

THE PROGRESS OF AUTHENTICATION ANALYSIS OF FATS AND OILS USING VIBRATIONAL SPECTROSCOPY AND CHEMOMETRICS ANALYSIS: NARRATIVE REVIEW

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ABSTRACT

Food authenticity, including edible oils and fats (EOFs), is an interesting issue since unethical players try to adulterate high priced EOFs with lower priced oils to gain the economical profits. Vibrational spectroscopy (VS) is considered a fingerprinting analytical tool capable of differentiating authentic and unauthentic fats and oils. Combined with multivariate data analysis or chemometrics, VS has been reported as the common method used for the authentication of EOFs. Chemometrics has been defined as the science providing the extraction of chemical data to get the maximum information employing statistics and mathematical methods. VS of EOFs involved very large chemical data and therefore the use of chemometrics is a must. The main objective of this review was to highlight the employment of VS in combination with chemometrics for the authentication of EOFs. In order to achieve this purpose, a search strategy using databases of SCOPUS, PubMed and DOAJ along with several keywords was carried out. VS such as Fourier transform infrared (FTIR), near infrared (NIR), and Raman spectroscopy in conjunction with chemometrics offered the most reliable outcome for the authentication analysis of EOFs. In addition, the combination of VS and chemometrics is a rapid and reliable analytical method with minimum sample preparation. Among those techniques, FTIR and NIR spectroscopy combined with chemometrics offer a more effective and efficient technique for the authentication of EOFs.

Keywords: edible fats and oils, FTIR spectroscopy, multivariate calibrations, pattern recognition, Raman spectroscopy.

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INTRODUCTION

As an important source of essential fatty acids, edible oil and fats (EOFs) are vital components in the human diet needed for the appropriate development of the human body. Oils and fats are also essential components to be applied in pharmaceutical preparations, cosmetics and personal care products as well as food products. The typical framework of EOFs is the glycerol backbone, which is esterified by three fatty acids and is called triacylglycerols (TAG). Besides the main TAG, EOFs also contain some minor components such as sterols and fat-soluble vitamins (A, D, E and K). The composition of TAG in terms of chain length, substitution order and

saturation degree and minor components present in EOFs can be used to differentiate types of oils and fats. EOFs are composed of approximately 98% TAG and 2% of minor components including glycolipids, phospholipids, vitamins, sugars, sterols and carotenoids. In recent year, some edible oils such as corn oil, soybean oil, coconut oil, palm oil and edible fats mainly animal fats are used as good ingredients in the foodstuffs, cosmetics and pharmaceutical products (Jamwal *et al.*, 2021).

Chemically, edible fats (EFs) and edible oils (EOs) are TAG with different fatty acids (FAs) in terms of chain length (C12, C14, C18, C18:1 *etc.*), saturation degree which can be saturated FAs such as lauric, stearic, palmitic and myristic acids, mono-unsaturated FAs such as palmitoleic and oleic acids or poly-unsaturated FAs such as linoleic and linolenic acids. The difference in saturation and chain length determined the physico-chemical properties of EOFs. Besides, the specific FAs can also be used as markers for their quality controls (Baeten and Aparicio, 2000). EOFs also provide the essential FAs including omega-3 and omega-6 needed for brain function (Gouilleux *et al.*, 2018). Due to the increase in demand for EFs and EOs in the fats and oils industry, the adulteration practices of high quality EOs and EFs have escalated tremendously due to the monetary profits based on the price difference between high-quality oils and low-quality ones. In addition, EU legislation (EU Regulation 166/2011: Food Information) stated that in the case of blended or mixed vegetable oils, the oils composition must be clearly informed and identified in the package. For instance, in the case of vegetable fat products, it must be labelled as follows on the package: "Vegetable oil (palm oil)" (Osorio *et al.*, 2014). Thus, the detection of adulteration practices in EFs and EOs is very significant for consumers, producers and regulatory authorities to warrant the authenticity of EFs and EOs.

