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Postharvest Characterization of Olive Oil Fruits Texture by NIR and Vis/NIR Spectroscopy

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For olive oil fruits, textural properties could be used as indices of ripeness to meet requirements for technological process and oil characterization. Texture measuring instruments are time consuming and envisage high cost for devices. Increasing demand for rapid, cost-effective and non-invasive measurement of texture remains a challenge in the food process.

This work studied the applicability of vis/NIR (400-1,000 nm) and NIR (1,000-2,000 nm) spectroscopy as rapid techniques for the characterization of olives texture, directly at the mill just before oil extraction process. Mechanical analyses (breaking point force, total deformation energy, stiffness) were performed on fruit flesh using a laboratory dynamometer. Moreover, a firmness (N) analysis was done using a digital penetrometer. The destructive analyses and the optical acquisitions were carried out on 100 olives harvested in November 2012.

Principal component analysis (PCA) was performed on vis/NIR and NIR spectra to examine sample groupings and a partial least square (PLS) regression algorithm was used to correlate samples spectra and physical properties. Regarding the vis/NIR results, PCA pointed out a good separation among samples according to texture parameters; the best PLS models, in validation, were elaborated for stiffness (R^2 = 0.85 and RPD = 2.53) and firmness (R^2 = 0.86 and RPD = 2.67). Slightly better results were obtained for NIR spectroscopy. PCA showed a fairly good separation among classes and the best PLS models were achieved again for stiffness (R^2 = 0.86 and RPD = 2.72) and firmness (R^2 = 0.87 and RPD = 2.62).

The study provides the sector with postharvest methods and sorting systems for a quick evaluation of olive oil fruits texture. Therefore, the vis/NIR and NIR spectroscopy could give support to producers for preliminary decisions about the destination of olives before the oil extraction process.

1. Introduction

For fruit and vegetables textural features are widely used as indices of ripeness to meet requirements during handling, storage and acceptability by the consumer (Chen and Opara, 2013). For olive oil fruits, texture could be used as indices of ripeness to meet requirements for technological process and oil characterization.

During ripening, olive oil fruits undergo biochemical changes. Cherubini et al. (2009) studied sugar and oil content during ripening of olive oil fruits; Salas et al. (2000) investigated biochemistry of lipid metabolism in olive; Marsilio et al. (2001) examined free sugar and polyphenolic compositions of some European olive fruit varieties suitable for table olive purposes and Borzillo et al. (2000) assessed biomolecular components for *Oinotria* table olives during ripening.

Regarding texture properties, Mafra et al. (2001) evaluated effect of ripening on texture, microstructure and cell wall polysaccharide composition of olive fruit (*Olea europea* L.); Beltra et al. (2004) affirmed that during maturation fruit weight increase and flesh texture is related to the dry matter content for table olive fruits. Yousfi et al. (2006) studied changes in quality and phenolic compounds of virgin olive oils during fruit maturation and confirmed that firmness allowed better discrimination at the initial maturity stages than the other methods tested (harvest date, amount of chlorophylls and carotenoids in the oil) on olive oil fruits.

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Texture measuring instruments range from simple hand-held devices to the Instron machine and texture analyzer which provide time-series data of product deformation thereby allowing a wide range of texture attributes to be calculated from force–time or force–displacement data (Chen and Opara, 2013). The texture measurement is time consuming and is characterized by high costs for instrumentation. Therefore, increasing demand for quick, cost-effective and non-invasive measurement of texture remains a challenge in the food sector.

In the modern oil industry there is a strong need for a simple, rapid, and easy-to-use method for objectively evaluating the level of olive ripening. A tool enabling real-time analysis at the receiving station would allow preliminary decision-making about olives during consignment thanks to the rapid analysis of ripening parameters. In recent times, the application of emerging non-invasive technologies such as near-infrared spectroscopy (NIR) to measure texture attributes has increased in both fresh and processed foods. NIR spectroscopy has been shown to be one of the most efficient and advanced tools to monitor process and control product quality in the food industry. It is widely used for rapid quality control of several products (Guidetti et al., 2012). Studies available in the literature discuss quality evaluation of intact olives using optical analysis. Beghi et al. (2013) characterized intact olive fruit by using visible/near infrared spectroscopy for the analysis of firmness on olive for oil; Bellincontro et al. (2012) studied the application of a portable NIR for on-field prediction of phenolic compounds during the ripening of olives; Mailer (2004) calibrated chemical factors, including free fatty acids (FA), induction time, polyphenol content, and FA profiles, for NIR analysis and Morales-Sillero et al. (2011) studied the feasibility of NIR spectroscopy for non-destructive characterization of table olives.

