A portable Raman sensor for the rapid discrimination of olives according to fruit quality

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ABSTRACT

In the real marketplace, providing high-quality olive oil is important from the perspective of both consumers and producers. Quality control should meet all requirements in the production process, from farm to packaging. The quality of olive oil can be affected by several factors, including agricultural techniques, seasonal conditions, farming systems, maturity, method and duration of storage, and process technology.

The quality of oil produced also depends largely on the quality of the olives. In an enterprise aimed at producing high-quality oils, olives with defects ('ground'; i.e., fallen to the ground) should be separated from healthy fruit ('sound'; i.e., collected directly from the tree), because a very small portion of low-quality fruit can ruin the whole batch.

The fruit falls partly because of its maturation process, but also because of pest and disease attack or weather conditions (strong wind). Fruit that has fallen to the ground can suffer a rapid deterioration in quality.

Currently, the separation of fruits is based mainly on visual inspection or information provided by the farmer. These are not very reliable procedures. Methods using analytical parameters to characterize the oil, such as acidity and peroxide value, can be applied, but they require a lot of time and materials. Alternative techniques are therefore needed for the rapid and inexpensive discrimination of olives as part of a quality control strategy.

The work described here aims to determine the potential of low-resolution Raman spectroscopy for the discrimination of olives before the oil processing stage in order to detect whether they have been collected directly from the tree (i.e., healthy fruit) or not. Low-resolution Raman spectroscopy was applied together with multivariate procedures to achieve this aim. PCA was used to find natural clusters in the data. Supervised classification methods were then applied: Soft Independent Modeling of Class Analogy (SIMCA), PLS Discriminate Analysis (PLS-DA) and K-nearest neighbors (KNN). The best results were obtained using the KNN method, with prediction abilities of 100% for 'sound' and 97% for 'ground' in an independent validation set.

These results demonstrated the potential of a portable Raman instrument for detecting good quality olives before the oil processing stage, by developing models that could be applied before this stage, thus contributing to an overall improvement in quality control.

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1. Introduction

A series of important stages, from farm to packaging, are involved in producing good quality olive oil. The quality of the oil can be affected by several factors, including agricultural techniques used, seasonal conditions, farming systems, maturity, method and duration of storage, and process technology. The harvesting stage is a very important one in the production of good quality olive oil. When harvesting olives, it is important to check the state of ripeness in order to ensure that, during the oil processing stage, the extraction yield and oil quality are optimal. Harvesting can have an important influence on the quality of the oil produced, as well as on the production costs and therefore on the olive farm economy. In terms of quality, there are three main issues to consider when harvesting olives: the collection time, the origin of the fruit, and the method of collection [1].

Under normal conditions, variety and agronomy have no clear influence on the quality regulated. Any variety and a range of agronomic conditions can provide oils that can be classified as extra virgin, if obtained from healthy olives collected at the optimum

and appropriate time and put through the correct milling process [2,3].

A delay in harvesting olives can lead to the natural fall of the fruit (over-ripe olives), accelerated by wind; the degree to which this happens depends on the variety [4].

The fruit on the ground can suffer from a variety of defects caused by diseases, pests and ground frost, reducing the quality of the oil subsequently produced. In an earlier study, it was shown that some quality indexes for oil were not affected by frostbite, but the oil became less stable and there were some sensory changes.

When olives are on the ground for several days, this leads to a deterioration of the fruit pulp which, in turn, adversely affects oil quality. This loss of quality results in increased acidity, a higher peroxide index and a deterioration in the sensory characteristics of the oil, as demonstrated in several previous studies [5].

After harvesting, the most important factor affecting fruit quality is storage prior to production, which, if inadequate, can lead to higher acidity and peroxide values and promote enzymatic activities, leading to deterioration in sensory characteristics [6].

For all these reasons, it is very important to collect, transport and process healthy fruit separately from defective fruit, as small amounts of defective fruit can significantly alter the organoleptic characteristics of oils obtained from healthy fruits and thus reduce their quality. Fruit that has the potential to provide good quality oils (i.e., healthy olives picked from the tree) must follow a different route from the outset – from collection on the farm and factory reception and milling process to storage of the oil produced.

