Application of low-resolution Raman spectroscopy for the analysis of oxidized olive oil

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ABSTRACT

The aim of this study was to evaluate the potential of low-resolution Raman spectroscopy for monitoring the oxidation status of olive oil. Primary and secondary oxidation parameters such as peroxide value, K_{232} and K_{270} were studied. Low-resolution Raman spectra ranging from 200 to 2700 cm^{-1} in a set of 126 oxidized and virgin olive oil samples were collected directly using a probe. Partial Least Squares was used to calibrate the Raman instrument for the different targeted parameters. The performance of the models was determined by using validation sets, and the best results obtained were: $R^2 = 0.91$, RMSEP = 2.57 for the peroxide value content; $R^2 = 0.88$, RMSEP = 0.37 for K_{232}; and $R^2 = 0.90$, RMSEP = 0.08 for K_{270}. These results demonstrated that low-resolution Raman spectroscopy could be a relevant technique for evaluating the oxidation status of olive oils because the key oxidation parameters can be determined quickly and in a non-destructive and direct way.

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1. Introduction

The quality of olive oil can be affected by several factors, such as inherent agronomical factors, including seasonal conditions or different cultivation and ripening systems. Other factors relate mainly to technical parameters, such as storage method and duration or the technology of the process.

Oxidative rancidity, or the oxidation of oil, is the main parameter affecting its quality and takes place mainly during the production and storage of oil (Kiritsakis, Nanos, Polymenopulos, Thomai, & Sfakiotakis, 1998). Some of the important parameters related to the oxidative deterioration of olive oil feature in the official regulations, including the peroxide value and the spectrophotometric UV absorption of olive oil at 232 nm (K_{232}) during the initial stages of oxidation and absorption at 270 nm (K_{270}) during secondary oxidation. Another important parameter is the anisidine index (Muik, Lendl, Molina-Díaz, Ortega-Calderón, & Ayora-Cañada, 2004), which is related to the measurement of secondary products for oxidation and produces rancidity in the oil. Peroxides are important indicators of oxidation and rancidity in foods; they are chemical compounds composed mainly of O—O bonds.

Peroxides negatively affect the nutritional value and global sensorial quality of foods (Vercellotti, St. Angelo Allen, Spanier, & Arthur, 1992). They are unstable and they are easily transformed, as a result of the secondary product accumulation of oxidation, into other products, such as conjugated aldehydes, ketones, conjugated dienes and trienes (double bonds C=C). The major secondary oxidation products formed are alcohols, aldehydes, saturated epoxy compounds and α, β-unsaturated epoxy compounds (Frankel, Selke, Neff, & Miyashita, 1992). These products reduce the sensory and nutritional quality of oil. A parameter such as K_{232} measures the oxidative state of oil compounds, such as conjugated dienes with an absorbance at 232 nm; K_{270} also measures conjugated dienes and trienes absorbing at 270 nm.

According to European Commission Regulation 1989/03 (EC Commission Regulation, 2003), extra virgin olive oil cannot have a peroxide value higher than 20 meq O2/kg, a UV absorption K_{232} value higher than 2.50 or a UV absorption K_{270} value no higher than 0.22.

Oils with peroxide content and UV absorption K_{232} and K_{270} values higher than these, indicate the presence of diene- and triene-conjugated systems and are then considered to be lampante oils; these oils need to be refined in order to make them acceptable for consumption. (Boskou, 1996; García, Seller, & Pérez-Camino, 1996).

The official method used for determining the peroxide value is based on the iodine index. This is obtained by titration with a sodium

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thiosulfate standard solution. The spectrophotometric absorptions at 232 nm (K_{232}) and 270 nm (K_{270}) are expressed as a specific extinction of a solution of oil dissolved in cyclohexane, respectively. These methods are highly empirical and their precision depends on several experimental factors, such as technician skill, light exposure and atmospheric oxygen. There are many factors that can affect the quality of olive oil, such as inherent agronomical factors or factors related to the various steps in olive oil processing, from extraction to bottling. Some of these factors could be changed by controlling the oil at the time of production, thus avoiding mixing oils of different qualities and thereby improving the quality of extra virgin oil. Oil analysis at the production stage is a laborious, costly and time-consuming procedure. There is not yet a method to directly determine the oxidative state of oil at the production stage and thus to improve oil production quality control.

