Comparative analysis of quality parameters of Italian extra virgin olive oils according to their region of origin

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ABSTRACT

Italian extra virgin olive oils from four regions covering different latitudes of the country were considered. They were analyzed by means of absorption spectroscopy in the wide 200-2800 nm spectral range, and multivariate data processing was applied. These spectra were virtually a signature identification from which to extract information on the region of origin and on the most important quality indicators. A classification map was created which was able to group the 80 oils on the basis of their region of origin. Furthermore, a model for the prediction of quality parameters such as oleic acidity, peroxide number, K232, K270 and Delta K, was developed.

Keywords: extra virgin olive oils, UV-VIS-NIR absorption spectroscopy, multivariate data processing, quality parameters, geographic authentication, chemical composition

1. MOTIVATION AND SCOPE

The olive tree was the first type of tree to be cultivated by the people living along the Mediterranean basin, and anyone coming from the Mediterranean region would tell you about the wonderful flavor and taste of a good dose of virgin olive oil on salads, pasta, fish and almost anything else. The olive oil called 'virgin', because it is uncontaminated and unprocessed, is the natural juice squeezed and cold-pressed from the best fruits of the olive tree, one day after the harvest. Virgin olive oils are classified in order of ascending acidity: the extra virgin olive oil is less than 0.8% acid, the virgin olive oil is less than 2% acid, while the *lampante* or *fino* olive oil can be more than 2% acid [1].

Extra virgin olive oil (EVOO) is a completely natural product, high in monounsaturated fat – the 'good fat' – and is a source of antioxidants, making it a healthier alternative to butter, margarine, and other vegetable oils, both as a dressing and in cooking. Nutritionists the world over are now recommending that consumers replace the other less healthy fats in their diets with EVOO as part of a diet designed to help people live healthier lives [2, 3, 4, 5, 6, 7, 8, 9]. Consequently, EVOO, as a light and delicate addition to many wonderful dishes, is also becoming one of the most health-promoting types of oils available.

Today, the olive tree is cultivated beyond the Mediterranean in such places as California, Texas, Argentina, Australia, South Africa and China. The different qualities of the product are not only related to the different olive varieties and blends, but also to the different soils and meteorological conditions which confer specific sensory and chemical properties. Moreover, the price of EVOO varies in large proportion, and the most expensive products are protected by labels certifying the high standard of oil quality, such as the 'protected denominations of origin' (PDO). Many studies and techniques have been recently addressed to the search of origin and authenticity of EVOO. A variety of analytical methodologies, frequently associated with a chemometric data processing, have proved to be suitable for authentication of oils, such as nuclear magnetic resonance [10, 11], gas chromatographic analyses [12, 13], and Fourier transform infrared

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spectroscopy [14, 15]. However, they require expensive instrumentation and trained personnel that not everyone can afford. Recently, a cheaper technique as the one based on near infrared spectroscopy has become popular to study the composition and quality of edible oils for authentication purposes [16, 17].

Unmatched for freshness and flavor, 100% Italian extra virgin olive oil is considered one of the finest and fruitiest of the olive oils and is therefore also the most expensive. The Italian regions, which cover a wide range of latitudes, are characterized by different types of soils in different climatic conditions. Consequently, EVOO is different according to the region of production. The purpose of this work is to demonstrate that absorption spectroscopy carried out over the wide ultraviolet-visible-near infrared (UV-VIS-NIR) spectral range is able to discriminate EVOO from different regions and is also able to provide quality indicators characteristic of these oils. This is a completion of a previous work, in which a smaller spectral range was used for discriminating Italian EVOO according to three regions of origin, and for predicting some important fatty acids [18].

In this paper, eighty EVOO samples selected from four regions were considered. The regions were spanning the extension of the Italian country. Absorption spectroscopy in the wide 200-2800 nm spectral range was used for their analysis, so that each sample was characterized by means of a large number of spectral variables. Multivariate data processing was applied allowing to group the oils according to their region of production, and also to predict important quality indicators such as oleic acidity, peroxide number, K232, K270 and Delta K.

2. CHOICE OF EXTRA VIRGIN OLIVE OILS AND THEIR QUALITY PARAMETERS

In order to have a complete figure of the EVOO Italian production, the considered regions were Lombardy, Tuscany, Calabria and Sicily. Lombardy is located in the northern part of Italy, Tuscany in the center, while Calabria and Sicily in the south, being Sicily the southest region. Because of the different meteorological conditions, tree varieties, soils and production practices, EVOOs from these regions are different and identified by means of different PDO labels.

