



HAL
open science

Applications of vibrational spectroscopy techniques

A Malechaux, Nathalie Dupuy, J. Artaud

► **To cite this version:**

A Malechaux, Nathalie Dupuy, J. Artaud. Applications of vibrational spectroscopy techniques. Michael G. Kontominas. Authentication and Detection of Adulteration of Olive Oil., Nova Science Publishers, 2018, Food Science and Technology, 978-1-53614-596-0. hal-01937476

HAL Id: hal-01937476

<https://hal.science/hal-01937476v1>

Submitted on 28 Nov 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

VIRGIN OLIVE OILS: AUTHENTICATION AND DETECTION OF ADULTERATION

Applications of vibrational spectroscopy techniques

A. MALECHAUX, N. DUPUY, J. ARTAUD

Aix Marseille Univ, Univ Avignon, CNRS, IRD, IMBE, Marseille, France

CONTENTS

Introduction.....	4
1. Bibliometrics.....	5
2. Spectroscopy	7
3. Chemometrics	8
4. Near Infrared Spectroscopy.....	9
5. Mid Infrared Spectroscopy.....	14
6. Raman Spectroscopy	21
7. Multiblock analysis / concatenation of spectral data	26
Conclusion	28
References.....	29

ABBREVIATIONS

ANN: artificial neural networks

ATR: attenuated total reflectance

CP-ANN: counter-propagation artificial neural networks

CVA: canonical variate analysis

DA: discriminant analysis

DTGS: deuterated triglycine sulphate

ESM: external standard method

EVOO: extra-virgin olive oil

FDA: factorial discriminant analysis

FT: Fourier transform

GA: genetic algorithm

HCA: hierarchical cluster analysis

IECVA: interval extended canonical variate analysis

IOC: international olive council

kNN: k-nearest neighbours

LDA: linear discriminant analysis

LOD: limit of detection

LS-SVM: least-square support vector machine

MCTA: mercury cadmium telluride-A

MIR: mid infrared

MLR: multiple linear regression

MRM: multivariate range modelling

MSC: multiple scatter correction

NCC: nearest centroid classification

NMR: nuclear magnetic resonance

NIR: near infrared

PC: principal component

PCA: principal component analysis

PC-OSC: principal-component orthogonal signal correction

PCR: principal component regression

PDO: protected designation of origin

PLS: partial least square

PLSR: partial least square regression

PLS-DA: partial least square discriminant analysis

POTFUN: potential function

QDA: quadratic discriminant analysis

R²: coefficient of determination

RMSEC: root mean square error of calibration

RMSECV: root mean square error of cross-validation

RMSEP: root mean square error of prediction

SECV: standard error of cross-validation

SEP: standard error of prediction

SG: Savitzky-Golay

SIMCA: soft independent modelling of class analogies

SLDA: stepwise linear discriminant analysis

SNV: standard normal variate

SVM: support vector machine

UNEQ: unequal dispersed classes

UV: ultra-violet

VOO: virgin olive oil

INTRODUCTION

One of the main issues facing the food industry to this day is the authentication of its products. Due to their high price compared to other edible oils, especially when they benefit from a certification like the Protected Designation of Origin (PDO), Extra Virgin Olive Oils (EVOOs) and Virgin Olive Oils (VOOs) are an attractive target for fraudsters. They can indeed be subjected to more or less sophisticated fraudulent practices, the most common ones being the falsification or adulteration of VOOs with lower-price oils such as seed oils, refined olive oil or olive pomace oil. Many studies have thus been conducted in order to fight frauds that disrupt the market and deteriorate the positive image of VOOs.

First of all, the quality criteria which have been set by the International Olive Council (IOC) allow the classification of olive oils in different categories (extra virgin, virgin, lampante virgin) according to their free acidity, peroxide value, UV absorbance, alkyl esters contents and sensory properties. In the second place, molecular markers including fatty acids (Z and E), sterols, triterpene dialcohols, waxes or stigmastadienes are used to detect possible frauds.

However, the authentication of varietal or geographical origins, as well as the affiliation of a VOO to a PDO, often represent a real analytical challenge. Numerous research works, based on various physicochemical determinations associated with chemometric data processing, have sought to answer this problem. These studies can be classified into two main groups: those analysing the chemical composition of the oil, and those relying on spectroscopic techniques like nuclear magnetic resonance, infrared, Raman or fluorescence spectroscopies. For instance vibrational spectroscopic analyses, namely Near Infrared (NIR), Mid Infrared (MIR) and Raman, coupled with the predictive chemometric methods of Partial Least Squares (PLS) regression and PLS discriminant analysis (PLS-DA), have been successfully applied to the authentication of French VOOs from different PDOs.^{1,2}

1. BIBLIOMETRICS

A quick search of the terms “olive oil”, “authentication” and “spectroscopy” in Google Scholar, restricted to articles published between 1990 and 2016, gives an idea of the vast amount of studies on these subjects. Figure 1 also indicates that “olive oil” is almost 3 times more often associated with “spectroscopy” than with “authentication”, however “spectroscopy” is present in 94% of the articles containing both “olive oil” and “authentication”. This tends to show that olive oil authentication is often studied in relation with spectroscopic analyses but that these analytical techniques also have other purposes, such as characterisation of oil components or measurement of quality parameters. It can also be noted that the number of articles containing “olive oil” and “chromatography” is higher than that for “olive oil” and “spectroscopy”. However, this is no longer the case when the term “authentication” is added.

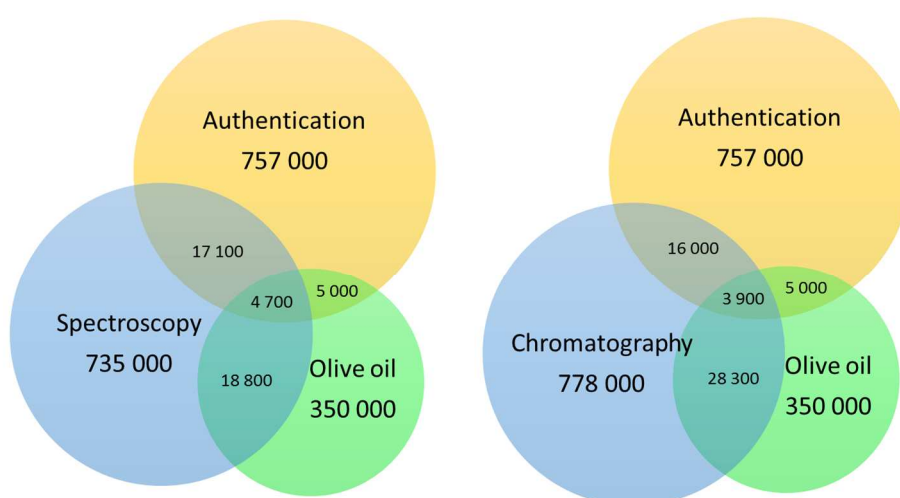


FIGURE 1: NUMBER OF ARTICLES CONTAINING THE WORDS “OLIVE OIL”, “AUTHENTICATION”, “SPECTROSCOPY” OR “CHROMATOGRAPHY” AND THEIR COMBINATIONS (GOOGLE SCHOLAR, 20TH MARCH 2017, FIGURE NOT TO SCALE)

A more specific search on Web of Science confirms that the authentication of virgin olive oil using vibrational spectroscopy has been a subject of interest since the 1990s, and even more so during the past 10 years. This is evidenced by the growing number of publications that are reported in Figure 2. The number of studies focused on NIR has been steadily increasing since 2002, while MIR has seen a more recent and sharper rise of interest. Raman spectroscopy used to be the most popular in the late 1990s and early 2000s, but has since then been overtaken by the other two techniques. On average, around 20% of the articles included experiments with at least two of the analytical methods of interest.

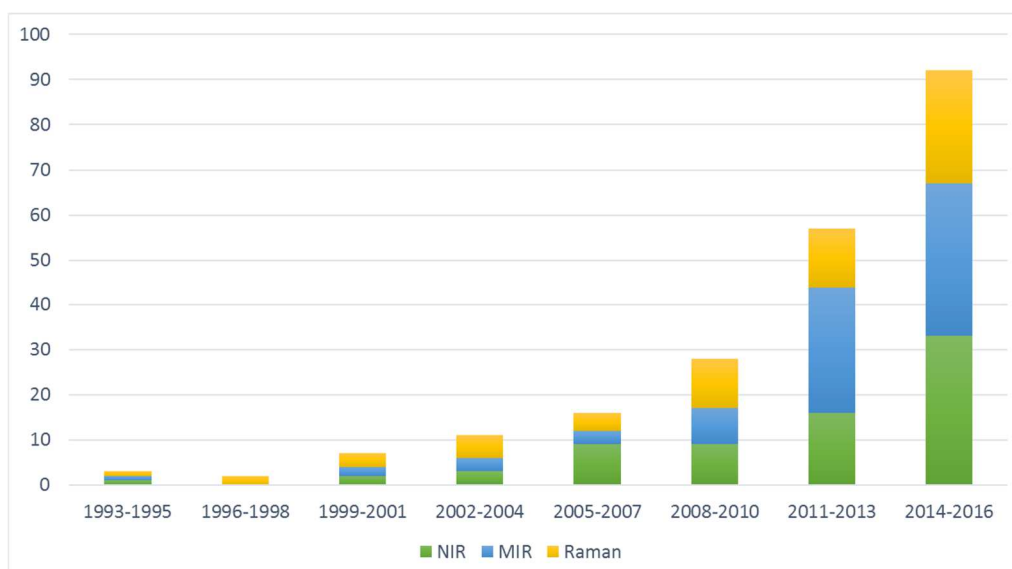


FIGURE 2: EVOLUTION OF THE NUMBER OF PUBLICATIONS FOUND FOR THE QUERY “OLIVE OIL” AND AUTHENTIC* AND (NIR OR “NEAR INFRARED”) OR (MIR OR “MID INFRARED”) OR RAMAN (WEB OF SCIENCE, 20TH MARCH 2017)

In the year 2016 alone, six reviews dealing with the applications of spectroscopic and/or chemometric methods for the quality control and authentication of VOOs have been published.³⁻⁸ Moreover, a book summing up the latest advances in food authenticity has also been edited and contains chapters regarding vibrational spectroscopy, chemometrics, the confirmation of geographical origin of food and the analysis of adulterated vegetable oils.⁹

The free software Wordle allowed the identification of the most frequently used keywords in the titles of the articles from the previous Web of Science search, and the result is presented in Figure 3. The terms “olive oil” and “spectroscopy” were removed in order to have a better view of the other words. Thus, the importance of Fourier-transform instruments and the predominance of studies using MIR over NIR and Raman spectroscopies appear. Other analytical techniques are mentioned, such as UV-visible, fluorescence or NMR spectroscopies, as well as the possibility to combine several methods. The association with chemometrics for multivariate analysis is also highlighted and a few specific models are cited, the most prominent one being PLS. The detection and quantification of extra-virgin or virgin olive oil adulteration with other vegetable or edible oils seems to be the main application, followed by the authentication or determination of geographical and varietal origins.



FIGURE 3: WORD CLOUD GENERATED BY THE TITLES OF THE ARTICLES FROM WEB OF SCIENCE QUERY (WORDLE, 20TH MARCH 2017, FONT SIZE REPRESENTATIVE OF FREQUENCY OF APPEARANCE)

2. SPECTROSCOPY

Vibrational spectroscopic techniques, such as infrared and Raman spectroscopies, have gained in popularity during the past decades, and their applications to food analysis have been extensively studied. Compared to chromatographic methods they allow simple, non-destructive, time- and cost-saving analyses. Moreover, technological advances like the introduction of interferometers, attenuated total reflection instruments or detectors with increased sensitivity and resolution made them more user-friendly. The spreading use of chemometrics has also significantly improved the ability to extract meaningful information from spectral data, and to obtain reliable quantitative results.

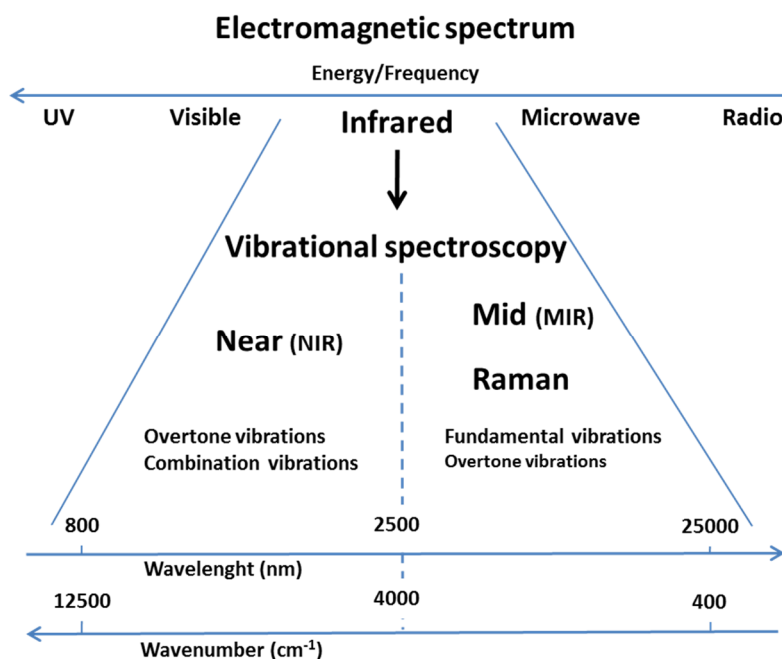


FIGURE 4: SPECTROSCOPIC TECHNIQUES RELATED TO THE INFRARED REGION OF THE ELECTROMAGNETIC SPECTRUM

Vibrational spectroscopy relies on changes in the energy levels of the molecules, due to the interaction between a sample and an electromagnetic radiation. Each bond between two atoms has a characteristic vibration frequency depending on parameters such as the reduced mass of these two atoms and bending force constants. The excitation brought by the radiation causes the bonds to stretch or bend. In the case of infrared absorption the molecular vibration is related to a change in the intrinsic dipole moment, while Raman inelastic scattering depends on a change in the electronic polarizability of the molecule. The amount of energy absorbed by the sample also influences the vibrations, as summarised in Figure 4. In the MIR region (4000-400 cm⁻¹), the transitions between energy levels correspond mainly to fundamental vibrations and a few overtones, whereas in the more energetic NIR area (12500-4000 cm⁻¹) lower intensity bands of overtones and combinations of the fundamental vibrations can be observed. As a consequence, these three techniques provide complementary information about the chemical composition and physical state of a sample. For instance, some infrared absorption bands arise from polar groups such as C=O and O-H, while Raman spectra show more pronounced scattering bands for nonpolar groups like C=C or C-C. It also worth noting that Raman is prone to fluorescence interference, which can be reduced by using a Fourier Transform (FT) interferometer and a laser source of lower energy.^{10,11}

3. CHEMOMETRICS

Chemometrics is the use of multivariate statistical analyses to extract information from chemical data. Since its creation by Svante Wold and Bruce Kowalski in the 1970s^{12,13} different methods have been developed to serve various purposes, such as data pre-processing, qualitative or quantitative analysis.