Various techniques to solve this problem have been proposed in the literature. Techniques such as infrared spectroscopy have been studied and successfully used for characterizing some olive oil parameters (Armenta, Garrigues, & De la Guardia, 2007; Mailer, 2004; Sinelly, Tura, & Casiragui, 2008), for quality control and for determining the geographic origin of virgin olive oils (Bendini et al., 2007). Studies have also been done, using infrared spectroscopy, on the various parameters of oxidation of some edible oils: analyzing lipids by spectroscopy (Dobson, 1995), determining peroxide values in palm oil (Moh, 1999), monitoring the peroxide in soybean and corn oil (Yildiz, Randy, Wehling, & Susan, 2002), determining peroxide values in oxidized soybean oils (Yildiz, Randy, Wehling, & Susan, 2003), and determining the oxidation state in oxidized vegetal oils (Dreau, Dupuy, Artaud, Ollivier, & Kister, 2009). Raman spectroscopy is a promising tool in analytical chemistry because of its interesting characteristics, which include being non-destructive, fast and relatively inexpensive; it does not involve any chemical products and requires very little sample preparation. In addition, Raman spectra are the result of bands of fundamental vibrational transitions, which offer a large quantity of information about the molecular structure.

In the olive oil sector, the Raman spectroscopy technique has been used to determine unsaturation (Baeten, Hourant, Morales, & Aparicio, 1998), to detect adulteration in virgin olive oil and for authentication (Baeten & Meurens, 1996; Marigheto, Kemsley, Defernez, & Wilson, 1998). More recently, it has been used to determine the fat and moisture content in olives and for olive discrimination (Muik, Lendl, Molina-Díaz, Ortega-Calderón, & Ayora-Cañada, 2003). Work comparing Fourier Transform Infrared (FTIR) and Raman techniques for studying the oxidation of lipids in edible oils (Muik et al., 2007) and for monitoring lipid oxidation in edible oils by Raman spectroscopy (Muik, Lendl, Molina-Díaz, & Ayora-Cañada, 2005) has been also proposed.

Recent advances in Raman instrumentation have led to the development of portable Raman equipment. These portable systems, although they have a lower resolution than classic FT-Raman equipment, have contributed to increased industrial use of Raman spectroscopy, reflecting increased demand for online analysis (Xiaohua, Zhang, & Zou, 2008).

The aim of this study was to evaluate the potential of a portable Raman instrument with low resolution and chemometrics for determining quality parameters related to the oxidative state, such as the peroxide values, K_{232} and K_{270}, in virgin olive oil.

2. Material and methods

2.1. Samples and sample preparation

Four virgin olive oil samples freshly collected from the 2008–2009 harvest at the Instituto de Investigación y Formación

Agraria y Pesquera (IFAPA) center 'Venta Del Llano' (Mengíbar, Jaén) were used.

The samples consisted of two oil varieties, Picual (P) and Arbequina (A), in different proportions (P:A): 100:0, 60:40, 40:60 and 20:80. For each mixture, 32 glass containers of 30 ml of oil were produced, except for the last proportion where only 30 containers were produced. In total, 126 samples were available. These containers were subjected to a thermal oxidation process based on the Schaal Oven Storage Stability Test for olive oil (Frankel, July 1993; Malcolmson, 1992; Muik et al., 2007). This test involved placing the samples in an oven at a temperature of 100 °C for 189 h in order to extract typical oxidation compounds. Every 4 h, a container of each mixture was removed from the oven and left until it reached room temperature; the Raman spectra were then recorded.

2.2. Raman spectroscopy analysis

The instrument used was a portable Raman spectrometer model RH-3000 (Ocean Optics) with a low resolution; it had a 785 nm laser diode and was linked to an optical fiber that enabled measurements to be taken through a glass container. The Raman spectra were recorded from 200 to 2700 cm^{-1}, with a spectral resolution of 10 cm^{-1}. This measurement corresponds to the average value of the three scans performed for each sample. The laser diode of the instrument had an intensity range of 0–290 mW. Spectra were acquired with a laser intensity set at 190 mW, with an integration time of 10 s.

