

Quality Evaluation of Olives, Olive Pomace and Olive Oil by Infrared Spectroscopy

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1. Introduction

Olive oil extraction starts by crushing olives and ends by obtaining olive oil, vegetative water and partially de-oiled olive pomace (Petrakis 2006; Di Giovacchino 2000). In the industry it is important to know the amount of oil and water present in both olive fruits and olive pomace. In fact, the amount of oil is the parameter that establishes the price of raw materials and by-products and is critical for the optimization of extraction procedures.

There are publications compiling the various technological aspects of olive oil production, its quality, authenticity, chemical composition and the numerous analytical methodologies used for its characterization (Boskou 2006; Hardwood & Aparicio 1999; Hardwood & Aparicio 2000 Kiritsakis 1998; EC Reg No 2568/1991 and its amendment EC Reg No 1989/2003).

The intrinsic characteristics of the production demand fast decisions based on rapid analytical results. Therefore, conventional analytical determinations of oil, water and acid value should be replaced by short time or real-time/in-line measurements. Rapid characterization of raw material allows the selection of olives according to quality, enabling the production of higher quality oils.

Nowadays, infrared spectroscopy has become widely used as a non-invasive tool for fast analyses with less to no sample pre-preparation. There are numerous publications on the use of infrared spectroscopy for the analysis of oils, some of them will be referred, later in this document.

Baeten et al. (2000) published a paper on infrared and Raman spectroscopies and their potential for olive oil analysis. They described the instrumental techniques, interpretation of the spectra, data treatment and present potential applications.

This chapter reviews various applications of infrared spectroscopy for the analysis of olive oil, presents some results of the authors' work and emphasizes that infrared spectroscopy coupled with proper chemometric tools is an advantageous instrument, to be used in the industry, for olive quality evaluation and olive oil characterization.

2. Overview of the olive oil quality parameters

As mentioned previously the most relevant parameters for olives and olive pomace are fat and water content. Another important parameter is the free fatty acids (FFA) content of the oil of the fruit, which will determine the acid value of the produced olive oil .

Olive oil, after its extraction, classification and quality evaluation should be labeled and priced. Quality evaluation and authenticity are based on organoleptic assessment and chemical characterization according to the European Commission Regulation (EC Reg No 2568/1991 and its later amendments EC Reg No 1989/2003), the Codex Alimentarius Norm (Codex Alimentarius Commission Draft, 2009) and International Olive Oil Council (IOOC) Trade standards (IOC/T.15/NC n° 3/Rev.4, 2009). Usual adulterations of olive oil are the addition of olive residue oil, refined olive oil, low-price vegetable oils, and even mineral oil (Wahrburg et al. 2002; Dobarganes & Marquez-Ruiz 2003).

IOOC standards for olive oil and olive pomace oils contain a set of values and limits for the following parameters: fatty acid composition, *trans* fatty acid content, sterol composition and total sterol content, content of erythrodiol + uvaol, wax content, aliphatic alcohol content, stigmastadiene content, 2-glycerol monopalmitate, unsaponifiable matter, free acidity, peroxide value, specific absorbance in ultra-violet, moisture and volatile matter, insoluble impurities in light petroleum, flash point, trace metals, α -tocopherol, traces of heavy metals and traces of halogenated solvents (IOC/T.15/NC n° 3/Rev.4, 2009). Olive oil chemical characterization involves complex, time consuming and expensive analytical methodologies, which also destroy the sample.

3. Interpreting and using the infrared spectra

Spectroscopic techniques are neither invasive nor sample destructive and may contribute to rapid quality and authenticity evaluation, with low operating cost. From a physicochemical point of view, infrared spectroscopy is based on the vibrational transitions occurring in the ground electronic state of the molecules. The infrared absorption requires a change of the intrinsic dipole moment with the molecular vibration. The regions of the infrared spectrum which are used for applications in food analysis are: mid-infrared (MID-IR) and near-infrared (NIR).

Mid-infrared spectra present well resolved bands showing absorbances of varying intensity in the range of 4000 to 400 cm^{-1} originating from the fundamental vibrations.

Figure 1 shows a representative olive oil spectrum in the 4000 - 900 cm^{-1} region, where several characteristic bands related to lipid functional groups can be observed. In the 3100 - 2800 cm^{-1} spectral region appear the signals, assigned to C-H stretching mode from methylene and methyl groups of fatty acid and triacylglycerols. The low intensity peak near 3100 cm^{-1} may be explained by the CH=CH elongation and the signals of weak absorption around 2800 cm^{-1} are the result of the presence of secondary oxidation products, such as aldehydes and ketones. At 1800-1700 cm^{-1} the C=O stretching mode is found. The very strong band located at 1743 cm^{-1} can be ascribed to the triacylglycerol n-C=O ester group and a shoulder found around 1710 cm^{-1} is characteristic of the presence of free fatty acids (carboxylic n-C=O). The C-H deformation is detected between 1400 and 900 cm^{-1} , spectroscopic region which is also known as fingerprint region (Tay et al. 2002).