Pre-treatment of raw spectra is often necessary to reduce the effect of interferences and artefacts on the subsequent development of a predictive model. Wavelet filtering¹⁴ or Savitzky-Golay (SG) smoothing¹⁵ can be used to improve the signal to noise ratio, while detrending or SG 1st and 2nd derivatives provide a correction of the baseline shift. Moreover, 2nd derivative can resolve overlapping peaks. Other algorithms, like Standard Normal Variate (SNV)¹⁶ and Multiplicative Scatter Correction (MSC)¹⁷, are useful when both additive and multiplicative effects caused by light scattering are present. Normalisation or scaling can also be applied to ensure that each spectrum has the same importance in the model.

Before the development of analytical models, the spectral data can be explored through Principal Component Analysis (PCA)^{18,19} which decomposes the initial matrix into sets of scores and loadings allowing to reduce its dimensions. When enough variability is taken into account by the PCs, the loadings show which variables have more influence on the PCs and a representation of the scores can provide insight into the similarities among samples or the presence of outliers.

The discrimination between oils of different botanical, varietal or geographical origins involves the use of qualitative analyses. Unsupervised classification methods, such as Hierarchical Cluster Analysis (HCA)²⁰, separate the samples into different groups without prior knowledge of their category membership. On the other hand, supervised methods like classification by Linear Discriminant Analysis (LDA)²¹ or class-modelling by Soft Independent Modelling of Class Analogy (SIMCA)²², assign new samples to previously defined categories. LDA reduces the space dimensions by selecting directions that maximise the separation between classes, whereas SIMCA performs a PCA on each class to minimise its internal differences. More recently, artificial intelligence algorithms such as Artificial Neural Networks (ANN)²³ have been developed to categorise samples after a phase of training by iterative adjustments.

The development of quantitative models is required to determine the amount of adulterant that may have been added to a sample. Multiple Linear Regression (MLR)²⁴, Partial Least Squares (PLS)²⁵ or Principal Component Regression (PCR)²⁶ are the most commonly used methods. They are based on the construction of a linear relationship between the variations of spectral data and the chemical parameter to be explained. However, other methods using non-linear models, such as ANN or Support Vector Machines (SVM)²⁷, also have the ability to perform quantitative analyses.^{3,11,28}

4. NEAR INFRARED SPECTROSCOPY

1. Spectra interpretation

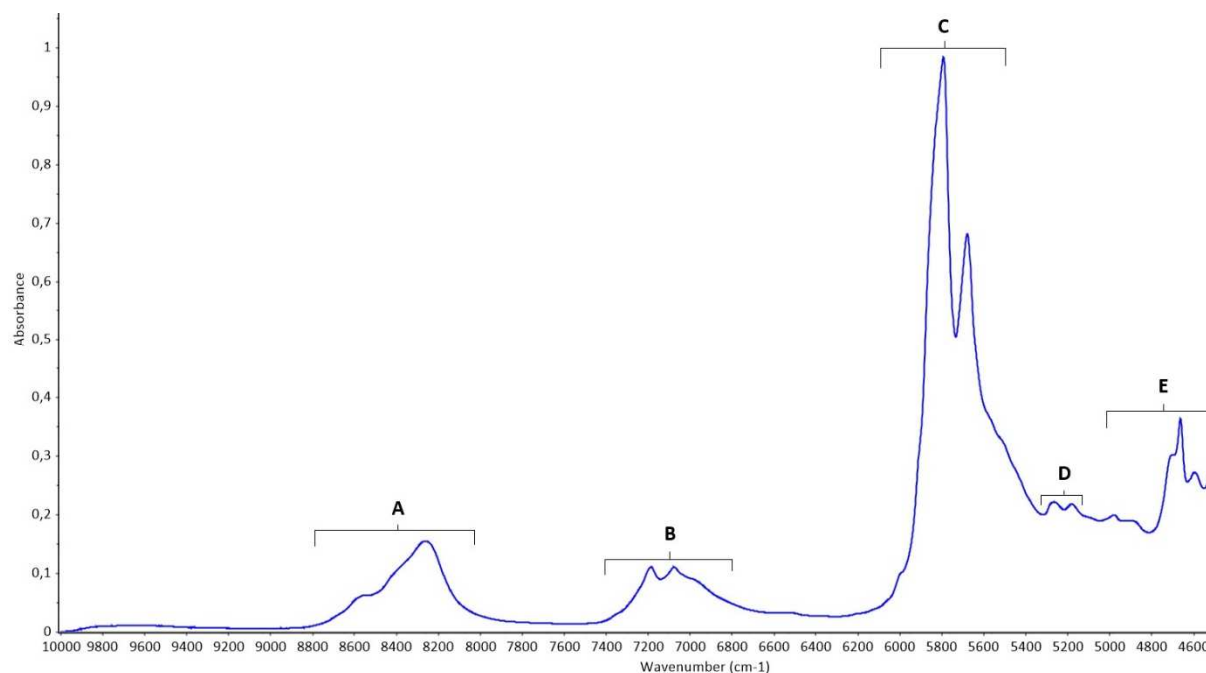


FIGURE 5: NEAR INFRARED SPECTRUM OF EVOO WITH IDENTIFICATION OF MAIN ABSORBANCE BANDS

As can be seen in Figure 5, characteristic NIR absorbance bands arise in several regions of the EVOO spectrum. Region A ($8700\text{--}8000\text{ cm}^{-1}$) is attributed to the 2nd overtone of C-H stretching vibrations, while B ($7400\text{--}6700\text{ cm}^{-1}$) results from combinations of C-H stretching and bending, and C ($6000\text{--}5500\text{ cm}^{-1}$) corresponds to the 1st overtone of C-H stretching vibrations. These three regions contain information regarding the degree of unsaturation of the fatty acids and triacylglycerols present in a sample. The two bands in region D ($5300\text{--}5100\text{ cm}^{-1}$) have been attributed to the 2nd overtone of C=O stretching vibration from carbonyl functional groups. Finally, region E ($5000\text{--}4500\text{ cm}^{-1}$) presents combination bands of =C-H and C=C stretching vibrations.^{9,11,29,30}

2. Identification of Virgin Olive Oils vs other oils

The first step of authentication is to differentiate olive oil from other oils and fats. This can be achieved through the analysis of their major compounds, such as fatty acids and triacylglycerols, usually conducted by gas chromatography and high performance liquid chromatography respectively. However, differences in the composition of the samples are also reflected in their NIR spectra, as can be seen in the examples presented in Table 1. Hourant *et al.*³¹ indeed showed that the absorption intensity of the bands around 5814 cm^{-1} (1720 nm), 4668 cm^{-1} (2142 nm) and 4595 cm^{-1} (2176 nm) could be related to the degree of total unsaturation in the sample. This allowed the classification of eighteen different oils and fats with the modelling of a dendroid structure based on seven linear discriminant functions. Yang *et al.*³² confirmed that LDA could discriminate pure edible oils and fats using FT-NIR spectra, but obtained more satisfying classification rates with Canonical Variate Analysis (CVA).

TABLE 1: EXAMPLES OF NIR SPECTROSCOPY APPLICATIONS TO DIFFERENTIATE OLIVE OILS FROM OTHER OILS

References	Other oils	Materials	Chemometrics	Results
³¹	Almond, Brazil nut, coconut, grape seed, high oleic sunflower, hydrogenated fish, maize, palm, peanut, rapeseed, safflower, sesame, soya, sunflower, tallow, walnut	NIR, 1 mm quartz cell, range: 9090-4000 cm ⁻¹	Canonical discrimination after variable selection by SLDA	Combination of 7 equations gives 90% correct classification
³²	Butter, coconut, cod liver oil, lard, maize, peanut, rapeseed, safflower, soya	FT-NIR, DTGS detector, quartz cell, range: 8000-2000 cm ⁻¹ , resolution: 16 cm ⁻¹	CVA after normalisation and data compression by PCA	92.2% correct classification

3. Adulteration of Virgin Olive Oils with other oils

Several articles focusing on the ability of NIR to analyse binary mixtures of VOOs with other kinds of oils have been published over the past 20 years (Table 2). Dispersive and FT-NIR have been equally used in these studies, and three of them report results obtained with a fibre optic probe although not in an on-line setting³³⁻³⁵.

Downey *et al.*³⁶ developed a SIMCA model that gave 100% of correct classification for VOOs versus adulterated samples containing 1 to 5% of sunflower oil. Karunathilaka *et al.*³⁷ also applied SIMCA to FT-NIR spectra to successfully detect the addition of 10 to 20% of various vegetable oils in EVOOs. Mignani *et al.*³³ obtained spectra through an integrating sphere and fibre optic detector. In this study, the application of PCA followed by LDA enabled the discrimination between EVOOs adulterated with refined olive oil, deodorised olive oil, olive pomace oil and refined olive pomace oil, with 75% of correct classification.

In addition to the detection of adulteration, most of the articles are interested in the use of regression models to quantify the amount of adulterant. For instance, Downey *et al.*³⁶, Wesley *et al.*³⁸ and Christy *et al.*³⁹ applied PLS regression after various pre-treatments to predict the amount of sunflower oil added to olive oil. They all obtained R² values superior to 0.9 and Standard Errors of Prediction (SEP) under 2%. The analysis of VOOs adulterated with maize, soya, rapeseed, safflower, peanut, walnut, hazelnut or palm oils yielded similar results according to Azizian *et al.*³⁴, Wesley *et al.*³⁸, Christy *et al.*³⁹ and Mendes *et al.*⁴⁰. The latter constructed different models to quantify the addition of high linoleic oils, high oleic oils or palm olein, based on the absorption ratio at 5280 and 5180 cm⁻¹, attributed respectively to volatile and non-volatile compounds. Mignani *et al.*³³, Azizian *et al.*³⁴, Yang and Irudayraj³⁵, Wesley *et al.*³⁸ and Wojcicki *et al.*⁴¹ also tried to quantify the adulteration of EVOOs by refined olive oil or olive pomace oil. These studies tend to show higher errors of prediction, ranging from 1.78 to 13%, which may be due to the higher similarity between the composition of pure and adulterated samples. Finally, Ozdemir and Ozturk⁴² developed a Genetic Inverse Least Square model, capable of predicting the concentration of tertiary mixtures with SEP of 1.42%, 5.42% and 6.38% for the amount of VOO, sunflower oil and maize oil respectively.

TABLE 2: EXAMPLES OF NIR SPECTROSCOPY APPLICATIONS TO ANALYSE VOOs ADULTERATED WITH OTHER OILS

References	Adulterants	Materials	Chemometrics	Results
33	Olive pomace, refined olive pomace, refined olive, deodorised olive oils (5 to 95%)	NIR, fibre optic source and detector, integrating sphere, range: 25000-5880 cm^{-1}	LDA and PLS regression after SG smoothing	LDA: 75% correct classification PLS: $R^2 = 0.932$ to 0.997, RMSEP = 2% to 13%
34	Refined olive oil (3 to 60%) and soya, sunflower, maize, rapeseed, hazelnut, safflower, peanut, palm oils (3 to 30%)	FT-NIR, fibre optic probe, InGaAs detector, range: 8000-4500 cm^{-1} , resolution: 8 cm^{-1}	PLS regression on the absorption ratio 5280/5180 cm^{-1}	$R^2 = 97.6$ to 99.9, RMSECV = 3.7% to 0.9%
35	Olive pomace oil (5 to 100%)	NIR, fibre optic probe, InGaAs DAD, range: 25000-5880 cm^{-1}	PLS regression after MSC	$R^2 = 0.990$, SECV = 3.48%, SEP = 3.27%
36	Sunflower oil (1 and 5%)	NIR, 0.1 mm camlock cell, range: 25000-4000 cm^{-1}	SIMCA and PLS regression after SG 1 st derivative	SIMCA: 100% correct classification PLS: $R^2 = 0.93$, RMSEP = 0.8%, LOD = 1.6%
37	Sunflower, soya, rapeseed, maize, hazelnut, safflower, peanut oils, palm olein (10 and 20%)	FT-NIR, 8 mm glass vials, range: 12500-4000 cm^{-1} , resolution: 8 cm^{-1}	SIMCA after SG smoothing, SG 1 st derivative and SNV	100% correct classification
38	Refined olive oil, maize, sunflower oils (5 to 30%)	NIR, 1 mm quartz cell, range: 12500-4000 cm^{-1}	PLS regression after SG smoothing and 1 st derivative	$R^2 = 0.97$, SECV = 1.31%, SEP = 1.78%
39	Hazelnut, walnut, maize, soya, sunflower oils (0 to 100%)	FT-NIR, Ge diode detector, 4 mm quartz cell, range: 12000-4000 cm^{-1} , resolution: 4 cm^{-1}	PLS regression after MSC and SG smoothing	$R^2 = 0.999$ SEP = 0.56% to 1.32%
40	Soya oil (1.5 to 100%)	FT-NIR, Te-InGaAs detector, 8 mm glass vials, range: 12000-4000 cm^{-1} , resolution: 4 cm^{-1}	PLS regression	$R^2 = 0.998$, RMSECV = 1.71, RMSEP = 1.76
41	Mildly deodorised and refined olive oils (2.5 to 75%)	NIR, 2 mm quartz cell, range: 6150-4500 cm^{-1}	PCR after MSC and 1 st derivative	$R^2 = 0.98$, RMSEP = 2.7%
42	Sunflower and maize oils (4 to 96%)	FT-NIR, PbSe detector, 2 mm quartz cell, range: 10000-4000 cm^{-1}	Genetic Inverse Least Squares	SEP = 1.42% to 6.38% for tertiary mixtures

4. Authentication of geographical or varietal origins

The most recent and prominent application of NIR spectroscopy has been the classification of VOOs according to their geographical or varietal origins. Table 3 summarises some of the articles published on this subject, with a majority preferring FT-NIR to dispersive instruments.

