



Review

Chemometric applications to assess quality and critical parameters of virgin and extra-virgin olive oil. A review



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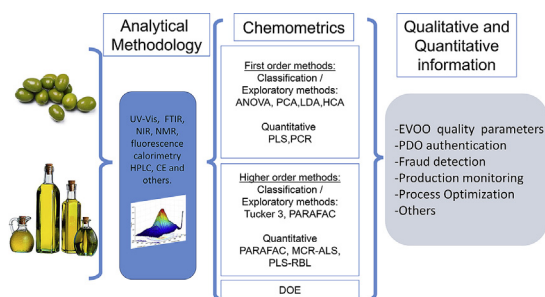
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HIGHLIGHTS

- First work review addressing chemometrics coupled to almost all analytical methods used for EVOO/VOO.
- Discussion on some practical aspects about implementing chemometrics on EVOO/VOO.
- Screening a wide range of techniques used for EVOO/VOO analysis.
- Perspective of the application of chemometrics in EVOO/VOO analysis in the coming years.

GRAPHICAL ABSTRACT



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ABSTRACT

Today virgin and extra-virgin olive oil (VOO and EVOO) are food with a large number of analytical tests planned to ensure its quality and genuineness. Almost all official methods demand high use of reagents and manpower. Because of that, analytical development in this area is continuously evolving. Therefore, this review focuses on analytical methods for EVOO/VOO which use fast and smart approaches based on chemometric techniques in order to reduce time of analysis, reagent consumption, high cost equipment and manpower.

Experimental approaches of chemometrics coupled with fast analytical techniques such as UV–Vis spectroscopy, fluorescence, vibrational spectroscopies (NIR, MIR and Raman fluorescence), NMR spectroscopy, and other more complex techniques like chromatography, calorimetry and electrochemical techniques applied to EVOO/VOO production and analysis have been discussed throughout this work. The advantages and drawbacks of this association have also been highlighted.

Chemometrics has been evidenced as a powerful tool for the oil industry. In fact, it has been shown how chemometrics can be implemented all along the different steps of EVOO/VOO production: raw material input control, monitoring during process and quality control of final product.

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1. Introduction

Among vegetable oils, virgin olive oil (VOO) and extra-virgin olive oil (EVOO) have nutritional and sensory characteristics that make them unique and basic components of the Mediterranean diet. Olive oil has been used over the centuries for its preventive and therapeutic properties, as well as a precious and valuable dietary lipid ingredient [1]. In fact, compared to other vegetable oils normally subjected to a refining process, EVOO is well-known for having higher quality in terms of health and sensory aspects, and because of its characteristic oxidative stability. These properties are related not only to the fatty acid composition of its lipid matrix, but especially to the presence of several minor compounds. Among these minor compounds there are:

- volatile compounds, mainly related to typical odours;
- phenolic compounds, responsible for its oxidative stability, taste and healthy properties;
- tocopherols, that contribute to oxidative stability and to healthy proprieties;
- squalene, related to their healthy proprieties

In the last three decades, many efforts have been made in order to correlate the chemical structures of these naturally occurring molecules in EVOO/VOO with its quality and genuineness, health benefits and sensory characteristics [2]. Other important aspect is the fluctuation of EVOO/VOO components (macro and micro) due to factors of different origins [3]. Some of these factors are listed below:

- agronomic variables (environment conditions, agricultural and harvesting methods, olive cultivar, olive ripening stage during the transformation phase)
- technological variables (milling, malaxation and separation of phases)
- storage/distribution parameters (time, temperature, light, packaging)

Due to its quality and genuineness, it is important to underline that EVOO is the most expensive edible oil. For economic reasons, it may be adulterated by the addition of cheaper oils such as refined olive oil, residue oil, synthetic olive oil-glycerol products, seed oils and nut oils. To avoid this kind of practice, a rapid method is

important for quality control and labeling purposes [3].

The study of the different molecules present in EVOO/VOO has required the use of different sample preparation methodologies and analytical techniques. Among these techniques can be listed spectrometric techniques and separation techniques coupled to different detection systems, as diode array detection (DAD), mass spectrometry (MS) and nuclear magnetic resonance (NMR). In recent years, also chemometrics has been coupled to these analytical techniques as can be seen in Fig. 1.

The analyses performed by the different analytical tools provide a huge amount of data which most of the times, is difficult to process or poorly exploited. Usually, researchers applied univariate analysis to their data as analysis of variance (ANOVA), t-tests for normally distributed data, etc. However, developments in computer science have allowed the extensive use of multivariate procedures. This important step has made possible to cope with the vast amount of data that new and sophisticated analytical instruments provide. The application of mathematical algorithms has allowed to reach conclusions that some years ago were unthinkable [4].

Some reviews works have collected applications of some analytical techniques combined with multivariate analysis to authenticate, detect adulteration and determine intrinsic quality parameters in edible fats and oils. However, they are not at all doomed to the EVOO/VOO analysis or showed only partial point of view of EVOO/VOO analysis (only one or two analytical techniques coupled to chemometrics were revised) [5–9].

Nowadays, chemometrics is increasingly being applied in food analysis. In the VOO and EVOO field specifically, chemometrics is helping to find cultivar markers, to differ samples by cultivar/origin, to guarantee the authenticity of olive oil and/or detect adulteration with other oils.

Despite all described above, chemometrics has not already been considered by EU Regulation (EC No 2568/1991 Regulation and amendments), International Olive Council (IOC) trade standard (Trade standard applying to olive oils and olive-pomace oils, COI/T.15/NC No 3/Rev. 10 November 2015) nor USA Regulation (United States standards for grades of olive oil and olive-pomace oil) as a reliable tool for EVOO/VOO data treatment and quality assessment. Therefore, the potential of chemometrics should be highlighted and, thus, the aim of this review is to summarize the main applications of chemometrics coupled to the most important analytical techniques for the analysis of VOO and EVOO in the last 20 years.

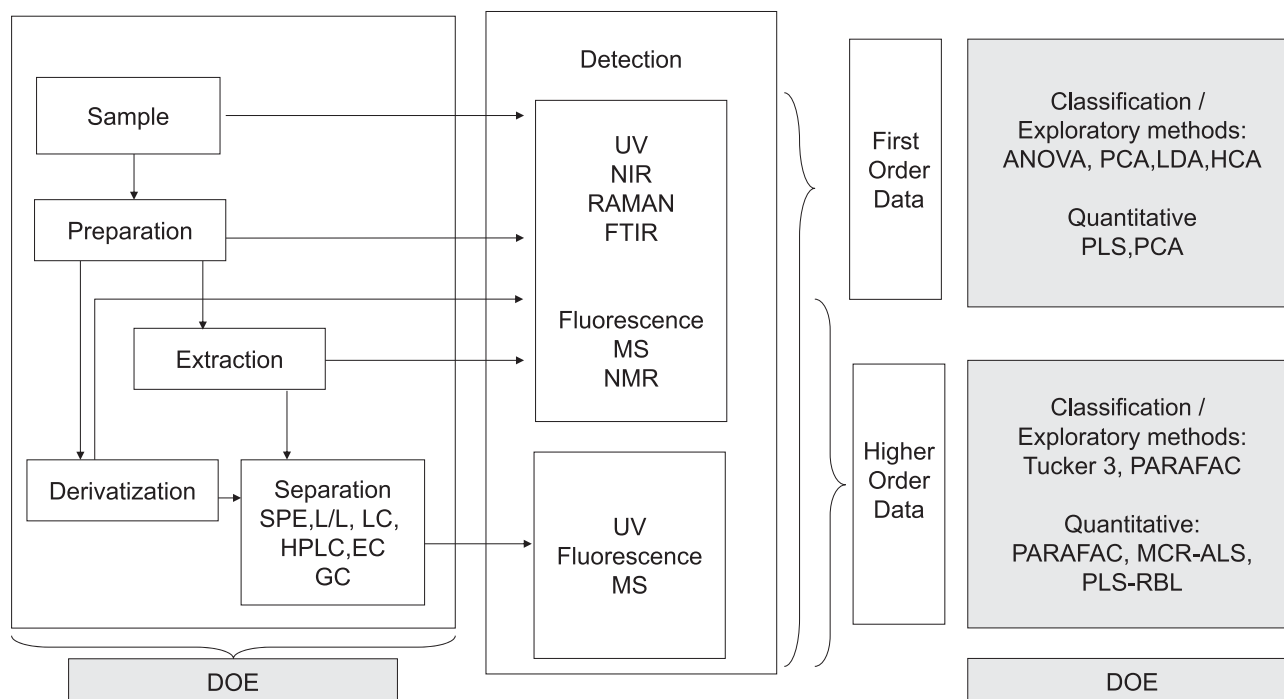


Fig. 1. Application fields of most common chemometric techniques on several process of EVOO/VOO samples analysis. Generation of DOE, quantitative and clustering data to be analysed.

2. Chemometric methods

Chemometrics could be defined as the science of extracting information from chemical systems by mathematical modeling of data. Svante Wold, coined the term in 1972 [10]; however Massart suggested a wide definition in 1997 “Chemometrics is a chemical discipline that uses mathematics, statistics and formal logic (a) to design or select optimal experimental procedures; (b) to provide maximum relevant chemical information by analysing chemical data; and (c) to obtain knowledge about chemical systems” [11].

As stated in the definition Chemometrics is an inter-disciplinary field that uses methods such as multivariate statistics, mathematics and computer science applied to chemical data [12]. The scopes of chemometrics are both quantitative and qualitative analysis and design of experiments (DOE). A short introduction to chemometric methods, its classification and a brief theoretical background are discussed herein. The basis and specific applications of each methodology exceed the scope of this revision work, and they were discussed elsewhere.

2.1. Chemometrics qualitative analysis and classification methods

Among chemometrics qualitative analysis it can be found methods from very different nature and origins. These methods hold different abilities and fields of application.

Principal component analysis (PCA) is the most widespread qualitative analysis in social and natural sciences [13]. PCA, Tucker and PARAFAC, called “display methods”, carry out a multi-linear or linear decomposition of the data. These methods decompose the array into sets of scores and loadings, which describe the data in a lower dimensional space than the original data array. Tucker3 could be defined as multi-way version of PCA, while PARAFAC is restricted version of the first, where the core tensor is diagonal.

Another significant field is “clustering analysis”, which consists to discover unknown patterns in complex data sets. These methods

are also called “unsupervised classification methods” because, they do not have *a priori* knowledge of the groups present in the population. In this type of classification, the “objects” or samples have a set of features with hidden relationships with a class or category. Then, the purpose is the discovery of groups of “objects” which have related characteristics and allow their separation into different classes. Hierarchical clustering analysis (HCA) [14] and self-organizing maps (SOM) [15] are the more common examples of linear and non-linear of this kind of methods.

Classification is the task of assign a new object to a set of categories. This process has basis of a previous set of elements whose category membership is known, so these kind of methods are named “supervised methods”. Thus, classification methods are included into pattern recognition methodologies. Two major sub-categories could be found among supervised methods, properly classification methods such as LDA [16] and class-modeling ones like SIMCA [17]. LDA is the most widely used supervised classification method. LDA is a linear and parametric method that focuses on finding optimal boundaries between classes. LDA, like PCA, is a feature reduction method, however, it selects the space directions that achieve a maximum separation among the different classes and it uses Euclidean distance to classify unknown samples.