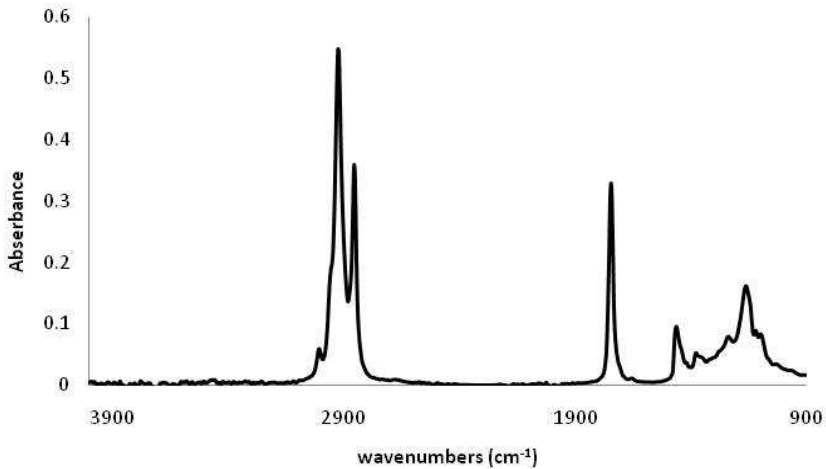


Fig. 1. Typical ATR-Mid-IR spectrum of olive oil.

Near-infrared spectra present less well resolved bands in the range of 14000 to 4000 cm^{-1} corresponding to overtones and combinations of fundamental vibrations.

Figure 2 a) and b) show NIR spectra of olive oil, hammer milled olive and olive pomace. The following main spectroscopic regions can be observed: the region between 9000 – 8000 cm^{-1} , can be ascribed to the second overtone of the C-H stretching vibration of modes of methyl, methylene and ethylene groups of fatty acids and triacylglycerols; the region between 7500 and 6150 cm^{-1} can be attributed to the first overtone of the O-H stretching vibrations; whereas the absorptions located around 6000 – 5700 cm^{-1} correspond to the first overtone of the C-H stretching vibration modes of methyl, methylene and ethylene groups; in next region bands between 5350 and 4550 cm^{-1} result from combinations of fundamentals of the C-H stretching vibration and of bands of water molecules (specially in olives and olive pomace); finally, the 4370 – 4260 cm^{-1} region can be ascribed to the C-H stretching combination of methyl and methylene groups (Galtier et al. 2007; Muick et al. 2004).

Several aspects must be considered when spectroscopic data are used in order to achieve multiple parameter determination, by direct analysis of spectra. A careful calibration framework should be devised, comprising: 1) an adequate sampling strategy, taking in account sampling variability and a suitable physicochemical range set; 2) a robust spectroscopic equipment in order to detect and quantify olive oil parameters in lower amounts, which is particularly important in the industrial in-line process; 3) a proper validation of the results given by infrared spectra and multivariate models; 4) a careful control of the outcome from the instrumental results and chemometric models, by employing control charts to evaluate the performance of the methodology and 5) a plan to address models sustainability through a periodic assessment of models performance, e.g. by performing traditional analysis and comparing to the outcome of the infrared spectra, in order to correct possible deviations. This last aspect is very important due to the nature of the samples (e.g. different harvest periods and samples origin, etc.) and equipment efficacy.

