PAPER

RAPID DETERMINATION OF CRUCIAL PARAMETERS FOR THE OPTIMIZATION OF MILLING PROCESS BY USING VISIBLE/NEAR INFRARED SPECTROSCOPY ON INTACT OLIVES AND OLIVE PASTE

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ABSTRACT

The aim of this work is the application of vis/NIR spectroscopy in order to correlate spectral data acquired on intact olives just before or in pastes during the milling process, to the crucial parameters for the optimization of the process. Physical measurements (i.e. yield point force and total deformation energy) were performed on the olive samples; after the fruit were crushed for olive paste production, chemical analysis (moisture, oil and sugars content) and maturity index (MI) were measured and correlated to the spectral data. The obtained results were encouraging for chemical, texture and MI parameters, demonstrating the feasibility of real-time prediction of important indices for the milling plant settings.

Keywords: chemometrics, milling plant, olive pastes, optical analysis, ripening, texture

1. INTRODUCTION

In olive fruits, physical parameters such as weight, color, pulp-to-stone ratio, and texture, and chemical parameters such as oil content, composition of fatty acids, levels of polyphenols, tocopherols, and sterols, change during the ripening process (BELTRÁN *et al.*, 2004; YOUSFI and GARCÍA, 2005). These features are of high commercial importance as they influence the olive oil shelf life. In fact, olive oils derived from ripe fruit results in a less stable shelf life due to an increase in polyunsaturated fatty acids and a decrease in total polyphenol content (CAPONIO *et al.*, 2001; MARSILIO *et al.*, 2001; MORELLO *et al.*, 2004; BELTRÁN *et al.*, 2005). Phenolic compound content is considered an important parameter in the evaluation of virgin olive oil quality because of phenols contribute to oil flavour and aroma. Phenols also, protect oil from autoxidation. In addition, olives processed at an over ripened stage may result in unstable oil during shelf-life owing to the low phenolic compound content (CHERUBINI *et al.* 2009). Early-harvested fruits produce oil with high polyphenol concentrations and a degradation may occur during the processing and shelf-life. Degradation may result in variations in nutritional quality of the product since antioxidant content decreases and free radical content increases. This can lead to sensory modification and to an appreciation reduction of the product, since aroma, colour, taste and flavour attributes change and some unpleasant sensory attributes may occur (ZANONI *et al.*, 2005; DIRAMAN and DIBEKLIOGLU, 2009).

For these reasons, the influence of harvesting time on the quality stability and sensory characteristics of olive oils is of crucial interest for the growers. An investigation of the olives' characteristics before the milling process could allow the quality of the oil output to be controlled. Better monitoring of the oil production process also depends on controlling the paste, the intermediate product between the olives inlet in the process and the oil outlet from the mill, to establish correlations among olives, paste and oil. Nowadays, established methods for quality assessment are generally based on tedious and time-consuming techniques that are impractical for processing a large number of samples. Therefore, there is a lack of real-time information during the milling process in order to monitor the operating parameters continuously. Hence, there is a strong need in the modern oil industry for a simple, rapid, and easy-to-use method for (i) objectively evaluating the level of olive ripening and the characteristics of the paste, (ii) early detection of possible failure, (iii) permanent monitoring of the production process, and (iv) assessment of oil process at any desired time in order to control the oil quality deriving from the process. The rapid analysis of olives during consignment and paste during the process would allow preliminary separation of homogeneous classes and a more efficient decision-making process about the destination of lots. Therefore, the sector could be helped by optical non-destructive and rapid applications for olive oil chain optimization.

Despite there being some works regarding the application of NIR spectroscopy for olive oil analysis (ARMENTA *et al.*, 2010), few works about the characterization of intact olives and olive pastes using spectroscopy can be found. FERNÁNDEZ-ESPINOSA (2016) combined chemometric analysis with NIR spectroscopy to monitor quality parameters in intact olives to determine the optimal harvesting time; SALGUERO-CHAPARRO *et al.* (2013) used NIR spectroscopy for the online determination of the oil content, moisture and free acidity parameters in intact olive fruits; and BELLINCONTRO *et al.* (2012) studied the application of a portable NIR for on-field prediction of phenolic compounds during olive ripening. CAYUELA *et al.* (2009) determined the effectiveness of a portable NIR spectrometer for the prediction of oil free acidity, oil yield, oil content in fresh fruit, oil content in fruit dry matter and fruit moisture content, analyzing intact fruits.