On the other hand, SIMCA puts more emphasis on similarity within a class than on discrimination between classes. SIMCA considers each class separately and a PCA is performed which leads to a model. Then the new object is challenged to every class model and it is assigned to the class that produces the smallest residue during the prediction.

The most common algorithms used for qualitative analysis and reference literature are listed in Table 1.

2.2. Chemometric methods for quantitative analysis

Chemometrics quantitative methods could be classified in two general groups: first order methods and higher order methods

Table 1
Common chemometrics methods for qualitative and quantitative analysis, acronyms and references.

Preprocessing methods			Methods for qualitative analysis		
Mean centering	(MC)		<i>Exploratory methods</i>		
Derivatives/smoothing (Savitzky-Golay)	(D°, D', D'')		Principal component analysis	(PCA)	[13]
De-trending (baseline corrections)	(Dt)	[23] [25]	Parallel factor analysis	(PARAFAC)	[26]
			TUCKER3 model	(TUCKER)	[27]
Standard normal variate	(SNV)		Factor analysis	–	[28]
Multiplicative scatter correction	(MSC)		<i>Unsupervised methods</i>		
			Hierarchical clustering analysis	(HCA)	[14]
			Kohonen neural networks or self-organizing maps	(SOM)	[15]
			Gaussian mixture models	(GMM)	[29]
			K-means		[29]
			<i>Supervised classification methods</i>		
Quantitative methods			Linear discriminant analysis	(LDA)	[16]
<i>First order methods</i>			Canonical discriminant analysis	(CDA)	[31]
Partial least squares	(PLS)	[20,21]	Partial least squares and discriminant analysis	(PLS-DA)	[32,33] [34]
Backpropagation neural network	(ANN)	[30]			
Principal component in regression	(PCR)	[22]	Extended canonical variates analysis	(ECVA)	[35]
			Soft independent modelling of class analogy	(SIMCA)	[17]
<i>Higher order methods</i>			Backpropagation neural network	(ANN)	[30]
Parallel factor analysis	(PARAFAC)	[26]	Support vector machines	(SVM)	[38]
Multivariate curve resolution – alternating least squares	MCR-ALS	[36]			
Unfolded-PLS and Bilinear least squares	(U-PLS-RBL)	[37]			

[18,19]. First order methods use a data vector for each sample as input signal as UV, NIR, IR, or fluorescence spectra (a tensor of order 1), whereas higher order methods use a data matrix. As examples of data matrices could be quoted fluorescence excitation-emission matrix (EEM) or chromatograms from hyphenated techniques (HPLC-DAD, HPLC-Mass spectrometric and others). Within first order methods, PLS [20,21] has become the reference or first choice method, due to the wide applicability and availability of the algorithm in many kind of software (statistics-s, chemical-s, instrumental-s, spreadsheets, as toolbox in mathematical platforms, and others). PLS belongs to the family of “full-spectrum” methods, as its ancestor principal component in regression (PCR) [22].

High order methods are also known as multi-way techniques because data for a single sample are contained in a multidimensional array. These methods hold the ability to perform determinations in the presence of interferences, even when interferences were not taken into account in the calibration step (“the second-order advantage”).

PARAFAC and multivariate curve resolution coupled to alternating least squares (MCR-ALS), the calibration samples and test (unknown) samples are put together and decomposed by the model, so the number of factors necessary to perform the regression model is determined at once and, in theory, are equal to the total number of independent chemical species presents in the calibration and test samples (Fig. 2).

More calibration algorithms can be found in Table 1.

2.2.1. Preprocessing methods

In many cases raw data should be treated before its analysis to develop better predictive models. A careful preprocessing often turns out to be more effective than the modelling process of interferences and irrelevant artefacts in multivariate calibrations [23]. Typical pretreatment of data are listed in Table 1.

2.3. Design of experiments (DOE)

DOE is a systematic approach to understand how process and product parameters affect response variables such as product performance or analytical signal. There are two kinds of problems that typically need experimental design to improve their solution. The first one is to discover which factors may significantly affect the response of the experiment, the “screening phase”, and the scope of this phase is to perform a minimum number of experiments

exploring a maximum number of factors [24].

The second problem is to find factor values which optimize the response [39]. This task could be carried out following the next steps, (1) setting of the objective and the planning of the experiment, (2) data collection, (3) analysis (by multiple linear regression or ANN) and (4) find the optimum value of the response by the model. If many responses need to be optimized simultaneously Derringer's desirability function should be calculated in this step [40].

3. Methods applications

3.1. UV and fluorimetric techniques and chemometrics

UV–Vis spectroscopy is widely used due to its great versatility, easy handling, high sample turnover and automation feasibility. However, the low selectivity of this technique makes its application, without a previous pre-treatment, an almost impossible task. In fact, its direct application on VOO and EVOO analysis is limited to a few cases (anisidine value, peroxide value, general colour, carotenoids and chlorophylls). Nevertheless, chemometrics has proven to be very useful to deal with the major issues of this methodology. A similar scenario appears in the application of fluorimetric techniques, which find selectivity and improve their performances in combination with chemometric techniques.

A good example of this tendency is the work of Torrecilla et al. [41] where UV–Vis measurements done to monitor adulterated samples of EVOO with refined olive oil or refined olive pomace oil. Using a SOM, the signals were identified and clustered into five groups depending on the concentration of adulterant agents. When validation set was tested by projection on SOM and calculation of Euclidean and Manhattan distances the clustering error was estimated as 1.3%.

Adulterations of EVOO with refined olive oil, refined olive-pomace oil, sunflower or corn oil have also been studied using the entire 190–900 nm region containing UV–Vis. Data was treated using two mathematical methods, MLR and radial basis ANNs (a non-linear method) and they could estimate the adulteration with a mean correlation coefficient (R^2) greater than 0.80 and 0.97, respectively [42]. Additionally, when validation set was analysed mean square error (MSE) was 1% for MLR and 0.051% for ANN.

Classification of Spanish EVOO was also accomplished by data

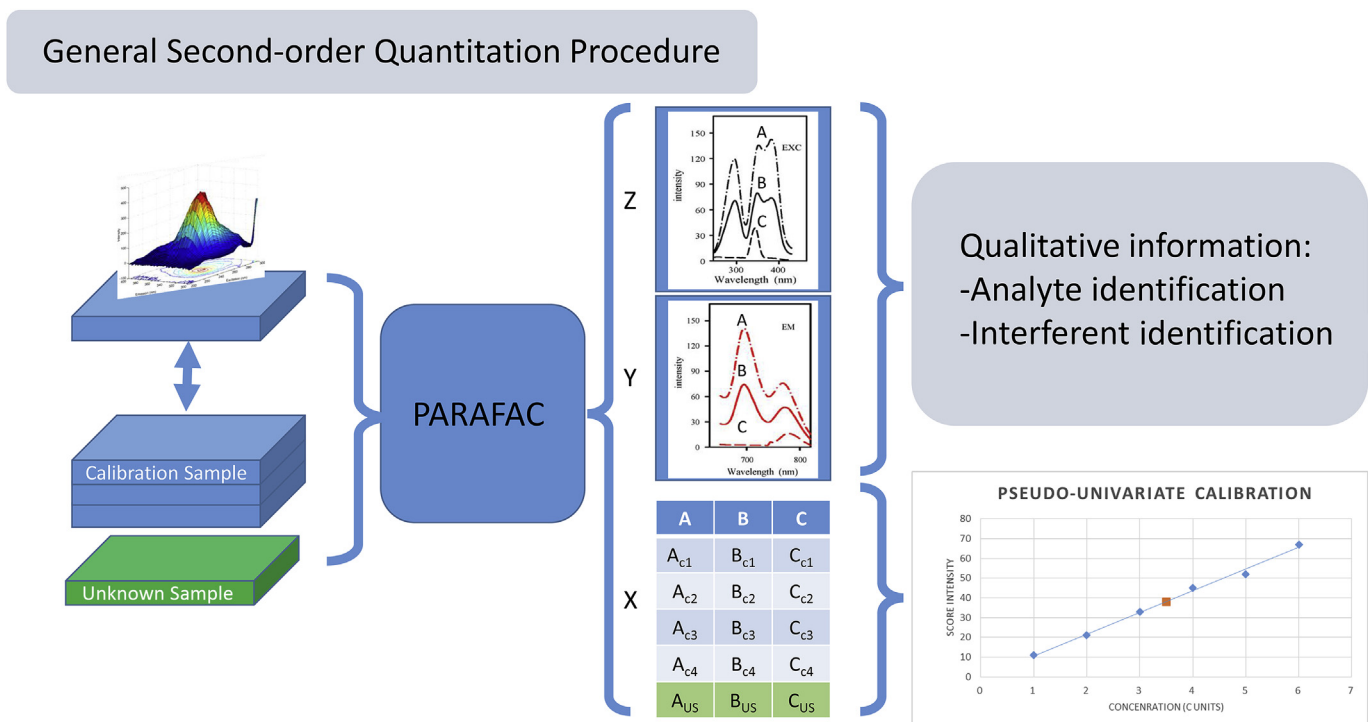


Fig. 2. General second-order calibration procedure, using PARAFAC for signal processing. Data array construction, signal decomposition, recognition of signal analyte using PARAFAC loadings and construction of pseudo-univariate curve with PARAFAC scores.

fusion of visible spectroscopic fingerprints and quality parameters matrices. Both groups of data were processed individually and then jointly for their further classification using LDA and PLS-DA. The results revealed a perfect discrimination between the defined categories after performing PLS-DA on the fused matrix, reaching 100% of correct classifications and showed a clear improvement in the overall prediction rates (92.5%) [43]. Another application of data fusion has been presented by Casale et al. [44]. They fuse visible spectroscopy and headspace mass data for the classification of the Ligurian olive oils using LDA and SIMCA. LDA reach excellent classification rates in cross-validation procedure (100%) and test-set (89.1%), giving a high level of confidence to the future results. SIMCA as a class-modelling tool, were not so effective, but also confirmed that the results improve using the synergy between different analytical techniques.

Guimet et al. studied the potential of fluorescence EEM and three-way methods of analysis to detect olive-pomace oil adulteration in “Siurana” EVOO (Fig. 3). Unfold-PCA and PARAFAC for exploratory analysis were applied. Loadings of both (PARAFAC and PCA) exploratory methods were related to fluorescence profiles of Vitamin E and some oxidation product, which are present in different amount through sample classes. LDA and discriminant N-PLS regression in training and validation sets gave classification rate close to 100%. Finally, the level of adulterant (limit of quantification; LOQ = 5%) could be quantified using N-PLS obtaining a root mean square error (RMSE) on prediction error of 1.2% [45].

Besides, the feasibility of the determination of polycyclic aromatic hydrocarbons in EVOO and sunflower oils via U-PLS-RBL and PARAFAC using fluorescence EEM has also been studied. Seven heavy polycyclic aromatic hydrocarbons were successfully examined and the limit of detection (LOD) ranged from 0.07 to 2 $\mu\text{g kg}^{-1}$, a comparable value to that obtained by HPLC with fluorescence detection [46].

3.2. Vibrational spectroscopy and chemometrics: NIR, MIR and Raman

In the last years, near-infrared (NIR) and mid-infrared (MIR) spectroscopy have emerged as a very powerful and general techniques for investigating the structure of food components and for monitoring changes in the quality of food [47–49]. Spectroscopic techniques do not need any time-consuming and labor-intensive sample pretreatments, destructive and complex chemical analysis or high quantities of organic solvents; conversely, it provides rapid analysis with minimum sample preparation. Thus, IR results in time and cost savings and increase throughput of samples. Most applications of NIR and MIR spectroscopy have been done coupled to Fourier transform (FT), named FT-NIR and FT-MIR or FTIR, respectively.