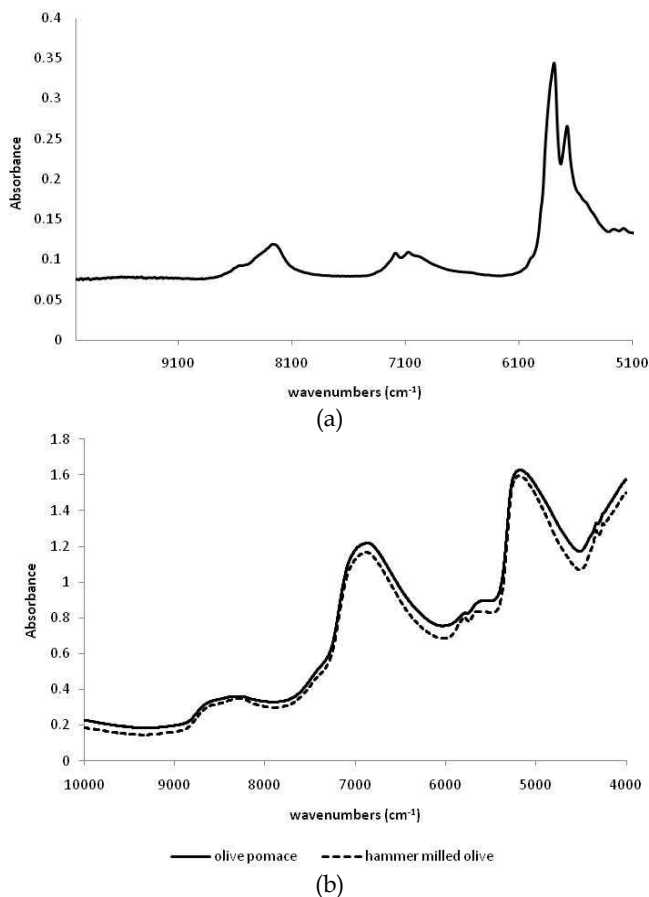


Fig. 2. Typical NIR spectra of (a) olive oil and (b) hammer milled olive and olive pomace.

4. Quantification of chemical parameters in olive oil

To ensure a more reliable control of every step in the extraction process, a good sampling system is necessary. For industrial in-process analysis of olive oil, spectroscopic techniques (mostly, NIR and MID-IR spectroscopy) in tandem with chemometric methods are the cornerstone for quality control. According to Marquez et al. (2005) these techniques have shown a high potential as an alternative to time-consuming and expensive chromatographic or wet chemistry analysis. In fact the application of optical on-line NIR sensor for olive oil characterization is an appealing approach for real-time chemical evaluation, allowing the estimation of acid value, bitter taste (K_{255}) and fatty acids (Marquez et al. 2005). Near infrared spectroscopy has been valuable for the assessment of physicochemical parameters of vegetable oils (Sato 1994; Hourant et al. 2000; Takamura et al. 1995; Franco et al. 2006). Infrared spectroscopy (NIR and MID), has also been applied successfully for olive oil evaluation and geographical origin determination using chemometric approaches (Tapp et al. 2003; Iñón et al. 2003; Galtier et al. 2007). In addition, NIR technique was employed to detect fraudulent

addition of other vegetable oils and olive pomace oil, to virgin olive oil (Wesley et al. 1995; Yang & Irudayaraj 2001; Downey et al. 2002; Vlachos et al. 2006); and for olive oil authentication (Bertran et al. 2000; Downey et al. 2003; Woodcock et al. 2008). The chemical characterization of fatty acids and sterols (Ollivier et al. 2006; Ollivier et al. 2003; Aranda et al. 2004; Leardi and Paganuzzi 1987), is useful for assessing quality and authenticity.

The authors attempted to apply NIR for the quantification of fatty acids, sterols and wax in an industrial scenario (for in-line analysis). 40 chemically characterized olive oil samples, from different origins, were used for this study. Partial Least Squares regression (PLS1) was applied in combination with NIR spectra in the 9000 - 4500 cm^{-1} range. Model validations were carried out using Monte-Carlo Cross-Validation (MCCV) (500 runs to evaluate models robustness); the predictive power of each one of the models were assessed through the computation of 1) Root Mean Square Error of Cross Validation (RMSECV); 2) Root Mean Square Error of Prediction (RMSEP); 3) Coefficient of Determination (R^2) and 4) the cross-validated coefficient of determination (Q^2). At the same time several data pre-treatments were tested in order to find the most suitable ones (predictive ability).

A summary of the results obtained is described in Table 1. Two data pre-treatments were selected: 1) Standard Normal Deviate (SNV) and 2) 2nd derivative computed with the Savitzky-Golay procedure, using a 2nd degree polynomial with 11 points (5+5+1). As it can be seen from the table the obtained models have from reasonable to good predictive power.