For olive oil fruits, textural properties could be used as indices of ripeness to meet requirements for the technological processes and oil characterization. Texture-measuring instruments are time-consuming, and there are high costs for the devices. The parameter setting of the process operations (i.e. crushing, malaxation, and extraction using decanter) is highly influenced by ripeness degree and olive texture. Therefore, there is nowadays a lack of available information that could allow feedback-based real-time control of the plant, for better oil quality and the reduction of process wastes. BEGHI *et al.* (2013) and GIOVENZANA *et al.* (2015) conducted preliminary studies on the laboratory scale of the capability of portable visible/near infrared (vis/NIR) and NIR spectrophotometers to investigate different textural indices for the characterization of olive fruits entering the milling process.

On olive paste, GARCÍA SÁNCHEZ *et al.* (2005) tested the suitability of NIR and NMR spectroscopy for the determination of moisture and fat contents, while GALLARDO *et al.* (2005) used near-infrared spectroscopy for the real-time determination of moisture and fat content in olive pastes and solid-liquid wastes. HERMOSO *et al.* (1999) examined the applicability of NIR spectroscopy for the measurement of oil content and humidity in olive pomace.

The challenge of producing high-quality olive oil is of great concern, and the selection of olive fruit with defined properties that ensure positive attributes in olive oil is foreseeable using vis/NIR and NIR spectroscopy in olive oil production (ARMENTA *et al.*, 2010). The olive oil sector is increasingly becoming more interested in the implementation of quality control systems in a mill industry context. However, limited work has been undertaken about the implementation of vis/NIR and NIR spectroscopy directly in the mill. Research regarding the application at the factory level is desirable, mainly concerning the definition of parameters related to the on-line spectrum acquisition (SALGUERO-CHAPARRO *et al.*, 2012) and the testing of compact and low-cost devices also usable for the SME of the sector. Hence, in this study, the applicability of a vis/NIR low-cost and compact system was tested on intact olives, acquired just before the milling process, and on olive pastes, in order to correlate spectral data to the crucial parameters (yield point force, total deformation energy, moisture, oil and sugars content, and maturity index) for the optimization of the milling process. The predictive models calculated here could be applied in future on-line for the rapid monitoring of crucial parameters for the enhancement of extraction oil yield and the control of semi-finished products of the process.

2. MATERIALS AND METHODS

Two olive varieties were considered: Frantoio and Moraiolo (~50% of each). These varieties are typical of the Tuscan hills, in the province of Florence, Italy, and are cultivated in several European olive growing areas.

2.1. Sampling

Sampling was performed in 2013, from September to December, to obtain a wide sample variability. The sampling was conducted by hand once a week at 08:00 a.m. on a selected number of plants (about 10), belonging to the two different cultivars selected for the experiment. The olives were picked along plant circumference at approx. 1.7 m from the soil. A total of 54 olive samples (400-500 g), which presented no infection or physical damage, were quickly transported to the laboratory to be analysed and for each sample a homogeneous batch of olives (i.e. approx. 300 g) was selected. For each sample, 30 olive fruit vis/NIR spectra were acquired, for a total of 1620 optical measurements. Using a portable spectrophotometer, two spectral measurements were taken in reflectance mode on individual fruit along their equatorial region and averaged. All the olives composing a sample were crushed using a laboratory crusher (Zeutec, Rendsburg, Germany), obtaining olive paste. Five acquisitions were performed for each paste sample through disposable laboratory cuvettes (12.5 mm x 12.5 mm x 45.0 mm).

2.2. Texture analysis

The firmness was assessed using a laboratory dynamometer (MTS Criterion® Systems, Eden Prairie, MN, USA) providing time-series data of product compression, allowing the calculation of textural attributes from load-extension traces. Table 1 shows the settings for the compression test. The measurements were carried out using a 5 cm diameter plate coupled with a load cell of 100 N. The sample was placed under the plate, without holder, with the major axis perpendicular to the direction of the compression test.