When olives arrive at the factory, there should be a control check whereby their quality is continuously evaluated. The oil production sector is making a major effort to improve the quality of virgin olive oil, but sometimes there is inadequate control and verification at the point when olives first enter the factory. In most cases, quality control at this stage is based on visual observation of the olives or information provided by the farmer. Thus, the method of olive harvest is an important checkpoint in the process of producing high quality olive oils, and alternative techniques are needed for the rapid and inexpensive discrimination of olives at this stage, as part of a quality control strategy. An important first step, therefore, lies in the quality control of the fruit at the factory reception stage and the classification of olives at the start of the production process, and the need to avoid mixing of olives of different qualities by using fast, safe and clean analytical methodologies.

The characterization of olive fruit by means of optical technologies has been developed mainly by NIR and Raman spectroscopies. With this purpose, NIR technology has been applied to the direct analysis of intact olives for the determination of fat content and moisture, including in some cases other parameters like free acidity, fatty acid composition, olive variety and fruit traits [7–13]. In other contributions, NIR spectra have been collected after grinding of olive fruits, in the resulting pulp [14–17]. On the other hand, Raman spectroscopy has been proposed for the determination of several compositional and quality parameters in olives after grinding. Thus, fat and moisture [18,19], free acidity [20], carotenoids and phenolic compounds [18] have been evaluated.

Concerning olive oil analysis, Raman spectroscopy has been mainly applied to authentication purposes, to classify PDO olive oils [21,22] and to detect adulteration with other low price oils [23–34]. This technique has been also applied to the determination of the oxidative degradation [35], free acidity [36,20] and the characterization of antioxidant olive oil biophenols [37].

To our knowledge, there are only two contributions dealing with the evaluation of fruit quality, from a point of view of origin of fruit (tree or soil) or status (sound or affected by some disease, frostbite or fermented). For this purpose, NIR [38] and Raman [39] spectroscopies have been applied, achieving a high classification capability.

Fig. 1. System designed for this work in order to take Raman measurements.

In this study, a portable low-resolution Raman spectroscopy method was applied for the discrimination of olives according to their 'ground'/'sound' origin. The work aimed to ensure the quality of olives before they entered the oil production process. In an earlier study, some applications of this technique for determining the quality parameters in olive oil oxidation [40] were reported. This technique was based on using an instrument that was small, inexpensive and easily installed for checking the quality of oil production process.

2. Materials and methods

2.1. Samples and sample preparation

One hundred ninety-two olives samples from 11 Spanish varieties, mainly Picual, were harvested and analyzed from October to March over 2 years (the 2009–2010 and 2010–2011 harvests) at the Instituto de Investigación y Formación Agraria y Pesquera (IFAPA) center 'Venta Del Llano' in Mengíbar, Jaén, Spain.

The samples included 86 samples of 'sound' olives picked from the tree and 106 olives collected from the ground, including frozen and fermented olives. Table 1 shows, for both harvests, the quality parameters for these samples, including humidity and oil content, as well as the quality parameters of the oil extracted in a laboratory mill [41]: free acidity, peroxide value, and spectrophotometric absorptions at 232 nm (K_{232}) and 270 nm (K_{270}).

Before the Raman measurements, the olives went through a system which was designed for this work in order to take measurements of several probes with different instruments simultaneously in the same experience (NIR, Raman and VIS measurements). This system is a roller mill that had a circular stainless steel component (4 cm in diameter) linked to the optical fiber probe Raman equipment.

All the olives entered the mill through a hopper and passed through the circuit where the Raman measurement was taken from the olive paste using a glass window (2 mm thick).

Fig. 1 shows the structure that is designed to take the Raman steps.