Parameter	Range	LV	Q^2	R^2	RMSECV (%)	RMSEP (%)	Pre-treatment
Fatty acids							
16:0	9.0 - 12.1 %	4	0.88	0.82	0.270	0.570	2 nd derivative
16:1	0.7 - 1.3 %	5	0.88	0.82	0.050	0.101	2 nd derivative
18:0	2.8 - 3.8 %	9	0.81	0.98	0.123	0.216	SNV
18:1	73.3 - 78.9 %	9	0.86	0.98	0.521	1.47	SNV
18:2	5.3 - 9.0 %	8	0.91	0.99	0.263	0.32	SNV
18:3	0.7 - 0.8 %	4	0.64	0.81	0.027	0.038	2 nd derivative
24:0	0.0 - 0.1 %	7	0.76	0.80	0.021	0.087	SNV
Sterols							
Campesterol	2.97 - 3.64 %	7	0.82	0.98	0.070	0.131	2 nd derivative
Cholesterol	0.07 - 0.27 %	6	0.85	0.96	0.020	0.052	2 nd derivative
Stigmastenol	0.23 - 0.33 %	9	0.80	0.96	0.012	0.027	SNV
Stigmasterol	0.52 - 1.21 %	8	0.85	0.96	0.088	0.106	SNV
Sitosterol	94.6 - 98.3 %	7	0.63	0.99	0.111	0.175	2 nd derivative
Total Sterols	1434 - 1636 (mg/kg)	9	0.70	0.96	23.90	57.0	SNV
Others							
Wax	59.42 - 240.67 (mg/kg)	5	0.71	0.95	29.20	37.7	2 nd derivative

Nomenclature: palmitic acid (16:0), palmitoleic acid (16:1), stearic acid (18:0), oleic acid (18:1), linoleic acid (18:2), linolenic acid (18:3), lignoceric acid (24:0).

Table 1. Fatty acids, sterols and wax determination for olive oil by NIR and PLS1 regression in the spectral range of 9000 - 4500 cm^{-1} .

Several factors may reduce the predictive ability of such modeling techniques: 1) low amount of some parameters present in the olive oil; 2) NIR instrument characteristics (selectivity, specificity, signal to noise ratio, etc.) and 3) sampling distribution. At this stage seven fatty acids can be estimated using NIR, but many more could be quantified. It will be necessary to add more samples with wider ranges of parameters in order to enhance the robustness of the models. Galtier et al. (2007) have managed to quantify 14 fatty acids, squalene and triacylglycerols.

The spectral profiles extracted from infrared spectra using chemometric methods could be in many cases a substitute for the traditional analysis, for olive oil overall characterization.

5. Identification and quantification of olive oil adulterants

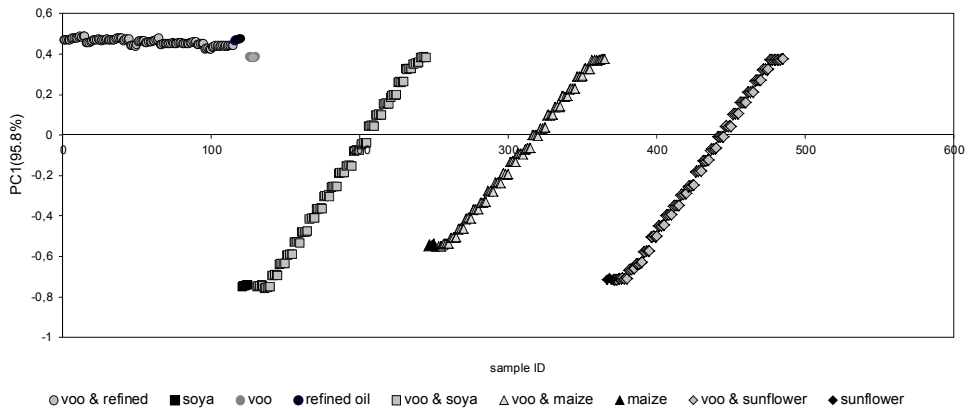
Extra virgin olive oil is adulterated with oils of low quality or price. The natural variation due to geographical origin, weather effect during growth and harvesting makes the task of detecting adulteration difficult. Analytical methods applied in the examination of chemical composition include the determination of fatty acid profiles by gas liquid chromatography (Firestone et al. 1988), high-pressure liquid chromatography (Cortesi 1993; Mariani & Fedeli 1993), pyrolysis mass spectrometry (Goodacre et al. 1993), measurement of iodine values and many other determinations. Rapid, non destructive spectroscopic methods such as Raman (Davies et al. 2000), ultraviolet (Calapaj et al. 1993), MID-IR (Lai et al. 1995; Dupuy et al. 1996; Guillen & Cabo 1999; Küpper et al. 2001) and NIR (Wesley et al. 1995; Bewig et al. 1994; Sato 1994; Wesley et al. 1996; Hourant et al. 2000) have all been applied to quantify adulterants in olive oil.

NIR spectroscopy in tandem with PCA and PLS1 regression, as studied in this laboratory, was found to be suitable for the identification and quantification of adulterants (refined olive oil, sunflower oil, maize oil and soya oil) in virgin olive oil. Binary mixtures were prepared with extra virgin olive oil and each one of the selected potential adulterants. Different amounts of refined olive oil and 3 commercial oil samples (sunflower, soya and maize) were mixed with olive oil giving four different data sets. 25 samples were prepared for each data set (binary mixture), containing additions from 5 to 95 mL of adulterant. Additionally, for each adulterant, an independent prediction set of 8 samples was prepared.