Despite the fact that food heterogeneity provides very complex spectra and, this makes the detection/determination of minor components of the samples difficult, the association of IR with chemometrics allow the extraction of significant and valuable information from large and complex data sets. As a consequence, many studies have been carried out by using NIR and MIR coupled to exhaustive chemometric analyses in the last years. These techniques have been confirmed as a rapid, nondestructive, authenticity measuring tool for edible oils, particularly for EVOO [49].

Visible–NIR and MIR spectroscopy have been applied to a study of VOO subjected to thermal stress. The spectra obtained were elaborated by PLS to individualize regions and bands where critical variations were present [50]. In this study, two spectral bands were found as principal influential ones ($1245\text{--}1180\text{ cm}^{-1}$ and $1150\text{--}1030\text{ cm}^{-1}$) on MIR, whereas one primary region was identified on Vis–NIR ($22,000\text{--}13,250\text{ cm}^{-1}$).

Inarejos-García et al. carried out the evaluation of minor components, sensory characteristics and quality of EVOO by NIR

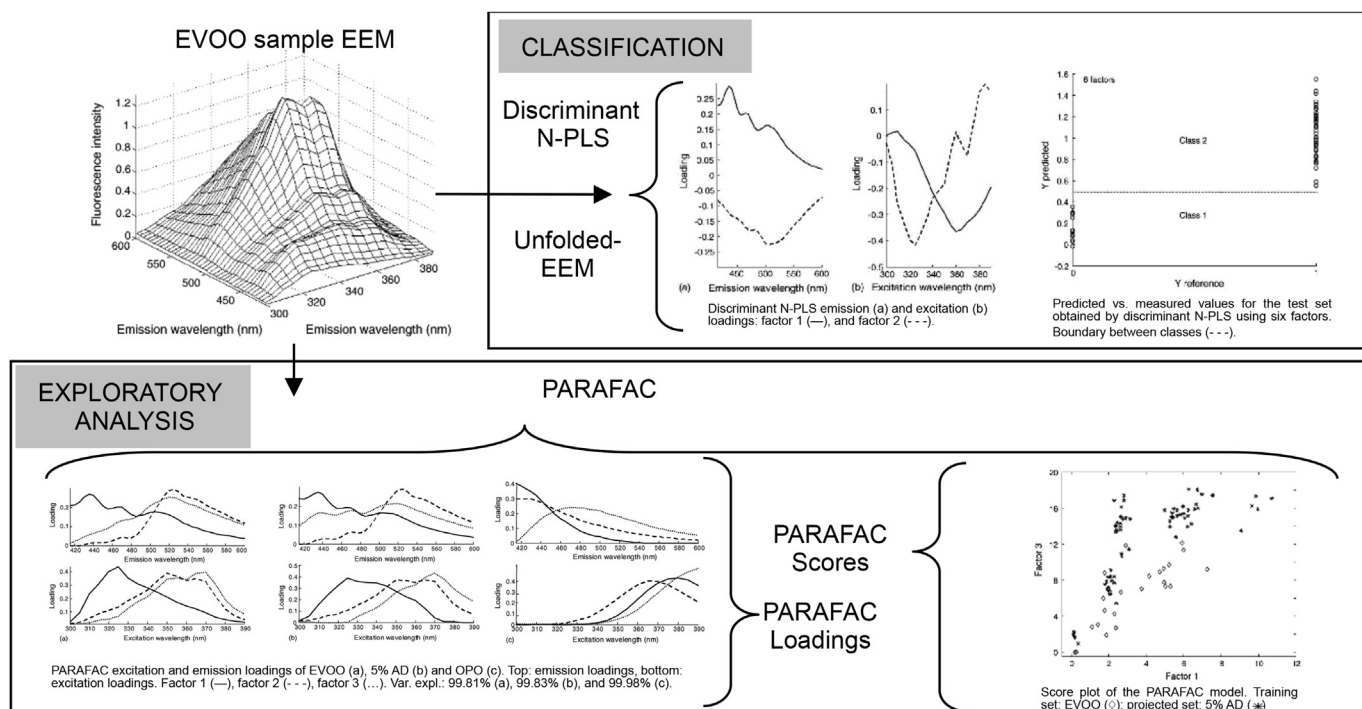


Fig. 3. EEM data qualitative analysis using high order chemometrics methods to determine EVOO adulterated samples. Exploratory analysis using PARAFAC and classification of the genuine samples using Discriminant N-PLS. Figure built using graphics reprinted from Ref. [45].

spectroscopy empowered by PLS [48]. PLS models were obtained for VOOs' fatty acid profile ($R = 0.84$ – 0.96) and minor components; such as hydroxytyrosol derivatives ($R = 0.86$ – 0.88) and C6 alcohols ($R = 0.69$ – 0.80); with acceptable reliability. Among positive sensory attributes 'fruity' ($R = 0.87$) and 'bitter' ($R = 0.85$), were also well modeled by PLS.

Detection and quantification of adulteration in EVOO was also accomplished by chemometric analysis of NIR spectra of olive oil mixtures containing different adulterants as corn, sunflower, soy, walnut and hazelnut oils. The authors carried out a PCA and several PLS models. However, they get confused when stated they used PCA models for classification, since PCA is only a display method. In fact, the authors used PCA to display what is the fat used for the adulteration using only score plot and human power. At this point, it will be desirable to use classification method such as LDA, in order to determine the nature of the adulterant previous to PLS analysis. On the other hand, PLS models were conducted and they predicted the amount of adulterants with 1% w/w of error in validation samples in the range 0–100% w/w of adulterant [51]. It deserves to be mentioned, the range 0–100% w/w for adulterants in a quite wide, a 0–30 or 0–50% w/w range should be more appropriate. This and other applications of NIR spectroscopy coupled to chemometric techniques to EVOO/VOO analysis are shown in Table 2.

Concerning MIR, most applications are coupled to FT (usually named as FTIR); thus, Table 3 summarizes the main applications of FTIR coupled to chemometric treatments to the quality control analyses of EVOO/VOO.

Raman spectroscopy or Raman scattering arising from vibrational, rotational, and other low-frequency transitions in molecules. Raman signal provides well-defined and separated spectral fingerprints, which are closely related to molecular structures. Thus, the application of Raman has almost been coupled to chemometrics for EVOO analysis, exclusively. The task tackled for this methodology include authentication and classification [62,64], the detection of deterioration [67], oil oxidation [44] and adulteration [58–61]. A

complete list of chemometric methods coupled to Raman spectroscopy is detailed in Table 4.

3.3. NMR spectroscopy coupled to chemometrics

NMR spectroscopy has extensively been used for oil analysis and it has been established as a valuable tool for the assessment of the quality and authenticity of olive oil. In the case of NMR signals for functional moieties are almost separated, the issue to address is interpretation of the large amount of data emerging from this signals. Thus, it is almost essential to have suitable multivariate methods for compressing such information in some few variables.

Detection of adulterations has been one of the principal scopes in the application of NMR to EVOO/VOO samples. A ^1H NMR (600 MHz) analytical protocol for the detection of refined hazelnut oils was developed by Mannina et al. [111], coupling NMR signals with PCA and LDA, allowing detection of adulteration down to 10%. An alternative approach to deal with hazelnut oil adulterations was informed by Agiomyrgianaki et al. [112], where, different mixtures of refined olive oils with refined hazelnut oils were analysed by ^1H and ^{31}P NMR spectroscopy. Subsequent application of forward stepwise CDA and a nonlinear variant of the binary tree method to the NMR data allowed the detection of the presence of refined hazelnut oils in refined olive oils at 5%.

Also, NMR was applied to measure diffusion coefficients of a number of EVOO. Qualitative prediction of adulteration was achieved by LDA [113] and the minimum adulteration levels detected by changes in diffusion coefficients were 10% for sunflower and soybean oil, and 30% for hazelnut and peanut oil.

NMR has extensively been used to develop accurate analytical fingerprinting methods for the authentication or certification of the geographical origin of olive oils aided by suitable chemometric analysis. NMR coupled to PLS-DA and SIMCA to trace European olive oils (896 samples) of three consecutive harvesting years (2005, 2006, and 2007) from Mediterranean areas were analysed

Table 2

Chemometric methods applied to NIR (stand alone), UV–Vis + NIR and NIR + MIR spectroscopy for the analysis of olive oil.