The potential of PLS-DA modelling applied to NIR spectra to discriminate VOOs from different cultivars or regions of origin has been highlighted by several authors, amongst which Dupuy *et al.*¹, Sinelli *et al.*⁴³, Woodcock *et al.*⁴⁴, Galtier *et al.*⁴⁵ and Bevilacqua *et al.*⁴⁶. Indeed, all of them obtained 85 to 100% of correct classification rates. Other discriminant analysis algorithms, like FDA or LDA, have also been rather successfully tested by Downey *et al.*⁴⁷, Casale *et al.*⁴⁸ and Sinelli *et al.*⁴⁹. Class modelling techniques such as SIMCA seem to give less satisfying results overall, although Casale *et al.*⁵⁰, Oliveri *et al.*⁵¹ and Laroussi-Mezghani *et al.*⁵² managed to correctly predict the origin of 84.5 to 98.5% of their samples. Oliveri *et al.*⁵¹, Casale *et al.*⁵³ and Forina *et al.*⁵⁴ also used POTFUN or UNEQ class models giving 83 to 100% of correct classification. In another study, Oliveri *et al.*⁵⁵ developed a novel Multivariate Range Modelling technique yielding a classification rate of 94.9%. Devos *et al.*⁵⁶ achieved a classification rate of 86.3% with a SVM supervised learning model coupled with genetic algorithm for pre-treatment selection.

TABLE 3: EXAMPLES OF NIR SPECTROSCOPY APPLICATIONS TO DETERMINE THE ORIGIN OF VOOS

References	Origins	Materials	Chemometrics	Results
¹	6 French PDOs, 5 harvest years	FT-NIR, 2 mm quartz cell, range: 10000-4500 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA	85% correct classification for PDOs
⁴³	3 Italian regions	FT-NIR, 8 mm vials, range: 12500-4500 cm ⁻¹ , resolution: 8 cm ⁻¹	PLS-DA after SG 2 nd derivative	93% correct classification with commercial oils
⁴⁴	Liguria and other European regions, 3 harvest years	NIR, 0.1 mm camlock cell, range: 9090-4000 cm ⁻¹	PLS-DA after SG 1 st derivative	92.8% correct classification for Ligurian oils, 81.5% for other oils
⁴⁵	5 French PDOs, 4 harvest years	FT-NIR, 2 mm quartz cell, range: 10000-4500 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA	100% correct classification for PDOs
⁴⁶	PDO Sabina and other Mediterranean regions, 2 harvest years	FT-NIR, integrating sphere, 19 mm glass cell, range: 10000-4000 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA after MSC, detrend, or SG 1 st derivative	100% correct classification for Sabina and 95.5% for other origins
⁴⁷	3 Greek regions	NIR, 0.1 mm camlock cell, range: 25000-4000 cm ⁻¹	FDA	94% correct classification for geographic origin
⁴⁸	3 cultivars from 3 Italian regions	FT-NIR, 8 mm vials, range: 12500-4500 cm ⁻¹ , resolution: 8 cm ⁻¹	LDA after SNV, SG 1 st derivative and variable selection (SELECT)	82.9% correct classification for cultivars
⁴⁹	3 cultivars from 3 Italian regions	FT-NIR, 8 mm vials, range: 12500-4500 cm ⁻¹ , resolution: 8 cm ⁻¹	LDA after SNV, SG 1 st derivative and variable selection (SELECT)	83% correct classification
⁵⁰	Liguria and other Italian regions	FT-NIR, 5 mm quartz cell, range: 10000-4000 cm ⁻¹ , resolution: 8 cm ⁻¹	SIMCA after SG 1 st derivative and variable selection (SELECT)	92.4% correct classification for Ligurian oils
⁵¹	Liguria and other European regions, 3 harvest years	NIR, 0.1 mm camlock cell, range: 9090-4000 cm ⁻¹	SIMCA or POTFUN after SG 1 st derivative	84.5% correct classification with SIMCA, 83% and higher confidence level with POTFUN
⁵²	6 Tunisian cultivars and other countries, 2 harvest years	FT-NIR, 2 mm quartz cell, range: 10000-4500 cm ⁻¹ , resolution: 4cm ⁻¹	SIMCA after SNV and SG 1 st derivative	89.55 to 98.50% correct classification for cultivars
⁵³	PDO Chianti Classico and other Italian regions	FT-NIR, 5 mm quartz cell, range: 10000-4000 cm ⁻¹ , resolution: 4 cm ⁻¹	UNEQ after SNV, SG 1 st derivative and variable selection (SELECT)	97.5% correct classification
⁵⁴	PDO Chianti Classico and other Italian regions	FT-NIR, 5 mm quartz cell, range: 10000-4000 cm ⁻¹ , resolution: 4 cm ⁻¹	QDA-UNEQ after SG 1 st derivative and variable selection (STEP-LDA)	100% correct classification
⁵⁵	PDO Chianti Classico and other Italian regions	FT-NIR, 5 mm quartz cell, range: 10000-4000 cm ⁻¹ , resolution: 4 cm ⁻¹	MRM after SNV	94.9% correct classification
⁵⁶	Liguria and other Italian regions, 3 harvest years	NIR, 0.1 mm camlock cell, range: 9090-4000 cm ⁻¹	SVM after detrend	86.3% correct classification

5. MID INFRARED SPECTROSCOPY

1. Spectra interpretation

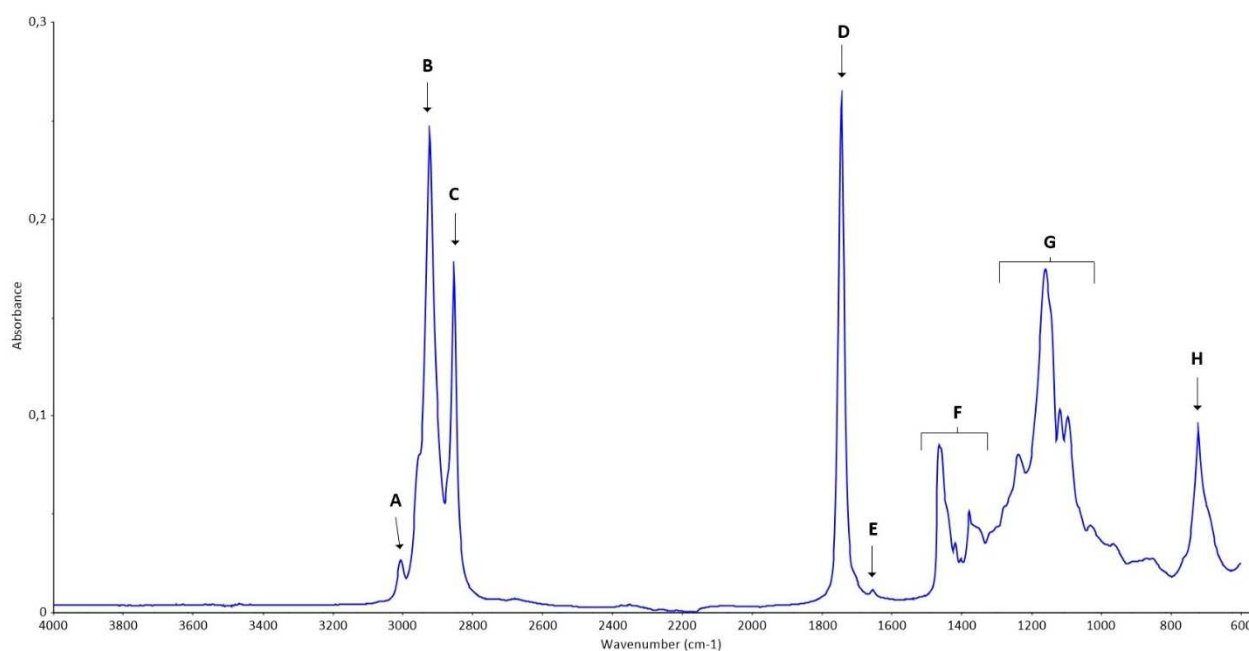


FIGURE 6: MID INFRARED SPECTRUM OF EVOO WITH IDENTIFICATION OF MAIN ABSORBANCE BANDS

Figure 6 shows a characteristic MIR spectrum of EVOO, presenting sharper absorption bands than the NIR spectrum. Band A, around 3005 cm⁻¹, is associated to the =C-H stretching vibrations of cis (Z) double bonds. Bands B and C (2920 and 2850 cm⁻¹) arise respectively from C-H aliphatic asymmetric and symmetric stretching vibrations. D (1740 cm⁻¹) corresponds to the C=O stretching of carbonyl groups, and E (1650 cm⁻¹) to C=C stretching vibrations. The fingerprinting region, under 1500 cm⁻¹, presents overlapping peaks that are less easily attributed. However, region F between 1500 and 1300 cm⁻¹ can be related to C-H aliphatic bending vibrations and region G (1250-1000 cm⁻¹) to C-C and C-O bending vibrations. Finally, band H (700 cm⁻¹) is attributed to the C-H bending of CH₂.^{9,11,29,30}

2. Identification of Virgin Olive Oils vs other oils

The discrimination between VOOs and other fats and oils has been more extensively studied using MIR than NIR spectroscopy, and always with FT instruments (Table 4).

Several authors, such as Lai *et al.*⁵⁷, Marigheto *et al.*⁵⁸, Tay *et al.*⁵⁹, Obeidat *et al.*⁶⁰, Lerma-Garcia *et al.*⁶¹, de la Mata *et al.*⁶², reported a classification rate of 100% with the use of various discriminant analysis techniques including PLS-DA and LDA. Javidnia *et al.*⁶³ reached the same result by using interval extended canonical variate analysis (iECVA). Yang *et al.*³² obtained better results with CVA applied to MIR spectra of olive and sunflower oils compared to NIR, since 98.9% of the samples were correctly classified versus 92.2% for NIR spectra. In two different studies, Baeten identified refined olive oil and hazelnut oil using either ANN⁶⁴ or stepwise linear discriminant analysis (SLDA)⁶⁵.

TABLE 4: EXAMPLES OF MIR SPECTROSCOPY APPLICATIONS TO DIFFERENTIATE VOOS FROM OTHER OILS

Reference	Other oils	Materials	Chemometrics	Results
32	Butter, coconut, cod liver oil, lard, maize, peanut, rapeseed, safflower, soya	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-400 cm^{-1} , resolution: 16 cm^{-1}	CVA on 1800-1400 cm^{-1} region, after normalisation and data compression by PCA or PLS	98.9% correct classification
57	Grapeseed, groundnut, maize, rapeseed, refined olive, walnut	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4800-800 cm^{-1} , resolution: 4 cm^{-1}	DA on PC scores	100% correct classification for extra virgin vs refined olive oil
58	Coconut, grapeseed, hazelnut, maize, mustard, palm, peanut, rapeseed, refined olive, safflower, sesame, soya, sunflower, sweet almond, walnut	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-800 cm^{-1} , resolution: 4 cm^{-1}	LDA after normalisation, baseline correction and data compression by PLS	100% correct classification
59	Maize, peanut, rapeseed, sesame, soya, sunflower, walnut	FT-MIR, MCTA detector, ZnSe ATR crystal, range: 4000-700 cm^{-1} , resolution: 2 cm^{-1} , 128 averaged scans	DA	100% correct classification
60	Cottonseed, maize, sunflower	FT-MIR, DTGS detector, range: 4000-400 cm^{-1}	PLS-DA after mean centring and normalisation	100% correct classification
61	Hazelnut, maize, soya, sunflower	FT-MIR, KBr disks, range: 4000-500 cm^{-1} , resolution: 4 cm^{-1}	LDA after normalisation and variable selection	100% correct classification
62	Flaxseed, grapeseed, maize, peanut, rapeseed, safflower, sesame, soya, sunflower	FT-MIR, MCTA detector, diamond ATR crystal, range: 3800-600 cm^{-1} , resolution: 2 cm^{-1}	PLS-DA after normalisation, detrend and SG 1 st derivative	100% correct classification
63	Butter, maize, rapeseed, soya, sunflower	FT-MIR, range: 4000-450 cm^{-1} , transmittance mode	iECVA after MSC	100% correct classification
64	Hazelnut	FT-MIR, ZnSe ATR crystal, range: 4000-400 cm^{-1} , resolution: 4 cm^{-1}	CP-ANN	Good classification for olive and hazelnut oils
65	Hazelnut	FT-MIR, ZnSe ATR crystal, range: 4000-900 cm^{-1} , resolution: 4 cm^{-1}	SLDA after SG smoothing, SG 1 st derivative and selection of variables related to unsaponifiable matter	95.5% correct classification for olive vs hazelnut oil

3. Adulteration of Virgin Olive Oils with other oils

Numerous articles, gathered in Table 5, focus on the qualitative or quantitative analysis of mixtures of olive oil and other oils based on MIR data. Once again, only FT-MIR instruments were used.

