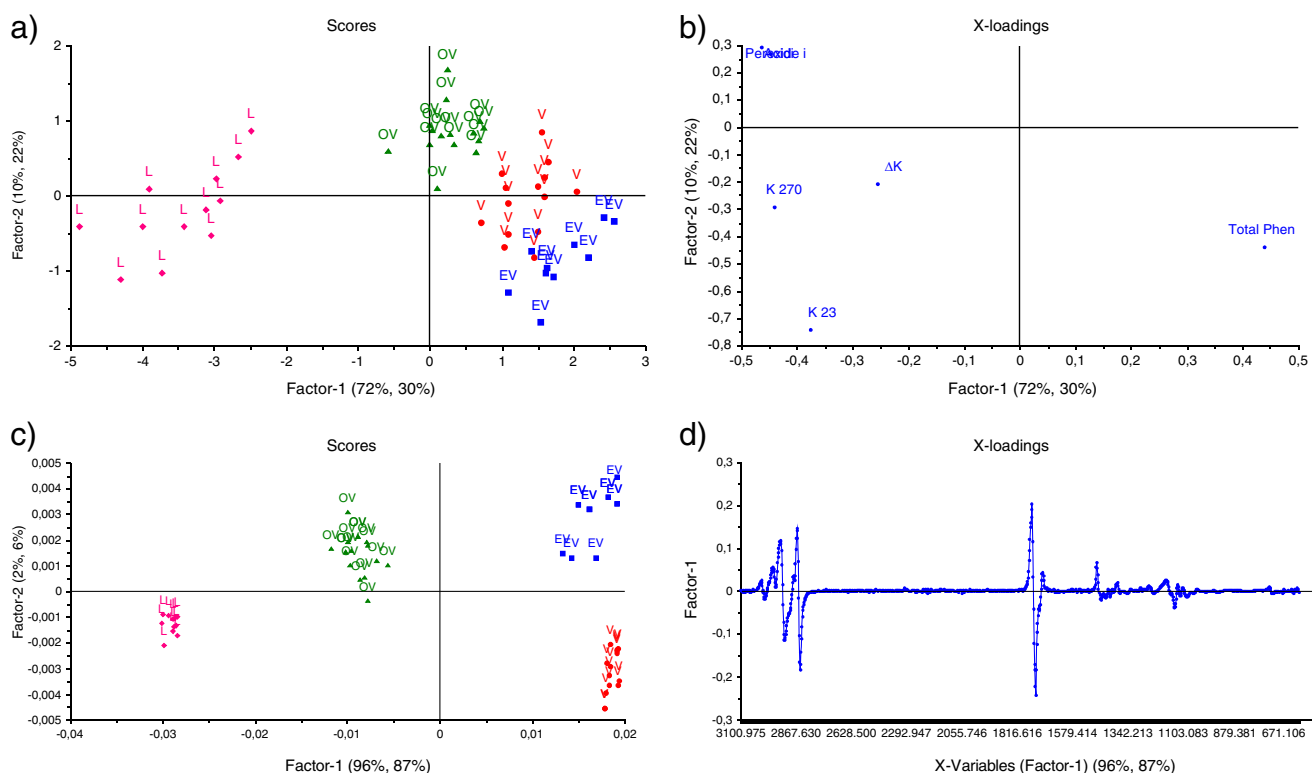


Fig. 2 PLS2-DA scores and loading plots (LV1 vs LV2) in the analysis of the physicochemical data (**a** and **b**) and in the analysis of FTIR spectral data (**c** and **d**)

right side on the plot) and the rest of investigated parameters (on the left side on the plot with negative loadings). It was possible to conclude that polyphenols are able to differentiate the VOO quality. EV, V, and OV were richer on total polyphenols and show less acidity and peroxide index than the lampante grade; therefore, they were better quality. However, the obtained model was not able to distinguish among the better quality EV, V, and OV oils, resulting in less satisfactory figures of merit, as reported in Table 2.