Numerous methods based on physical, biological and chemical methods have been optimised and developed for the purpose of authentication of EFs and EOs, mainly based on searching the specific markers in authentic EFs and EOs using chromatographic techniques. However, chromatographic-based methods such as gas chromatography and liquid chromatography coupled with mass spectrometer (gas chromatography-mass spectrometer or GC-MS and liquid chromatography-mass spectrometer or LC-MS) are typically time-consuming, expensive involving huge solvents and reagents, and requiring complex sample preparation and clean up. In addition, the modern industries of EFs and EOs require rapid and reliable quality control of EFs and EOs with low consumption of chemical reagents to support green analytical chemistry. Vibrational spectroscopy (VS) is an ideal technique

for authentication studies due to its nature as a fingerprinting analytical technique. Moreover, it offers rapid and reliable techniques without requiring much chemical reagents. Therefore, it is promising to be used as an authentication technique for EOFs (Rohman, 2017).

VS including near infrared (NIR), Fourier transform Infrared (FTIR) applying mid infrared region, hyperspectral imaging and Raman spectroscopies provide large data sets, even from the single measurements since these spectra can be characterised with each peak and shoulders. The intensities and position of each peak and shoulders correlated to the infrared absorption of functional groups present in the analysed samples (EOFs). Furthermore, each peak and shoulder can be characterised by intensities (absorbance or transmittance) and the exact frequency of the corresponding peaks, therefore, the use of chemometrics to treat these datasets is inevitable. Some definitions of chemometrics existed and the most accepted ones state the following: "Chemometrics is the chemical discipline that uses mathematical, statistical and other methods employing formal logic to design or select optimal measurement procedures and experiments, and to provide maximum relevant chemical information by analysing chemical data" (Aleixandre-Tudo *et al.*, 2022). As per this definition, it is very clear that the treatment and analysis of chemical data is the main objective of chemometrics (Arendse *et al.*, 2021). In general, in relation to food authenticity using FTIR spectroscopy, chemometrics techniques were widely applied for FTIR spectral pre-processing, qualitative analysis or pattern recognition (discrimination and classification of authentic and adulterated samples) and prediction of analyte in authentic and adulterated samples using multivariate calibrations (Moros *et al.*, 2010). Recently, the experimental design which is a part of chemometrics was also applied for the optimisation of instrumental-based methods intended for the authentication analysis of EFs and EOs (Peris-Díaz and Kręzel, 2021).

This review highlighted the application of such VS techniques using FTIR, NIR, and Raman spectroscopy in combination with chemometrics for the authentication of EOFs. The detailed methods of each technique along with the results were discussed to provide a clear overview of the authentication of EOs using VS techniques. This information would be very useful for readers in choosing the VS techniques for the authentication of EOs.

METHODS

During performing this review, some databases such as DOAJ, PubMed and Scopus were investigated and explored. The keywords were

used during the search and re-search of the relevant articles namely "Authentication edible fats OR Edible oils AND FTIR spectroscopy", "oil OR fat authentication AND FTIR spectroscopy", "fat OR oil authentication AND chemometrics", "oil NOT engine oil AND vibrational spectroscopy". To find the relevant references, some Boolean functions (AND, OR, NOT) were also used. The inclusion criteria of the selected papers were articles studying and discussing the authentication of edible fats using FTIR, NIR, and Raman spectroscopy between 2000-2023 and articles that are written in English. Meanwhile, articles which are not related to edible fats and oils analysis using vibrational spectroscopy, articles without the use of chemometrics, and articles which are written using other English language are excluded.