2.3. Reference chemical analysis

For all the samples, the references values for the peroxide (or index of peroxides [IP]) and the specific UV absorption at 232 nm (K_{232}) and 270 nm (K_{270}) were obtained following EU Regulations EEC/2568/91 and EEC/1429/92, which focus on the characteristics of olive oil and olive-residue oil and on relevant methods of analysis (EC Commission Regulation, 1991, 1992). The samples used in this study varied widely in oxidation level, as shown in Table 1, which presents the minimum and maximum values, the average values and the standard deviation for each of the chemical indices.

The peroxide value is the amount of peroxide in a sample (expressed in milliequivalents of active oxygen per kg fat) that causes the oxidation of potassium iodide. The sample, dissolved in acetic acid and chloroform, was treated with a potassium iodide solution. The liberated iodine was titrated with a sodium thiosulfate solution.

The K_{232} and K_{270} values were spectrophotometric measures for quantifying the UV absorption, at 232 nm (K_{232}) and 270 nm (K_{270}), of a solution of the oil in cyclohexane. Spectrophotometric analysis in UV provides information about the quality of the fat, the state of conservation of the oil and any deterioration occurring during the technological processes. High values of K_{232} and K_{270} indicate the presence of diene- and triene-conjugated systems.

2.4. Chemometrics

Two classic multivariate procedures were applied: the exploratory Principal Component Analysis (PCA) technique (Massart,

Table 1
Standard deviation, mean and min-max values of the reference values used in the study.

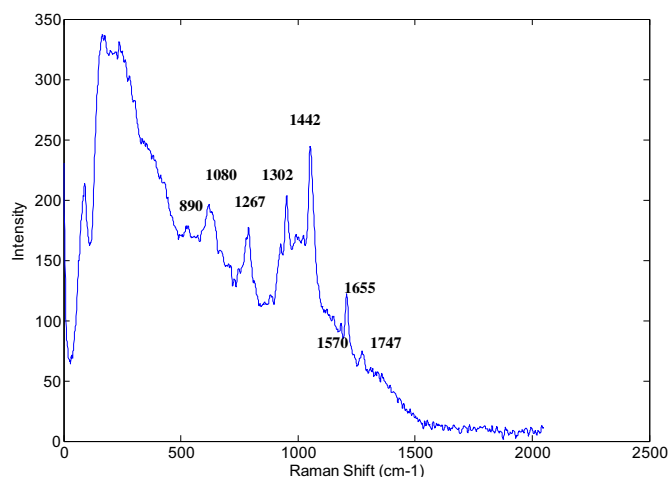|	Max	Min	Mean	SD
IP (meq O$_2$/kg)	74.59	3.68	22.22	10.57
K_{232} (UV absorption)	6.52	1.30	3.18	0.74
K_{270} (UV absorption)	1.02	0.09	0.48	0.20

Fig. 1. Typical Raman spectrum of a virgin olive oil obtained with the portable Raman instrument.

Vandeginste, & Buydens, 1998); and the supervised Partial Least Squares (PLS) method (Wold, 1988).

PCA involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables, called principal components. This technique was used to make an initial exploratory analysis of the data showing evidence of the presence of some aberrant data or outliers. PLS reduces the spectral data to a series of key variables (latent variables) that take into account both the spectral values as reference values. It aims to identify the underlying factors, or linear combination of the X variables, that best model the Y-dependent variables. PLS can deal efficiently with datasets where there are many variables that are highly correlated and involve substantial random noise.

PLS models were validated by using the 'leave-one-out' cross validation (LOOCV) and 'leave-more-out' cross validation (LMOCV) approaches, and by using external validation. For LOOCV, each individual sample was used in turn for validation. For external validation, 97 samples were used to build the calibration model while another group of external samples (22) was used to validate the calibration model. For LMOCV, instead of using each sample for validation, a group of samples was used. Here, because of the different mixtures available, each mixture was taken out in order to use it for validating the model constructed with the other mixtures.