Table 1. Settings for the compression test.

Settings	Units	
Gage adjustment speed	mm s^{-1}	0.2
Gage adjustment load	N	0.6
Experimental speed	mm s^{-1}	1.0
Date acquisition rate	Hz	400.0
Break Threshold	N	5.0
Break sensibility	%	50.0
Strain end point	%	80.0

The textural parameters obtained from the elaboration of the load-extension curve were as follows:
- Yield point force (N): the maximum force recorded during the elastic deformation phase;
-Total deformation energy (mJ): the work required for complete compression of the olive pulp.
In Figure 1 is shown an example of load-extension curve obtained from the compression test for the identification of yield point force (N) and total deformation energy (mJ).

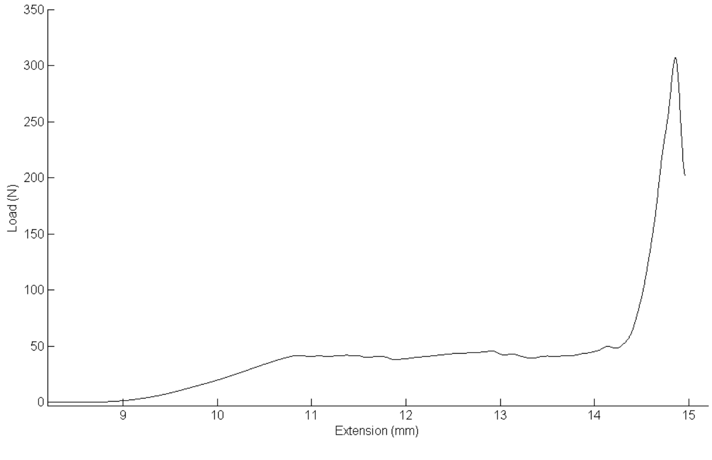

Figure 1. Example of load-extension curve obtained from the compression test.

2.3. Chemical analyses

The olive paste was used for the following chemical analyses.

2.3.1 Water content

The water content was measured on olive paste by heating 60 g of sample in an oven at 105°C until reaching constant weight (CECCHI *et al*. 2013). The results were expressed as moisture content (%).

2.3.2 Oil content

The total oil content was determined on 5 g of dried olive paste (see the oven method above). Samples were extracted with hexane in an automatic extractor (Randall mod. 148, VELP Scientifica, Milan, Italy), following the method of CHERUBINI *et al*. (2009). The results were expressed as oil content on dry matter basis (g kg^{-1}).

2.3.3 Sugar content

8 g of olive paste was cold extracted (6 ± 2°C) with distilled water in a 200 mL flask for 2 hours. The content of the flask was filtered on paper, and 10 mL of the obtained solution was diluted with water in a 20 mL flask. The measurements were performed by analyzing the obtained solution with an enzymatic method using an automatic ChemWell analyzer (Awareness Technology, ChemWell 9210, Palm City, FL). Three enzymatic kits were used to measure, respectively, (i) the sum of two monosaccharides contents, namely glucose and fructose; (ii) the sum of disaccharide sucrose content with glucose and fructose contents; (iii) the mannitol content. All kits were purchased from R-Biopharm (Darmstadt, Germany). The measurements were performed by means of external calibration standards: fructose and glucose (purity > 99%, Sigma Aldrich SrL, Milano, Italy), and mannitol (purity > 98%, Sigma Aldrich Srl, Milan, Italy). The results provided by the instrument were expressed in g L^{-1}; they were also converted in sugar content on dry matter basis (g kg^{-1}) as the average of two readings, carried out for each sample. The sucrose contents were determined by multiplying by 0.95 the difference between the sum of glucose, fructose, sucrose contents and the sum of glucose and fructose contents.

2.4. Maturity Index

MI was based on visual assessment according to UCEDA and FRIAS (1975). A sample of 100 drupes was classified into eight different classes according to pulp and skin colors. The values ranged from 0 (skin color deep green) to 7 (skin color black with all the flesh purple to the stone).