RESULTS AND DISCUSSION

Vibrational Spectroscopy

In recent years, spectroscopic methods such as VS namely Raman, near infrared and mid infrared have evolved as very effective and efficient analytical tools to be used as a reliable analytical technique for authentication purposes, including EFs and EOs. VS offers a fast, non-destructive, green analytical method with minimum use of chemical reagents and solvents and provides fingerprinting analytical tools (Tahir *et al.*, 2022). VS is frequently applied for the characterisation, identification, or classification of food samples including EFs and EOs. Currently, VS is widely applied for quantitative analysis of food adulterants in high quality food products (Gómez-Caravaca *et al.*, 2016). However, the obtained vibrational spectra typically consisted of a huge number of variables including highly overlapping vibrational spectral peaks which made them difficult to interpret. Therefore, to assist in the interpretation of spectral data, sophisticated statistical and chemometrics software are very helpful (Arendse *et al.*, 2021).

Near infrared (NIR) spectroscopy is a versatile analytical technique for the analysis of solid and liquid samples based on the interaction between electromagnetic radiations at wavelength 780-2500 nm to provide vibrational transitions of functional groups present in the analytes. Another VS technique is NIR spectroscopy which is also a simple and non-invasive analytical technique in which the samples are scanned and then can be further subjected to other instrumental analyses (Wang and Paliwal, 2007). NIR spectra of EFs and EOs originate from the interaction between EFs or EOs in the NIR region to provide the correlation between wavelength or wavenumbers and intensities either in absorbance or transmission values. Peaks in NIR

spectra are due to the overtones and combination vibrations of functional groups (Fermi resonance). The functional groups of C-H, N-H, O-H and S-H were observed as major peaks in NIR spectra. Due to the low sensitivity, this technique is not suitable for analysing trace levels of samples (Agelet and Hurburgh, 2014).

Infrared spectroscopy at mid infrared region (MIR) is the most applied VS technique typically used for qualitative and quantitative analyses of the analyte of interest including EOFs. This technique employed the IR radiation at wavenumbers of 4000-400 cm^{-1} absorbed by functional groups to provide the vibrational vibrations of functional groups in the analysed samples. Each peak and shoulder in FTIR spectra could be used as tools for the identification of functional groups, while the intensity of peaks (absorbance) can be utilised as variables during the quantification of EFs and EOs based on Lambert-Beer law (Candoğan *et al.*, 2020). Equipped with sophisticated chemometrics software and Fourier transformation instrumentation, FTIR spectroscopy is a powerful tool employed in the authentication of food commodities including EFs and EOs (Putri *et al.*, 2021; Rohman and Man, 2012) and other food products (Rohman *et al.*, 2016; Siddiqui *et al.*, 2021).

Raman spectroscopy is the complementary method to MIR spectroscopy, based on Raman scattering effects due to the interaction between the laser and the analysed samples. The incident laser is absorbed by functional groups in the samples, and the emitted beam has the same wavenumbers as the incident beam to provide Raman shift, as represented in Raman spectra (the correlation between the intensity of the scattered light and Raman shift). Each band in Raman spectra represent the vibrational characteristics related to functional groups or chemical bonds present in the molecules. Raman spectra are unique for each compound; therefore, Raman spectra are fingerprinting tools which can be used for the characterisation and differentiation of the studied samples. Besides, according to Lambert-Beer, Raman spectroscopy is also widely applied to quantitative analysis, since the intensity of specific bands in Raman spectra is linearly proportional to the concentration of the analyte of interest (Xu *et al.*, 2020). Raman spectroscopy in combination with chemometrics is a popular method to be used in the authentication of food products including fats and oils (Nunes, 2014).

Chemometrics Analysis

Chemometrics involving the use of multivariate data analysis (MDA) is a new discipline combining statistical tools and chemical data. Chemometrics has been well-defined as "the employment of statistics and mathematics

to extract the chemical data (absorbance values from spectroscopic measurements, chromatogram from chromatographic evaluations, pH value, electropherogram, *etc.*) in order to provide more understandable information" (Mazivila and Olivieri, 2018). Chemometrics is related to big data analysis used to treat a very large number of chemical responses obtained from the modern instrumental analysis even from single measurements. Vibrational spectra provide large data including the number of peaks and shoulders, the intensities of peaks and the exact wavenumbers (frequencies) which can be used as variables during chemometrics analysis (Xu *et al.*, 2020). There are three groups of chemometrics techniques widely applied in authentication analytical purposes in relation to VS, namely (1) preprocessing spectral data, (2) unsupervised and supervised pattern recognition techniques and (3) multivariate calibrations (Moros *et al.*, 2010).