The quality of the models was assessed using various statistical parameters: the coefficient of determination (R_2); the root mean squared error for calibration (RMSEC); the root mean squared error for cross-validation (RMSECV), which represents the model and the validation errors, respectively; and the residual predictive deviation (RPD). The model with the smallest RMSECV was assumed to have the best fit to the data, and the external validation set was then predicted. The RMSEP described the model's predictive ability based on the results of the external test set of 22 samples.

2.5. Software

All computations, chemometric analyses and graphics were performed using Matlab v7.4.0. (The Mathworks, Inc., Natick, MA, USA). For PCA and PLS, the PLS toolbox v. 4.11 (Eigenvector Research, Inc.) was used.

3. Results

Using FT-Raman, well-defined bands could be obtained that were associated with changes in oils during oxidation. Part of these
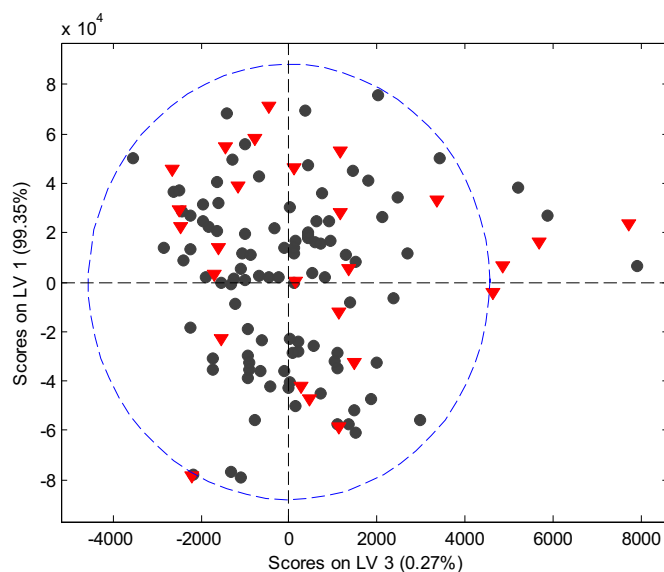

Fig. 2. LV1 vs. LV3 (calibration [circle] and validation [triangle] sets).

bands was in the region below 1800 cm^{-1}, about 1267 cm^{-1} (symmetric rock double bond in cis δ [= CH]), 1302 cm^{-1} (in-phase twist methylene), 1442 cm^{-1} (methylene scissoring mode of δ [CH2]), 1655 cm^{-1} (cis double bond stretching v (C=C) and 1747 cm^{-1} (ester stretching v (C=O). (Baeten, 1998)).

In the spectrum obtained from the portable Raman instrument, there is an important area below 800 cm^{-1} that does not match the FT-Raman spectra and has not yet been described in the literature.

Fig. 1 shows a typical Raman spectrum of a virgin olive oil obtained using the portable Raman instrument.

The dataset was initially split randomly into the calibration set and the test set. The calibration set consisted of 100 spectra and was used to build the model; the test set contained 26 spectra and was used to validate it.

In order to detect the presence of outliers, various tests were performed based mainly on applying different pre-treatments and using PCA and PLS factors. As an example, Fig. 2 shows the first latent variable vs the third one after centering the data; there are clearly a few samples outside the 95% percentile range. These samples (three samples for the calibration set, and four for the test set) were removed from the dataset. In addition, the Backward Variable Selection PLS (BVSPLS) method (Fernandez Pierna, 2009) was applied in order to select the most important spectral regions. The results (not shown) indicated that any particular region showed improved results compared with the models using the whole spectra.

Once the outliers had been removed, regression models for the three properties studied (peroxide value and UV extinction coefficients K_{232} and K_{270}) were constructed using PLS. Table 2 shows a summary of the PLS results obtained using LOOCV for the calibration set (97 samples) in terms of R_2 and RMSECV, and the

Table 2
A summary of the results obtained using leave-one-out cross-validation (LOOCV) procedures.