Marigheto *et al.*⁵⁸ applied LDA after data compression by PLS and obtained 99% correct classification for olive oil adulterated with as little as 5% of various vegetable oils. Similarly, Oussama *et al.*⁶⁶ used PLS-DA after variable selection to correctly classify 100% of the samples containing 1 to 24% of soya or sunflower oils, and de la Mata *et al.*⁶² to discriminate between VOOs adulterated with more and less

than 50% of other oils. Discriminant analyses also allowed Tay *et al.*⁵⁹ to successfully detect the addition of 2 to 10% of sunflower oil, while Rohman and Che Man reached 100% correct classification for samples adulterated with palm oil⁶⁷, lard⁶⁸, rice bran oil⁶⁹, maize and sunflower oils⁷⁰ and 97.4% with rapeseed oil⁷¹. Other techniques seem to give satisfying results, for instance Sun *et al.*⁷² reached 96.6% correct classification with a Nearest Centroid algorithm after dimension reduction. Mixtures of hazelnut oil in VOO appear to be more difficult to detect. Indeed, Ozen and Mauer⁷³ achieved a correct classification rate of 100% with DA but only for samples containing at least 25% of hazelnut oil. Baeten *et al.*⁶⁵ reached a LOD of 8% for Turkish hazelnut oil in refined olive oil by applying SLDA on variables characterising the unsaponifiable matter. Georgouli *et al.*⁷⁴ obtained a correct classification rate of 75% for samples adulterated with as little as 1% of hazelnut oil, with the use of k-NN after Continuous Locality Preserving Projections. The application of CP-ANN by Baeten and Novi⁶⁴ only resulted in a partial separation between VOOs with and without the addition of 2 to 20% of hazelnut oil. As for the quantification of adulterants, most authors found that PLS regression after various pre-treatments gave satisfactory results. For instance, Wojcicki *et al.*⁴¹, Tay *et al.*⁵⁹, Oussama *et al.*⁶⁶, Sun *et al.*⁷², Rohman and Che Man⁷⁵, Lai *et al.*⁷⁶, Küpper *et al.*⁷⁷, Gurdeniz *et al.*⁷⁸ and Nigri and Oumeddour⁷⁹ all obtained R^2 superior to 0.97 and RMSECV or RMSEP below 2.5% when predicting the concentration of diverse vegetable oils mixed with olive oil. However, Yang and Irudayaraj³⁵, Mendes *et al.*⁴⁰ and Maggio *et al.*⁸⁰ had higher errors of prediction for the analysis of added olive pomace oil, soya oi and hazelnut oil respectively. PCR was usually shown to be less efficient than PLS regression, except for Jovic *et al.*⁸¹ who managed to quantify the amounts of olive oil, sunflower, high oleic sunflower and rapeseed oils in binary and ternary mixtures with R^2 over 0.99 and RMSEP under 2.3%. Another method, based on linear regression between the amount of adulterant and a ratio of peak heights, was applied by Vlachos *et al.*⁸² and Poiana *et al.*⁸³ using the absorbance at 3006 and 2925 cm^{-1} which can be related to the degree of unsaturation. Allam and Hamed⁸⁴ employed a similar method, but focused on the peaks at 1118 and 1097 cm^{-1} that were assigned to C-O stretching.

TABLE 5: EXAMPLES OF MIR SPECTROSCOPY APPLICATIONS TO ANALYSE VOOs ADULTERATED WITH OTHER OILS

References	Adulterants	Materials	Chemometrics	Results
40	Soya oil (1.5 to 100%)	FT-MIR, RT-DLaTGS detector, range: 4000-350 cm^{-1} , resolution: 4 cm^{-1}	PLS regression	$R^2 = 0.986$, RMSECV = 14.71, RMSEP = 4.89
35	Olive pomace oil (0 to 100% in 5% increments)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 3200-600 cm^{-1} , resolution: 4 cm^{-1}	PLS regression after MSC	$R^2 = 0.991$, SECV = 4.74%, SEP = 3.28%
41	Mild deodorised and refined olive oils (2.5 to 75%)	FT-MIR, ATR crystal, range: 4000-650 cm^{-1} , resolution 4 cm^{-1}	PLS after MSC and 1 st derivative	$R^2 = 0.99$, RMSEP = 2.1%
58	Refined olive oil, sunflower, rapeseed, peanut, soya, maize oils (5 to 45%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-800 cm^{-1} , resolution: 4 cm^{-1}	LDA after normalisation, baseline correction and data compression PLS	99% correct classification LOD = 5%
59	Sunflower oil (2 to 10%)	FT-MIR, MCTA detector, ZnSe ATR crystal, range: 4000-700 cm^{-1} , resolution: 2 cm^{-1}	DA, PLS regression	DA: 100% correct classification PLS: $R^2 = 0.974$, RMSECV < 1%
60	Sunflower, maize oils (25 to 75%)	FT-MIR, DTGS detector, range: 4000-400 cm^{-1}	PLS-DA after mean centring and normalisation	Good separation between pure and adulterated samples

References	Adulterants	Materials	Chemometrics	Results
61	Sunflower, maize, soya, hazelnut oils (5 to 100%)	FT-MIR, KBr disks, range: 4000-500 cm ⁻¹ , resolution: 4 cm ⁻¹	MLR after normalisation	R ² = 0.91 to 0.99%, SEP = 1.5 to 2%, LOD = 1.3 to 4.8%
62	Rapeseed, maize, flaxseed, grape seed, peanut, safflower, sesame, soya, sunflower oils (10 to 90%)	FT-MIR, MCTA detector, diamond ATR crystal, range: 3800-600 cm ⁻¹ , resolution: 2 cm ⁻¹	PLS-DA and PLS regression after normalisation, detrend and SG 1 st derivative	PLS-DA: 95% correct classification for samples >50% adulterant PLS: R ² = 0.79, RMSECV = 8.28
64	Hazelnut oil (2 to 20%)	FT-MIR, ZnSe ATR crystal, range: 4000-400 cm ⁻¹ , resolution: 4 cm ⁻¹	CP-ANN	partial separation between mixtures and olive oil
65	Hazelnut oil (2 to 20%)	FT-MIR, ZnSe ATR crystal, range: 4000-900 cm ⁻¹ , resolution: 4 cm ⁻¹	SLDA after SG smoothing, SG 1 st derivative and selection of variables related to unsaponifiable matter	100% correct classification, LOD = 8% of Turkish hazelnut oil in olive oil
66	Soya, sunflower oils (1 to 24%)	FT-MIR, DTGS detector, ATR crystal, range: 4000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA and PLS regression after variable selection (VIP)	PLS-DA: 100% correct classification PLSR: R ² = 0.996, RMSECV = 0.63, RMSEP = 0.41, LOD = 1.2%
67	Palm oil (1 to 50%)	FT-MIR, DTGS detector, ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 4 cm ⁻¹	LDA and PLS regression after SG 1 st derivative	LDA: 100% correct classification PLSR: R ² = 0.998, RMSECV = 0.285, RMSEP = 0.616
68	Lard (1 to 50%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 4 cm ⁻¹	DA and PLS regression after SG 1 st derivative	DA: 100% correct classification PLSR: R ² = 0.987, RMSEC = 0.070, RMSEP = 1.99
69	Rice bran oil (1 to 50%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 4 cm ⁻¹	LDA and PLS regression after normalisation	LDA : 100% correct classification PLSR: R ² = 0.981, RMSECV = 1.34%, RMSEP = 2.15%
70	Maize and sunflower oils (1 to 50%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 4 cm ⁻¹	DA and PLS regression after SG 1 st derivative	DA: 100% correct classification PLSR: R ² = 0.987 to 0.997, RMSEC = 0.034 to 0.404, RMSEP = 1.13 to 2.02
71	Rapeseed oil (1 to 50%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 4 cm ⁻¹	DA and PLS regression after SG 1 st derivative	DA: 97.4% correct classification PLSR: R ² = 0.997, RMSEC = 0.108, RMSEP = 1.52
72	Camelia, soya, sunflower, maize oils (1 to 90%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-400 cm ⁻¹ , resolution: 2 cm ⁻¹	Nearest centroid classification after SLLE dimension reduction, PLS regression after	NCC: 96.6% correct classification PLSR : R ² = 0.971 to 0.999,

References	Adulterants	Materials	Chemometrics	Results
			mean centring, normalisation and SG 1 st derivative	RMSECV = 0.095 to 0.017
73	Hazelnut oil (5 to 50%)	FT-MIR, MCTA detector, ZnSe ATR crystal, range: 3200-800 cm ⁻¹ , resolution: 4 cm ⁻¹	DA	100% correct classification for hazelnut adulteration > 25%
74	Refined and crude hazelnut oils (1 to 90%)	FT-MIR, DTGS detector, diamond ATR crystal, range: 4000-550 cm ⁻¹ , resolution: 4 cm ⁻¹	kNN after SNV, SG smoothing and Continuous Locality Preserving Projections	75% correct classification
75	Virgin coconut oil (1 to 50%)	FT-MIR, DTGS detector, ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS regression	R ² = 0.997, RMSEC = 0.756, RMSEP = 0.823
76	Refined olive oil, walnut oil (0 to 22%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4800-800 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS regression after mean centring and variance scaling	SEP = 0.68 to 0.92
77	Sunflower oil (2 to 10%)	FT-MIR, silver halide probe, range: 3000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS regression after variable selection	SEP = 1.2%
78	Rapeseed, cotton, maize, sunflower oils (2 to 20%)	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 2 cm ⁻¹	PLS regression after mean centring and wavelet analysis	R ² = 0.93 to 0.98, SEP = 1.04 to 1.4 LOD = 5%
79	Olive pomace oil	FT-MIR, KBr disk, range: 4000-450 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS regression	R ² = 0.98
80	Olive pomace, oleic and linoleic sunflower, rapeseed, hazelnut oils (5 to 40%)	FT-MIR, ZnSe ATR crystal, range: 4000-700 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS regression after mean centring and SG 1 st derivative	R ² = 0.935 to 0.999, SEP = 1.13 to 20.8%
81	Sunflower, high oleic sunflower, rapeseed oils (10 to 90%)	FT-MIR, diamond ATR crystal, range: 4000-600 cm ⁻¹ , resolution: 2 cm ⁻¹	QDA and PCR after mean-centring	QDA: 89% correct classification for binary and ternary mixtures PCR: R ² = 0.992 to 0.998, RMSEP = 2.27% to 1.22%
82	Olive pomace, sunflower, soya, sesame, maize oils (2 to 90%)	FT-MIR, DTGS detector, KBr disks, range: 4000-400 cm ⁻¹ , resolution: 4 cm ⁻¹	linear regression on the ratio of peak height 3006/2925 cm ⁻¹	R ² = 0.991 to 0.996 LOD = 6 to 9%
83	Refined soya oil (10 to 90%)	FT-MIR, ATR crystal, range: 4000-400 cm ⁻¹ , resolution: 4 cm ⁻¹	linear regression on the ratio of peak height 3006/2925 cm ⁻¹	R ² = 0.998 LOD = 6%
84	Refined sunflower, soya, maize oils (25 to 100%)	FT-MIR, DTGS detector, KBr disks, range: 4000-400 cm ⁻¹ , resolution: 4 cm ⁻¹	linear regression on the ratio of peak height 1118/1097 cm ⁻¹	R ² = 0.963 to 0.985

4. Authentication of geographical or varietal origins

Similarly to NIR, the ability of FT-MIR spectroscopy to differentiate VOOs from various origins has been the subject of numerous research works, as can be seen in Table 6.

EVOOs from three different Italian regions were correctly classified by Sinelli *et al.*⁴³ using PLS-DA, while Galtier *et al.*⁸⁵ discriminated virgin olive oils from France and other countries with the same technique. Moreover, PLS-DA allowed Galtier *et al.*⁸⁵ and Dupuy *et al.*¹ to reach a correct classification of 96% and 98% respectively between VOOs from the six French PDOs, with samples collected over several harvest years. Bevilacqua *et al.*⁴⁶ also correctly identified 92.3% of the samples from PDO Sabina versus other Mediterranean regions by applying PLS-DA to MIR data, even though NIR data provided better results. De Luca *et al.*⁸⁶ built a model based on PLS-DA after cluster analysis and variable selection by Martens test to separate VOOs from 4 Moroccan regions, and obtained satisfactory results with R^2 over 0.986 and RMSEP under 0.049. LDA has also been used by several authors. For instance, Tapp *et al.*⁸⁷ applied it after variable selection by genetic algorithm (GA), resulting in a correct classification rate of 100% for the country of origin of VOO samples. Casale *et al.*⁴⁸ and Sinelli *et al.*⁴⁹ both obtained a correct classification of 86.6% between three Italian cultivars with LDA after variable selection, and Abdallah *et al.*⁸⁸ correctly classified 100% of the samples from seven Tunisian cultivars. Additionally, in this last study the concentrations of binary mixtures of cultivars were predicted by MLR, giving R^2 over 0.956 and SEP under 3.88%. Although supposedly less efficient than discriminant analyses, SIMCA was applied by Gurdeniz in several studies^{89–91} and allowed the discrimination of Turkish olive oils according to their region of origin, harvest year and cultivar. PLS regression was also used to predict the concentration of cultivars in binary mixtures with R^2 between 0.84 and 0.91 and RMSEP between 3.14 and 20.9%. In another study, Casale *et al.*⁵³ developed a UNEQ model and achieved a correct classification of 92.5% between olive oils from PDO Chianti Classico and other Italian regions. This was however a less satisfactory result than that obtained with NIR data. Finally, SVM analyses were employed by Devos *et al.*⁵⁶ and Caetano *et al.*⁹², resulting in mixed outcomes.