Pre-processing spectra. Quantitative analysis of analyte including EOFs using VS was based on Beer-Lambert law stating that a linear relationship existed between absorbance values and the concentration of analyte(s) of interest. In certain circumstances, this linear relationship can be disturbed by some chemical or physical phenomena such as the interaction among molecules, the scattering (drift) of particulates, the width changes of spectra in terms of peaks or position shifts, the change of refractive index, and stray radiation at high optical densities. Some pre-processing spectra can transform multivariate data so that the data follows Beer's law, therefore, pre-processing can improve the linear correlation between the actual value of analyte concentration and responses of spectral data (Kumar and Chandrakant, 2017). The purpose of signal preprocessing can be either signal correction or signal enhancement.

Signal correction can be performed by some pre-processing spectra including off-set elimination based on Kubelka-Munk transformation, Polynomial baseline correction capable of reducing the non-linearity, derivatisation of spectra intended to resolve the extensive overlapping peaks, multiplicative scatter correction (MSC) for correcting the baseline, standard normal variate (SNV), and orthogonal signal correction (OSC) intended for removing the information which is not related to the target variables (Moros *et al.*, 2010). Meanwhile, signal enhancement can be accomplished by mean centering (MC) and variance scaling. MC could enhance the differences among the samples to provide a more accurate and precise predictions. Variance scaling capable of emphasising slight variations in the data responses by giving all data values equal weightage and this preprocessing technique is suitable when analysing

low-levels of analytes having overlapping spectral bands (Wang *et al.*, 2009).

Pattern recognition techniques. Different pattern recognition techniques have been introduced including exploratory data analysis (EDA) or classification models which can be chosen relying on data characteristics, the data structure and the specific purposes. Pattern recognition is considered the most used chemometrics technique in the authentication of EFs and EOs for the classification and discrimination of EFs and EOs. However, it is rather problematic to make the decision for choosing certain pattern recognition models. The information on the data structure is important to decide what types of pattern recognition are used. If the correlation between the used variables and class modelling is linear, linear models such as PCA are suitable. Linear partial least square-discriminant analysis (PLS-DA) is an ideal chemometrics model for the classification and discrimination of the samples if the class variability within a group is greater than that between several groups. In addition, if the correlation between the used variables and class modelling is non-linear such as the quadratic model and artificial neural network (ANN), there will be a tendency to give large errors in prediction (Singh *et al.*, 2013).

The chemometrics of pattern recognition can be categorised into unsupervised pattern recognition (UPR) and supervised pattern recognition (SPR) with the main objective being the differentiation and classification of objects. The objective of UPR is to find the hidden and interesting pattern in unlabelled data which can be done using PCA and HCA. Furthermore, SPR models used the responses or variables from the instrumental measurement and the well-known class modelling to build the classification models. SPR provides a rule to assign the class membership to new objects (Marini, 2009). From the operational perspectives, the classification or pattern recognition models can be further subdivided into discriminant models and class-modelling. PLS-DA, Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) and k-nearest neighbors (k-NN) are discrimination models focusing on the differentiation among samples belonging to different classes, whereas class-modelling tools, such as Soft Independent Modelling Class Analogy (SIMCA) and UNEQ (chemometrics for supervised pattern recognition based on the assumption of multivariate normally-distributed groups) focused on the similarities among objects of the same group, and these models were used to decide whether a new object fits in a certain class or not (Rohman *et al.*, 2020). Some parameters used for pattern recognition chemometrics include sensitivity, specificity, efficiency, precision and accuracy (Noviana *et al.*, 2022).