2.5. Visible/Near Infrared device

Spectral acquisitions were performed on samples (olives and pastes) using an optical portable system (JAZ vis/NIR spectrophotometer, OceanOptics, Inc., Dunedin, FL, USA) operating in the 400-1000 nm wavelength range. The system is composed of five components: 1) vis/NIR lighting system; 2) fiber-optic probe for reflection measurement; 3) spectrophotometer; 4) hardware for data acquisition and instrument control; 5) power battery.

Spectra were acquired in reflectance mode: light radiation was guided to the sample through a Y-shaped, bidirectional fiber optic probe (OceanOptics, Inc., Dunedin, FL, USA). A Y-shaped fiber allowed light from a halogen lamp to be guided to illuminate the sample while simultaneously collecting the radiation coming from the berry and guiding it back to the spectrophotometer. The tip of the optical probe was equipped with a soft plastic cap to ensure contact with sample skin during measurements, minimizing environmental light interference. White background and black background were acquired before each acquisition session. The integrated spectrophotometer was equipped with a diffractive grating for spectral measurements, optimized in the range 400-1000 nm, and a CCD sensor with a 2048 pixel matrix, corresponding to a nominal resolution of 0.3 nm. Each spectrum corresponds to the average of five spectral acquisitions.

2.6. Data analysis

The data acquired were processed using chemometric techniques to extract maximum data information. Chemometric analysis was performed using The Unscrambler software package (version 9.8, CAMO ASA, Oslo, Norway). Different pre-treatments were applied to the vis/NIR spectra in order to maximize the model accuracy. Moving-averaged smoothed spectra (15 point-wide window corresponding to a window of 4.5) and multiplicative scatter correction (MSC) were applied before building the calibration models. These pre-treatments were applied to improve the signal-to-noise ratio in order to reduce the effects caused by the physiological variability of olive and paste samples.

The olive samples available were used for the calculation of a chemometric regression model for reference parameters by using partial least squares (PLS) regression analysis. The vis/NIR spectra acquired on the single olives were correlated to the textural parameters (one-to-one correlation) using the PLS regression algorithm, while the 30 olive spectra representing each experimental sample were averaged, and the resulting mean spectrum was correlated to the chemical indices and MI. Similarly, the olive paste samples were also correlated to chemical reference data and to MI to create PLS models.

To evaluate model accuracy, the statistics used were the coefficient of determination in calibration (R^2_{cal}), coefficient of determination in cross-validation (R^2_{cv}), root mean square error of calibration (RMSEC), and root mean square error of cross-validation (RMSECV). Calibration models were evaluated using a cross-validation leave-more-out procedure using five cancellation groups randomly selected. With a small number of cancellation groups, the resulting training sets are very different, and the measure of the predictive ability is not optimistic, possibly pessimistic (CASALE *et al.*, 2008). Moreover, the Ratio Performance Deviation (RPD) value was calculated. RPD is defined as the ratio between the standard deviation of the response variable and RMSECV. RPD values below 1.5 indicate that the calibration is not useful. When the RPD value is higher than 2, quantitative predictions are possible. Between 1.5-2.0, the algorithm has the possibility to distinguish between high and low values (WILLIAMS and NORRIS, 1987). The best model calibrations were selected based on minimizing the RMSECV and maximizing the RPD.

3. RESULTS AND DISCUSSIONS

The average spectra of both olives and pastes showed three main peaks: around the 670 nm band, corresponding to the chlorophyll absorption peak (MCGLONE *et al.*, 2002); around the 730 nm band, equal to the maximum reflectance peak; and the 780 nm band, representing the third overtone of OH bond stretching (CLEMENT *et al.*, 2008).

Changes in spectra reflected modifications in chemical parameters. For a better visualization, two arbitrary classes based on oil content (a, Level 1 ≤ 358.3 g kg^{-1}; and Level 2 > 358.3 g kg^{-1}) and on moisture content (b, Level 1_m ≤ 53.5 %; and Level 2_m > 53.5 %) were created to show changes in the optical data. The average vis/NIR spectra acquired on intact olives are grouped into two classes by oil and moisture content, and are shown in Figures 2a and 2b, respectively.