	Spectroscopic information	Chemometric analysis	Results/remarks	Ref.
Chemical/quality parameter				
Phenolic compounds (hydroxytyrosol derivatives)	FT-NIR (12500–4000 cm ⁻¹ , 8 mm vials)	PLS Pretreatment: 1st and 2nd derivative Multiplicative scatter correction (MSC)	A set of monovarietal Cornicabra VOOs produced in the PDO "Montes de Toledo" were used to generate calibration (n = 66), cross-validation and validation (n = 31) models in order to predict target parameter. Acceptable PLS models were obtained for VOOs' fatty acid profile, some minor components (hydroxytyrosol derivatives and C6 alcohols) and positive sensory attributes ('fruity' and 'bitter').	[48]
Volatile compounds (C6 alcohols)	Sensory parameters		The PLS methods were <i>a priori</i> developed in the laboratory using 190 VOO samples. Validation sets (n = 35–45) gave R ² over 0.992. PLS models, prior to a slope/bias correction, were used to monitor on-line values of the modeled parameters (acidity, oleic, linoleic and bitterness levels) during virgin olive oil production, during the processing of virgin olive oils in real olive mills. The results of t-tests indicate similarity between information both NIR and reference laboratory methods.	[52]
Organoleptic attributes (fruity, bitter)			FTIR* spectroscopy was found to be the most efficient in classification of oils and fats (80 samples for calibration and 30 for validation) when used with CVA yielding about 98% classification accuracy, followed by FT-Raman (94%) and FT-NIR (93%) methods.	[53]
Degree of unsaturation				
On-line quality control and characterization of VOOs	NIR (2500–750 cm ⁻¹ , 1 mm flow cell of 120 μl)	PLS		
Discriminant analysis of edible oils and fats	FT-NIR (2000 and 8000 cm ⁻¹ , Transmission cell) FT-MIR (4000–400 cm ⁻¹ , ATR)	LDA CVA		
Determination of free fatty acid (FFA), Polyphenol, Chlorophyll, and major fatty acid (FA) content. PV and Induction time parameters.	NIR spectroscopy (400–2500 nm, Reflectance spectroscopy / Cell)	PLS Pretreatment: SNV, MSC and 1st derivative	A set of 216 olive oil samples from throughout the Australian olive-growing areas. The variation in the oils tested covered the range of International Olive Oil Council. Correlation coefficients for minor components ranged 0.85–1.00 for minor and major components provided high levels of accuracy in the models.	[54]
Olive oil stability index (OSI), free fatty acids, peroxide value, and conjugated dienes were also developed	Vis-NIR (350–2300 nm (5 mm quartz cell))	PLS	The determination of the OSI using the Rancimat instrument was used as a reference method. Predictive Vis/NIRS models were obtained from PLS for the OSI, showing satisfactory performance in independent test samples. Predictive models for the determination of FFA, PV and conjugated dienes were also satisfactory.	[55]
Olive fat content, moisture and free acidity	FT-NIR (12500–3600 cm ⁻¹) - Olive paste: diffuse reflectance - Oil samples: transmission	PLS Pretreatment: Straight line subtraction and D'	Olive lots (287) and (161) olive oil samples were collected at three industrial plants which utilize different extraction technology. Results indicate good similarity between PLS-NIR and reference laboratory methods, allowing a rapid and less expensive screening analysis. The correlation between the oil yield and NIR was not satisfactory.	[56]
Sensory analysis (Defective: yes or not; Fruity aroma: low, medium and high)	FT-NIR (12500–4500 cm ⁻¹ , 8 mm vials) FT-MIR (4000–400 cm ⁻¹ , ATR)	LDA SIMCA	A sensory analysis of 112 virgin olive oils was performed by a fully trained taste panel. LDA showed better performance than SIMCA, with an average of samples correctly classified around 100% for both defective and fruity aroma using NIR or MIR spectroscopy.	[57]
PDO/origin/cultivar				
Authenticity of the Italian PDO extra virgin olive oil (Chianti Classico) and content of oleic and linoleic	UV–Vis (190–1100 nm, 5 mm quartz-cell) FT-NIR (10000–4000 cm ⁻¹ , 5 mm quart cell) FT-MIR (4000–700 cm ⁻¹ , ATR)	Unequal Class Models (UNEQ) SIMCA PLS	UNEQ and SIMCA were employed both on the MIR, NIR and UV–vis spectra, individually and jointly, in order to construct classification model. Samples were divided in two classes according to their geographical origin, 23 Chianti Classico PDO and 34 from Maremma region. PLS was applied on the UV–vis, NIR and MIR spectra, in order to predict the content of oleic and linoleic acids in the extra virgin olive oils.	[58]
Classification 5 PDOs from France Quantification of fatty acids and triacylglycerols (TAG)	FT-NIR (4500 and 10000 cm ⁻¹ , quartz cell 2 mm)	PLS-DA PLS	PLS-NIR was set up for the quantification of fatty acids and triacylglycerols in 125 virgin olive oil samples. PLS-DA was used to classify five near French PDOs and the spectroscopic interpretation of regression vectors showed the correlation among each PDO and one or two specific components of EVOO according to cultivar compositions.	[59]
Quantitative analysis of FA and TAG. Identifying PDO of extra virgin olive oils.	FT-NIR (12500–4500 cm ⁻¹ , 8 mm vial) FT-MIR (4000–700 cm ⁻¹ , ATR)	PLS PLS-DA Hierarchical-PLS (H-PLS)	Both spectral signals were used separately and concatenated matrix using PLS and PLS-DA regressions of 412 VOOs commercial samples. Multiblock method using H-PLS models were constructed at the second time. The H-PLS methodology seems to be very interesting for quantitative analysis, but for PDO identification the use of H-PLS was less efficient.	[60]
Cultivar discrimination of Italian monovarietal EVOO	FT-NIR (10000–4500 cm ⁻¹) FT-MIR (4000 and 600 cm ⁻¹)	LDA	LDA was applied on spectral data, NIR and MIR both separately and jointly, as a classification technique according to olive cultivar (Casaliva, Leccino, and Frantoio). Most accurate results were obtained using the fused NIR and MIR data, with either feature selection or data compression.	[61]

(continued on next page)

Table 2 (continued)

	Spectroscopic information	Chemometric analysis	Results/remarks	Ref.
Ligurian EVOO origin confirmation.	FT-NIR (10000–4000 cm ⁻¹ , 5 mm quartz cells) UV-Vis (190–1100 nm, 10 mm quartz cell) HS-MS	PCA, UNEQ-QDA and SIMCA Samplig: Kennard Stone, Potential Function	Samples labelled as Ligurian EVOO (26, 6 of them as PDO) and as provenient different geographical origin (37 from other Italian regions and Spain) were studied. Chemometrics was used to extract and combine the information from several multivariate and non-specific data (HS-MS, UV-Vis and NIR) and to build a class model for Liguria EVOO. The results confirmed the fusion of data is more appropriate for testing food authenticity.	[62]
Ligurian and non-Ligurian origing confirmation	NIR (1100–2498 nm, Transflectance) FT-MIR (4000–600 cm ⁻¹ , ATR)	Classification PLS-DA SVM Pre-processing: GENOPT (genetic algorithm)	EVOO samples (210 Ligurian and 700 non-Ligurian) were collected over three consecutive harvests. Both NIR as MIR, showed higher accuracy with SVM optimised by pre-processing than with PLS-DA on pre-processed data. Furthermore, this study demonstrates that even SVM models have to be developed on the basis of well-corrected spectral data in order to obtain higher classification rates.	[63]
Sabina PDO EVOO tracing	FT-MIR (4000–630 cm ⁻¹ , ATR) FT-NIR (10000–4000 cm ⁻¹ , 19 mm cylindrical glass cell)	PLS-DA SIMCA	Coupling MIR/NIR spectroscopy fingerprinting and chemometric classification methods for the traceability of EVOO PDO Sabina samples was investigated. It was still possible to build models that are transferable from one year to another with good accuracy.	[64]
Confirmation of declared provenance EVOO	NIR (1100–2498 nm, Transflectance)	PCA PLS-DA	EVOO samples (210 Ligurian and 703 non-Ligurian) were collected over three consecutive harvests. NIR fingerprint coupled to PLS-DA (following examination by PCA) using a first-derivative data pretreatment rendered the best models. Which correctly predicted the origins of samples, 92.8% for Ligurian and 81.5% non-Ligurian samples.	[65]
Origin authentication of virgin olive oils	NIR	ANN Logistic Regression (LR)	EVOO of “Siurana” and “Les Garrigues” PDOs, which are made from at least 90% of olives of the Arbequina variety, were discriminated. The results obtained for ANN and LR were quite satisfactory, in spite of the similarity between the two PDO.	[66]
Varietal discrimination of EVOO	FT-NIR (12,500–4500 cm ⁻¹) FT-MIR (4000–700 cm ⁻¹)	LDA and SIMCA using algorithm SELECT	82 monovarietal samples (‘Casaliva’, ‘Leccino’ and ‘Frantoio’) of EVOOs were analysed. NIR and MIR are interesting techniques compared with traditional chemical index for classifying EVOO samples on the basis of the varietal origin. Particularly, LDA and SIMCA, gave a high percentage of correct classification and prediction for ‘Leccino’ cultivar.	[67]
Characterisation of the PDO Chianti Classico olive oil	FT-NIR (10,000–4000 cm ⁻¹) UV-visible (190–1100 nm) Artificial nose	PCA, STEP-LDA, LDA, Quadratic Discriminant Analysis-UNEQ dispersed classes (QDA-UNEQ)	217 EVOOs were collected from 5 geographical origins. The non-specific information obtained allowed to build reliable models for checking the origin and authenticity of the Italian PDO Chianti Classico.	[68]
Geographical authentication of Ligurian EVOO	FT-NIR 10,000–4380 cm ⁻¹	Potential functions techniques (POTFUN), SIMCA, QDA-UNEQ	195 EVOOs were analysed by NIR: 126 were authentic oils from Liguria and 69 were commercial samples. In general, Liguria EVOOs were clearly differentiated from the other oils. Multivariate analysis allowed the construction of Liguria class models with good predictive ability and high sensitivity.	[69]
Authentication of Tunisian virgin olive oils	NIR 10000–4500 cm ⁻¹	PCA, SIMCA	Fatty acid composition and NIR spectra associated to chemometric treatment allowed to characterise and authenticate six Tunisian olive oil varieties. These oils were distinguished from Maghrebien (Algerian and Moroccan) and French PDO VOOs. The models build with NIR spectroscopy data give 89.55%, 92.53% and 98.50% of correct classifications for Chemlali Sfax, Chetoui and Oueslati oils, respectively	[70]
Adulteration EVOO adulteration with Pomace olive oil	NIR (400–1700 nm) FT-MIR (3200–600 cm ⁻¹) ATR/photoacoustic spectroscopy (PAS) FT-Raman (3200–800 cm ⁻¹)	PLS Spectral treatment: MSC	The concentration of olive pomace oil in EVOO was in the range between 0 and 100% by weight, with 5% increments. Of the methods studied, FT-Raman gave the highest correlation ($R^2 = 0.997$) and lower standard error ($SD = 1.7\%$).	[71]
Process control Fat loss and Pomace moisture content On-line determinations	NIR (1100–2250 nm, Acousto-optic tunable filter and transfectance probe)	ANN	Spectra were acquired on line into the olive mill. A three-layer ANN was trained and tested with two independent data sets of 68 samples. The results indicate a very good predictive capacity of the model with values of $R = 0.961$ and for fat content and $R = 0.970$ for moisture. The model to make possible a rapid regulation of the extraction process to correct any failure.	[72]

by ^1H NMR spectroscopy. PLS-DA and SIMCA modeling analyses were used to build up statistical models both to discriminate between Ligurian and non-Ligurian olive oils and to define the Ligurian olive oil class to confirm the declared provenience [114].

Longobardi et al. [115] also carried out the classification of olive oils according to geographical origin by using ^1H NMR fingerprinting combined with multivariate analysis. ^1H NMR (simple one pulse and with multiple saturation of the lipid signals experiment) was applied to each sample in combination with PCA, CDA, and k-Means clustering analysis. Monte-Carlo embedded cross-validation was used to demonstrate suitability of the methods.

Multivariate analysis of ^1H NMR data has been used for the characterization commercially available in the U.S. as Italian products. PCA allowed good discrimination and gave some affinity indications for the U.S. market olive oils compared to other single cultivars of EVOO such as Coratina and Ogliarola from Italy, Picual (Spain), Kalamata (Greece) and Sfax (Tunisia). The study revealed that most EVOO tested were closer to Greek and Spanish olive oils than Italian EVOO. The PCA loadings disclose the components responsible for the discrimination as unsaturated (oleic, linoleic, linolenic) and saturated fatty acids [116].

Many works have dealt with the influence of harvest year, cultivar and geographical origin on olive oils composition, Agiomyrigianaki et al. performed a study on Greek EVOO study by NMR spectroscopy and biometric analysis [117]. The samples were chemically analysed by means of ^1H and ^{31}P NMR spectroscopy and other chemical parameters. The influence of cultivars on the compositional data of the EVOO samples according to harvest year and geographical origin was examined by means of forward stepwise CDA and binary tree. They found which variables most satisfactorily classified Greek olive oils.

The influence of harvest period and harvest method on olive oil composition was also studied by NMR spectroscopy and by some quality parameters in a previous work [118]. The work focused on this secondary factors and investigated their interactions with primary (genetic and pedoclimatic) and other secondary factors. To avoid misinterpretation MLR was used to adjust the result obtained from the ANOVA, factors were corrected for the effects of the other factors that influence the variables under investigation. The weight of each factor was evaluated by the variance component analysis. Additionally, PCA and LDA were applied showing that samples were well grouped on the basis of the harvest period and method.

Studies of time, thermal and oxidative stability of olive oils by NMR analysis were also powered by multiway chemometric methodologies. That is the case of a multiway chemometric and kinetic study to evaluate the thermal stability of edible oils published by Cordella et al. [119]. Their approach used the NMR fingerprint corresponding to aldehydes in a multivariate data analysis procedure in order to give the major trend in the thermo stability phenomena. The application of 3 and 4 way Tucker3 models, a general model of PARAFAC, led to a better understanding of the chemical stability of the oils studied and was used to determine the order of stability of these oils. This work shows that a fully chemometric study of NMR spectra allows to rank the oils according to their thermal stability.