TABLE 6: EXAMPLES OF MIR SPECTROSCOPY APPLICATIONS TO DETERMINE THE ORIGIN OF VOOS

References	Origins	Materials	Chemometrics	Results
¹	6 French PDOs, 5 harvest years	FT-MIR, DTGS detector, diamond ATR crystal, range: 4000-600 cm^{-1} , resolution: 4 cm^{-1}	PLS-DA after mean centring and normalisation	98% correct classification for PDO
⁴³	3 Italian regions	FT-MIR, DTGS detector, Ge ATR crystal, range: 4000-700 cm^{-1} , resolution: 4 cm^{-1}	PLS-DA after SG 2 nd derivative	100% correct classification
⁴⁶	PDO Sabina and other Mediterranean regions, 2 harvest years	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-630 cm^{-1} , resolution: 2 cm^{-1}	PLS-DA after MSC and detrend	92.3% correct classification for Sabina, 95.5% for other origins
⁴⁸	3 cultivars from 3 Italian regions	FT-MIR, DTGS detector, Ge ATR crystal, range: 4000-700 cm^{-1} , resolution: 4 cm^{-1}	LDA after SNV, SG 1 st derivative and variable selection (SELECT)	86.6% correct classification for cultivars
⁴⁹	3 cultivars from 3 Italian regions	FT-MIR, DTGS detector, Ge ATR crystal, range: 4000-700 cm^{-1} , resolution: 4 cm^{-1}	LDA after SNV, SG 1 st derivative and variable selection (SELECT)	86.6% correct classification

References	Origins	Materials	Chemometrics	Results
53	(PDO Chianti Classico and other Italian regions	FT-MIR, DTGS detector, Ge ATR crystal, range: 4000-700 cm ⁻¹ , resolution: 4 cm ⁻¹	UNEQ after SNV, SG 1 st derivative and variable selection (SELECT)	92.5% correct classification
56	(Liguria and other Italian regions, 3 harvest years	FT-MIR, Ge ATR crystal, range: 4000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	SVM after SG smoothing, SG 1 st derivative and normalisation	82.2% correct classification
85	(6 French PDOs and other countries, 4 harvest years	FT-MIR, DTGS detector, diamond ATR crystal, range: 4000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA after MSC	100% correct classification for France vs other countries, 96% correct classification for PDOs
86	4 Moroccan regions	FT-MIR, DTGS detector, range : 4000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA after variable selection by Martens test	R ² = 0.986 to 0.993 RMSEP = 3.55 to 4.90%
87	Spain, Italy, Greece, Portugal	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-800 cm ⁻¹ , resolution: 4 cm ⁻¹	LDA after variable selection by genetic algorithm	100% correct classification
88	7 Tunisian cultivars, 2 harvest years / binary mixtures	FT-MIR, ATR crystal, range: 4000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	LDA and MLR (binary mixtures) after normalisation	LDA: 100% correct classification for cultivars MLR: R ² = 0.956 to 0.998, RMSEC = 2.40 to 5.90, SEP = 1.09 to 3.88%
89	3 Turkish cultivars / binary mixtures	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 2 cm ⁻¹	PLS regression	R ² = 0.84 to 0.91, RMSE = 3.14 to 2.09%
90	5 cultivars from 2 Turkish regions, 2 harvest years	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 2 cm ⁻¹	Coomans plot on PCA after wavelet compression	R ² = 0.759 to 0.953 for geographical origin, effect of harvest year and cultivar
91	Turkey, 2 harvest years	FT-MIR, DTGS detector, ZnSe ATR crystal, range: 4000-650 cm ⁻¹ , resolution: 2 cm ⁻¹	SIMCA after Orthogonal Signal Correction and wavelet analysis	discrimination for area of origin and harvest year
92	Italy, Greece, Spain, France, Turkey, Cyprus, 2 harvest years	FT-MIR, Ge ATR crystal, range: 4000-600 cm ⁻¹ , resolution: 4 cm ⁻¹	SVM after SG 1 st derivative	88.7 to 94.2% sensitivity and 50 to 76.9% selectivity for Italian vs other countries / 58.5 to 65.2% sensitivity and 91.4 to 94.8% selectivity for Ligurian vs other regions

6. RAMAN SPECTROSCOPY

1. Spectra interpretation

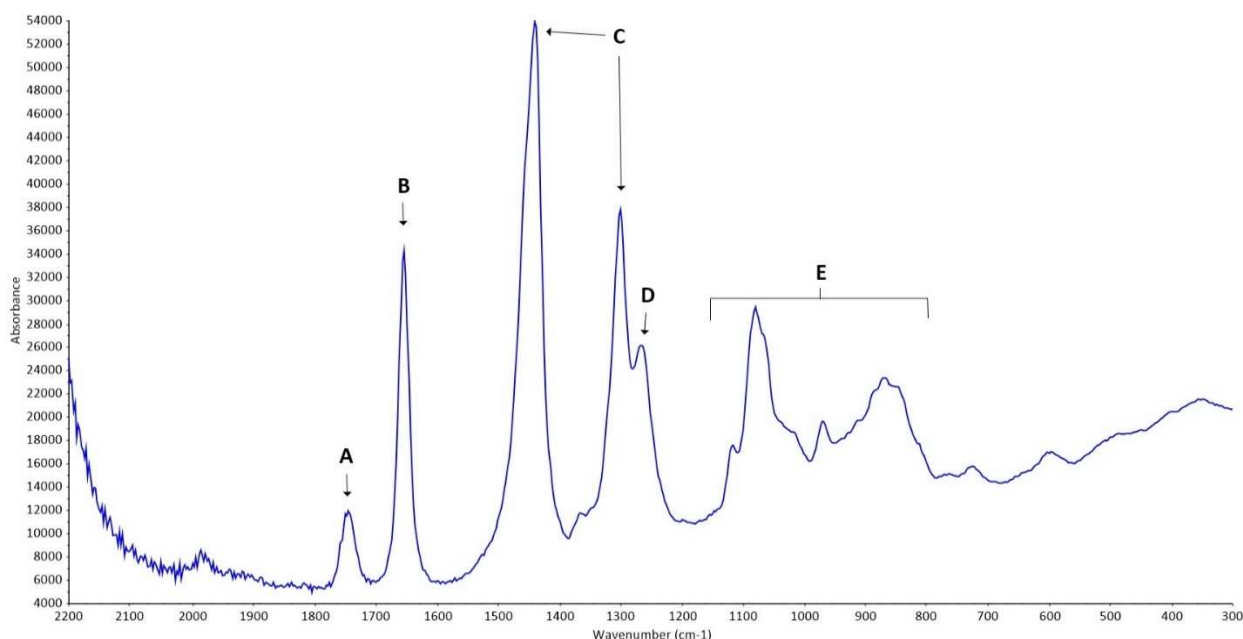


FIGURE 7: RAMAN SPECTRUM OF EVOO WITH IDENTIFICATION OF MAIN ABSORBANCE BANDS

The Raman spectrum of EVOO presented in Figure 7 gives complementary information compared to the MIR spectrum. Peak A (1750 cm^{-1}) results from C=O stretching vibrations, and peak B (1660 cm^{-1}) is related to cis C=C stretching. They correspond to the peaks D and E of the MIR spectrum, although their relative intensities are reversed. The two peaks labelled C ($1450\text{--}1300\text{ cm}^{-1}$) are associated with C-H aliphatic bending vibrations, thus matching the region F of the MIR spectrum. Peak D, at 1270 cm^{-1} , is attributed to =C-H bending vibrations of cis double bonds and is not identified on the MIR spectrum. Region E ($1150\text{--}800\text{ cm}^{-1}$) is also characteristic of the Raman spectrum and related to C-C stretching vibrations. ^{9,11,29,30}

2. Identification of Virgin Olive Oils vs other oils

Although it is less frequently used than NIR or MIR, several authors have studied the potential of Raman spectroscopy to authenticate olive oils (Table 7). In this case, as for MIR, only FT-Raman instruments were used.

Baeten *et al.* ^{93,94} demonstrated the ability of Raman spectra to discriminate between various oils and fats, including VOO. SLDA indeed allowed to classify the samples depending on their saturated, mono-unsaturated and poly-unsaturated fatty acids content. In another study ⁶⁵, SLDA on selected variables related to unsaponifiable matter gave a correct classification of 95% between refined olive oil and hazelnut oil, which is a similar result to that obtained with MIR data. Marigheto *et al.* ⁵⁸ reached a correct classification rate of 93% for EVOO versus other vegetable oils with LDA after data compression by PCA, although the same method applied to MIR spectra correctly identified 100% of the samples. Similar results were obtained by Yang *et al.* ³² using CVA after Raman data treatment by PLS, which gave 94.4% correct classification.

TABLE 7: EXAMPLES OF RAMAN SPECTROSCOPY APPLICATIONS TO DIFFERENTIATE VOOS FROM OTHER OILS

References	Other oils	Materials	Chemometrics	Results
³²	Butter, coconut, cod liver oil, lard, maize, peanut, rapeseed, safflower, soya	FT-Raman, laser: HeNe, 2 W, InGaAs detector, range: 3700-400 cm ⁻¹ , resolution: 32 cm ⁻¹	CVA after normalisation and data compression by PLS	94.4% correct classification
⁵⁸	Coconut, grapeseed, hazelnut, maize, mustard, palm, peanut, rapeseed, refined olive, safflower, sesame, soya, sunflower, sweet almond, walnut	FT-Raman, laser: Topaz, 1064 nm, 0.9 W, Ge detector, range: 3500-500 cm ⁻¹ , resolution: 4 cm ⁻¹	LDA after normalisation, baseline correction and data compression by PCA	93% correct classification
⁶⁵	Hazelnut	FT-Raman, laser: Nd:YAG, 1064 nm, 0.6 W, InGaAs detector, range: 4000-900 cm ⁻¹ , resolution: 4 cm ⁻¹	SLDA after SG smoothing, SG 1 st derivative and selection of variables related to unsaponifiable matter	95% correct classification
⁹³	Almond, Brazil nut, butter, coconut, grapeseed, hazelnut, high oleic sunflower, hydrogenated fish, maize, margarine, palm, peanut, rapeseed, safflower, sesame, soya, sunflower, tallow, walnut	FT-Raman, laser: Nd:YAG, 1064 nm, 0.5 W, Ge detector, range: 3250-0 cm ⁻¹ , resolution: 4 cm ⁻¹	SLDA after SG smoothing, normalization and variable selection	Classification by type of oil according to their fatty acid contents
⁹⁴	Coconut, high oleic sunflower, hydrogenated fish, maize, palm, peanut, rapeseed, soya, sunflower, tallow	FT-Raman, laser: Nd:YAG, range: 3250-0 cm ⁻¹ , resolution: 4 cm ⁻¹	SLDA	Discrimination of oils depending on their fatty acid contents

3. Adulteration of Virgin Olive Oils with other oils

Table 8 presents some articles studying the ability of Raman spectroscopy to detect and quantify the adulteration of VOOs. A majority of these works used FT-Raman, but an interest for confocal benchtop and handheld instruments can be noticed.

Marigheto *et al.*⁵⁸ employed Raman spectroscopy to detect the adulteration of EVOOs with different vegetable oils and reached a correct classification of 97% with PLSR, but these results were less satisfactory than with MIR spectra. Baeten *et al.*^{65,94} also showed that SLDA could discriminate genuine olive oil from adulterated samples, and even obtained a correct classification of 97.5% for samples of refined olive oil adulterated with as little as 2% of hazelnut oil. A method involving Raman measurements at increasing temperatures to enhance spectral differences between pure and adulterated samples was successfully tested by Kim *et al.*⁹⁵. Temperatures of 80 and 90°C allowed a correct classification of 100% by applying LDA on the PCA scores of the spectra.

Regarding quantitative analyses, several authors such as Mendes *et al.*⁴⁰, Yang and Irudayaraj³⁵, El-Abassy *et al.*⁹⁶, Davies *et al.*⁹⁷, Lopez-Diez *et al.*⁹⁸ or Heise *et al.*⁹⁹, applied PLS regression to Raman spectra to predict the concentrations of added sunflower, soya oil, hazelnut or olive pomace oils to VOO. They obtained quite satisfactory results, with R^2 over 0.97 and SEP below 3.6%. Yang and Irudayaraj³⁵ concluded that Raman spectroscopy was slightly more efficient than NIR and MIR to quantify the adulteration of EVOO with olive pomace oil, whereas Mendes *et al.*⁴⁰ detected no statistically significant difference between the three techniques for the analysis of soybean and olive oil mixtures. Baeten *et al.*¹⁰⁰ used stepwise linear regression analysis (SLRA) to measure the amount of trilinolein added to VOO, yielding a R^2 of 0.998 for concentrations between 1 and 10% of adulterant. The same method applied to VOOs adulterated with maize, soya or olive pomace oils gave a R^2 of 0.92. Zhang *et al.*¹⁰¹ developed an external standard method (ESM) resulting in R^2 over 0.99 and RMSE below 3.2%, while Dong *et al.*¹⁰² generated a LS-SVM model after parameter optimization by Bayesian framework that gave a R^2 of 0.997 and RMSEP of 0.051.