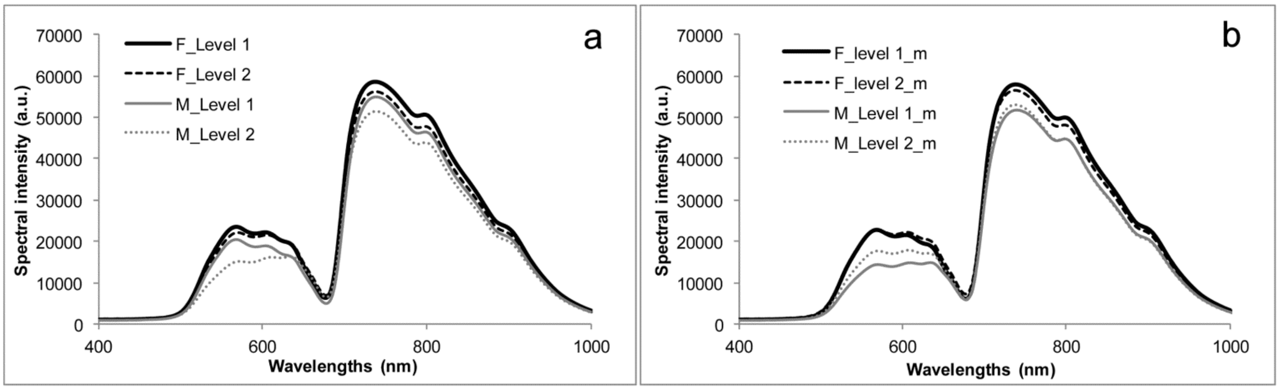

Figure 2. Average vis/NIR smoothed spectra of intact olives, Frantoio (F) and Moraiolo (M) cultivar, grouped in two classes of oil content (a, level 1 ≤ 358.3 g kg^{-1}; level 2 > 358.3 g kg^{-1}) and in two classes of moisture content (b, level 1_m ≤ 53.5 %; level 2_m > 53.5 %).

Vis/NIR spectra exhibited differences for both the cultivars among the two classes, with relevant changes particularly in the visible range occurring from Level 1 to Level 2 for Moraiolo cultivar. The spectra of Moraiolo cultivar showed higher absorption in the visible range compared to Frantoio cultivar. This is linked to anthocyanin pigmentation during ripening from green berries to the completely black-pigmented olives, which leads to a strong decrease in reflectance in the visible band associated with the anthocyanin absorption peak centered on 540 nm. This different behavior in the spectral reflectance is confirmed by the maturity index (UCEDA and FRIAS, 1975). This parameter is based on the subjective evaluation of the progressive pigmentation of olive skin and flesh. The index is the main reference utilized by the olive oil chain to characterize the olive ripeness degree at the mill or on the tree (GARCÍA *et al.*, 1996), and by scientists to identify the ripeness levels of olives for harvesting all over the world, e.g. in Israel (DAG *et al.*, 2011) in Spain (GUTIÉRREZ *et al.*, 1999); BELTRÁN *et al.*, 2005) in Tunisia (MRAICHA *et al.*, 2010), and in Italy (SINELLI *et al.*, 2008). When the olives are fully ripe, the MI reached values equal to 6 on Barnea and Souri cultivars (DAG *et al.*, 2011) and 7 on Chemlali cultivar (MRAICHA *et al.*, 2010). Instead, for the two analyzed cultivars, the MI achieved at harvest maximum values of 3.39 for Moraiolo cv and 2.31 for Frantoio cv. Frantoio remains substantially green even when fully ripe, hence the spectra in the visible range not showing evident changes between the two classes considered.

In Figure 2, as expected, an opposite trend can be noticed between spectra grouped by oil content and by moisture content; the oil accumulation in the fruit caused greater absorption in the spectra of both cultivars, which results in lower average values of reflectance in the whole spectra of the class Level 2. In particular, this behavior is evident for the Moraiolo cv, due to an increase of oil content and a simultaneously external pigmentation of the berries. This leads to a decrease in reflectance in the visible band associated with the anthocyanin absorption peak centered around 540 nm.