2.2. Raman spectroscopy analysis

The instrument used was a portable Raman spectrometer model RH-3000 (Ocean Optics); 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

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

	Harvest 2009/2010				Harvest 2010/2011			
	Max	Min	Mean	SD	Max	Min	Mean	SD
Humidity (%)	53.07	40.69	45.77	2.83	61.82	40.51	48.58	4.65
Oil content (%)	32.52	17.94	26.02	2.89	30.09	10.09	21.45	3.57
IP (meq02/kg)	7.5	0.6	3.42	2.09	22.37	0.91	5.42	3.40
K_{232} (UV abs.)	1.72	1.28	1.49	0.11	2.74	1.23	1.56	0.25
K_{270} (UV abs.)	1.24	0.1	0.19	0.21	1.34	0.09	0.17	0.13
Acidity (%oleic ac.)	2.06	0.21	0.99	0.58	12.69	0.17	1.55	2.02

$2700 \, cm^{-1}$, with a spectral resolution of $10 \, cm^{-1}$. 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, and were the average of 10 scans, resulting in an acquisition time of 5 min.

The equipment used a laptop, with the physical dimensions of 20 $(L) \times 18 \, (A)$ and weighing about 4 kg, as a preliminary simulation of the measurements that could be taken by coupling this equipment in the factory mill, enabling it to be used during the production process.

2.3. Chemometrics

The first step involved classification, which was carried out using an exploratory analysis with Principal Components Analysis (PCA) in order to find trends that would group the samples based only on their spectral characteristics. PCA is an unsupervised technique that reduces the dimensionality of the original data matrix, retaining the maximum amount of variability. It is an important tool for in the good exploration of data [42].

In the second step, three supervised classification methods were used: Soft Independent Modeling of Class Analogy (SIMCA) [43], PLS Discriminant Analysis (PLS-DA) [44] and K-nearest neighbor (KNN) [45].

SIMCA classifies samples/spectra based on their similarities in a principal components space. A principal components model is built for each available class. For each modeled class, the mean orthogonal distance of training data samples from the line, plane or hyper-plane (calculated as the residual standard deviation) is used to determine a critical distance for classification. Based on these distances, the classification of a new set of samples is obtained by adjusting each of these samples to each model and deciding, at a 95% confidence level, if the sample belongs to the corresponding class or not. In this model, the distance of a point from a class was determined by the out-of-space distance; that is, by the Euclidean distance of the point from the subspace spanned by the k principal components used to model the class [46].

PLS-DA is performed in order to sharpen the separation between groups of observations, by rotating PCA components so that a maximum separation among classes is obtained, and to understand which variables carry class-separating information. PLS-DA consists of a classical PLS regression where the response variable is a categorical one (replaced by the set of dummy variables describing the categories) expressing the class membership of the statistical units [47].

KNN is a method for classifying objects based on the closest training examples in the feature space. By comparing the distances between the unknown object and the training samples, whose closeness is known in advance, KNN with shortest distances is selected, and the classification type represented by a simple majority of the KNN is assigned to the known object. The Euclidean distance is the most common algorithm used for this purpose [48].
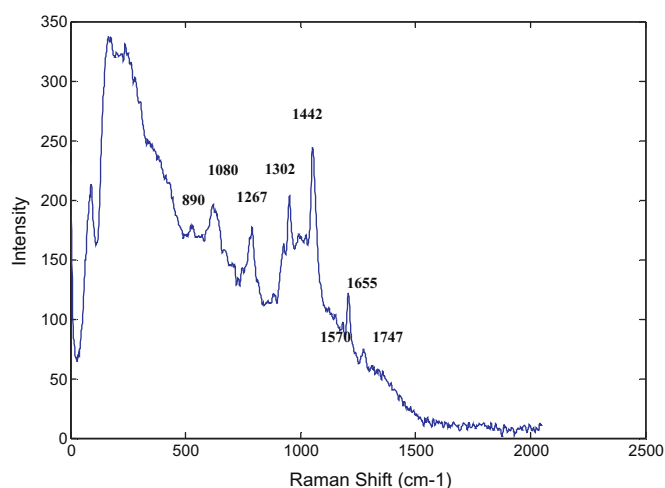

Fig. 2. Raman spectra of oil olive using dispersive Raman spectrometry.