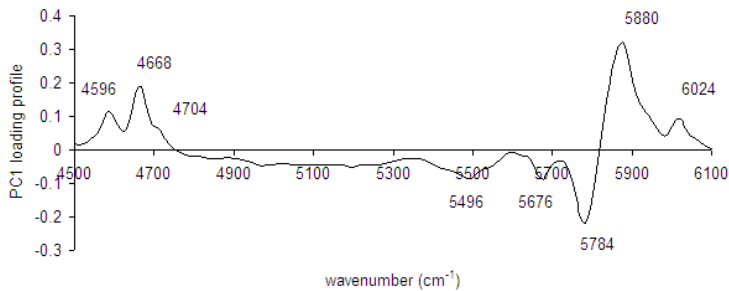
NIR spectra from the samples were obtained with a Perkin Elmer Spectrum One NTS FT-NIR spectrometer. The data were recorded in the spectral range between 10000 – 4500 cm^{-1} , by co-adding 30 scans with a resolution of 8 cm^{-1} . Each sample was acquired five times. PCA allowed the characterization of the sample relationships (scores plans) and the recovery of their sub-spectral profiles (loadings) (Jolliffe 2002). For this analysis, the 6100 - 4500 cm^{-1} region was selected and each spectrum was SNV corrected. A calibration model was built for each adulterant and was validated with the external and independent prediction data sets.

Oil samples are distributed across PC1 axes according to the olive oil content (Figure 3a). The bands located at 4596, 4668 4704, 5880 and 6024 cm^{-1} are related with the samples with larger amount of olive oil (Figure 3b).

Parameters of the best calibration models built for each adulterant are shown in Table 2. The four calibration models were built in the spectroscopic region of 4536-6108 cm^{-1} .



(a)



(b)

Fig. 3. (a) Scores plot of the first principal component (PC1), obtained for the set of virgin olive oil (voo) adulterated with refined oil, sunflower oil, maize oil and soya oil. (b) PC1 loading profile.

Spectral region (cm ⁻¹)	Pre-treatment	LV	RMSEP(%)	R ²	RMSEC(%)
Model 1: quantification of sunflower oil in virgin olive oil					
4536-6108	SNV	6	0.20	0.99	0.29
Model 2: quantification of maize oil in virgin olive oil					
4536-6108	SNV	5	0.23	0.99	0.34
Model 3: quantification of soya oil in virgin olive oil					
4536-6108	SNV	2	0.38	0.99	0.67
Model 4: quantification of refined olive in virgin olive oil					
4536-6108	1 st derivative	7	2.81	0.99	3.74

Table 2. Statistical parameters obtained for the calibration models built for each adulterant.

The coefficient of determination higher than 0.99, and the low root mean squared error of prediction (RMSEP) suggest a good predictive power. PLS1 regression based calibration models were used to predict the percentage of adulterant in the independent data sets. Results presented in Table 3 suggest that NIR spectroscopy in tandem with PLS1 regression is suitable to detect and quantify adulteration with other edible oils (sunflower, soya, maize refined olive oil) in extra virgin olive oil up to 2% (w/w).

Prediction Sample n°	Observed Oil Content in Virgin Olive Oil (%)	Predicted Oil Content in Virgin Olive Oil (%)							
		Model 1 (Sunflower)		Model 2 (Maize)		Model 3 (Soya)		Model 4 (Refined Olive Oil)	
P1	0.3	0.1	± 0.1	0.3	± 0.2	0.0	± 0.2	0.4	± 0.4
P2	2.0	1.9	± 0.1	1.8	± 0.3	1.0	± 0.1	1.7	± 1.9
P3	8.0	7.8	± 0.1	7.7	± 0.1	7.5	± 0.1	10.0	± 2.2
P4	16.0	16.1	± 0.1	15.6	± 0.1	15.2	± 0.1	14.9	± 0.7
P5	37.0	36.9	± 0.2	34.5	± 0.1	36.9	± 0.3	36.1	± 2.9
P6	58.0	57.9	± 0.2	56.1	± 0.1	57.7	± 0.1	56.9	± 0.6
P7	71.0	71.1	± 0.1	69.0	± 0.1	70.6	± 0.2	71.2	± 0.8
P8	87.0	86.9	± 0.1	84.9	± 0.2	83.3	± 0.1	82.6	± 1.9

Table 3. Predicted values using the calibration model built for each adulterant.