TABLE 8: EXAMPLES OF RAMAN SPECTROSCOPY APPLICATIONS TO ANALYSE VOOS ADULTERATED WITH OTHER OILS

Reference s	Adulterants	Materials	Chemometrics	Results
40	Soya oil (1.5 to 100%)	FT-Raman, laser: Nd:YAG, 1064 nm, 0.2 W, Ge detector, range: 3500-50 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS regression	R ² = 0.998, RMSECV = 1.61, RMSEP = 1.57
35	olive pomace oil (0 to 100% in 5% increments)	FT-Raman, laser: 1064 nm, 0.5 W, InGaAs detector, range: 4000-400 cm ⁻¹ , resolution: 8 cm ⁻¹	PLS regression after MSC	R ² = 0.997, SECV = 2.23%, SEP = 1.72%
58	Refined olive oil, sunflower, rapeseed, peanut, soya, maize oils (5 to 45%)	FT-Raman, laser: Topaz, 1064 nm, 0.9 W, Ge detector, range: 3500-500 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS after normalisation, baseline correction and data compression by PCA	97% correct classification LOD = 45% for refined olive oil, 5% for others
65	Hazelnut oil (2 to 20%)	FT-Raman, laser: Nd:YAG, 1064 nm, 0.6 W, InGaAs detector, range: 4000-900 cm ⁻¹ , resolution: 4 cm ⁻¹	SLDA after SG smoothing, SG 1 st derivative and selection of variables related to unsaponifiable matter	97.5% correct classification
94	Olive pomace oil, maize, sunflower, soya oils (1 to 10%)	FT-Raman, laser: Nd:YAG, range: 3250-0 cm ⁻¹ , resolution: 4 cm ⁻¹	SLDA	discrimination of genuine vs adulterated samples
95	Soya oil (5%)	Raman, laser: 785 nm, 0.1 W, 8 temperatures (20 to 90°C), range: 1500-690 cm ⁻¹ , resolution: 4 cm ⁻¹	LDA after normalisation, baseline correction and data compression by PCA	80 or 90°C gives 100% correct classification
96	Sunflower oil (5 to 100%)	Raman, laser: Ar, 514 nm, 0.01 W, CCD detector, range: 3100-700 cm ⁻¹	PLS regression after baseline correction	R ² = 0.971 to 0.988, RMSECV = 1.33 to 3.59 LOD = 0.05%
97	Sunflower Oil (2 to 10%)	FT-Raman, laser: Nd:YAG, 1064 nm, 1 W, range: 3600-100 cm ⁻¹	PLS regression	RMSEC = 2.40%, RMSEP = 2.86%
98	Hazelnut oil (5 to 100%)	Raman, laser: 780 nm, 0.02 W, range: 3000-1000 cm ⁻¹ , resolution: 6 cm ⁻¹	PLS regression after baseline correction, normalisation and SG smoothing	R ² = 0.979, RMSEP = 0.94
99	Sunflower oil (1 to 10%)	FT-Raman, laser: Nd:YAG, 1064 nm, 1 W, resolution: 4 cm ⁻¹	PLS regression after SG 1 st derivative and variable selection (Tabu)	SEP = 1.26%
100	Trilinolein, olive pomace, maize, soya oils (1 to 10%)	FT-Raman, laser: Nd:YAG, 1064 nm, 0.5 W, Ge detector, range: 3250-100 cm ⁻¹ , resolution: 4 cm ⁻¹	SLRA after SG smoothing, SG 1 st derivative and variable selection	R ² = 0.998 for trilinolein R ² = 0.92 for oils
101	Soya, sunflower, maize oils (1 to 100%)	Handheld Raman, laser: 785 nm, 0.2 W, range: 2000-200 cm ⁻¹ , resolution: 8 cm ⁻¹	External standard method after normalisation	R ² = 0.996 to 0.991, RMSE = 1.40 to 3.13%
102	Soya, maize, sunflower oils (2 to 100%)	Handheld Raman, laser: 785 nm, 0.375 W, 10 mm quartz cell, range: 2100-150 cm ⁻¹ , resolution: 6 cm ⁻¹	LS-SVM with Bayesian network	R ² = 0.997, RMSEC = 0.020, RMSEP = 0.051

4. Authentication of geographical or varietal origins

Few studies have been published regarding the confirmation of VOOs declared geographical origin or cultivar with Raman spectroscopy, all of them using confocal instruments, as shown in Table 9.

Korifi *et al.*² applied PLS-DA to Raman spectra, yielding a correct classification of 92.3% for the six French PDOs with samples collected over several harvest years. A similar method gave Sanchez-Lopez *et al.*¹⁰³ a correct classification of 86.6% for three Andalusian PDOs. In this study, PLS-DA on Raman data was also able to discriminate the EVOOs based on their harvest year, region of origin and olive variety with correct results of 94.3%, 89% and 84% respectively. Finally, Gouvinhas *et al.*¹⁰⁴ used LDA to correctly classify 81.9% of Portuguese EVOO samples depending on their maturation stages.

TABLE 9: EXAMPLES OF RAMAN SPECTROSCOPY APPLICATIONS TO DETERMINE THE ORIGIN OF VOOS

References	Origins	Materials	Chemometrics	Results
²	6 French PDOs, 6 harvest years	Raman, laser: Nd:YVO4 DPSS, 532 nm, 0.15 W, CCD detector, range: 1800-440 cm ⁻¹	PLS-DA after SNV and MSC	92.3% correct classification for PDOs
¹⁰³	3 Andalusian PDOs and other Spanish regions, 6 harvest years	Raman, laser: Nd:YAG, 1064 nm, 0.3 W, range: 3100-100 cm ⁻¹ , resolution: 4 cm ⁻¹	PLS-DA after SG smoothing and normalisation	94.3% correct classification for harvest year, 89% for geographical origin, 86.6% for PDOs, 84% for olive variety
¹⁰⁴	3 Portuguese cultivars, 3 maturity stages	Raman, laser: Ar, 488 nm, 0.1 W, CCD detector, range: 3050-250 cm ⁻¹	LDA after SNV and data compression by PCA	81.9% correct classification for maturation stage

7. MULTIBLOCK ANALYSIS - CONCATENATION OF SPECTRAL DATA

1. Adulteration of Virgin Olive Oils with other oils

A couple of studies focusing on the combination of data from several analytical methods have recently been published and are presented in Table 10.

Wojcicki *et al.*⁴¹ applied PLS regression to concatenated data from NIR, MIR, visible and fluorescence spectra, yielding a R^2 of 0.96 and RMSEP of 4.1%. However these results showed no significant improvement compared to those obtained with separate spectra. On the other hand, Nigri and Oumeddour¹⁰⁵ obtained better results with concatenated MIR and fluorescence data than with individual datasets. In this case, PLS regression gave a R^2 of 0.992 and RMSECV of 2.67.

TABLE 10: EXAMPLES OF CONCATENATED DATA APPLICATIONS TO ANALYSE VOOS ADULTERATED WITH OTHER OILS

References	Adulterants	Materials	Chemometrics	Results
⁴¹	Mild deodorised and refined olive oils (2.5 to 75%)	NIR, 2 mm quartz cell, range: 6150-4500 cm^{-1} FT-MIR, ATR crystal, range: 4000-650 cm^{-1} , resolution: 4 cm^{-1} Fluorescence, 10 mm quartz cell, range: 40000-14285 cm^{-1}	PLS regression	No improvement vs separate spectra $R^2 = 0.96$, RMSEP = 4.1%
¹⁰⁵	Sunflower, olive pomace oils (5 to 50%)	FT-MIR, DTGS detector, KBr disks, range: 4000-450 cm^{-1} , resolution: 4 cm^{-1} Fluorescence, xenon lamp source, 10 mm quartz cell, range: 45455-11110 cm^{-1}	PLS regression after normalisation and SG 1 st derivative	Better results vs separate spectra $R^2 = 0.992$, RMSECV = 2.67

2. Authentication of geographical or varietal origins

Diverging conclusions have been drawn regarding the usefulness of spectral data concatenation for the authentication of virgin olive oils, as can be seen in the articles from Table 11.

Harrington *et al.*¹⁰⁶ reached 100% of correct classification between oils from five French PDOs by applying Principal-Component Orthogonal Signal Correction (PC-OSC) and PLS-DA to fused NIR and MIR data. However, this result was not compared to that obtained with each technique alone. In another study, Dupuy *et al.*¹ obtained 99% of correct classification for six French PDOs with PLS-DA on concatenated NIR and MIR spectra, but this did not significantly improve the result compared to MIR data alone. On the contrary, in three different articles^{48,53,107}, Casale *et al.* obtained an improved rate of correct classification by combining data from various analytical instruments. For instance, LDA on fused NIR and MIR spectra gave a correct classification rate of 90.2% for three Italian cultivars, versus respectively 82.9% and 86.6% for NIR and MIR data alone⁴⁸. UNEQ class modelling applied to combined NIR, MIR and UV-visible spectral data gave a correct classification of 100% for PDO olive oil Chianti Classico and improved the predictive ability of the model⁵³. Concatenation of NIR, UV-visible and MS data also resulted in 100% discrimination between EVOOs from Liguria and other Italian regions, which was not possible with each separate technique¹⁰⁷.

TABLE 11: EXAMPLES OF CONCATENATED DATA APPLICATIONS TO DETERMINE THE ORIGIN OF VOOS

References	Origins	Materials	Chemometrics	Results
1	6 French PDOs, 5 harvest years	FT-NIR, 2 mm quartz cell, range: 10000-4500 cm^{-1} , resolution: 4 cm^{-1} FT-MIR, DTGS detector, diamond ATR crystal, range: 4000-600 cm^{-1} , resolution: 4 cm^{-1}	PLS-DA after mean centring and normalisation	No improvement vs separate spectra 99% correct classification for PDO
48	3 cultivars from 3 Italian regions	FT-NIR, 8mm vials, range: 12500-4500 cm^{-1} , resolution: 8 cm^{-1} FT-MIR, DTGS detector, Ge ATR crystal, range: 4000-700 cm^{-1} , resolution: 4 cm^{-1}	LDA after SNV, SG 1 st derivative and variable selection (SELECT)	Better results vs separate spectra 90.2% of correct classification for cultivars
53	PDO Chianti Classico and other Italian regions	FT-NIR, 5mm quartz cell, range: 10000-4000 cm^{-1} , resolution: 4 cm^{-1} FT-MIR, DTGS detector, Ge ATR crystal, range: 4000-700 cm^{-1} , resolution: 4 cm^{-1} UV-Visible, 5 mm quartz cell, range: 52360-9090 cm^{-1}	UNEQ after SNV, SG 1 st derivative and variable selection (SELECT)	Better results vs separate spectra 100% correct classification
106	5 French PDOs, 5 harvest years	FT-NIR, 2 mm quartz cell, range: 10000-4500 cm^{-1} , resolution: 4 cm^{-1} FT-MIR, DTGS detector, diamond ATR crystal, range: 4000-600 cm^{-1} , resolution: 4 cm^{-1}	PLS2-DA after PC- OSC	100% correct classification for PDO
107	Liguria and other regions	FT-NIR, 5 mm quartz cell, range: 10000-4000 cm^{-1} , resolution: 4 cm^{-1} , transmittance mode Headspace mass spectrometer UV-Visible, 10 mm quartz cell, range: 52630-9090 cm^{-1}	UNEQ-DA after SG 1 st derivative and variable selection (SELECT)	Better results vs separate data 100% correct classification

CONCLUSION

Bibliometric results show a growing interest in vibrational spectroscopic techniques as an alternative method for the authentication of VOOs and EVOOs. The ability of NIR, MIR and Raman spectroscopies to detect and quantify the adulteration of VOOs with cheaper oils, and to identify the geographical or varietal origins of samples, has been demonstrated in numerous research works. Even though MIR is more often studied, no significant difference appears in the quality of the results obtained with the three techniques. Thus, this apparent preference may be due to the greater availability of MIR instruments. Despite these promising results, vibrational spectroscopic techniques are not currently recognised as reference analytical methods by international standards and regulations.

The importance of chemometrics pre-treatment and modelling, allowing to treat the large amount of complex data generated by the vibrational spectroscopic analyses, should also be noted. Indeed, NIR, MIR and Raman spectra represent “fingerprints” of the samples, and only chemometrics can reveal the slight differences between two VOOs spectra.

In the future, more studies could be focused on the use of multiblock models to explore the interest of combining complementary information from several analytical techniques. The use of on-line instruments, for instance with fibre optic probes, could be an interesting way to monitor the varietal origin and quality parameters during olive oil extraction. However, the issue of NIR, MIR and Raman instrumental drift should be addressed if they are to be used on a routine basis.

REFERENCES

- (1) Dupuy, N.; Galtier, O.; Ollivier, D.; Vanloot, P.; Artaud, J. Comparison between NIR, MIR, Concatenated NIR and MIR Analysis and Hierarchical PLS Model. Application to Virgin Olive Oil Analysis. *Anal. Chim. Acta* **2010**, *666* (1–2), 23–31.
- (2) Korifi, R.; Le Dréau, Y.; Molinet, J.; Artaud, J.; Dupuy, N. Composition and Authentication of Virgin Olive Oil from French PDO Regions by Chemometric Treatment of Raman Spectra. *J. Raman Spectrosc.* **2011**, *42* (7), 1540–1547.
- (3) Gómez-Caravaca, A. M.; Maggio, R. M.; Cerretani, L. Chemometric Applications to Assess Quality and Critical Parameters of Virgin and Extra-Virgin Olive Oil. A Review. *Anal. Chim. Acta* **2016**, *913*, 1–21.
- (4) Messai, H.; Farman, M.; Sarraj-Laabidi, A.; Hammami-Semmar, A.; Semmar, N. Chemometrics Methods for Specificity, Authenticity and Traceability Analysis of Olive Oils: Principles, Classifications and Applications. *Foods* **2016**, *5* (4), 77.
- (5) Nenadis, N.; Tsimidou, M. Z. Perspective of Vibrational Spectroscopy Analytical Methods in on-Field/official Control of Olives and Virgin Olive Oil. *Eur. J. Lipid Sci. Technol.* **2016**.
- (6) Sørensen, K. M.; Khakimov, B.; Engelsen, S. B. The Use of Rapid Spectroscopic Screening Methods to Detect Adulteration of Food Raw Materials and Ingredients. *Curr. Opin. Food Sci.* **2016**, *10*, 45–51.
- (7) Valli, E.; Bendini, A.; Berardinelli, A.; Ragni, L.; Riccò, B.; Grossi, M.; Gallina Toschi, T. Rapid and Innovative Instrumental Approaches for Quality and Authenticity of Olive Oils: Innovative Approaches for Quality of Virgin Olive Oils. *Eur. J. Lipid Sci. Technol.* **2016**, *118* (11), 1601–1619.
- (8) Wang, P.; Sun, J.; Zhang, T.; Liu, W. Vibrational Spectroscopic Approaches for the Quality Evaluation and Authentication of Virgin Olive Oil. *Appl. Spectrosc. Rev.* **2016**, *51* (10), 763–790.
- (9) Downey, G. *Advances in Food Authenticity Testing*; Elsevier: Boston, MA, **2016**.
- (10) Sun, D.-W. *Modern Techniques for Food Authentication*; Elsevier/Academic Press: Amsterdam; Boston, **2008**.
- (11) *Handbook of Olive Oil*; Aparicio, R., Harwood, J., Eds.; Springer US: Boston, MA, 2013.
- (12) Wold, S. Spline Functions in Data Analysis. *Technometrics* **1974**, *16* (1), 1–11.
- (13) Kowalski, B. R. Chemometrics: Views and Propositions. *J. Chem. Inf. Model.* **1975**, *15* (4), 201–203.
- (14) Barclay, V. J.; Bonner, R. F.; Hamilton, I. P. Application of Wavelet Transforms to Experimental Spectra: Smoothing, Denoising, and Data Set Compression. *Anal. Chem.* **1997**, *69* (1), 78–90.
- (15) Savitzky, A.; Golay, M. J. E. Smoothing and Differentiation of Data by Simplified Least Squares Procedures. *Anal. Chem.* **1964**, *36* (8), 1627–1639.
- (16) Barnes, R. J.; Dhanoa, M. S.; Lister, S. J. Standard Normal Variate Transformation and De-Trending of Near-Infrared Diffuse Reflectance Spectra. *Appl. Spectrosc.* **1989**, *43* (5), 772–777.
- (17) Geladi, P.; MacDougall, D.; Martens, H. Linearization and Scatter-Correction for Near-Infrared Reflectance Spectra of Meat. *Appl. Spectrosc.* **1985**, *39* (3), 491–500.
- (18) Hotelling, H. Analysis of a Complex of Statistical Variables into Principal Components. *J. Educ. Psychol.* **1933**, *24* (6), 417–441.
- (19) Wold, S.; Esbensen, K.; Geladi, P. Principal Component Analysis. *Chemom. Intell. Lab. Syst.* **1987**, *2* (1–3), 37–52.
- (20) Bridges, C. C. Hierarchical Cluster Analysis. *Psychol. Rep.* **1966**, *18* (3), 851–854.
- (21) Fisher, R. A. The Use of Multiple Measurements in Taxonomic Problems. *Ann. Eugen.* **1936**, *7* (2), 179–188.
- (22) Wold, S.; Sjöström, M. SIMCA: A Method for Analyzing Chemical Data in Terms of Similarity and Analogy. In *Chemometrics: Theory and Application*; Kowalski, B. R., Ed.; American Chemical Society: Washington, D. C., **1977**, *52*, 243–282.