Alonso et al. used ^1H NMR fingerprinting to evaluate VOO stability over time [120]. PCA of the NMR data allowed visualizing the evolution of the oil within the 3 years and seven months of the study. The PCA loadings disclose the chemical compounds responsible for the compositional changes taking place in VOO. Small changes in the signals, and the appearance of low intensity ones, indicate that oxidative (primary oxidation products) and hydrolytic degradation of the VOO started after one year. Moreover, the characteristic resonances of aldehydes (main secondary oxidation products) were not detected in the VOO over the studied

time period; therefore the secondary oxidation process had not yet occurred.

To date, a large number of research and review articles have been published with regards to the analysis of olive oil reflecting the potential of the NMR technique, some of them coupled with chemometric analysis have been discussed elsewhere [6,121].

Other applications of NMR coupled with chemometrics for determining quality parameters in olive oil are shown in Table 5.

3.4. Chemometrics and separation techniques

Techniques such as liquid chromatography, gas chromatography (GC) and capillary electrophoresis (CE) are used for the separation, purification and/or the analyses of complex samples. These techniques provide a huge amount of data that can offer the analyst plenty of information; however, the conventional data treatment can only give a small part of the information contained therein. Therefore, chemometrics has proven to be a very useful tool for chromatography data treatment as a technique of exploratory data analysis and unsupervised and supervised pattern recognition [138].

Liquid chromatography has been widely coupled to chemometrics for the analysis of olive oils. Polar compounds such as phenolic compounds of olive oil have been extensively studied by HPLC, many of these studies have used chemometrics for the treatment of data set. Evangelisti et al. [139] used PLS regression to obtain models that show a significant correlation between the phenolic composition of olive oils and the healthy state of the olives sampled. These models allowed tracing the state of health of the olives through the analysis of the phenolic compounds of VOO with a high degree of accuracy. Besides, they could predict the oil's expected shelf life.

Other authors used MCR-ALS and PARAFAC2, a PARAFAC modification to deal with three-linearity loss, to resolve overlapping of phenolic compounds after the chromatographic analysis. These chemometric models allowed shortening the analysis time and to obtain good resolution for the determination of four phenolic acids [140]. Chemometrics has also been of great usefulness for the geographical origin discrimination of olive oils. PCA demonstrated the relationship of the quali/quantitative phenolic profile of Oueslati olive oil and the geographical origin of olives. Additionally, the use of the model permitted the use of phenolic fractions as an indicator of each region [141]. CDA has also shown to discriminate the geographical origin of an olive oil variety depending on the phenolic profile [142,143]. Another study showed how PCA was able to discriminate among different varieties of EVOO oil depending on the phenolic profile; while LDA classified the samples depending on their geographical origin in Tunisia (North, Centre and South) [144].

HPLC-MS has also been combined with chemometric for the classification and prediction of different olive oil cultivars by means of diacylglycerols, triacylglycerols (TAGs) and sterols. LDA allowed classifying/predicting the samples with a very high accuracy: 100% classification and 99% prediction rate on by cross validation procedure [145]. Other authors have evaluated the possibility of getting parameters to classify within the cultivars according to quali/quantitative determination of pigments oils (chlorophylls, pheophytins and carotenoids) in monovarietal olive [146].

The complete evaluation by PCA, PLS-DA and MCR, in combination with suitable preprocessing of the chromatograms of triacylglycerides (TAGs) profiles of 126 samples of different categories and varieties of olive oils, and types of edible oils was carried out by de la Mata-Espinosa et al. [147]. The two clusters (olive and non-olive oils) were explored using PCA, from properly de-trended (Dt) HPLC data. Using PLS-DA on the same data the classification

Table 3
Chemometric methods coupled to MIR (specifically FTIR) spectroscopy for the analysis of olive oil.

Determination	Mode	Spectral region	Chemometric analysis	Results	Ref.
Chemical/quality parameter					
Characterization of edible fats and oils	Optical fibre	3060–2750 cm ⁻¹ 1500–1000 cm ⁻¹	PCA	Different concentrations of linoleic acid allows characterization of sunflower seed oil compared to olive and peanut.	[47]
Quantitative determination of isolated trans fatty acids and conjugated linoleic acids in oils and fats	ATR	1000–850 cm ⁻¹	PLS	Trans fatty acids and conjugated linoleic acids (CLA) have been quantitatively determined simultaneously.	[73]
Monitoring of fatty acid composition in VOO	ATR	4000–700 cm ⁻¹	PLS	The validation set exhibited nearly quantitative recoveries (100% and 98% for oleic and linoleic acid, respectively) and relative standard deviations below 7%. The proposed method provided results comparable to official procedures, with the advantages of being less expensive and more rapid.	[74]
Comparison of fatty acid profiles and mid-infrared spectral data for classification of olive oils	ATR	4000–650 cm ⁻¹	PCA, PLS, SIMCA	FT-IR spectra in combination with PLS could be a useful and rapid tool for the determination of some of the fatty acids of olive oils.	[75]
Detection of low-quality EVOOs by fatty acid alkyl esters evaluation	ATR	4000–700 cm ⁻¹	PLS	FTIR-PLS methodology proved to be useful for analytical predictions of the sum of FAMEs and FAEEs content and ratio between ethyl esters and methyl esters in EVOOs. Results were statistically similar to official procedures.	[76]
Discrimination of edible oils and fats	Transmittance (with NaCl cell windows)	4000–450 cm ⁻¹	PCA, PLS-DA, ECVA	All used methods could distinguish butter from vegetable oils; however, interval-ECVA resulted in the best performances for calibration and external test set with 100% sensitivity and specificity.	[77]
Classification EVOO on the basis of fruity attribute intensity	ATR	4000–400 cm ⁻¹	LDA, SIMCA	Best results were obtained using only the “not defective oils”, which were grouped into three classes: ‘low fruity’ (class 1), ‘medium fruity’ (class 2) and ‘high fruity’ (class 3). The prediction rate varied between 71.6% and 100%, as average value.	[57]
Determination of the peroxide value in EVOO through the application of the stepwise orthogonalisation of predictors to mid-infrared spectra	Flow liquid cell with a standard holder and ZnSe window	4000–375 cm ⁻¹	SELECT-Ordinary Least Squares (OLS)	SELECT-OLS regression model finally proposed for peroxide value modelling showed a similar accuracy to the respective reference method. This encourages the transfer of the methodology to industry to notably reduce analytical time, efforts, and cost of assessing this quality index, allowing a near real-time determination to be used to control EVOO quality and possible quality changes.	[78]
Identification of olive oil sensory defects	Horizontal attenuated total reflectance, HATR	4000–600 cm ⁻¹	PCA, PLS-DA	PLS-DA models were able to discriminate the defective versus non-defective oil categories with predictive abilities between 70% and 90%, as evaluated by cross- and test set validations. This methodology advances instrumental determination of results previously only achievable with a human test panel.	[79]
PDO/origin/cultivar					
Differentiation of mixtures of monovarietal olive oils	ATR	4000–650 cm ⁻¹	PCA, PLS	PCA successfully classified each cultivar and differentiated the mixtures from pure monovarietal oils. Quantification of two different monovarietal oil mixtures (2–20%) is achieved using PLS regression models	[80]
Geographical classification of olive oils	ATR	4000–600 cm ⁻¹	CART and SVM	Discrimination between Italian and Ligurian olive oils, using both Classification and regression trees (CART) and SVM.	[81]
Characterization and classification of Italian VOO	ATR	4000–700 cm ⁻¹	LDA, PLS, SIMCA	Mid-infrared spectroscopy was able to classify both monovarietal and industrial olive oils allowing a high correct classification of samples (>95%)	[82]
Confirmation of EVOO origin claims by FTIR and chemometrics	ATR	4000–600 cm ⁻¹	PCA, FDA, PLS-DA	The most successful chemometric models were those derived from data sets that contained samples from three harvest seasons incorporating variation due to weather conditions in the models. However, the model had 20% of error, but the speed and low cost of measurements suggest that it could certainly be used as a screening technique.	[83]
FTIR spectroscopy for cluster analysis and classification of morocco olive oils	ATR	4000–600 cm ⁻¹	CA, PCA, PLS-DA	Morocco olive oils were separated into four classes by CA and PLS-DA. The proposed model proved the ability of the chemometric techniques applied on FTIR data for a rapid and accurate classification of olive oils without the need for sample preparation	[84]
Origin of EVOOs by infrared spectroscopy and chemometrics	ATR	4000–630 cm ⁻¹	PLS-DA, SIMCA	PLS-DA evidenced a rather high classification accuracy and SIMCA confirmed the results. It was evidenced that the different production year can influence on the spectroscopic fingerprint. However, it was still possible to build models that are transferable from one year to another with good accuracy.	[85]

Table 3 (continued)

Determination	Mode	Spectral region	Chemometric analysis	Results	Ref.
Discrimination of the geographical origin of Italian olive oil (Ligurian and non-Ligurian)	ATR	4000–600 cm ⁻¹	PLS-DA, SVM, GENOPT-SVM	SVM with optimized pre-processing give models with higher accuracy than the one obtained with PLS-DA on pre-processed data.	[63]
Adulteration					
Analysis of potential adulterants of EVOO using infrared spectroscopy	ATR	4800–800 cm ⁻¹	PLS	Quantitative determination of the level of typical adulterants in extra virgin olive oil such as refined olive oil and walnut oil	[86]
Authentication of edible oils	ATR	3500–500 cm ⁻¹	PLS, LDA, ANN	Classification rates according to botanical origin and adulteration detection levels. Comparison Raman vs MIR.	[87]
Authentication of olive oil adulterated with vegetable oils	Single-bounded ATR	4000–500 cm ⁻¹	PLS-DA, PLS	PLS-DA successfully classified pure vs. adulterated samples. PLS successfully quantified the degree of adulteration in the olive oil. DA-PLS classified EVOO and other vegetable oils.	[88]
Detection of the presence of hazelnut oil in olive oil	ATR	4000–900 cm ⁻¹	Stepwise LDA	Discrimination between olive and hazelnut. Adulteration detection at de level of 8%. The limit of detection is higher when the blends are of edible oils from diverse geographical origins.	[89]
FT-MIR spectroscopy and counter-propagation artificial neural networks for tracing the adulteration of olive oil	ATR	3074–728 cm ⁻¹	CP-ANN	The models obtained a good separation of the different groups and classify correctly pure olive oil and hazelnut oil. Indeed, a reasonable discrimination between both mixtures and pure oils was achieved.	[90]
Detection of adulteration of EVOO	ATR	4000–650 cm ⁻¹	PCA, PLS-DA	PCA and PLS-DA predict the adulterants, corn-sunflower binary mixture, cottonseed and rapeseed oils, in olive oil with LOD around 1%. Also, models detect adulteration regardless of the type of adulterant oil. LOD 10%.	[91]
Estimation of EVOO adulteration with edible oils	ATR	4000–700 cm ⁻¹	PLS	PLS model developed was very suitable for the determination of modelled adulterants (canola, hazelnut, pomace and high linoleic/oleic sunflower). Additionally, it may also reveal an adulteration even if it does not derive from the studied adulterants.	[92]
FTIR spectroscopy for the analysis of EVOO adulterated with palm oil	ATR	4000–650 cm ⁻¹	PLS, PCR, DA	PLS and PCR revealed the best calibration models for predicting the concentration of adulterated EVOO samples (R ² > 0.999) and root mean standard error of cross validation (RMSECV) of 0.285 and 0.373, respectively. DA could classify pure and adulterated samples with no misclassified group obtained. DA was also effective enough to classify EVOO samples and potential adulterant of vegetable oils.	[93]
Authentication of EVOO by FTIR	KBr disks	4000–500 cm ⁻¹	LDA, MLR	LDA was able to discriminate EVOO according to their botanical origin. Indeed, MLR models could detect sunflower, corn, soybean and hazelnut oils presence in EVOO until contents of 5%.	[94]
Detection of olive oil adulteration	ATR	4000–600 cm ⁻¹	PLS, PLS-DA	PLS model was able to predict the concentration of sunflower and soybean oil adulterants in the 1–24% range. PLS-DA explained 99.9% of variance and predicted with 100% accuracy both adulteration.	[95]
Quantification and classification of corn and sunflower oils as adulterants in olive oil	ATR	4000–650 cm ⁻¹	PLS	PLS calibration using FTIR normal spectra and first derivative FTIR spectra was used to determine de level CO and SFO, respectively,	[96]
FTIR spectral data for the analysis of rice bran oil in EVOO	Deuterated triglycine sulphate (DTGS) as a detector and a KBr/Germanium as beam splitter	4000–500 cm ⁻¹	PCA, DA, PLSR, PCR	DA can discriminate EVOO and EVOO adulterated with rice bran oil, with an accuracy of 100%. PLSR demonstrated to be a reliable technique for the quantification of rice bran oil in EVOO.	[97]
Rapid authentication of EVOO	ATR	4000–650 cm ⁻¹	PLS, PCR, LDA	In order to quantify the level of canola oil in EVOO, PLS using FTIR normal spectra was preferred to derivative treatments. LDA allows one to make the classification between EVOO and EVOO adulterated with canola and other vegetable oils.	[98]
Process control					
Classification of VOO subjected to thermal stress	ATR	4000–700 cm ⁻¹	PLS	PLS distinguished among the oils and the thermal treatments. This approach could be useful for monitoring the oxidative status of cooked oils, both in industrial scale or in food-catering field.	[50]