6. Quality evaluation of the olives at the oil extraction plant

6.1 Determination of oil and water content in olives and olive pomace

Information about olive quality is very important for the olive and olive oil producers as fruits with larger amounts of oil are highly priced. In addition to water content, fat content is also an important parameter for the optimization of the extraction procedures. Olive pomace can be re-extracted in the same industrial facilities or dried and sold in the form of dried olive pomace (O'Brien 2004).

Conventional oil and water analytical determinations could be replaced by real-time methods that avoid mixtures of high quality with low quality fruits. Muick and coworkers (2004) applied NIR and Raman spectroscopy to the determination of oil and water content in olive pomace. Later on, Bendini et al. (2007) were able to determine fat content, moisture and acid value directly in olives, using a Fourier Transform near-infrared (FT-NIR) instrument located in an industrial mill.

Here, the application of NIR in tandem with a multivariate regression method for the quantification of oil and water directly in fresh hammer milled olive and olive pomace samples is discussed (Barros et al. 2009). A total of 159 olive and olive pomace samples were used to build the calibration set. In order to validate the built models (for oil and water), 108 olive and olive pomace samples were used as independent set. In order to build the calibration models for the quantification of oil and water in hammer milled olive and olive

pomace using NIR and PLS1 regression, a Monte Carlo Cross-Validation (MCCV) (Xu & Liang 2001) framework was used. This approach was needed for building robust calibration models for real-time industrial application.

The model for water content estimation was built by a preliminary spectrum pre-treatment by computing the 1st derivative, in order to minimize the baseline effect, followed by Standard Normal Deviate (SNV). A PLS1 regression model with 3 LVs (Latent Variables) was needed to obtain predictive power with a Q^2 of 0.96 and a relative RMSECV of 1.1%. The **b** vector plot for the water calibration models and the relationship between measured and predicted water values using a PLS1 are presented, respectively, in Figure 4a and Figure 4b.

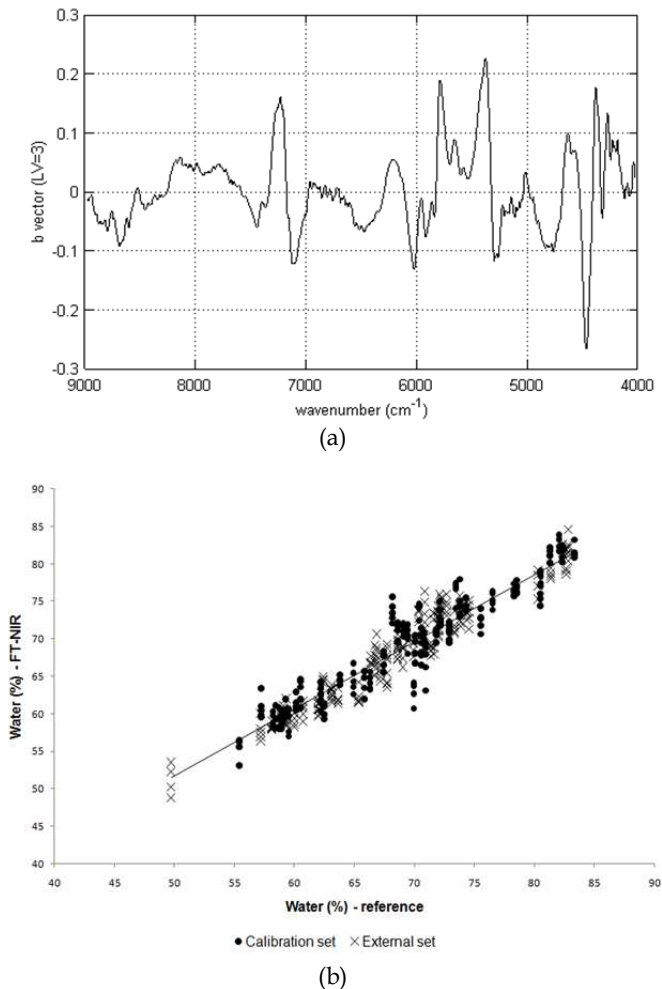
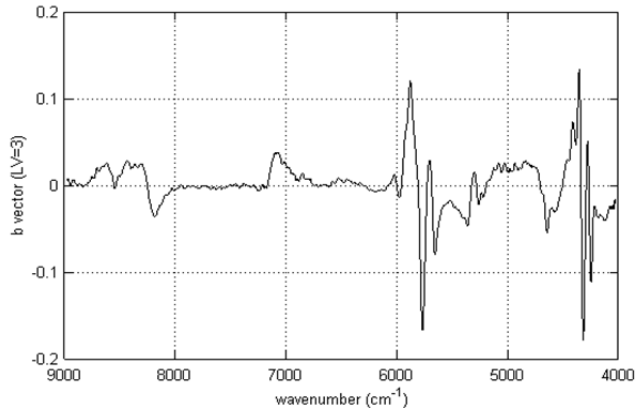
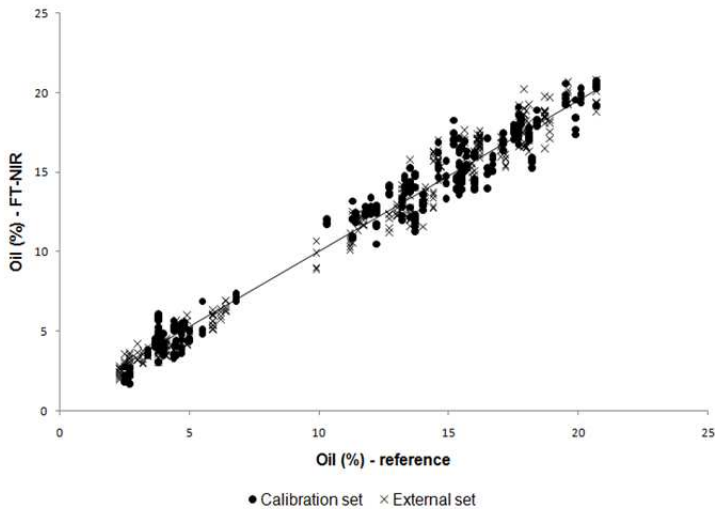