Conversely, the spectra of the berries richer in water (Level 2_m) showed slightly higher values of reflectance, especially in the visible spectral range for the Moraiolo cv. Similar behavior, as shown in Figure 3, can be noticed for the average spectra of olive pastes grouped by the same two classes of oil and moisture content. In particular, the spectra of pastes richer in water (Level 2_m) showed the highest values of reflectance. Also, in this case, the behavior is more evident for the Moraiolo cv.

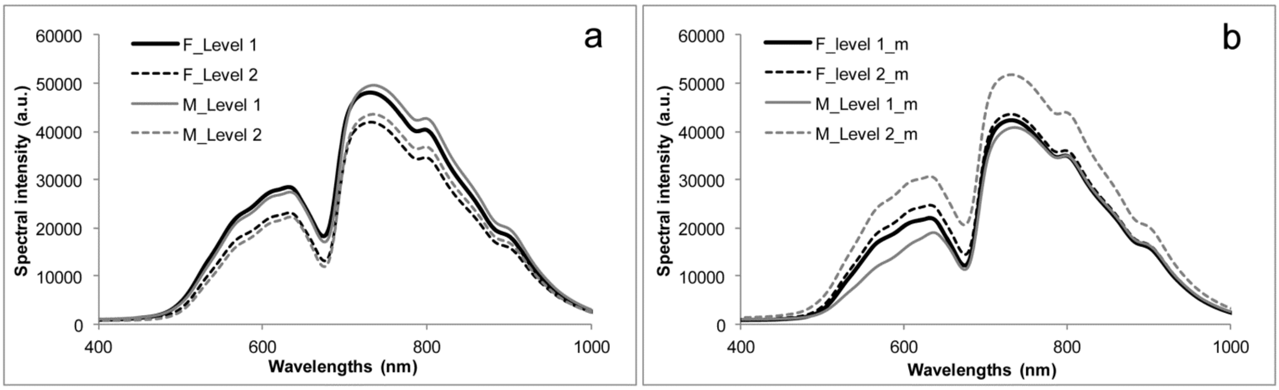

Figure 3. Average vis/NIR smoothed spectra of olive pastes, *Frantoio* (F) and *Moraiolo* (M) cultivar, grouped in two classes of oil content (a, level 1 ≤ 358.3 g kg^{-1}; level 2 > 358.3 g kg^{-1}) and in two classes of moisture content (b, level 1_m ≤ 53.5 %; level 2_m > 53.5 %).

PLS regression models were built for each parameter measured. In Table 2, the results of the PLS regression models arising from spectra on 30 intact olives for the predictions of moisture, oil and sugars content, of yield point force, total deformation energy, and MI are shown.

Regarding textural parameters the possibility to use the reference data on a single berry allowed us to obtain acceptable results for the prediction of indices usually difficult to predict in an optical non-destructive way. Interesting results were obtained for the prediction of the yield point force. Similar results were obtained for firmness prediction on intact olives by KAVDIR *et al.* (2009) and by BEGHI *et al.* (2013), using FT-NIR spectroscopy in the wavelength range 780-2500 nm in reflectance mode and vis/NIR spectroscopy (400-1000 nm), respectively. Instead, regarding the prediction of the total deformation energy, results are not satisfactory and similar to those obtained in a previous study by GIOVENZANA *et al.* (2015): R^2 in cross-validation equal to 0.58 for vis/NIR range and equal to 0.33 for NIR range.

The application of vis/NIR and NIR spectroscopy for the analysis of textural parameters often encounters considerable difficulties, which was highlighted elsewhere (ZUDE *et al.*, 2006; NICOLAÏ *et al.*, 2008). This difficulty is usually due to several factors: first, the extreme variability of this parameter among berries; the high instrumental error of the penetrometer; and the difficulty of calibrating a model for the estimation of an index not directly associable with a chemical species (and consequently the absorption bands of those chemical bonds).

Encouraging results were also obtained for chemical parameters, in particular for the prediction of moisture and oil content, with RPD values of about 2.