All these oils were made in a handcrafted manner, with the scope of producing a product with regional characteristics for niche markets, instead of an large-scale-produced oil addressed to larger markets. The oil collection, belonging to the 2006 crop, was made of eighty samples, that is, twenty samples for each region. Before the optical characterization, each oil was analyzed in specialized laboratories and the values of the most important quality parameters were available.

The measured quality parameters for all oils were: oleic acidity, peroxide index, K232, K270 and Delta K. The acidity is the quantity of KOH (or NaOH) required to neutralize the fatty acids of 1 g of oil, assuming that the fatty acids have the same molecular weight as oleic acid (PM=282). It is expressed in % of free fatty acids (considered as oleic acid) per g of sample. Peroxide value (PV) is one of the most widely used tests for oxidative rancidity and it is a measure of the concentration of peroxides and hydroperoxides. The peroxide value is reported in units of millimole of hydroperoxide per kilogram of oil (or expressed as milliequivalents of iodine per kilogram of oil). K232 and K270 are measurements of the absorption of light at 232 and 270 nm wavelengths. Finally, Delta K is the absorbance at 270 nm with respect to UV absorbance curve of non oxidated EVOO. In addition, for the Sicilian oils, a wider information about most of the fatty acids was available as reference data.

3. EXPERIMENTAL RESULTS

A commercially available spectrophotometer was used for spectral measurements (Perkin Elmer – Model Lambda 19). Quartz cuvettes with 10 mm optical path were used. Transmission measurements were carried out in the 200-2800 nm spectral range, with a spectral resolution of 1 nm. As reference channel, the empty cuvette was used.

Figure 1 shows the results of transmission measurements of the EVOO collection. Chemometrics was used for spectral data processing [19, 20]. Principal Component Analyis (PCA) [21] and Linear Discriminant Analysis (LDA) [22] were used for grouping the oils according to the region of production, while Partial Least Square (PLS) [23] regression was used for predicting the quality parameters. All the programs were custom written in Matlab code for this specific application.

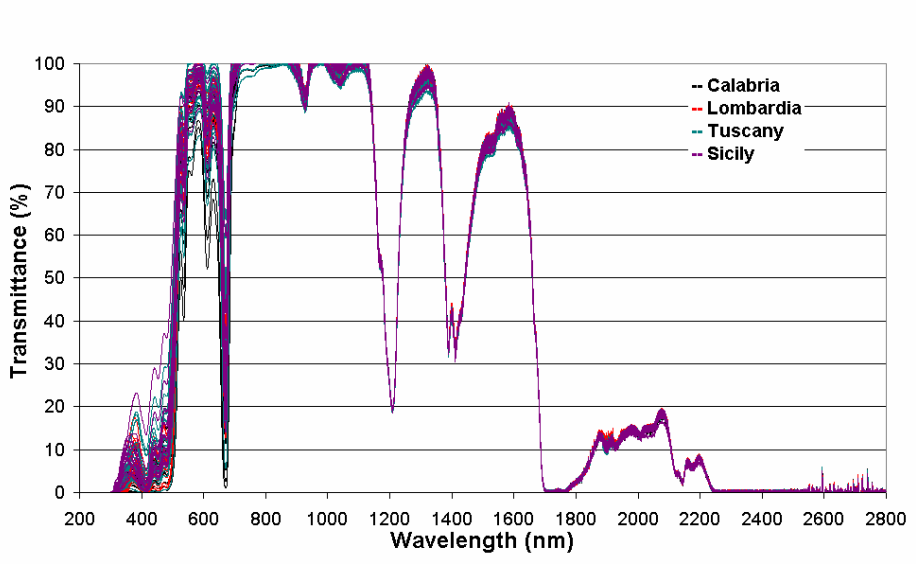

Figure 1. Transmission spectra of the entire EVOO collection.

3.1 Extra virgin olive oil grouping according to geographic region of origin

The oil absorption spectra were first submitted to an explorative exam, using PCA to reveal a possible clustering of samples coming from the same region. For this purpose the spectra were arranged in a matrix in which each row represent a sample and each column a wavelength. The spectral bands demonstrating a good discrimination capability towards the geographic origin determination were: 300-700 nm, 1000-1650 nm, and 1800-2230 nm. PCA processing of individual bands, showed a partial discrimination among the different origins, but none of this bands, alone, was able to discriminate all four oil classes. To improve the classification rate the discrimination capability of all the three bands was combined. This was achieved taking as workspace the cartesian product of the three score spaces, operating in this way a data fusion. LDA was then employed to find those axes showing the best possible separation among the four classes. First of all, the 80 available samples were split in two groups: 64 samples as training set and 16 samples as validation set. This distinction was necessary because supervised methods, as LDA, have to be validated in order to check the robustness of the model. Then, the three PCA models, one for each of the previously mentioned bands, were evaluated using only the training set. This compressed of the spectral information into a limited number of scores.