	(LOOCV)			
	R2	RMSECV	RMSEP	RPD
IP	0.91	2.36	2.57	4.11
K_{232}	0.88	0.36	0.37	2.00
K_{270}	0.90	0.05	0.08	2.50

R² = 0.911
7 Latent Variables
RMSEC = 1.9903
RMSECV = 2.3633
RMSEP = 2.5743
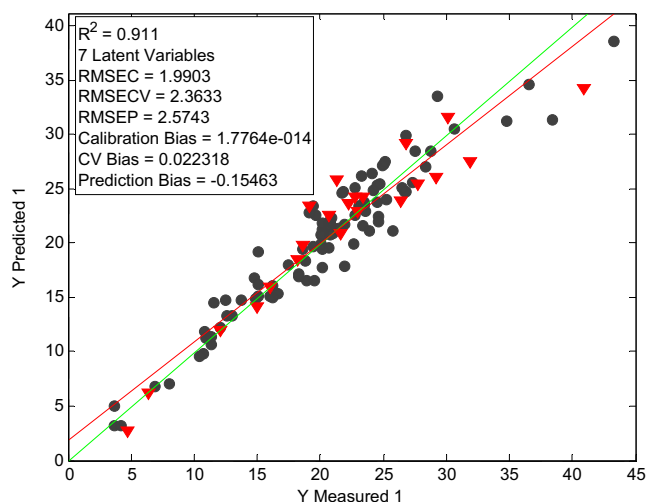Calibration Bias = 1.7764e-014
CV Bias = 0.022318
Prediction Bias = -0.15463

Fig. 3. Scatter plot of the actual Peroxide Value (IP) and predicted IP for calibration (circle) and validation (triangle) sets.

R^2 = 0.901
7 Latent Variables
RMSEC = 0.054476
RMSECV = 0.069165
RMSEP = 0.07851
Calibration Bias = -1.6653e-016
CV Bias = 0.00044252
Prediction Bias = -0.0088974

Fig. 5. Scatter plot of the actual K_{270} and predicted for parameter K_{270} for calibration (circle) and validation (triangle) sets.

prediction results for the validation set (22 samples) in terms of RMSEP and RPD.

For determining the peroxide values shown, the final PLS regression model (Fig. 3) for determining the peroxide value in olive oil was built using seven latent variables; it had an RMSECV of 2.36 and an RMSEP of 2.57. The RPD was 4.11, indicating that the model could be useful for initial screening purposes.

For determining the UV extinction coefficient K_{232}, the best PLS model was built with spectra without pre-treatment, using six PLS factors; it had an RMSECV of 0.36 and an RMSEP of 0.37. The model developed gave an RPD value of 2, so it could be used for the initial screening of olive oil. Fig. 4 shows the results for the external validation set. These results indicate that the model is consistent and gives a good prediction for a validation sample set.

For determining the UV extinction coefficient K_{270}, the PLS model was built using seven factors; it had an RMSECV of 0.07 and an RMSEP of 0.09 (Fig. 5). As in the case of K_{232}, the RPD of 2.50 suggested that this model could be used as a screening method. These results show that the model was consistent and gave the correct prediction for a validation sample set. It was more stable
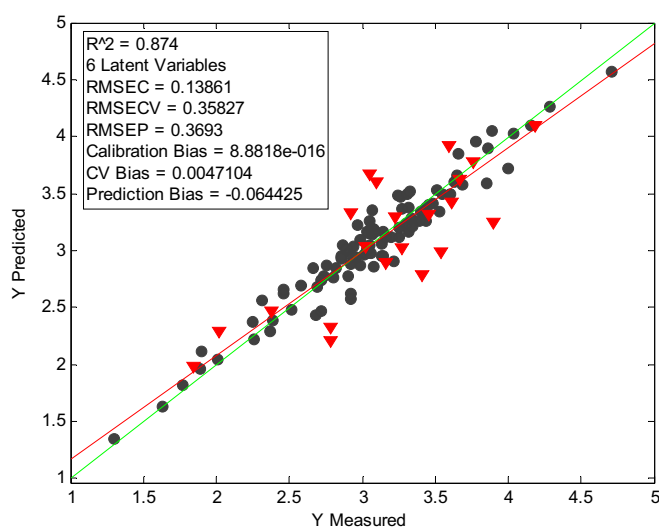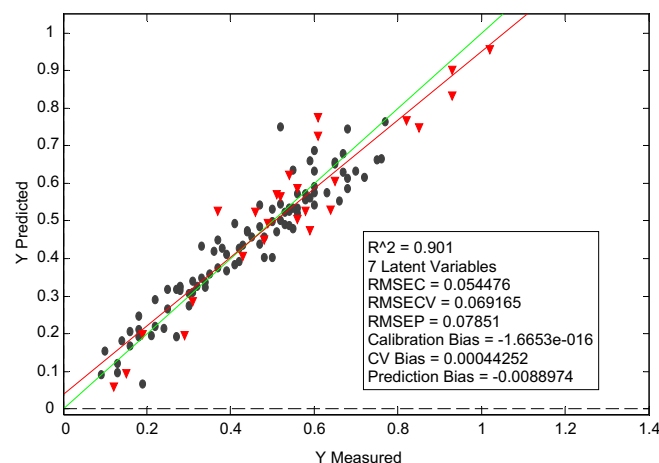
than the other models, as reflected in the lower RMSECV, and it had a slightly better predictive ability than other parameters (Sundaran, 2010).