The R -squared equal to 0.9 was the best, and RMSEC and RMSECV (0.14 and 0.15, respectively) were the lowest for lampante VOO grade. Figures of merit obtained for the rest VOO grades were poorer. For example, RMSECV in the internal model validation did not exceed 0.50 for the other three grades. All these facts revealed that the obtained PLS2-DA model based on the six physicochemical parameters was not efficient to predict accurately the four quality grades of VOO, probably requiring new parameters to be included in the analysis, and this will imply increasing the overall time and cost of the analysis.

PLS2-DA model using FTIR data was built considering the spectral range 3100–600 cm^{-1} as X variables, while the Y variables had the four VOO grade classes (one y variable for each class). The obtained model was able to distinguish satisfactorily the four grades (EV, V, OV, and L), as it can be seen from the PLS2-DA score plot in Fig. 2c, where the four clusters of samples are much better distinguishable than those

obtained from PLS2-DA of physicochemical parameters data (see Fig. 2a). The first latent variable, LV1, explains 87 % of Y variance with 96 % of X variance, discriminates among the four quality grades, from the left to the right on Fig. 2c plot. The lower quality VOO grades were located on the left side of

Table 2 Figures of merit achieved by PLS2-DA discrimination of the four different types of virgin olive oil samples (EV, V, OV, and LV)

Classes ^a	Physicochemical parameter data		
	Figures of merit ^b		
	R^2_{cal}	RMSEC	RMSECV
EV	0.54	0.27	0.29
V	0.17	0.41	0.43
OV	0.51	0.32	0.34
LV	0.90	0.14	0.15
Classes ^a	FTIR data		
	Figures of merit ^b		
	R^2_{cal}	RMSEC	RMSECV
EV	0.96	0.08	0.12
V	0.97	0.06	0.1
OV	0.96	0.08	0.16
LV	0.98	0.04	0.10

^a Investigated classes by PLS-DA

^b Reported model figures of merit: R^2_{cal} R -squared in calibration, RMSEC root mean squared error in calibration, RMSEP root mean squared prediction error in external validation

the plot, starting with the lampante grade (L, with largest negative scores on the very left side on the plot) and followed by the ordinary virgin grade, OV. On the right side of the plot, the better quality virgin (V) and extra virgin (EV) were located. Figure 2d shows the loadings of LV1. Different chemical group substitution patterns, differing in the chain length of the acyl moieties, as well as in the unsaturation degree of the four VOO grades can be observed.

EV and V oil grades were characterized by different bands of symmetric and asymmetric stretching and bending vibrations of the aliphatic $-\text{CH}_2$ and $-\text{CH}_3$ groups (Vlachos et al. 2006) at 2964, 2927, 2857, and 1961 cm^{-1} (with strong positive loadings on Fig. 2d). Also, the typical band for the ester carbonyl functional group stretching of triglycerides is located at 1751 cm^{-1} band (with positive loadings for LV1).

On the contrary, the lower quality OV and L grades were characterized by the stretching of the $-\text{C}=\text{O}$ (free fatty acids) located at around 1723 cm^{-1} (Vlachos et al. 2006; Lerma-Garcia et al. 2010) with negative loadings in Fig. 2d.

The second latent variable explains a rather small percentage of variance of \mathbf{Y} (6 %) and also a small amount of variance in \mathbf{X} (2 %). High-quality oil grades (EV from V) were distinguished on LV2, as it can be seen in Fig. 2c. EV samples had positive scores, while V samples had negative scores. Positive loadings (not shown in Fig. 2) on LV2 were found for some bands at 2911 and 2846 cm^{-1} , typical for asymmetric stretching of $-\text{CH}_2$ groups together with the band at

1654 cm^{-1} , which represents vibration of *cis*-olefins (Vlachos et al. 2006).

Figures of merit obtained by PLS2-DA model of FTIR spectral data using the calibration sample subset (see “Material and Methods” section) are given in Table 2. In this case, high correlations between measured and predicted grades (R^2 was around 0.96 and 0.98 in all cases) and low prediction errors (RMSEC ranging between 0.04 and 0.08) were observed.