rate of olive oils on validation set was 100%. Finally, MCR was used to detail the chemical behaviour of samples and chemical base of classification.

TAGs analysis by HPLC coupled to PLS analysis was also able to predict olive oil concentrations with reasonable errors in other edible oils. The model could quantify the concentration of olive oil with errors lower than 10% [148].

The non-polar fraction of olive oil is usually determined by GC and chemometrics also plays an important role to manage the data obtained by this technique. The main purpose of applications of GC and chemometrics is the discrimination of olive oils depending on their variety and geographical origin and their authentication.

Fatty acid composition data obtained by GC (raw chromatograms and concentration data) from 144 EVOO samples was used

Table 4
Chemometric methods coupled to Raman spectroscopy for the analysis of olive oil.

	Spectroscopic information	Chemometric analysis	Results/remarks	Ref.
Chemical/quality parameter				
Discriminant analysis of edible oils and fats	FT-NIR (2000 and 8000 cm ⁻¹) Transmission cell FT-IR (4000–400 cm ⁻¹) ATR FT-Raman (400–3700 cm ⁻¹)	LDA CVA	FTIR spectroscopy was found to be the most efficient in classification of oils and fats (80 samples for calibration and 30 for validation) when used with CVA yielding about 98% classification accuracy, followed by FT-Raman (94%) and FT-NIR (93%) methods.	[53]
Analysis of oxidized olive oil (peroxide value, k232 and k270)	Raman spectra (200–2700 cm ⁻¹) Spectroscopic Probe	PLS	Raman spectra of 126 oxidized EVOO and VOO samples were collected directly using a measure probe. PLS was used to calibrate the Raman instrument for the different targeted parameters. The performance of the PLS developed models was determined by using validation sets.	[99]
FA and TAG composition and origin authentication of French PDO regions	Confocal Raman spectroscopy	PLS PLS-DA	FA and TAG compositions were determined by PLS, FAs at very low percentages showed some troubles in their predictions. PLS-DA on Raman spectra was able to correctly classify 92.3% of French PDOs and 100% of PDO samples made with only one principal cultivar. This work confirms that fatty acid and TAG percentages may be used to authenticate PDO of French VOOs.	[100]
FFA in VOO and olives	Raman 800–3200 cm ⁻¹ flow cell (Oils) dedicated sample cup (Milled olives)	PLS	Both external and internal validation were used to assess the predictive ability of the PLS calibration models for FFA content in oil (0.20–6.14%) and olives (0.15–3.79%). The predicted FFA contents were used to classify oils and olives in different categories according to the EU regulations, 90% of the oil samples and 80% of the olives were correctly classified.	[101]
FFA in EVOO	Raman 700–3100 cm ⁻¹ 1800 μl quartz cell	PLS	The FFA content of olive oil in terms of oleic acid percentage ranged from 0.14 to 0.40% as was measured by the titration analysis. Pure oleic acid was used to expand the upper limit of the FFA range to 0.8%. The best performance was achieved using the fingerprint region 945–1600 cm ⁻¹ of the Raman data, which yielded an accurate, robust and precise model.	[102]
Adulteration				
EVOO adulteration with Pomace olive oil	NIR 400–1700 nm MIR 3200–600 cm ⁻¹ ATR/photoacoustic spectroscopy (PAS) RAMAN (3200–800 cm ⁻¹)	PLS Spectral treatment: MSC	The concentration of olive pomace oil in EVOO was in the range between 0 and 100% by weight, with 5% increments. Of the methods studied, FT-Raman gave the highest correlation (R ² = 0.997) and lower standard error (SD = 1.7%).	[71]
Determination of soybean oil adulteration VOO	Raman spectra (1217–690 cm ⁻¹) Temperature controlled manifold (20–90 °C)	LDA	An LDA strategy was evaluated for the identification of soybean oil-adulterated olive oils using linear discriminant analysis (LDA). The discrimination accuracy was improved around 80–90 °C due to the enhanced spectral selectivity between olive and soybean oils.	[103]
Adulteration detection, sunflower seed oil, soybean oil and corn oil	Raman	LS-SVM ANN PLS	Olive oil samples (n = 117) adulterated with sunflower seed oil, soybean oil and corn oil were detected by Raman spectroscopy, and LS-SVM was used to identify the type of the adulterant oil. In addition, LS-SVM had the best performance to predict amount of adulterant than ANN and PLS.	[104]
Visible Raman spectroscopy for the discrimination of olive oils and the detection of adulteration	Raman 700–3100 cm ⁻¹ 1800 μl quartz cuvettes	PLS PCA	Different mixtures of EVOO with three different sunflower oil types were prepared between 5 and 100% (v/v) in 5% increments of sunflower oil. Raman spectroscopy in combination with PLS regression analysis was successfully applied for quantitative analysis, LOD down to 0.05% was achieved.	[105]
Hazelnut oil adulteration of EVOO	Raman 1000–3000 cm ⁻¹ 4 mL vial	PCA PLS and Genetic Programming (GP)	The relationship between Raman and cultivar/region for EVOO was evaluated by PCA. A set of Hazelnut oils was evaluated separately. It was found that two PCs accounting for 82% variation of EVOO/HO binary mixtures. Using a training set (0–100% of HO, every 10%) and a test set (5–95 of HO, every 10%) PLS and GP models were developed. PLS was a more simple and accurate approach.	[106]
EVOO authentication and adulteration quantification sunflower.	FT-Raman	PLS Pair-wise minima and maxima selection (PMMS)	Different strategies for wavelength selection were tested. PMMS provided robust calibration models with an small number of variables. TABU search strategy showed only punctual solution. Robustness was tested with a randomly cross-validation set (n = 20).	[107]
Characterizing different kinds of vegetable oils in the Raman region. Adulteration of EVOO detection.	Raman 800–1800 cm ⁻¹	Bayesian framework (Bay) LS-SVM PLS	Bay-LS-SVM was applied to find an adulteration prediction model using the Raman data of EVOO. The Bay-LS-SVM compared with PLS showed higher accuracy and computational efficiency.	[108]
Process control				
Discrimination of olives according to fruit quality	Raman 200–2700 cm ⁻¹	PCA SIMCA PLS-DA K-nearest neighbors (KNN) PLS	Low-resolution Raman was applied to detect whether olives have been collected directly from the tree or not (sound or ground, respectively). The best results were obtained by KNN, with prediction of 100% for 'sound' and 97% for 'ground' in an independent validation set.	[109]
				[110]

Table 4 (continued)

	Spectroscopic information	Chemometric analysis	Results/remarks	Ref.
Revealing heat-induced degradation of extra virgin olive oil carotenoids	Vis-Raman 700–3100 cm ⁻¹ 1800 µl quartz cuvette		A model PLS was established for monitoring carotenoids degradation during heating. A progressive degradation in carotenoids was observed, starting at 180 °C and 140 °C in microwave and conventional heating processes respectively; this was followed by a rapid disappearance among at 180–203 °C only with conventional heating. Loss of double bonds and slightly changes in FFA were also observed in both processes.	

for a deep chemometric analysis of French blends of EVOO (cultivars Aglandau, Grossane and Salonenque) [149]. Chromatograms were submitted to Correspondence Analysis, emerging 3 fatty acid-metabolic ways, C17-based, the 18:2w6 and unsaturated (1w7)-type, as responsible of discrimination among cultivars. In a second step, original set was divided in training and validation sets. Ten (pure) training samples were used to obtain an experimental domain based on simplex lattice design, which consisted in 66 simulated ternary mixture samples, raised to 1980 by bootstrapping. An LDA model was trained using only the concentration data of 6 fatty acids (5 chosen by correlation analysis). When validation set was tested the prediction error in variety composition was around 10%, which was in agreement with the variation of the simplex design. Additionally a PLS model was applied to determine variety composition of blends but no additional advantages were detected for its application.

Table 6 summarizes the main features of GC methodologies combined with chemometrics analyses.

Though, not as widely used as the previous techniques, CE has also been applied to determine some parameters in olive oil. As for HPLC and GC, chemometrics is also a useful tool for data treatment combined with CE. Most applications concern the analysis of phenolic compounds, present in the polar fraction. Carrasco-Pancorbo et al. used CE with UV detection to compare the phenolic profiles of EVOO oils belonging to Spanish and Italian PDOs and their relation to sensorial properties. In this study, Tukey's honest significant difference (HSD), one-way ANOVA, Pearson's linear correlations and PCA were used. The results showed that olive oil could be assigned to their PDO considering eight phenolic compounds present in the extracts [174].

Chemometrics, properly DOE, has also been used to optimize CE methodologies for the analysis of phenolic compounds. A response surface approach over a central composite design was used to optimize the electrophoretic separation of 13 phenolic compounds from EVOO oil. The application of Derringer's desirability was necessary to reach a multi-criteria target, providing maximum resolution between peaks and a shorter runtime [175]. Derringer's desirability function has also been used for the optimization of a CE method that allows determining 17 phenolic compounds in olive oil in just 19 min; a Doehlert design was used at this instance. This DOE approach appears to be useful to deal with optimization of peak separation, saving time and reagents as well as allowing mathematical analysis of the influence of each factor [176].