Fig. 4. (a) b vector plot for the water calibration and (b) relationship between measured and predicted water values using a PLS1 model with 3 Latent Variables (Reproduced with permission from Barros et al. 2009 © Springer 2009).

For oil calibration model the spectra pre-treatment was the same as for the water calibration model and, in this case, 3 LVs were needed to obtain predictive power with a Q^2 of 0.88 and a relative RMSECV of 2.64%. The **b** vector plot for the oil calibration models and the relationship between measured and predicted oil values are shown, respectively, in Figure 5a and Figure 5b.



(a)



(b)

Fig. 5. (a) **b** vector plot for the oil calibration and (b) relationship between measured and predicted oil values using a PLS1 model with 3 Latent Variables (Reproduced with permission from Barros et al. 2009 © Springer 2009).

The models showed a good predictive power considering the nature (heterogeneity) of the milled olive fruits and olive pomace samples. NIR technique in tandem with PLS1 regression was found suitable for the quantification of these two important parameters. At industrial scale, the results show that NIR can be used for an extensive screening process of the olive fruits and olive pomace. In fact, when compared to classical approaches of analysis, this methodology is faster, allows larger number of samples in real-time and is environmental sustainable.

6.2 Acid value quantification in olives

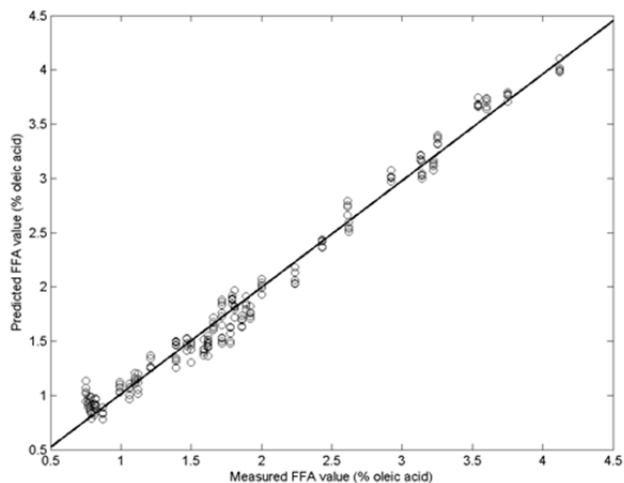
Several factors may affect the olive characteristics and consequently its quality (Muick et al. 2004) specially the increase of free fatty acids (FFA) due to the action of lipases (Morelló et al. 2003). Consequently, the classification of olive oils based on their FFA content prior to processing is an important measure to improve and guarantee the production of good quality olive oil.

Previous works (Muick et al. 2003) report the application of Raman spectroscopy to the direct determination of FFA in milled olives. It is not possible to predict FFA content directly in the milled olive by NIR, probably because of the complexity of the matrix: kernel, pulp and skin.