2.4. Software

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

3. Results and discussion

Figs. 2 and 3 shows characteristic dispersive Raman spectra of olive oil, 'ground' olive paste and 'sound' olive paste. In the dispersive Raman spectra, the same bands as in the FT-Raman spectra can be observed. The major bands of virgin olive oil are at 1267 (in plane
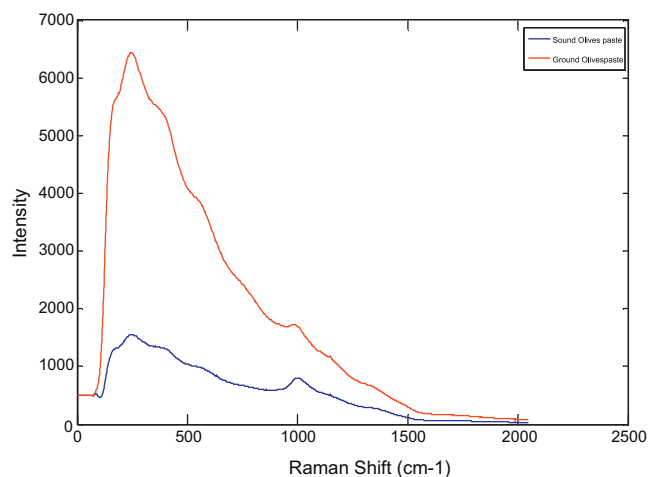

Fig. 3. Raman spectra of sound and ground olive paste using dispersive Raman spectrometry.
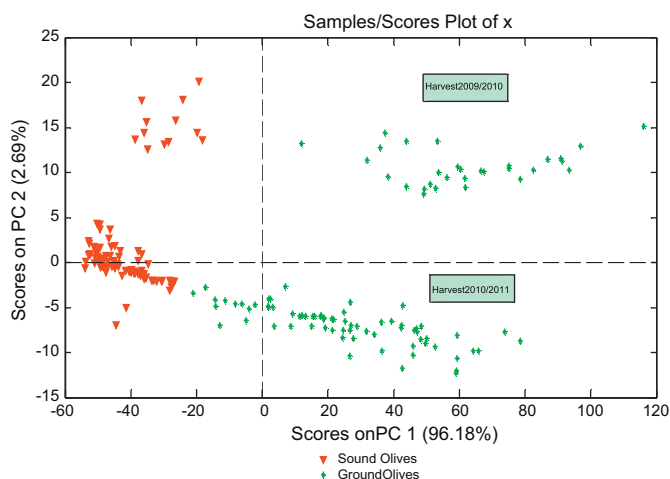
Fig. 4. PCA1 vs PC2 for calibration and validation set.

δ (=C—H) deformation in unconjugated *cis* double bond) 1302 (in-phase methylene twisting motion), 1442 (δ(CH$_2$)) and the band at 1655 (ν(C=C)), dominate the spectra. The band at 1747 cm^{-1}, which is assigned to the ν(C=O) ester vibration, can be found in both oil and the olive spectra [49,50].

The main difference in the spectra of the olives and olive oil is the high fluorescence background that characterizes the olive spectrum that overlaps with the typical oil bands. The difference between the spectra of the different kinds of olives ('ground' and 'sound') is also the fluorescence that is lower in the 'sound' olives and higher in the 'ground' olives or those olives with some type of damage (fermented and frostbite). This fluorescence is probably caused by the destruction of cell membranes and alterations in vegetable matter, such as oxidation and enzyme reactions. The olives are collected throughout the whole season (October–March) so that case the olives belong to all possible ranges of maturity indexes. In such a way, there are healthy and ground olives from green to black, therefore the color is not the factor that differentiates these classes.

Apart from this fluorescence phenomenon, there are several variations of the relative intensity, little change in band positions, and small changes in the spectral contours between classes [39].

To define the categories in the classification, the unsupervised PCA method was used. Data pretreatment comprised only auto-scale, which is a common preprocessing method that uses mean-centering followed by the division of each column (variable) by the standard deviation of that column. This approach is valid for correcting different variable scaling and units if the predominant source of variance in each variable is a signal rather than noise. Under these conditions, each variable will be scaled so that its useful signal has an equal footing with the signal of other variables.

Previously, the dataset had initially been randomly split into a calibration set and a test set. The calibration set consisted of 142 spectra and was used to build the model; the test set contained 50 spectra and was used to validate it.