The aim of this work was to study the applicability of vis/NIR (400-1,000 nm) and NIR (1,000-2,000 nm) spectroscopy as rapid techniques for the characterization of olives texture, directly at the mill just before oil extraction process in order to distinguish olives based on texture changes and build models for prediction of texture parameter of olive fruit. Chemometric tools were used for data exploration and for creating dedicated chemometric texture models.

2. Materials and Methods

2.1 Sampling

The experiment was carried out on 100 olives harvested in November 2012 on the Montepaldi experimental farm in Florence (Tuscany, Italy). Olive fruits used in this study were Moraiolo and Frantoio (approx. 50 % of each) cultivated in the Province of Florence; these varieties are typical for the Tuscan hills. Picked fruits taken at random from the bin were measured. Two spectral measurements were taken in reflectance mode on individual fruits along their equator region using a portable spectrophotometer and a laboratory NIR device. Subsequent to the spectral acquisition, analyses of texture of each olive were carried out using a laboratory dynamometer and a portable penetrometer.

2.2 Texture analyses

Firmness was assessed using a portable penetrometer (AGROSTA®100 by Agro-Technologie, Forges les Eaux, France). This device used a spring that is compressed onto the fruit and a tip (25 mm^2) that is displaced (Barreiro et al., 2004).

Table 1: Settings for the compression test deriving from dynamometer

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

A laboratory dynamometer provided time-series data of product compression allowing the calculation of texture attributes from load–extension traces. Table 1 shows the settings for the compression test deriving from the dynamometer. Measurements were carried out using a 5 cm diameter probe coupled with a load cell of 100 N.

Texture parameters obtained from the elaboration of the load–extension curve were the following:

- Stiffness (N mm^{-1}): the resistance offered by an elastic body to deformation;

- Total deformation energy (N mm): the work required to a complete compression of the olive pulp;
- Breaking point force (N): the maximum force registered during pulp compression.

In Figure 1 an example of mechanical pattern recorded by the compression test of olives is presented.

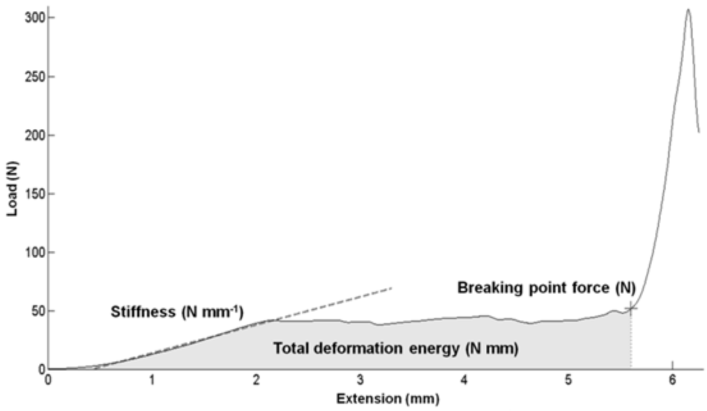

Figure 1: Example of a mechanical track for the analysis of firmness parameters

2.3 Visible/near infrared and near infrared devices

A total of 200 spectra were acquired in reflectance mode.
Spectral acquisitions were performed on samples using:

(i) an optical portable system JAZ vis/NIR spectrophotometer (OceanOptics, USA), wavelength range 400-1,000 nm. The system is composed of six components: a) vis/NIR lighting system; b) fiber optic probe for reflection measurement; c) spectrophotometer; d) hardware for data acquisition and instrument control; e) battery for power supplying; f) CCD sensor with a 2048 pixel matrix, corresponding to a nominal resolution of 0.3 nm.

(ii) an optical laboratory system TG-cooled NIR II (Hamamatsu Photonics, Japan), wavelength range 1,100-2,200 nm. The system is composed of: a) NIR lighting system (cool-red, Ocean Optics, USA); b) Y fiber optic probe; c) spectrophotometer; d) USB cable to connect the system with a PC; e) InGaAs detector corresponding to a resolution of 8 nm.