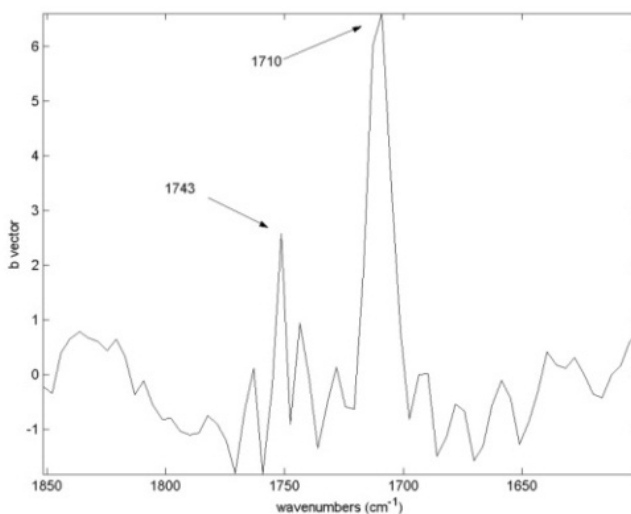
The authors proposed a method for a rapid determination of free fatty acids in olive (Nunes et al. 2009). This procedure combines Soxhlet extraction for 30 minutes with MID-IR spectroscopy coupled to a multivariate regression method (PLS1). The oil extracted from olives (crushed with a hammer mill) was used for infrared analysis and for free fatty acids determination according to UNE 55030 (AENOR 55030:1961) protocol. MID-IR spectra were acquired by ATR in a Golden Gate accessory (one reflection), in the range of 4000 to 600 cm^{-1} . The data set comprising a total of 210 spectra (42×5) was imported into an in-house developed procedure for performing PLS1 (Helland 2001; Martens 2001; Wold et al. 2001).

Figure 6a, shows a linear correlation between the actual olive oil acid values and those estimated by the PLS1 model within the considered values range. The corresponding b vector profile shown in Figure 6b clearly identifies the band located at 1710 cm^{-1} (carboxylic n-C=O) as the most important one, related to the quantified olive oil acid value. Moreover, the band located at 1743 cm^{-1} (assigned to triacylglycerols n-C=O ester group), although weaker than the previous one, also contributes to the modeling of the olive oil acidity.

The PLS1 calibration model with a Monte Carlo Cross-Validation approach was built in the spectroscopic region of 1850-1600 cm^{-1} (with SNV pre-treatment, 4 LVs, a RMSECV(%) of 8.7 and a Q^2 of 0.97). It represents an optimized method for calibration of FFA in extracted olive oil and a proposal for an indirect but quick acid value determination in olives and consequently fruit quality. The short extraction time and the spectroscopic determination of FFA from the MID-IR spectra instead of the titration step (with the consequent decreasing use of reagents and analysis time), provide more reliable results and permit a tight sampling control.



(a)



(b)

Fig. 6. (a) PLS1 regression relationship between actual and predicted value of olive oil acidity from the application of acidity calibration model and (b) the corresponding b vector plot (Reproduced with permission from Nunes et al. 2009 © Springer 2009).

7. Conclusions

The high sensitivity and reproducibility provided by the modern spectrometers allow in-depth studies of food systems, like olives and olive oil. The complexity of these matrices requires chemometric tools to extract both qualitative and quantitative information.

Infrared spectroscopic techniques have a potential in assisting and simplifying olive oil characterization. NIR spectroscopy in tandem with multivariate calibration models could provide a comprehensive chemical characterization of an olive oil sample for waxes, total sterols, sterol composition and free fatty acids composition.

NIR infrared may also contribute to the identification and qualification of adulterants in virgin olive oil (additions of refined olive oil, sunflower oil, maize oil and soya oil with "as low as 2% (w/w)).

Moreover, NIR and MID-IR spectroscopy as tool the advantage that it can be used to quantify oil and water content directly in olive and olive pomace and also to measure FFA directly in olives, allowing a quick quality evaluation that may reduce the processing time and cost.

The spectral profiles extracted from infrared spectra using chemometric methods could in many cases be a substitute for chromatographic and wet chemistry analysis, for olive oil overall characterization. Therefore, spectrometers of this type can be an important tool in modern olive oil analytical laboratory since they have so many advantages such as sensitivity, versatility (several type of analysis with only one equipment), real-time/in-line measurements, minimal sample preparation, relatively low cost implementation and high throughput.

8. Acknowledgment

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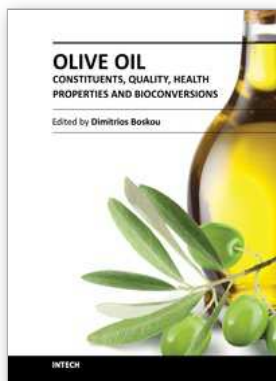
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