Table I summarizes the required number of components that satisfactorily represent the data and the percentages of explained variance for each considered spectral range. The cartesian product was then performed, concatenating the three score matrices and obtaining an 8-column data matrix for the application of LDA. Figure 2 shows the 3D map representing the training samples in the DF1-FD2-DF3 subspace: EVOOs appear well grouped according to their region of production. The 2D maps in the DF1-DF2 and DF1-DF3 subspaces are also shown in the figure. A 6-fold cross-validation was carried on the training set, and a Standard Error of Cross-Validation (SECV) of 15.9 % was obtaining. This figure was considered as reference value to assess the success of the validation test. Validation was carried out projecting the validation samples onto the three PCA subspaces (using the previously evaluated loadings), concatenating the resulting score matrices and projecting the joint matrix onto the LDA subspace (again using the previously calculated loadings). Validation provided a Standard Error of Prediction (SEP) of 18.8 % that had approximately the same magnitude of the SECV. Therefore, the reliability of the LDA model was successfully tested.

Spectral range (nm)	N° of PC	Explained variance (%)
300 – 700	3	98.2
1000 – 1650	3	95.5
1800 – 2230	2	94.7

Table I. Spectral data compression: number of PCs retained in each model and explained variance.

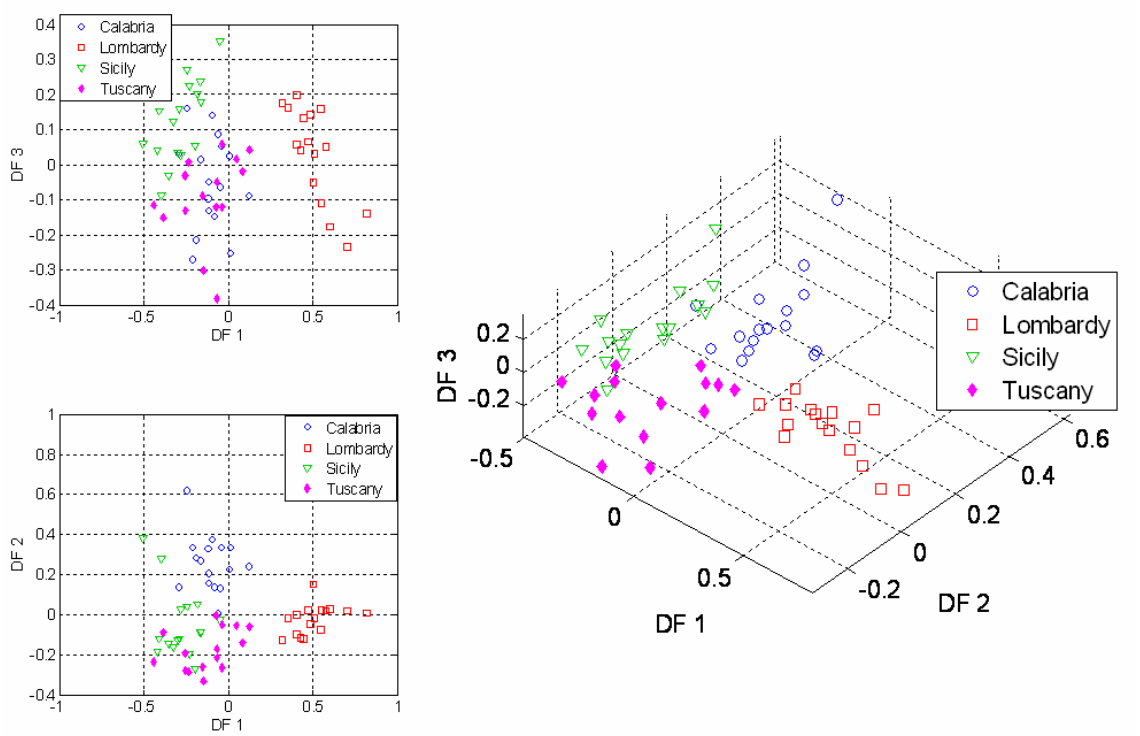

Figure 2. Grouping of EVOOs according to the region of production, achieved by means of LDA processing.