2.4 Data analysis

Vis/NIR and NIR spectra and texture parameters were used for multivariate analyses: principal component analysis (PCA) for explorative investigation and partial least square regression (PLS) to elaborate chemometric predictive models. Chemometric analysis was performed using The Unscrambler software package (version 9.8, CAMO ASA, Oslo, Norway). Moving average smoothing was applied to vis/NIR and NIR spectra, aiming at reducing noise. PCA was performed on spectra to examine sample grouping and to identify outliers. PCA allows to figure out the spectral difference among samples with different texture characteristics and consequently to define the sample sets to be used for the PLS analysis. The vis/NIR and NIR spectra were correlated with texture parameters (breaking point force, N¸ total deformation energy, N*mm; stiffness, N*mm^{-1} and firmness, N) using the PLS regression algorithm. Cross-validation was used as validation method. To evaluate model accuracy, the coefficient of determination in calibration (R^2_{cal}), the root mean standard error of calibration (RMSEC), the coefficient of determination in cross-validation (R^2_{cv}), the root mean standard error of cross-validation (RMSECV) and the ratio performance deviation (RPD) were applied. RPD is defined as the ratio between the standard deviation of the response variable. This ratio is desired to be larger than 2 for a good calibration (Sinnaeve et al., 2001). RPD ratio less than 1.5 indicates incorrect predictions and the model cannot be used for further prediction. RPD between 1.5 and 2 means that the model can discriminate low from high values of the response variable; a value between 2 and 2.5 indicates that coarse quantitative predictions are possible, and a value between 2.5 and 3 or above corresponds to good and excellent prediction accuracy, respectively.

3. Results and Discussion

Changes in spectra reflected modifications in texture parameters. For a better visualization, four arbitrary classes (≤20 N; 20 N<x≤40 N; 40 N<x≤60 N and >60 N) were created to identify different firmness ranges (texture parameter better related to spectral changes). The average vis/NIR and NIR raw spectra, grouped by these firmness classes, are shown in figure 2a and 2b, respectively.

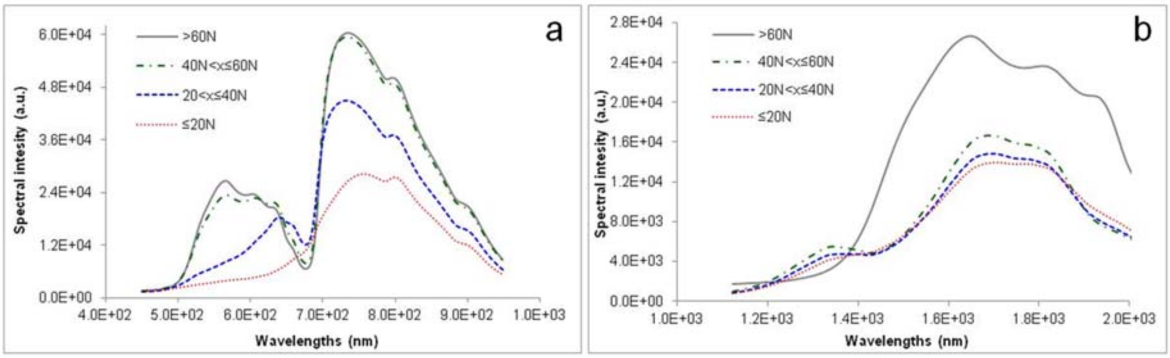

Figure 2: Average raw vis/NIR (a) and NIR (b) spectra of 100 olives grouped in four firmness classes (≤20N; 20N<x≤40N; 40N<x≤60N and >60N)

Regarding vis/NIR spectra, they exhibited significant differences among classes, with strong changes in the visible band occurring from hard olives (> 60 N) to the soft stages (≤ 20 N). This firmness behaviour is also linked to anthocyanin pigmentation during ripening and this leads to a strong decrease in reflectance in the visible band associated with the anthocyanin absorption peak centered on 540 nm.

Regarding NIR spectra, a significant difference was detectable for the > 60 N class in respect to the other classes. Smaller spectral differences are noticeable instead among the averaged spectra of the softest firmness stages.

PCA was performed on vis/NIR and NIR spectra to examine sample groupings (Figure 3).

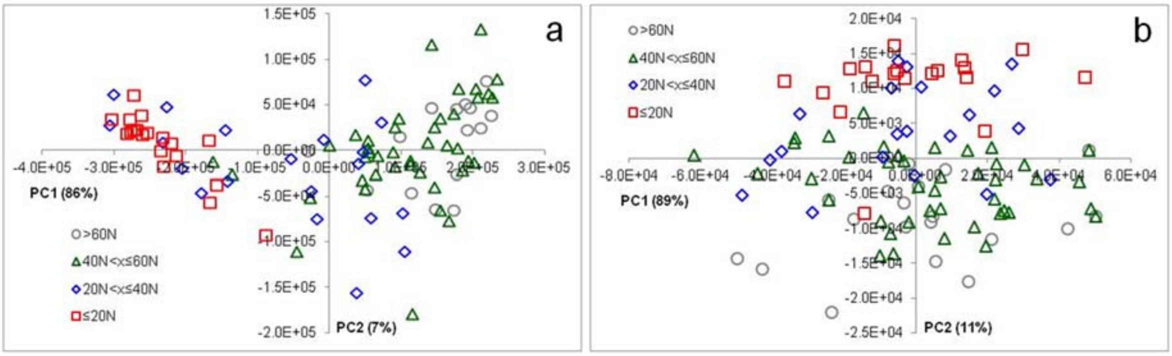

Figure 3: PCA scores plot of (a) vis/NIR and (b) NIR spectra. Olives dataset was grouped in four arbitrary firmness classes (≤20 N; 20 N<x≤40 N; 40 N<x≤60 N and >60 N)