Furthermore, MCR-ALS algorithm combined with non-aqueous CE with diode array detection (second-order data) has been applied for the simultaneous determination of six phenolic acids in virgin olive oil samples. MCR-ALS showed its versatility for the management of complex data without trilinearity [177].

However, CE and chemometrics have also been combined for the discrimination of different vegetable oils by their botanical origin. The analysis of fatty acids in vegetable oils by CE with indirect photometric detection was carried out and a LDA model was constructed to classify vegetable oils according to their botanical origin [178].

3.5. Alternative techniques (DSC, MS, electrochemical, and others)

Countless non common or less common analytical techniques still bearing high potential such as listed calorimetry, electrochemist, "electronic sensing" equipment, have also been used coupled to chemometrics to achieve compounds determination, characteristics, or classification of EVOO.

Corretani et al. applied several chemometric methods on calorimetry data to obtain quantitative and qualitative data. A PLS approach was applied to DSC data obtained from different vegetable oils to evaluate fatty acid composition Palmitic (Fig. 4A). DSC data first was unfolded in order to allow the access to all the information of profiles (cooling and heating profiles), then data was mean centred in order to avoid artifacts and remove uninformative tendencies (Fig. 4B). Palmitic, stearic, oleic and linoleic acids, saturated, mono- and poly-unsaturated fatty acids percentages, oleic/linoleic and unsaturated/saturated ratios were the chemical parameter inferred by different PLS models. The analysis of statistics and figures of merit (i.e. R² ranged 0.78–0.98, relative error in the calibration 2.1–10% and LOD 0.24–11%) and actual vs predict value curves (i.e. for palmitic acid Fig. 4C) allow to conclude that methods provide results statistically similar to traditional official procedures in terms of analytical performance [179]. Additionally, DSC was coupled with a PCA procedure to evaluate the effect of thermal stress on EVOO. Signals correlated with thermo-oxidation signs were found using this methodology [180]. Another instance was PLS applied to clarify the influence of TAG composition on the shape of DSC cooling curves of EVOO [181]. Results obtained by the application of algorithm on TAG concentration and digitized DSC curves showed that cooling transitions were markedly influenced by triolein, dioleoyl-linoleoyl-glycerol, dioleoyl-palmitoyl-glycerol and stearoyl-oleoyl-linoleoyl-glycerol, which are the most representative TAGs in EVOO. Finally, a chemical and thermal evaluation of olive oil during refining was correlated to different oxidative levels with PCA scores [182].

Torrecilla et al. developed two models based on the combination of DSC and the calculus of lag-k autocorrelation coefficients (decomposition base on a chaotic parameter) to quantify adulterations of EVOO with refined olive, refined olive pomace, sunflower and corn. The adulterant agent concentrations determined were always less than 14% w/w with a R² higher than 0.9 [183].

Electrochemical methods and especially e-sensing equipment produce signals which are not necessarily specific for any particular specie. Instead, the pattern of responses generated is a fingerprint of the sample studied. This pattern can be related to certain features or characteristics of the samples by means of chemometrics [184]. For example, using carbon paste electrodes and PLS-DA it has been possible to classify the olive oils groups according to their degree of bitterness. In addition, good correlations between redox processes observed in the electrodes and the analytical profile of the EVOO under study have been found. A similar correlation was found with sensorial characteristics [185].

The oxidation of EVOOs has also been considered at different storage periods and conditions. Then, LDA multivariate analysis has

Table 5
Chemometric methods coupled to NMR spectroscopy for the analysis of olive oil.

Determination	Analytical techniques	Chemometric analysis	Results	Ref.
Chemical/quality parameter				
Effect of agronomical practices on carpology, fruit and oil composition, and oil sensory properties, in olive	HRMAS-NMR	PLS-DA	Broad-spectrum analysis, such as HRMAS-NMR could be necessary to differ in the composition of fruits grown with different agronomical practices.	[122]
PDO/origin/cultivar				
Discrimination of the variety and region of origin of EVOOs using ^{13}C NMR and multivariate calibration with variable reduction	^{13}C NMR	PCA, PCR and PLS	Reduction of variables improved the PCA clustering, and the prediction results of PCR and PLS. Single models PCR2 and PLS2 models achieved a successful prediction rate of about 70%. However, multiple PLS models routinely achieved successful predictions of over 90% and in many cases 100% of the data in test sets.	[123]
Classification according to the variety and geographical origin of Italian olive oils by ^1H NMR	^1H NMR	LDA	A classification of the samples according to their variety with prediction ability of 100% was obtained with LDA, while the prediction ability of the DA model was 96% for the classification of olive oil varieties.	[124]
Chemometric classification of olive cultivars based on compositional data of oils	^{13}C NMR	PCA, HCA and LDA	The efficiency of official methods and ^{13}C NMR spectroscopy to distinguish oil composition of olive cultivars was demonstrated. The predictability of the LDA models from chromatographic and ^{13}C NMR were highly similar shielding 92 and 88% of right classification, respectively.	[125]
Study of the cultivar–composition relationship in sicilian olive oils from four different cultivars	^{13}C NMR	MANOVA, PCA, TCA, multidimensional scaling (MDS), and LDA	Grouping of olive oils according to their cultivars occurs for particular ^{13}C resonances all belonging to fatty chains in the sn 1,3 position of the glycerol moiety. TCA and MDS plots show Cerasuolo and Tonda Iblea well separated from the other cultivars, and Biancolilla appears very near Nocellara. While LDA shows a perfect separation among all the cultivars.	[126]
Classification of olive oils by geographical origin and processing using high throughput flow ^1H NMR fingerprinting	^1H NMR	PCA, LDA and PNN	PNN provided the best success rate for the classification of olive oils. Variability due to production year influenced less as a factor than the actual country of origin.	[127]
Geographical, ecological and agronomic characterization of olive oils from Lazio	^1H and ^{13}C NMR	ANOVA, PCA and LDA	NMR and statistical procedure is an important tool for the characterization of olive oils allowing, detection of minor compositional changes not obtainable with any other single analytical procedure. Olive oils were well grouped according to the irrigation practice as well as to the altitude at which olive trees were grown	[128]
Geographical characterization of Greek virgin olive oils (cv. Koroneiki)	^1H and ^{31}P NMR	CDA and classification binary trees (CBTs)	CDA showed that the geographical prediction at the level of three general regions is 87% and, becomes 74% when more specific origins are studied. The use of CBTs made possible the construction of a geographical prediction algorithm for unknown samples in a self-improvement fashion, which can be readily extended to other varieties and areas.	[129]
Multivariate analysis of ^1H NMR spectra of genetically characterized EVOO and growth soil correlations	^1H NMR	LDA	LDA afforded a high reliability degree for discriminating cultivars (almost 90% of prediction ability), and a good assigning ability for the geographical origin (100%).	[130]
Metabolomic approach for EVOO from secular olive trees of Apulia region	^1H NMR	PCA, OPLS-DA	EVOOs obtained from secular olive trees could be easily differentiated by OPLS-DA not only depending on the used cultivars but also according to their geographical origin within the different districts of the Apulia region.	[131]
Discrimination of vegetable oils using NMR spectroscopy and chemometrics	^1H and ^{13}C NMR	PCA	Results found virgin olive oils clustered close together in spite of the different geographical origin. Blends of 1% olive oil in sun-flower oil were detected using specific ^1H and ^{13}C signals.	[132]
Adulteration				
^1H and ^{13}C NMR techniques and ANN to detect the adulteration of olive oil with hazelnut oil	^1H and ^{13}C NMR	ANN	The designed and tested ANN mathematical model was a useful tool for detecting the presence of hazelnut oil in olive oil at percentages higher than 8%.	[133]
Detection of extra virgin olive oil adulteration with lampante olive oil and refined olive oil	^{31}P NMR	One-way ANOVA, HCA and DA	The variables with the highest discriminating power were selected by employing one-way ANOVA. EVOO, lampante olive oil and refined olive oil could be classified by HCA. In a first step, DA was able to group samples according to their quality with no error and, subsequent DA allowed detection of EVOO adulteration as low as 5% w/w for refined and lampante olive oils.	[134]
Fingerprint of the unsaponifiable fraction of virgin olive oils for authentication purposes	^1H NMR	LDA, PLS-DA, SIMCA, and CART	The spectral data of the unsaponifiable fractions of VOOs from Spain, Italy, Greece, Tunisia, Turkey, and Syria contained useful information for the geographical characterisation of VOOs. PLS-DA (PLS-1 approach) obtained the best classification results for all classes.	[135]
Virgin Olive Oil Authentication by Multivariate Analyses of ^1H NMR Fingerprints and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ Data	^1H NMR	PCA, LDA, PLS-DA	LDA and PLS-DA achieved consistent results for the characterization of PDO Riviera Ligure VOOs. More than 90% of oils were correctly classified in the in the cross-validation and more than 85% in the external validation.	[136]
60 MHz ^1H NMR spectroscopy for the analysis of edible oils	60 MHz ^1H NMR	Double cross-validated PLS	Bench-top 60 MHz ^1H NMR is a useful technique for the screening of pure olive oil, being able to detect adulteration with hazelnut oil at levels in excess of 11%w/w.	[137]

Table 6
Chemometric methods coupled to gas chromatography for the analysis of olive oil.