- (23) Kohonen, T. The Self-Organizing Map. *Proc. IEEE* **1990**, *78* (9), 1464–1480.
- (24) Brown, C. W.; Lynch, P. F.; Obremski, R. J.; Lavery, D. S. Matrix Representations and Criteria for Selecting Analytical Wavelengths for Multicomponent Spectroscopic Analysis. *Anal. Chem.* **1982**, *54* (9), 1472–1479.
- (25) Geladi, P.; Kowalski, B. R. Partial Least-Squares Regression: A Tutorial. *Anal. Chim. Acta* **1986**, *185*, 1–17.
- (26) Jolliffe, I. T. A Note on the Use of Principal Components in Regression. *Appl. Stat.* **1982**, *31* (3), 300.
- (27) Cortes, C.; Vapnik, V. Support-Vector Networks. *Mach. Learn.* **1995**, *20* (3), 273–297.
- (28) Engel, J.; Gerretzen, J.; Szymańska, E.; Jansen, J. J.; Downey, G.; Blanchet, L.; Buydens, L. M. C. Breaking with Trends in Pre-Processing? *Trends Anal. Chem.* **2013**, *50*, 96–106.
- (29) Baeten, V.; Dardenne, P. Spectroscopy: Developments in Instrumentation and Analysis. *Grasas Aceites* **2002**, *53* (1), 45–63.
- (30) Bertrand, D.; Dufour, É. *La Spectroscopie Infrarouge et Ses Applications Analytiques*, 2e ed.; Sciences et techniques agroalimentaires; Lavoisier: Paris (France), **2006**.
- (31) Hourant, P.; Baeten, V.; Morales, M. T.; Meurens, M.; Aparicio, R. Oil and Fat Classification by Selected Bands of Near-Infrared Spectroscopy. *Appl. Spectrosc.* **2000**, *54* (8), 1168–1174.
- (32) Yang, H.; Irudayaraj, J.; Paradkar, M. M. Discriminant Analysis of Edible Oils and Fats by FTIR, FT-NIR and FT-Raman Spectroscopy. *Food Chem.* **2005**, *93* (1), 25–32.
- (33) Mignani, A. G.; Ciaccheri, L.; Ottevaere, H.; Thienpont, H.; Conte, L.; Marega, M.; Cichelli, A.; Attilio, C.; Cimato, A. Visible and near-Infrared Absorption Spectroscopy by an Integrating Sphere and Optical Fibers for Quantifying and Discriminating the Adulteration of Extra Virgin Olive Oil from Tuscany. *Anal. Bioanal. Chem.* **2011**, *399* (3), 1315–1324.
- (34) Azizian, H.; Mossoba, M. M.; Fardin-Kia, A. R.; Delmonte, P.; Karunathilaka, S. R.; Kramer, J. K. G. Novel, Rapid Identification, and Quantification of Adulterants in Extra Virgin Olive Oil Using Near-Infrared Spectroscopy and Chemometrics. *Lipids* **2015**, *50* (7), 705–718.
- (35) Yang, H.; Irudayaraj, J. Comparison of near-Infrared, Fourier Transform-Infrared, and Fourier Transform-Raman Methods for Determining Olive Pomace Oil Adulteration in Extra Virgin Olive Oil. *J. Am. Oil Chem. Soc.* **2001**, *78* (9), 889–895.
- (36) Downey, G.; McIntyre, P.; Davies, A. N. Detecting and Quantifying Sunflower Oil Adulteration in Extra Virgin Olive Oils from the Eastern Mediterranean by Visible and Near-Infrared Spectroscopy. *J. Agric. Food Chem.* **2002**, *50* (20), 5520–5525.
- (37) Karunathilaka, S. R.; Kia, A.-R. F.; Srigley, C.; Chung, J. K.; Mossoba, M. M. Nontargeted, Rapid Screening of Extra Virgin Olive Oil Products for Authenticity Using Near-Infrared Spectroscopy in Combination with Conformity Index and Multivariate Statistical Analyses. *J. Food Sci.* **2016**, *81* (10), C2390–C2397.
- (38) Wesley, I. J.; Barnes, R. J.; McGill, A. E. J. Measurement of Adulteration of Olive Oils by near-Infrared Spectroscopy. *J. Am. Oil Chem. Soc.* **1995**, *72* (3), 289–292.
- (39) Christy, A. A.; Kasemsumran, S.; Du, Y.; Ozaki, Y. The Detection and Quantification of Adulteration in Olive Oil by Near-Infrared Spectroscopy and Chemometrics. *Anal. Sci.* **2004**, *20* (6), 935–940.
- (40) Mendes, T. O.; da Rocha, R. A.; Porto, B. L. S.; de Oliveira, M. A. L.; dos Anjos, V. de C.; Bell, M. J. V. Quantification of Extra-Virgin Olive Oil Adulteration with Soybean Oil: A Comparative Study of NIR, MIR, and Raman Spectroscopy Associated with Chemometric Approaches. *Food Anal. Methods* **2015**, *8* (9), 2339–2346.
- (41) Wójcicki, K.; Khmelinskii, I.; Sikorski, M.; Caponio, F.; Paradiso, V. M.; Summo, C.; Pasqualone, A.; Sikorska, E. Spectroscopic Techniques and Chemometrics in Analysis of Blends of Extra Virgin with Refined and Mild Deodorized Olive Oils: Spectroscopic Techniques and Chemometrics in Analysis of Blends of Olive Oils. *Eur. J. Lipid Sci. Technol.* **2015**, *117* (1), 92–102.
- (42) Ozdemir, D.; Ozturk, B. Near Infrared Spectroscopic Determination of Olive Oil Adulteration with Sunflower and Corn Oil. *J. Food Drug Anal.* **2007**, *15* (1), 40.

- (43) Sinelli, N.; Casiraghi, E.; Tura, D.; Downey, G. Characterisation and Classification of Italian Virgin Olive Oils by near- and Mid-Infrared Spectroscopy. *J. Infrared Spectrosc.* **2008**, *16* (1), 335.
- (44) Woodcock, T.; Downey, G.; O'Donnell, C. P. Confirmation of Declared Provenance of European Extra Virgin Olive Oil Samples by NIR Spectroscopy. *J. Agric. Food Chem.* **2008**, *56* (23), 11520–11525.
- (45) Galtier, O.; Abbas, O.; Le Dréau, Y.; Rebufa, C.; Kister, J.; Artaud, J.; Dupuy, N. Comparison of PLS1-DA, PLS2-DA and SIMCA for Classification by Origin of Crude Petroleum Oils by MIR and Virgin Olive Oils by NIR for Different Spectral Regions. *Vib. Spectrosc.* **2011**, *55* (1), 132–140.
- (46) Bevilacqua, M.; Bucci, R.; Magrì, A. D.; Magrì, A. L.; Marini, F. Tracing the Origin of Extra Virgin Olive Oils by Infrared Spectroscopy and Chemometrics: A Case Study. *Anal. Chim. Acta* **2012**, *717*, 39–51.
- (47) Downey, G.; McIntyre, P.; Davies, A. N. Geographic Classification of Extra Virgin Olive Oils From the Eastern Mediterranean by Chemometric Analysis of Visible and Near-Infrared Spectroscopic Data. *Appl. Spectrosc.* **2003**, *57* (2), 158–163.
- (48) Casale, M.; Sinelli, N.; Oliveri, P.; Di Egidio, V.; Lanteri, S. Chemometrical Strategies for Feature Selection and Data Compression Applied to NIR and MIR Spectra of Extra Virgin Olive Oils for Cultivar Identification. *Talanta* **2010**, *80* (5), 1832–1837.
- (49) Sinelli, N.; Casale, M.; Di Egidio, V.; Oliveri, P.; Bassi, D.; Tura, D.; Casiraghi, E. Varietal Discrimination of Extra Virgin Olive Oils by near and Mid Infrared Spectroscopy. *Food Res. Int.* **2010**, *43* (8), 2126–2131.
- (50) Casale, M.; Casolino, C.; Ferrari, G.; Forina, M. Near Infrared Spectroscopy and Class Modelling Techniques for the Geographical Authentication of Ligurian Extra Virgin Olive Oil. *J. Infrared Spectrosc.* **2008**, *16* (1), 39.
- (51) Oliveri, P.; Di Egidio, V.; Woodcock, T.; Downey, G. Application of Class-Modelling Techniques to near Infrared Data for Food Authentication Purposes. *Food Chem.* **2011**, *125* (4), 1450–1456.
- (52) Laroussi-Mezghani, S.; Vanloot, P.; Molinet, J.; Dupuy, N.; Hammami, M.; Grati-Kamoun, N.; Artaud, J. Authentication of Tunisian Virgin Olive Oils by Chemometric Analysis of Fatty Acid Compositions and NIR Spectra. Comparison with Maghrebian and French Virgin Olive Oils. *Food Chem.* **2015**, *173*, 122–132.
- (53) Casale, M.; Oliveri, P.; Casolino, C.; Sinelli, N.; Zunin, P.; Armanino, C.; Forina, M.; Lanteri, S. Characterisation of PDO Olive Oil Chianti Classico by Non-Selective (UV–visible, NIR and MIR Spectroscopy) and Selective (Fatty Acid Composition) Analytical Techniques. *Anal. Chim. Acta* **2012**, *712*, 56–63.
- (54) Forina, M.; Oliveri, P.; Bagnasco, L.; Simonetti, R.; Casolino, M. C.; Nizzi Grifi, F.; Casale, M. Artificial Nose, NIR and UV–visible Spectroscopy for the Characterisation of the PDO Chianti Classico Olive Oil. *Talanta* **2015**, *144*, 1070–1078.
- (55) Oliveri, P.; Casale, M.; Casolino, M. C.; Baldo, M. A.; Nizzi Grifi, F.; Forina, M. Comparison between Classical and Innovative Class-Modelling Techniques for the Characterisation of a PDO Olive Oil. *Anal. Bioanal. Chem.* **2011**, *399* (6), 2105–2113.
- (56) Devos, O.; Downey, G.; Duponchel, L. Simultaneous Data Pre-Processing and SVM Classification Model Selection Based on a Parallel Genetic Algorithm Applied to Spectroscopic Data of Olive Oils. *Food Chem.* **2014**, *148*, 124–130.
- (57) Lai, Y. W.; Kemsley, E. K.; Wilson, R. H. Potential of Fourier Transform Infrared Spectroscopy for the Authentication of Vegetable Oils. *J. Agric. Food Chem.* **1994**, *42* (5), 1154–1159.
- (58) Marigheto, N. A.; Kemsley, E. K.; Defernez, M.; Wilson, R. H. A Comparison of Mid-Infrared and Raman Spectroscopies for the Authentication of Edible Oils. *J. Am. Oil Chem. Soc.* **1998**, *75* (8), 987–992.
- (59) Tay, A.; Singh, R. K.; Krishnan, S. S.; Gore, J. P. Authentication of Olive Oil Adulterated with Vegetable Oils Using Fourier Transform Infrared Spectroscopy. *Leb.-Wiss U-Technol* **2002**, *35* (1), 99–103.