Predicting Quality of New Oil Samples

The predictive ability of PLS2-DA model using FTIR data was tested on 20 new samples, not used in the calibration step. These include four samples from extra virgin olive grade, six samples from virgin grade, six samples from ordinary virgin grade, and four samples with lampante olive oil grade. PLS-DA assigns an oil sample to a particular oil grade if the predicted value is comprised between 0.5 and 1.5 for that class. Table 3 shows the classification results with the comparison between known and predicted values for the four olive oil grades.

Table 3 shows that all samples from EV, V, OV, and L for the validation data set were correctly classified. This means that a 100 % accurate classification was achieved, i.e., all oil olive spectra of the validation data set matched correctly to the four corresponding grades. PLS2-DA predicted values were

Table 3 Prediction of VOO quality grades by chemometric analysis of MIR spectra in the external validation

Grades	Class EV		Class V		Classe OV		Classe LV	
	Y-pred	Y-known	Y-pred	Y-known	Y-pred	Y-known	Y-pred	Y-known
EV	0.99	1	0.005	0	0.03	0	-0.02	0
EV	0.66	1	0.31	0	0.10	0	-0.07	0
EV	1.15	1	-0.16	0	-0.005	0	0.01	0
EV	0.99	1	0.03	0	-0.04	0	0.02	0
V	0.13	0	0.84	1	0.07	0	-0.04	0
V	0.15	0	0.81	1	0.09	0	-0.04	0
V	0.12	0	0.85	1	0.07	0	-0.04	0
V	0.09	0	0.91	1	-0.05	0	0.05	0
V	0.08	0	0.95	1	-0.12	0	0.09	0
V	-0.02	0	1.05	1	-0.11	0	0.07	0
OV	-0.09	0	0.04	0	1.13	1	-0.08	0
OV	0.07	0	-0.08	0	1.01	1	-0.002	0
OV	-0.16	0	0.15	0	1.02	1	-0.01	0
OV	0.05	0	-0.08	0	1.04	1	-0.01	0
OV	0.2	0	-0.23	0	1.04	1	-0.01	0
OV	0.08	0	-0.05	0	0.92	1	0.05	0
L	0.003	0	-0.01	0	0.03	0	0.98	1
L	0.03	0	0.001	0	-0.09	0	1.05	1
L	-0.04	0	-0.02	0	0.12	0	0.94	1
L	0.002	0	0.01	0	-0.06	0	1.05	1

always very close to 0 or 1. These results confirm that the predictive ability of the developed PLS2-DA model was satisfactory good. Therefore, it was concluded again that FTIR spectroscopy coupled with the PLS2-DA chemometric method could be successfully used to discriminate VOO quality grades.

Prediction errors (RMSEP) were also satisfactory ranging between 0.1 and 0.16 (see Table 2). Therefore, the predictive ability of the developed PLS2-DA model was very promising.

Conclusion

FTIR spectroscopy can be applied for the prediction of virgin olive oil quality grades, giving similar results or even better than those obtained by more time-consuming and laborious classical physicochemical determinations using wet chemistry procedures. In fact, mid-infrared spectra give a complete fingerprint of olive oil samples, which contain information about their intrinsic quality and other influencing factors. Therefore, the use of FTIR spectroscopy coupled to chemometric methods such as PLS-DA is confirmed to be a reliable, cheap, and fast alternative tool for grade classification and prediction, able to verify the quality of virgin olive oil samples in a cheap and fast way, not requiring the use of traditional chemical analyses to discriminate among different oil quality classes.

Compliance with Ethical Standards

Funding Part of this study was funded by the grant CTQ2012-38616-C02-01 (Ministerio de Economía y Competitividad, Spain).

Conflict of Interest Aziz Hirri declares that he has no conflict of interest. Mahfoud Bassbasi declares that he has no conflict of interest. Stefan Platikanov declares that he has no conflict of interest. Roma Tauler declares that he has no conflict of interest. Abdelkhalek Oussama declares that he has no conflict of interest.

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

Informed Consent Not applicable.

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