3.2 Prediction of quality parameters

The data matrix columns were firstly autoscaled (mean=0, variance=1). PLS was then applied to predict the identified quality parameters, using cross-validation to asses the optimal number of PLS factors. The spectral ranges providing the best predictive performances were calculated at first. The prediction ability was measured in terms of the square correlation coefficient, R^2, also called determination coefficient. The limits of the spectral ranges were slightly modified with respect to those found in the literature [24], in order to improve R^2.

The obtained results are summarized in Table II, in which the variability ranges of the parameters, the optimal spectral bands, the optimal number of PLS factors and R^2 are reported. The prediction provided by means of the optical spectral measurements was excellent for K232, K270, and the peroxide value, it was good for oleic acidity, while it was poor for the parameter Delta K.

Quality parameters	Calibration range	Spectral range (nm)	Number of PLS regressors	R^2
Oleic acidity (% oleic acid)	0.12 - 1.555	780 - 2500	3	0.8407
Peroxide value (meq O / kg. oil)	3.76 - 13.98	1000 – 2333	2	0.9628
K232	0.922 - 1.548	1333 – 2222	3	0.9942
K270	0.062 - 0.1178	1333 – 2222	3	0.9825
ΔK	-0.004 - 0.01	1333 - 2222	2	0.4344

Table II. Prediction of quality parameters of the EVOO collection: results and summary of data processing parameters.

3.3 Fatty acid composition of Sicilian oils

As the analytical reference data for the complete fatty acid composition of the twenty Sicilian EVOOs were available, PLS was also applied to predict the fatty acids of this EVOO set. As in the previous determination of quality parameters, autoscaled transmittance spectra were employed to obtain prediction models. Several spectral ranges have been likewise

investigated for each component in order to determine the best prediction range of each particular compound. In some cases sensible benefits were obtained extending the range till the UV-VIS region. The same criteria described in the previous section were employed to assess the fitting performances and the optimal number of PLS factors.

Table III summarizes the prediction success of the spectral optical mesurements for determining the fatty acid composition of Sicilian EVOOs, together with the data processing parameters. All the fatty acids considered were well predicted, also those present in very low concentration, demonstrating that a wide UV-VIS-NIR spectral analysis is a powerful tool for product characterization. While NIR range was sufficient for predicting oleic acidity, peroxide number, K232, K270 and Delta K, UV and VIS ranges were necessary for the assessment of the complete fatty acid composition.

Components	Calibration range (%)	Spectral range (nm)	Number of PLS regressors	R^2
Oleic acid	65.847 - 76.334	1333 - 2222	1	0.9986
Palmitic acid	9.62 - 17.113	300 - 2300	2	0.9847
Linoleic acid	4.469 - 10.95	1333 - 2222	1	0.9553
Stearic acid	2.565 - 4.046	780 - 2500	2	0.9942
Palmiticoleic acid	0.367 - 1.457	1333 - 2222	2	0.9504
Linolenic acid	0.646 - 1.066	1000 - 2300	1	0.9822
Arachiric acid	0.382 - 0.642	1000 - 2222	1	0.9896
Eicosenoic acid	0.212 - 0.431	1000 - 2300	2	0.9821
Behenic acid	0.042 - 0.411	300 - 2300	2	0.8892
Heptadecenoic acid	0.053 - 0.356	300 - 2300	2	0.8081
Heptadecanoic acid	0.025 - 0.29	1000 - 2300	2	0.8337
Lignoceric acid	0.026 - 0.205	1333 - 2222	1	0.8532

Table III. Prediction of fatty acid composition of Sicilian EVOOs: results and summary of data processing parameters.

4. PERSPECTIVES

Extra virgin olive oils from four different Italian regions were analyzed by means of absorption spectroscopy carried out in the wide 200-2800 nm spectral range, and the spectral data were processed by means of chemometric techniques. The absorption spectra have provided signatures of the products from which to extract information about quality and nutritional parameters such as oleic acidity, peroxide index, K232, K270 and Delta K, as well as to predict important aspects of the chemical composition such as a wide set of fatty acids. The techniques of spectral data processing were particularly appropriate for the identification of the region of origin of EVOOs and the prediction of quality indicators.

This methodology is straightforward and does not require any preparation of the sample. It shows interesting potential to replace analytical instrumentation more expensive and cumbersome, in order to achieve a quick quality control and product classification. In fact, many new sources, detectors, and miniaturized components for spectroscopy applications are now available, which are suitable for implementing compact and low cost spectrophotometers that can be dedicated specifically to control olive oil samples. In addition, through fiber optic probes, it is possible to design devices capable of operating online, in one or more sections of the production process, to obtain timely information on important parameters of product quality.

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