- (60) Obeidat, S. M.; Khanfar, M. S.; Obeidat, W. M. Classification of Edible Oils and Uncovering Adulteration of Virgin Olive Oil Using FTIR with the Aid of Chemometrics. *Aust. J. Basic Appl. Sci.* **2009**, *3* (3), 2048–2053.
- (61) Lerma-García, M. J.; Ramis-Ramos, G.; Herrero-Martínez, J. M.; Simó-Alfonso, E. F. Authentication of Extra Virgin Olive Oils by Fourier-Transform Infrared Spectroscopy. *Food Chem.* **2010**, *118* (1), 78–83.
- (62) de la Mata, P.; Dominguez-Vidal, A.; Bosque-Sendra, J. M.; Ruiz-Medina, A.; Cuadros-Rodríguez, L.; Ayora-Cañada, M. J. Olive Oil Assessment in Edible Oil Blends by Means of ATR-FTIR and Chemometrics. *Food Control* **2012**, *23* (2), 449–455.
- (63) Javidnia, K.; Parish, M.; Karimi, S.; Hemmateenejad, B. Discrimination of Edible Oils and Fats by Combination of Multivariate Pattern Recognition and FT-IR Spectroscopy: A Comparative Study between Different Modeling Methods. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2013**, *104*, 175–181.
- (64) Baeten, V.; Novi, M. The Use of FT-MIR Spectroscopy and Counter-Propagation Artificial Neural Networks for Tracing the Adulteration of Olive Oil. *Acta Chim Slov* **2008**, *55*, 935–941.
- (65) Baeten, V.; Fernández Pierna, J. A.; Dardenne, P.; Meurens, M.; García-González, D. L.; Aparicio-Ruiz, R. Detection of the Presence of Hazelnut Oil in Olive Oil by FT-Raman and FT-MIR Spectroscopy. *J. Agric. Food Chem.* **2005**, *53* (16), 6201–6206.
- (66) Oussama, A.; Elabadi, F.; Platikanov, S.; Kzaiber, F.; Tauler, R. Detection of Olive Oil Adulteration Using FT-IR Spectroscopy and PLS with Variable Importance of Projection (VIP) Scores. *J. Am. Oil Chem. Soc.* **2012**, *89* (10), 1807–1812.
- (67) Rohman, A.; Man, Y. B. C. Fourier Transform Infrared (FTIR) Spectroscopy for Analysis of Extra Virgin Olive Oil Adulterated with Palm Oil. *Food Res. Int.* **2010**, *43* (3), 886–892.
- (68) Rohman, A.; Che Man, Y. B.; Hashim, P.; Ismail, A. FTIR Spectroscopy Combined with Chemometrics for Analysis of Lard Adulteration in Some Vegetable Oils Espectroscopia FTIR Combinada Con Quimiometría Para El Análisis de Adulteración Con Grasa de Cerdo de Aceites Vegetales. *CyTA - J. Food* **2011**, *9* (2), 96–101.
- (69) Rohman, A.; Man, Y. B. C. The Chemometrics Approach Applied to FTIR Spectral Data for the Analysis of Rice Bran Oil in Extra Virgin Olive Oil. *Chemom. Intell. Lab. Syst.* **2012**, *110* (1), 129–134.
- (70) Rohman, A.; Che Man, Y. B. Quantification and Classification of Corn and Sunflower Oils as Adulterants in Olive Oil Using Chemometrics and FTIR Spectra. *Sci. World J.* **2012**, *2012*, 1–6.
- (71) Rohman, A.; Che Man, Y. B.; Yusof, F. M. The Use of FTIR Spectroscopy and Chemometrics for Rapid Authentication of Extra Virgin Olive Oil. *J. Am. Oil Chem. Soc.* **2014**, *91* (2), 207–213.
- (72) Sun, X.; Lin, W.; Li, X.; Shen, Q.; Luo, H. Detection and Quantification of Extra Virgin Olive Oil Adulteration with Edible Oils by FT-IR Spectroscopy and Chemometrics. *Anal Methods* **2015**, *7* (9), 3939–3945.
- (73) Ozen, B. F.; Mauer, L. J. Detection of Hazelnut Oil Adulteration Using FT-IR Spectroscopy. *J. Agric. Food Chem.* **2002**, *50* (14), 3898–3901.
- (74) Georgouli, K.; Martinez Del Rincon, J.; Koidis, A. Continuous Statistical Modelling for Rapid Detection of Adulteration of Extra Virgin Olive Oil Using Mid Infrared and Raman Spectroscopic Data. *Food Chem.* **2017**, *217*, 735–742.
- (75) Rohman, A.; Che Man, Y. B.; Ismail, A.; Hashim, P. Application of FTIR Spectroscopy for the Determination of Virgin Coconut Oil in Binary Mixtures with Olive Oil and Palm Oil. *J. Am. Oil Chem. Soc.* **2010**, *87* (6), 601–606.
- (76) Lai, Y. W.; Kemsley, E. K.; Wilson, R. H. Quantitative Analysis of Potential Adulterants of Extra Virgin Olive Oil Using Infrared Spectroscopy. *Food Chem.* **1995**, *53* (1), 95–98.
- (77) Küpper, L.; Heise, H. M.; Lampen, P.; Davies, A. N.; McIntyre, P. Authentication and Quantification of Extra Virgin Olive Oils by Attenuated Total Reflectance Infrared Spectroscopy Using Silver Halide Fiber Probes and Partial Least-Squares Calibration. *Appl. Spectrosc.* **2001**, *55* (5), 563–570.

- (78) Gurdeniz, G.; Ozen, B. Detection of Adulteration of Extra-Virgin Olive Oil by Chemometric Analysis of Mid-Infrared Spectral Data. *Food Chem.* **2009**, *116* (2), 519–525.
- (79) Nigri, S.; Oumeddour, R. Fourier Transform Infrared and Fluorescence Spectroscopy for Analysis of Vegetable Oils. *MATEC Web Conf.* **2013**, *5*, 4028.
- (80) Maggio, R. M.; Cerretani, L.; Chiavaro, E.; Kaufman, T. S.; Bendini, A. A Novel Chemometric Strategy for the Estimation of Extra Virgin Olive Oil Adulteration with Edible Oils. *Food Control* **2010**, *21* (6), 890–895.
- (81) Jović, O.; Smolić, T.; Primožič, I.; Hrenar, T. Spectroscopic and Chemometric Analysis of Binary and Ternary Edible Oil Mixtures: Qualitative and Quantitative Study. *Anal. Chem.* **2016**, *88* (8), 4516–4524.
- (82) Vlachos, N.; Skopelitis, Y.; Psaroudaki, M.; Konstantinidou, V.; Chatzilazarou, A.; Tegou, E. Applications of Fourier Transform-Infrared Spectroscopy to Edible Oils. *Anal. Chim. Acta* **2006**, *573–574*, 459–465.
- (83) Poiana, M.-A.; Alexa, E.; Munteanu, M.-F.; Gligor, R.; Moigradean, D.; Mateescu, C. Use of ATR-FTIR Spectroscopy to Detect the Changes in Extra Virgin Olive Oil by Adulteration with Soybean Oil and High Temperature Heat Treatment. *Open Chem.* **2015**, *13* (1).
- (84) Allam, M. A.; Hamed, S. F. Application of FTIR Spectroscopy in the Assessment of Olive Oil Adulteration. *J. Appl. Sci. Res.* **2007**, *3* (2), 102–108.
- (85) Galtier, O.; Le Dréau, Y.; Ollivier, D.; Kister, J.; Artaud, J.; Dupuy, N. Lipid Compositions and French Registered Designations of Origins of Virgin Olive Oils Predicted by Chemometric Analysis of Mid-Infrared Spectra. *Appl. Spectrosc.* **2008**, *62* (5), 583–590.
- (86) De Luca, M.; Terouzi, W.; Ioele, G.; Kzaiber, F.; Oussama, A.; Oliverio, F.; Tauler, R.; Ragno, G. Derivative FTIR Spectroscopy for Cluster Analysis and Classification of Morocco Olive Oils. *Food Chem.* **2011**, *124* (3), 1113–1118.
- (87) Tapp, H. S.; Defernez, M.; Kemsley, E. K. FTIR Spectroscopy and Multivariate Analysis Can Distinguish the Geographic Origin of Extra Virgin Olive Oils. *J. Agric. Food Chem.* **2003**, *51* (21), 6110–6115.
- (88) Abdallah, M.; Vergara-Barberán, M.; Lerma-García, M. J.; Herrero-Martínez, J. M.; Simó-Alfonso, E. F.; Guerfel, M. Cultivar Discrimination and Prediction of Mixtures of Tunisian Extra Virgin Olive Oils by FTIR: EVOO Prediction of Cultivar and Mixtures by FTIR and LDA. *Eur. J. Lipid Sci. Technol.* **2016**, *118* (8), 1236–1242.
- (89) Gurdeniz, G.; Tokatli, F.; Ozen, B. Differentiation of Mixtures of Monovarietal Olive Oils by Mid-Infrared Spectroscopy and Chemometrics. *Eur. J. Lipid Sci. Technol.* **2007**, *109* (12), 1194–1202.
- (90) Gurdeniz, G.; Ozen, B.; Tokatli, F. Classification of Turkish Olive Oils with Respect to Cultivar, Geographic Origin and Harvest Year, Using Fatty Acid Profile and Mid-IR Spectroscopy. *Eur. Food Res. Technol.* **2008**, *227* (4), 1275–1281.
- (91) Gurdeniz, G.; Ozen, B.; Tokatli, F. Comparison of Fatty Acid Profiles and Mid-Infrared Spectral Data for Classification of Olive Oils. *Eur. J. Lipid Sci. Technol.* **2010**, *112* (2), 218–226.
- (92) Caetano, S.; Üstün, B.; Hennessy, S.; Smeyers-Verbeke, J.; Melssen, W.; Downey, G.; Buydens, L.; Heyden, Y. V. Geographical Classification of Olive Oils by the Application of CART and SVM to Their FT-IR. *J. Chemom.* **2007**, *21* (7–9), 324–334.
- (93) Baeten, V.; Hourant, P.; Morales, M. T.; Aparicio, R. Oil and Fat Classification by FT-Raman Spectroscopy. *J. Agric. Food Chem.* **1998**, *46* (7), 2638–2646.
- (94) Baeten, V.; Aparicio, R. Edible Oils and Fats Authentication by Fourier Transform Raman Spectrometry. *Biotechnol. Agron. Soc. Environ.* **2000**, *4* (4), 196–203.
- (95) Kim, M.; Lee, S.; Chang, K.; Chung, H.; Jung, Y. M. Use of Temperature Dependent Raman Spectra to Improve Accuracy for Analysis of Complex Oil-Based Samples: Lube Base Oils and Adulterated Olive Oils. *Anal. Chim. Acta* **2012**, *748*, 58–66.
- (96) El-Abassy, R. M.; Donfack, P.; Materny, A. Visible Raman Spectroscopy for the Discrimination of Olive Oils from Different Vegetable Oils and the Detection of Adulteration. *J. Raman Spectrosc.* **2009**, *40* (9), 1284–1289.

- (97) Davies, A. N.; McIntyre, P.; Morgan, E. Study of the Use of Molecular Spectroscopy for the Authentication of Extra Virgin Olive Oils. Part I: Fourier Transform Raman Spectroscopy. *Appl. Spectrosc.* **2000**, *54* (12), 1864–1867.
- (98) López-Díez, E. C.; Bianchi, G.; Goodacre, R. Rapid Quantitative Assessment of the Adulteration of Virgin Olive Oils with Hazelnut Oils Using Raman Spectroscopy and Chemometrics. *J. Agric. Food Chem.* **2003**, *51* (21), 6145–6150.
- (99) Heise, H. M.; Damm, U.; Lampen, P.; Davies, A. N.; McIntyre, P. S. Spectral Variable Selection for Partial Least Squares Calibration Applied to Authentication and Quantification of Extra Virgin Olive Oils Using Fourier Transform Raman Spectroscopy. *Appl. Spectrosc.* **2005**, *59* (10), 1286–1294.
- (100) Baeten, V.; Meurens, M.; Morales, M. T.; Aparicio, R. Detection of Virgin Olive Oil Adulteration by Fourier Transform Raman Spectroscopy. *J. Agric. Food Chem.* **1996**, *44* (8), 2225–2230.
- (101) Zhang, X.-F.; Zou, M.-Q.; Qi, X.-H.; Liu, F.; Zhang, C.; Yin, F. Quantitative Detection of Adulterated Olive Oil by Raman Spectroscopy and Chemometrics. *J. Raman Spectrosc.* **2011**, *42* (9), 1784–1788.
- (102) Dong, W.; Zhang, Y.; Zhang, B.; Wang, X. Quantitative Analysis of Adulteration of Extra Virgin Olive Oil Using Raman Spectroscopy Improved by Bayesian Framework Least Squares Support Vector Machines. *Anal. Methods* **2012**, *4* (9), 2772.
- (103) Sánchez-López, E.; Sánchez-Rodríguez, M. I.; Marinas, A.; Marinas, J. M.; Urbano, F. J.; Caridad, J. M.; Moalem, M. Chemometric Study of Andalusian Extra Virgin Olive Oils Raman Spectra: Qualitative and Quantitative Information. *Talanta* **2016**, *156–157*, 180–190.
- (104) Gouvinhas, I.; Machado, N.; Carvalho, T.; de Almeida, J. M. M. M.; Barros, A. I. R. N. A. Short Wavelength Raman Spectroscopy Applied to the Discrimination and Characterization of Three Cultivars of Extra Virgin Olive Oils in Different Maturation Stages. *Talanta* **2015**, *132*, 829–835.
- (105) Nigri, S.; Oumeddour, R. Detection of Extra Virgin Olive Oil Adulteration Using Fourier Transform Infrared, Synchronous Fluorescence Spectroscopy and Multivariate Analysis. *Riv. Ital. Delle Sostanze Grasse* **2016**, *93* (2), 125–131.
- (106) de B. Harrington, P.; Kister, J.; Artaud, J.; Dupuy, N. Automated Principal Component-Based Orthogonal Signal Correction Applied to Fused Near Infrared–Mid-Infrared Spectra of French Olive Oils. *Anal. Chem.* **2009**, *81* (17), 7160–7169.
- (107) Casale, M.; Casolino, C.; Oliveri, P.; Forina, M. The Potential of Coupling Information Using Three Analytical Techniques for Identifying the Geographical Origin of Liguria Extra Virgin Olive Oil. *Food Chem.* **2010**, *118* (1), 163–170.