Determination	Analytical techniques	Chemometric analysis	Results	Ref.
Chemical/quality parameter				
Classification of olive oils from different origins by fatty acid profile	GC-FID	FASTCLUS, a K-means based method	The used procedure provided the extra hyperspace for the successful classification of a number of olive oil samples.	[150]
Effect of climate on the chemical composition of VOO (fatty acids, alcohols, sterols, methylsterols and hydrocarbons)	GC-FID	Hottelling's T ² -test, stepwise LDA	It was found that sterols and some triterpenic alcohols and hydrocarbons changed systematically with altitude. Two LDA equations, with correct classifications greater than 90%, were obtained and verified with samples of another crop.	[151]
Stereospecific analysis of the TAG fraction and LDA in a climatic differentiation of Umbrian EVOO.	GC-FID and TLC on SiO ₂ plates	LDA	LDA allowed a partial or total separation of Umbrian EVOO oils according to their climatic characteristics.	[152]
Characterization of fatty acids composition in vegetable oils (sesame, perilla, soybean, corn germ, canola, rapeseed, olive and coconut oils).	GC-FID	PCA and DA	PCA plot showed that eight different vegetable oils could be clustered in different groups and each group could be distinguished clearly. LDA was used to assign unknown samples into one of those groups.	[153]
TAG determination based on fatty acid composition	GC-FID	PCA and MLR	PCA allowed to obtain information about the biosynthetic route of fatty acids and its regulation. MLR was proposed for determining the TAG composition of an oil according to its fatty acid composition.	[154]
Plant oils differentiation via volatile compounds	GC-MS and GC-FID	PCA and HCA	Multivariate analysis facilitated comparison of chromatographic profiles of characteristic volatile compounds for many plant oils and for monitoring oil quality in storage. PCA revealed how chromatographic data was related to sensory analysis when, similarities in sample clustering were observed.	[155]
Classification of vegetable oils characterized by the content of fatty acids	GC-FID	PCA, SOM, ANN and LDA.	PCA and SOM were both successful to cluster different oil samples. ANN provided a high predictive model for the oil classification (98.95% correct predictions) based on their composition. LDA also shield very high classification rate (96.84%) when it was submitted to cross-validation procedure.	[156]
Study of volatile compounds of defective VOO and sensory evaluation	GC-MS	PCA, LDA and Factorial analysis.	Chemometric data evaluation was carried out and samples were clustered on the basis of the headspace composition; the results were found to agree with those of the panel test.	[157]
Discrimination of single-cultivar EVOOs by sensorial analysis and volatile compounds	Electronic Nose and HS-SPME-GC-MS	PCA	Statistical treatment gave complementary information concerning the main chemical compounds interacting with the sensor array and concerning the predominance of some sensors of the array.	[158]
Comparison of the amounts of volatile compounds in French protected designation of origin VOO	HS-SPME-GC-FID	PCA and SIMCA	The method developed distinguished among different qualities of olive oils and highlighted the specificity of Nice PDOs (from commercial VOO and from other PDO oils). Three subgroups of Nice PDOs, were identified.	[159]
Characterization of 39 varietal VOO by their volatile compositions	DHS-GC-FID and GC-olfactometry	Brown-Forsythe test (ANOVA-1 variation) HCA and LDA	The methodology used showed the ability of the volatiles to cluster the varietal VOO according to their autochthonous geographical origin.	[160]
Influence of chemical composition of olive oil on the development of volatile compounds during frying	DHS-GC-MS	Genetic algorithms –PLS and MLR	EVOO components which influence spoilage during frying were screened. It was observed that high oleic acid content, chlorophylls, pheophytins, and carotenoids may prevent formation of toxic volatiles, such as acrolein, crotonal and others aldehydes, during frying.	[161]
Traceability of olive oil based on volatiles pattern	GC-MS	PCA, LDA and ANN	PCA was used to an initial exploration of data set. LDA and ANN models were carried out to characterize and distinguish Ligurian olive. Prediction of ANN ability on validation set was 81.1%, which substantially improved as compared to the LDA model (61.7%).	[162]
Dynamic headspace/GC-MS to control the aroma fingerprint of EVOO from the same and different olive varieties.	GC-MS	Screening (2 ³ factorial design) and RS (Box-Behnken design)	The developed method was able to detect minor quantitative differences between trademarks using the same varieties (Aceiroga and Val de Quiroga), and mayor quantitative differences between trademarks using different varieties (Aceiroga/Val de Quiroga vs. Aceites Abril)	[163]
Direct classification of olive oils by using ion mobility spectrometers (IMS)	GC-IMS and UV-IMS	PCA, LDA and KNN	The best results were obtained by using a GC in combination with IMS The classification rate for an independent validation set was 100%.	[164]
Characterization and olive oil quantification in mixtures with sunflower oil by fatty acid composition	GC-FID	PCA, Target factor analysis [165], SIMCA and PLS	A strong differentiation of blends according to the amount of olive oil contained and a quantification model with a standard error of prediction of 1.51% were obtained.	[166]
Optimization of a screening system to differentiate Olive oils (Lampant, VOO, and EVOO).	GC-IMS	PCA, LDA and KNN	A classification of VOO samples according to their sensory quality was developed. The model was able to classify 97% of VOO samples in their corresponding group and to predict with an accuracy of 87%.	[167]
Quantification of blending of olive oils and edible vegetable oils by TAG fingerprint	GC-MS	SIMCA, PLS and GA-PLS	The results showed the potential of the method that allowed quantification of blends of olive oil in the vegetable oils tested containing at least 10% of olive oil.	[168]
Determination of sterols and triterpene diols in olive oil as indicators of variety and degree of ripening	GC-MS	MANOVA, PCA and Stepwise-LDA	The results showed the possibility to predict the levels of sterols and triterpene diols in olive oils from different varieties during ripening and storage and/or to authenticate their origin with respect to these criteria.	[169]

(continued on next page)

Table 6 (continued)

Determination	Analytical techniques	Chemometric analysis	Results	Ref.
PDO/origin/cultivar				
Recognition of volatile compounds as markers in geographical discrimination of Spanish EVOOs	GC–MS	PCA, LDA and SLDA	The results obtained through the application of stepwise LDA method allowed a discrimination between the different Spanish geographical regions considered (La Rioja, Andalusia and Catalonia).	[170]
Adulteration				
Authentication of EVOO varieties by the chemical analysis using the official analytical methods and chemometrics	GC-FID and HPLC-refractive index	PCA, LDA and ANN	PCA and a Fisher's F method were used to reduce the number of variables. LDA and ANN were trained and used to classify and predict the samples in the test set.	[171]
Sequential detection, identification and quantitation of EVOO adulteration with four edible vegetable oils	GC–MS	PCA, SIMCA, KNN, PLS.	The method enabled to distinguish between pure EVOO samples and those adulterated, to identify the tested adulterant (sunflower, corn, peanut and coconut oils) and to determine the content of the latter in the sample.	[172]
Classification, prediction and detection of adulteration of oils and fats	¹ H NMR and GC–MS	PCA, PLS-DA, OPLS-DA, PLS	The results allowed to build a database for the discrimination and classification of oils and fats using both analytical techniques.	[173]

been applied on classical chemical determinations, electronic nose and electronic tongue responses. Results showed how the results obtained with electronic nose were good enough to define the EVOO oxidation and appeared to be able to describe the different storage conditions [186]. Additionally, characterization of olive oil by an electronic nose based on conducting polymer sensors has also been aided by PCA, achieving the differentiation of cultivars [187].

A voltammetric electronic tongue made from an array of polypyrrole modified screen printed electrodes has been used in the qualitative and quantitative analysis of phenolic compounds found in VOO. The obtained responses were pre-processed using the Kernel method. These coefficients were used as matrix input in PCA, SIMCA and PLS, which accomplished the quantification of total polyphenol content [188]. Another approach towards phenolic fraction evaluation has been presented by Rodríguez-Méndez et al. using an array of voltammetric sensors coupled to PCA and PLS-DA, and PLS [189]. In PLS showed a high correlation ($R^2 = 0.9908$) between redox processes observed in the electrodes and the bitterness index (chemical). Bitterness degree obtained from panel of experts was also on accord with PLS calculations. Furthermore, both electronic nose and electronic tongue in combination with ANN, have been used to verify the geographical origin and the uniqueness of specific EVOOs [190].

The electronic nose (head space–mass spectrometry: HS-MS) has been used to determine the volatile fraction of 105 EVOOs. The information collected and treated by PCA, LDA and stepwise LDA could discriminate the different aromas of olive oils coming from several geographical areas with a mean prediction ability of

80.0% after feature selection [191]. Electronic nose (HS-MS) and electronic tongue coupled to MRM and CMM models have also been capable of extracting useful information from the complex data generated in order to classify EVOOs according to their PDO [192].

A capacitive technique to assess water content in EVOOs using PLS regression reflectometric signals has been informed by Ragni et al. [193]. Ten different EVOO samples with water content ranging from 714 to 2008 mg of water/kg of oil were submitted to time domain reflectometry (TDR) measurement. The measures were carried out using a probe connected to a digital sample oscilloscope with time-domain reflectometer. TDR signals were processed by fast Fourier transform and the resulting spectra were correlated to water content using PLS algorithm. The best-fitting region of TDR spectra was found investigating the figures of merits of PLS trough calibration cross-validation and validation using external set. Optimal conditions found were 129–228 ps range, 5 PLS factors; which shield R^2 of 0.992 on calibration and a root mean square error (RMSE) of 53.3 and 55.1 mg water in kg of oil on cross-validation procedure and validation set respectively. This error is comparable with the requirements (50 mg/kg) of the official method [194,195].

4. Conclusions and perspective

In the last years, researchers and industry have explored and profited the possibilities offered by chemometrics in the field of VOO and EVOO quality evaluation. Chemometrics has not only been

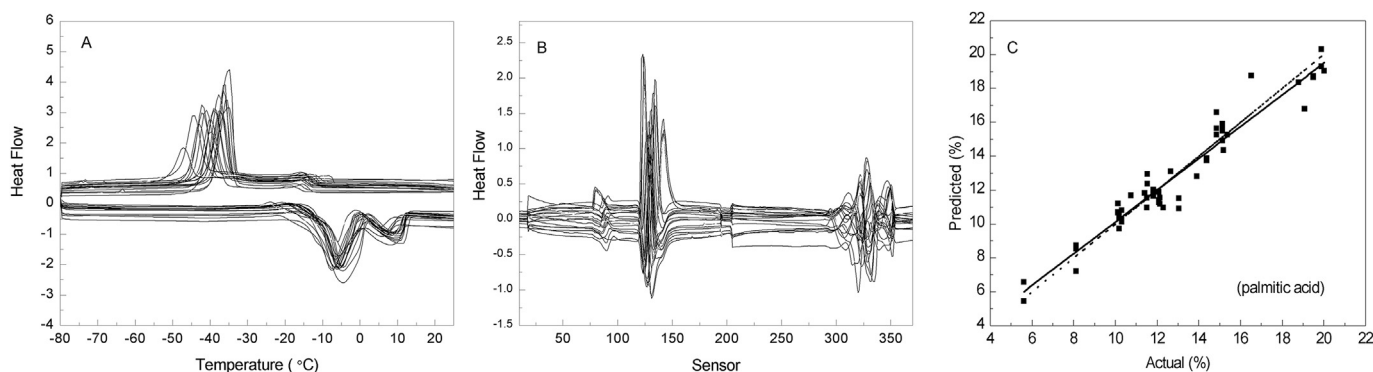


Fig. 4. DSC thermograms obtained from different origins oil samples (A); and unfolded and mean centred DSC data (B). Actual vs. DSC–PLS predicted values in the validation (■) set for palmitic acid, ideal fitting (intercept = 0, slope = 1, -) and actual fitting curves (- -) for predicted values (C). Reprinted from Ref. [179].

able to obtain quantitative knowledge concerning the major and minor components of VOO and EVOO, but also to predict the technological and organoleptic properties. The authentication of products, particularly those produced in a specific production region, was an additional scope successfully reached.

Along this review it has been highlighted how a wide set of analytical techniques, ranging from typical spectroscopy (UV–Vis, FTIR, NMR, and others) to less common techniques (calorimetry, electrochemical, CE, fluorescence), without excluding chromatographic techniques, has been coupled with chemometric algorithms to carry out the scopes listed before. That is why, even though the present review is focused on VOO and EVOO, the field of application of chemometrics is wider and can be applied to other vegetable oils or even to the entire food field.

Today EVOO/VOO is a food for which a large number of analytical tests are planned with the aim of ensuring quality and genuineness (EC No 2568/1991 Regulation and amendments). The official methods of analysis used to perform these determinations are often very different, but sometimes the parameters determined are inter-related and are usually taken into account as an overall data set. Both multivariate calibration and DOE could improve the analytical methodology in the official test by replacing or improving existing techniques, respectively.

Furthermore, interpretation and integration of data sample, when dealing with such a complex matrix like EVOO/VOO, are not straightforward tasks. Here, chemometrics could improve decisions on the basis of mathematical models and not only based on univariate fixed values. In this field, chemometric methods for classification play an irreplaceable role. In addition, chemometrics can help to find all the correlations between the content in micro and macro components and various factors (agronomic, technological and conservative) that may affect the content.

Despite the advantages of these methods and the high number of applications previously mentioned, EU Regulation about EVOO/VOO does not include chemometrics in its guidelines as a tool to assess the quality of these oils. It is, therefore, expected that in the next few years, chemometric combinations will continue to grow and become a reliable tool for understanding the molecular basis of EVOO/VOO and, as a consequence, it will be included in official regulations. This latter aspect is of primary importance to scientifically drive the process of production of EVOO/VOO.

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