The PCA model was calculated for seven principal components, with an explained variance of 96%. Fig. 4 shows the scores for the first two principal components of the model, where a separation of olives samples into different groups can be observed; the first PC shows the separation of samples according to 'sound' or 'ground', whereas the second component shows the separation of olives samples according to the period harvest to which they belong. These results show that the fruits could be differentiated according to harvest year, as reported by Gurdeniz et al. [51].

The preliminary exploratory analysis of data showed that Raman spectroscopy can see the grouping of olives according to their spectral characteristics and can be used for supervised classification

Table 2
Calibration and validation results in terms of classification ability given in percentage of PLSDA, SIMCA and KNN classification.

	SIMCA		PLS-DA		k-NN(3)	
	Cal set	Val set	cal set	Val set	Cal set	Val set
Sound olives	98%	100%	100%	92%	100%	100%
Ground olives	90%	73%	97%	100%	98%	97%

with two different classes or categories. This would allow a separation of the olives before their production, with 'sound' samples prepared separately from 'ground' samples as they enter the oil production process.

The next step involved multivariate classification, using three supervised methods: SIMCA, PLS-DA and KNN. The SIMCA and PLS-DA models were constructed with seven main latent variables for both classes. In the KNN method, the classification error depended on the number of the nearest neighbors chosen for the analysis (k) [52]. The best number of K neighbors was selected using a leave-one-out procedure [53], with K values between 3, 5 and 7. For $K = 3$, the recognition and classification abilities were 100% for the discrimination. However, for $K = 5$ and 7, the prediction abilities provided with KNN were 97% in both cases.

Table 2 provides a summary of the three model results for the calibration and validation sets in terms of correct classification ability (in percentage).

The linear classifiers (SIMCA, PLS-DA) gave good results for discrimination between olive classes, with a low error of classification, but KNN was found to be the most effective classification technique.

The most important point is that KNN is a non-parametric method where the quality of predictions depends on the distribution of some classes. Thus, the method can correctly classify objects, although classes are not linearly or quadratic separable. The KNN method sets irregular boundaries between classes, while the parametric methods such as SIMCA and PLS-DA depend on a distribution determined by the statistical limits (Bayesian theorem) to establish the boundaries between classes. In this study, the samples were highly clustered and therefore the KNN method, which uses distances to the nearest neighbor to classify the samples, was the most appropriate method.

The results obtained using the KNN method correctly classified all 'sound' olives samples in external validation, and only one 'ground' olives sample was misclassified; the similar values in classification and prediction indicate that the model is fairly stable. These results showed that the most appropriate classification technique for the classification task was the KNN method, which tended to produce more robust results, although good classification ability was obtained with the PLS-DA and SIMCA models.

Finally, with the data we had from different years, and using SIMCA and PLS-DA methods, we tried to use the data from one year to calibrate olive samples and from another year to do the sample validation, but the results were not satisfactory (not shown). The differences between different harvests were directly related to sources of variation not included in the PCA; there were large differences between samples and environmental conditions (temperature, humidity and rainfall), the harvesting period differed for the two consecutive harvest years and the composition (fatty acid profile) also changed. Geographical origin and harvest year are known to have a significant influence on the fatty acid profile of olive oil [54,55]. An earlier study on Cornicabra virgin olive oil revealed significant statistical differences in quality indexes, major fatty acids and sterol compositions in relation to year of production [56]. The data included sources of variation that were not completely eliminated by preprocessing, so it is necessary to establish a process for the transfer of calibration models in subsequent years because of these variations among different harvests.

In this study there were only 2 years of data, so prediction was difficult. More data from different years are needed in order to obtain reliable and robust prediction equations [11,57].

The combination of portable low-resolution Raman spectroscopy and multivariate discriminant analysis in olives could be an important tool for checking the quality of olives before they enter the oil production process. This is necessary to ensure good quality oil by creating more controlled production processes and saving much expense by avoiding unwanted mixing.

This method has many advantages. It is rapid and inexpensive because it does not need sample preparation. Also, it is non-destructive and uses no chemicals, and is therefore environmentally friendly. Apart from these advantages, this technique allows the possibility of coupling optical fibers, which can be directly inserted into the process or connected to a flow-cell through which the sample can be diverted from the production line. This would allow complete control of the quality of the oil before, during and after the processing of the olives.

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