Table 2. Descriptive statistics and statistics of the PLS models elaborated on vis/NIR spectra of intact olives for the prediction of chemical, maturity and textural parameters

					Calibration models		Cross-Validation models		
					Chemical parameters				
Sample	**n**	**Media**	**DS**	**LVs**	**R^2_{cal}**	**RMSEC**	**R^2_{cv}**	**RMSECV**	**RPD**
					Moisture (%)				
All samples	48	53.32	3.97	8	0.87	1.39	0.75	1.89	2.10
Frantoio cv	28	51.81	3.33	7	0.89	1.05	0.79	1.43	2.33
Moraiolo cv	18	55.42	4.07	5	0.91	1.13	0.74	2.12	1.92
					Oil content (g kg^{-1})				
All samples	44	371 110	49.93	9	0.85	18.67	0.74	25.85	1.93
Frantoio cv	28	361.34	49.88	2	0.67	28.01	0.67	31.12	1.60
Moraiolo cv	18	390.71	50.87	3	0.88	16.97	0.81	22.3	2.28
					Sugar content (g kg^{-1})				
All samples	46	38.87	5.69	7	0.65	3.31	0.42	4.35	1.31
Frantoio cv	24	35.91	3.76	10	0.95	0.77	0.75	2.03	1.85
Moraiolo cv	18	44.18	4.2	10	0.95	0.88	0.38	3.38	1.24
					Maturity Index				
Sample	n	Media	DS	LVs	R^2_{cal}	RMSEC	R^2_{cv}	RMSECV	RPD
					MI				
All samples	47	0.85	1.02	3	0.93	0.24	0.92	0.26	3.92
Frantoio cv	28	0.32	0.46	5	0.87	0.15	0.7	0.22	2.09
Moraiolo cv	18	1.71	1.08	3	0.96	0.21	0.94	0.28	3.86
					Textural parameters				
Sample	n	Media	DS	LVs	R^2_{cal}	RMSEC	R^2_{cv}	RMSECV	RPD
					Yield point force (N)				
All samples	1410	41.26	17.26	9	0.63	12.32	0.62	12.44	1.39
Frantoio cv	918	52.83	22.29	10	0.63	13.51	0.61	13.82	1.61
Moraiolo cv	486	43.6	17.81	9	0.74	8.04	0.72	8.31	2.14
					Total deformation energy (mJ)				
All samples	1373	450.35	103.69	10	0.42	78.83	0.4	79.96	1.30
Frantoio cv	876	467.11	106.65	10	0.54	71.96	0.52	73.59	1.45
Moraiolo cv	408	426.98	81.63	3	0.33	66.67	0.31	67.93	1.20

A similar study was performed by SALGUERO-CHAPARRO *et al.* (2013) for the evaluation of moisture and fat content in intact olive fruits from 50 varieties using an NIR instrument in the range 400-2500 nm. They achieved for PLS models on moisture, fat content and acidity RPD values of 2.32, 2.08 and 1.70, respectively. CAYUELA *et al.* (2009) obtained slightly worse results using an AOTF-NIR on intact olives in the range 1100-2300 nm for the prediction of oil content (R^2 equal to 0.65) and moisture (R^2 ranged 0.35-0.78) compared with those obtained by the authors of this study for the same parameters. Moreover, similar results were achieved by FERNÁNDEZ-ESPINOSA (2016) using an on-line AOTF-NIR system (1000-2300 nm) on intact olives for the estimation of the oil content (R^2 0.76), while better results were obtained by the same author for the prediction of the moisture content (R^2 0.88).

Excellent results were obtained for the estimation of the MI with RPD about 4. This result may have interesting applicative implications, since the MI requires time for measuring and sample preparation. GUZMÁN *et al.* (2015) classified intact olives based on MI using image analysis, obtaining positive predictive values of about 90%.

In Table 3, the results for the PLS regression models arising from spectra on olive pastes are shown. In this case, the considered parameters were obviously only the chemical ones and the MI. Slightly better results were obtained compared to those arising from the models calculated using spectra on intact olives. Also in this case, better results were achieved for the prediction of MI, in particular for the Moraiolo cultivar (RPD = 4.15). BENDINI *et al.* (2007) applied FT-NIR for in-process monitoring of different cultivar pastes in diffuse reflectance mode, obtaining models with R^2 equal to 0.92 and 0.91 for the prediction of oil content and moisture, respectively.

