Application of NIR and MIR spectroscopy to extra virgin olive oil classification

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INTRODUCTION

The extra virgin olive oil (EVOO) plays an important role amongst the Mediterranean typical food products. The European Union has recognized many EVOOs as Protected Designation of Origin (PDO) or Protected Geographical Indication (PGI). These typical oils are mainly known for their sensory properties (Caporale et al., 2006), which are deeply influenced by the cultivar of the olives used in production (Rotondi et al., 2011). Sensory and chemical properties of EVOO are also affected by the soil type on which the olives are grown, as well as by agronomic practices and climatic conditions (Tovar et al., 2002). Since EVOO is one of the more expensive vegetable oils, notably in presence of a PDO or PGI label, it is subjected to several commercial frauds. To protect consumers against fraudulent claims, rapid and easy analytical methods are necessary, at least for screening procedure. Spectroscopic techniques, associated with chemometric methods, have been shown to be useful for olive oil classifications (Galtier et al., 2007; Casale et al., 2010; Sinelli et al., 2010; De Luca et al., 2011; Casale et al., 2012).

AIM

The aim of this work was to verify the possibility to use NIR and MIR spectroscopy for the classification of EVOOs on the basis of their fruity flavor intensity, geographical origin, and varietal composition.



MATERIALS

The 245 oil samples used in this study belong to the "Innovative technologies, quality and typicality of Italian virgin oils from seeds and fruits" project (PRIN 2009, granted by the Italian Ministry for Education, University and Research) and were collected during two different Italian national competitions in which oils of different geographical origin and different olive cultivars were judged for their sensory properties. Sensory analysis was carried out according to the method developed by the International Olive Council, recognized by the European Community legislation (Commission Regulation (EC) No 1019/2002). On the basis of the fruitiness intensity and the other information available, samples were grouped in different classes, as reported in Table 1. Only samples deriving from one of the two competitions were used for classification on the basis of the varietal composition (214 samples).

Table 1. Class distribution of extra virgin olive oil samples, on the basis of different criteria.

Criterion	Fruitiness			Geographical				Varietal	
	intensity			origin				composition	
Class	LF	MF	IF	N	S	С	1	В	М
Sample no.	88	139	18	24	115	69	37	100	114

LF, light fruitiness intensity; MF, medium fruitiness intensity; IF, intense fruitiness intensity; N, North Italy; S, South Italy; C, Central Italy; I, Italian Isles; B, blend of different cultivars; M, monovarietal oil

METHODS

Oil samples were stored in the dark at 4°C until the analyses. Before spectral acquisition, the oil samples were conditioned at 25°C for at least 45 min. NIR spectra were recorded in transmission mode using vials of 8 mm path length, by means of an FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany), working in the range 12500-4000 cm⁻¹, with a resolution of 8 cm⁻¹ and 16 scans both for background and samples.

MIR analyses were carried out by means of an FT-IR spectrometer (VERTEX 70, Bruker Optics) equipped with a germanium crystal ATR cell. Spectra were acquired in the range 4000-700 cm⁻¹, with a 4 cm⁻¹ resolution and 16 scans both for background and samples.

All spectra were collected in duplicate, using the software OPUS v. 6.5 (Bruker Optics). Replicates of spectral data were averaged, standardized by different pretreatments (MSC or SNV alone or coupled with first or second derivatives), and processed with Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). LDA was applied working with Principal Components (PCs) or with the wavenumbers selected by the algorithm SELECT. Classification models were validated using both crossvalidation (5CV) and three different external test sets, randomly created, each containing about 30% of the spectra used for the analysis. Data elaboration was performed by the software The Unscrambler X (v. 10.2, Camo Software AS, Oslo, Norway) and V-PARVUS (Forina et al., 2008).

RESULTS AND DISCUSSION



Fig. 1. FT-NIR (a) and FT-IR (b) reduced raw spectra of oil sam

FT-NIR and FT-IR raw spectra of the EVOO samples analyzed are shown in Fig. 1. In order to eliminate not informative regions, spectral ranges were reduced as follows: 11251-4520 cm⁻¹ for FT-NIR; 3700-2600 and 2000-1200 cm⁻¹ for FT-IR.



Principal component analysis (PCA) was used as an exploratory tool, in order to visualize possible data structures. The score plots obtained did not show a good sample distribution according to the criteria of interest. As an example, the score plots obtained from the FT-NIR data pre-treated by SNV are shown in Fig. 2. In the different plots, the sample identification was made on the basis of the three criteria used for class distribution. Similar results were obtained with FT-IR data.



Fig. 3. Sample projection on the first two canonical variables of LDA performed on the 30 selected features of SNV pre-treated FT-NIR (a) and FT-IR (b) spectra. Full dots refer to calibration set samples; empty dots refer to external test set sam

Notwithstanding the poor results obtained by PCA, the use of the Linear Discriminant Analysis (LDA) gave satisfactory classification results. For all the classification criteria, the best LDA models were obtained using the 30 selected wavenumbers of the SNV pre-treated spectra.

The oil classification on the basis of fruitiness was quite successful: the three classes of samples (light, medium, and intense fruity flavor) were correctly classified in prediction with average percentages higher than 67 and 61 for NIR and MIR spectroscopy, respectively. Fig. 3 shows the sample projection on the first two canonical variables plane. The best distinguished class was that of the samples with intense fruitiness (green dots), but also the other two classes were guite well separated.

As regards the geographical origin, average percentages of correctly classified samples higher than 55 and 64 were obtained in prediction with FT-NIR and FT-IR data, respectively. As it can be observed in Fig. 4, the best classified EVOO samples belonged to Italian isles (green dots), whereas the most overlapped classes were those containing samples from the North (blue dots) and the Center (purple dots) of Italy.

Both the spectroscopy techniques correctly classified the 2 classes of blended and monovarietal oils, with average percentages in prediction ranging from 67 to 75 for FT-NIR and from 66 to 73 for FT-IR

CONCLUSIONS

FT-NIR and FT-IR spectroscopic methods, combined with suitable chemometric strategies, could represent a reliable, cheap and fast classification tool, able to describe EVOO intrinsic quality attributes. These attributes, related to the fruitiness intensity, the geographical origin and the varietal composition, are often reported in the product label. Thus IR spectroscopy could be used as an initial screening procedure in EVOO authentication, to protect consumers from misleading claims.

Results obtained are encouraging despite that the data set used was not well balanced in number of samples of each category



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