The explorative PCA conducted on the vis/NIR spectra (Figure 3a) resulted in two significant PCs explaining 93% of the total data variance (86% for PC1, 7% for PC2). The PCA pointed out a trend of samples from positive to negative values of PC1 according to firmness changes.

The scores plot resulting from PCA applied on NIR spectra was shown in Figure 3b. The first two components explained 100% of the data variance. Also in this case a quite good separation of samples was highlighted. Olives tend to soften from negative to positive values of PC2.

The results of the explorative analyses showed that the spectral data obtained by vis/NIR and NIR acquisitions are partially able to discriminate the olives in terms of firmness.

Quantative predictions were performed using PLS regression algorithm, correlating samples spectra and texture properties.

The best PLS models, in validation, were elaborated for stiffness (R^2_{cv} = 0.85 and RPD = 2.53) and firmness (R^2 = 0.86 and RPD = 2.67). Slightly better results were obtained for NIR spectroscopy. PCA showed a fairly good separation among classes and the best PLS models were achieved again for stiffness (R^2 = 0.86 and RPD = 2.72) and firmness (R^2 = 0.87 and RPD = 2.62).

Beghi et al. (2013) tested a portable vis/NIR system for texture on intact olive before the olive oil extraction process obtaining R^2 equal to 0.7 in validation. Similar results were found by Kavdir et al. (2009) using FTNIR spectroscopy (780-2500 nm) for firmness prediction on intact olives.

Table 2: Descriptive statistics and statistics of the PLS models elaborated on Vis/NIR and NIR spectra for the prediction of texture parameters of olives

							Calibration		Validation		
Parameters	Units	Spectral range	N samples	Mean	SD	LV	R^2_{cal}	RMSEC	R^2_{cv}	RMSECV	RPD
Breaking point	N	Vis/NIR	90	29.1	15.9	6	0.87	5.7	0.84	6.4	2.5
		NIR	92	29.3	16.3	7	0.82	6.8	0.79	7.6	2.2
Total deformation energy	N mm	Vis/NIR	89	29.4	16.3	6	0.69	9.1	0.58	10.4	1.6
		NIR	90	29.5	16.3	3	0.38	12.8	0.33	13.3	1.2
Stiffness	N mm^{-1}	Vis/NIR	91	12.9	8.5	4	0.86	3.2	0.85	3.3	2.5
		NIR	90	12.2	7.8	6	0.88	2.7	0.86	2.9	2.7
Firmness	N	Vis/NIR	90	43.2	17.7	3	0.88	5.9	0.86	6.9	2.7
		NIR	92	43.2	17.7	8	0.87	5.9	0.87	6.9	2.6

The application of vis/NIR and NIR spectroscopy on other fruits for the analysis of texture parameters often encounters considerable difficulties as was highlighted in literature on pears by Nicolaï et al. in 2008, and on apples by Zude et al. in 2006. These difficulties are usually due to some factors as well as the extreme variability of these parameters among fruits and the difficulty of calibrating a model for the estimation of an index not directly correlated with determined chemicals (and consequently the absorption bands of those chemical bonds). The possibility of using the reference data (firmness) on a single berry has allowed to obtain good results for the estimation of a parameter that is usually difficult to estimate such as the texture of a fruit by optical non-destructive systems.

4. Conclusions

This work studied the applicability of vis/NIR and NIR spectroscopy as rapid techniques for the texture analysis of olives directly at the mill just before oil extraction process. The obtained preliminary results were encouraging for some parameters. Specific models elaborated for each cultivar could improve predictive power and model robustness. Investigation of wavelength bands in order to highlight and select the most informative is desirable in order to design a simple and inexpensive device to monitor texture parameters and consequently ripeness degree and to classify olives entering the mill based on technological requirements.

Moreover, this techniques could also be applied to table olives before the fermentation process. The goal for the future is to provide the sector with post-harvest methods and sorting systems that can provide a quick evaluation of olive fruit ripeness indices and improve management of the oil-making process.

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