Table 3. Descriptive statistics and statistics of the PLS models elaborated on vis/NIR spectra of olive pastes for the prediction of chemical and maturity parameters.

					Calibration models		**Cross-Validation models**		
					Chemical parameters				
Sample	**n**	**Media**	**DS**	**LVs**	**R^2_{cal}**	**RMSEC**	**R^2_{cv}**	**RMSECV**	**RPD**
					Moisture (%)				
All samples	45	53.4	3.99	9	0.86	1.44	0.75	2	2.00
Frantoio cv	26	51.79	3.16	4	0.74	1.56	0.55	2.11	1.50
Moraiolo cv	18	55.42	4.07	4	0.86	1.42	0.79	1.91	2.13
					Oil content (g kg^{-1})				
All samples	46	378.23	50.98	5	0.78	23.46	0.69	28.64	1.78
Frantoio cv	26	372.19	44.83	2	0.68	24.56	0.7	27.32	1.64
Moraiolo cv	18	390.71	50.87	3	0.88	16.66	0.85	19.76	2.57
					Sugar content (g kg^{-1})				
All samples	45	51.68	7.3	4	0.61	4.5	0.51	5.2	1.40
Frantoio cv	28	48.67	5.72	4	0.6	3.53	0.51	4.42	1.29
Moraiolo cv	13	55.83	4.4	6	0.98	0.59	0.83	1.86	2.37
					Maturity Index				
Sample	n	Media	DS	LVs	R^2_{cal}	RMSEC	R^2_{cv}	RMSECV	RPD
					MI				
All samples	46	0.96	1.04	4	0.88	0.33	0.85	0.39	2.67
Frantoio cv	25	0.4	0.51	4	0.79	0.21	0.58	0.31	1.65
Moraiolo cv	18	1.71	1.08	7	0.98	0.12	0.95	0.26	4.15

Similar prediction performances were obtained starting from the spectra acquired on intact olives or on pastes. RPD values for the considered chemical parameters were 1.31–2.10 and 1.40–2.00 for the models calculated for intact olives and pastes, respectively. This result is very interesting with a view to future applications, as the possibility to perform optical analysis directly on the fruits before the process could be envisaged, without any sample preparation.

Regarding the MI, better results were obtained as expected starting from intact olives, due to the high correlation between ripeness and peel pigmentation; the evolution of MI values is driven by color evolution during ripening, which is mainly influenced by the external color of the fruits. The Moraiolo cultivar gave the best results overall. This is probably due to the evident evolution of external pigmentation of the fruits during the ripening process

that helps the correlation with the vis/NIR spectra, especially due to the contribution of the visible range.
Predictive models are usable for the monitoring of operative parameters in different steps of the milling process, i.e. crushing, malaxation, and extraction using decanter, for the enhancement of extraction oil yield and the control of semi-finished products of the process.

4. CONCLUSIONS

The olive oil sector is interested in new user-friendly systems for rapid analysis that can be performed directly on-line on the milling plant with the objective of using information from sensors to manage the product better, and to preserve consumers' expectations of high-quality extra virgin olive oil, closely related to the composition of phenols and of volatile compounds. Increasing demand for rapid, cost-effective and non-invasive measurement of texture remains a challenge for the oil extraction process. This study has interrogated the applicability of vis/NIR spectroscopy as a rapid technique for the analysis of olives directly on the tree or at the mill just before the oil extraction process, and the olive paste, for the monitoring of crucial parameters for the enhancement of extraction oil yield (moisture, oil, sugar content, MI and textural indices). Our results were encouraging for chemical, texture and MI parameters. Regression models could be used for real-time prediction of crucial indices to support specific requirements of the process, considering the technological characteristics of the different olives or olive pastes, in order to diversify quickly the oil production.
Investigation of wavelength bands in order to highlight and select the most informative ones is desirable in order to design a simple and inexpensive device to classify olives entering the mill based on technological requirements, and to monitor the operative parameters during the process. The olive oil sector could be provided with pre- and post-harvest methods and sorting systems for olive fruits and olive paste for quick evaluation of the essential features to optimize the oil-making process.

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