As some samples were mixtures with different concentrations of the two main varieties, it was decided to apply a different procedure, LMOCV. Each mixture was considered as a class and was used to perform CV. The LMOCV procedure consisted of using each class as an external validation set. A calibration model with three classes was developed and was validated by the fourth class; this process was repeated four times, each time using a class for the validation, and ultimately obtaining an average model for the whole calibration model.

The results obtained (not shown) indicated that the models used for the validation with an independent group of samples gave prediction and RSMECV values similar to those obtained using the LOOCV procedure. Then, because this procedure caters for more robust models, it was decided to keep these models.

4. Discussion and conclusions

In laboratories, the analyses of large numbers of oil samples are usually performed daily in order to obtain information about the main quality parameters of olive oil. It is therefore important to have analytical methods available for the rapid and inexpensive assessment of oil samples, which is essential for correctly classifying oils during preparation and in their subsequent sale. This led us to explore the possibility of dispersive Raman spectroscopy technology for analyzing the various quality parameters of virgin olive oil. For this study, an effective method for determining these three quality parameters (peroxide value, UV absorption K_{232} and UV absorption K_{270}) was proposed using a portable Raman spectrometer and some chemometric techniques.

This work demonstrated the usefulness of the portable technology, in this case a low-resolution Raman spectroscope linked to a laptop computer for determining the oxidative degradation of lipids in virgin olive oil. There is also an important area below 800 cm^{-1} in the spectra obtained from the portable Raman instrument different from that obtained with the FT-Raman spectra. The information included in this area in the portable Raman has not been described yet in the literature and could be an interesting area for future research.

The results obtained with the constructed PLS models correlated well with those obtained in the laboratory. The best models were selected on the basis of the standard error of prediction and the

R^2 = 0.874
6 Latent Variables
RMSEC = 0.13861
RMSECV = 0.35827
RMSEP = 0.3693
Calibration Bias = 8.8818e-016
CV Bias = 0.0047104
Prediction Bias = -0.064425

Fig. 4. Scatter plot of the actual K_{232} and predicted for parameter K_{232} for calibration (circle) and validation (triangle) sets.

RPD values. In all cases, the models had an RPD value lower than 5, which can be considered acceptable for screening and for generate ranking data, especially for the IP parameter. From these results, and for performing calibration models with larger groups of samples, it would therefore be possible to use this method for monitoring online the quality control process for olive oil The main drawback of this technique is that it is indirect; it requires using the reference and official methodologies as a first step in order to calibrate the instrument. There are several clear advantages of this methodology, however. It is faster than the official method, the samples do not need any preparation, it can be used online (in a factory or directly in the field), there is no need for contact with the samples, and it makes it possible to perform real-time analysis.

In summary, the use of portable Raman spectroscopy, combined with some chemometric tools for analyzing the oxidative state of olive oil, is feasible for analysis at the time of preparation and as a screening technique for quality control relating to traceability and storage.

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