Multivariate calibrations. The multivariate calibration is widely applied for the prediction of analyte of interest in the analysed samples based on the relationship between chemical responses (absorbance values) and concentrations. Some multivariate calibrations commonly used for the authentication analysis of EFs and EOs include principal component regression (PCR), partial least square regression (PLSR), ridge regression (RR), multiple linear regression (MLR), multivariate curve resolution-alternating least squares (MCR-ALS) and canonical correlation analysis (CCA). Some statistical parameters typically used for the assessment of multivariate calibration model performances are coefficient of determination (R^2) describing the model accuracy, root mean square error (RMSE) in calibration (RMSEC), in prediction (RMSEP) and in cross-validation (RMSECV). High R^2 and low RMSEC, RMSEP and RMSECV indicated that the developed multivariate calibrations are reliable with high accuracy and precision for the prediction of analyte in unknown samples (Naguib *et al.*, 2014).

The Employment of FTIR Spectra and Chemometrics for Authentication of EOs and EFs

The study involving the use of FTIR spectra and SPR of LDA for the discrimination and classification of EOs and EFs samples (135 samples) has been reported recently (Ye and Meng, 2022). The optimisation has been carried out by selecting the FTIR spectra regions along with FTIR spectral preprocessing (derivatisation, SNV, smoothing) capable of classifying edible oils with the highest correct classification rates (CCR) in the models (calibration and validation). The CCR is calculated as $CCR = N_{\text{correct}}/N \times 100$, in which N is the number of objects used during the classification and N_{correct} is the number of correctly identified samples. Based on the optimisation results, the best recognition ratio for the classification of studied edible oils (camellia, sunflower, soybean, peanut, rapeseed, linseed, olive, sesame and corn oils as well as animal fats of beef and lard) adulterated with gutter oil in the range of 0.5% to 50.0%, with CCR of 92.6% is achieved using the variable of absorbance values at wavenumbers of 3100-2800 in combination with absorbance values at 1330-1000 cm^{-1} . For the quantitative model, EFs and EOs were adulterated with gutter oil using multivariate calibration of BiPLS. The regression equation correlating the actual values and predicted values is highly linear, providing R^2 of 0.9942-0.9995, RMSECV of 1.09-5.49, RMSEC of 0.814-2.150, and RMSEP of 0.474-3.550. This result indicated that a combination of FTIR spectra and chemometrics of LDA and BiPLS is very effective for the classification and quantification of edible oils from potential adulterants.

FTIR spectroscopy combined with some chemometrics techniques including PCA, PLS-DA, SIMCA, kNN, and SVM has been employed for the quality control of Argan oil (AO), an oil extracted from Argan tree (*Argania spinosa* L.) with unique properties typically applied for cosmetic uses. This classification chemometrics were used for the classification and discrimination of extra virgin AO, virgin AO and low quality of AOs. The chemometrics of interval-PLS was used for the selection of regions (mid infrared region of 4000-400 cm^{-1}), and finally eight sub-intervals at the wavenumbers range of 3857-882 cm^{-1} were selected for the classification of AOs. The result showed that these classification chemometrics models exhibited perfect performance with a correct classification rate of 100% of AOs either in training or test sets (Kharbach *et al.*, 2021).

The feasibility of ATR-FTIR spectra for the detection of adulteration of Mustard oil (MO) from Argemone oil (AGO) has been studied, employing the chemometrics of PCA, LDA, PCR and PLSR. Twenty samples of pure MOs and 140 samples of MOs adulterated with AO at concentrations of 1%-30% v/v were prepared during this study. Based on the optimisation procedure, the variable of absorbance values at wavenumbers 3050-2750 combined with absorbance values at 1800-500 cm^{-1} was selected for the classification between MO from MO adulterated with AGO adulterants. Furthermore, LDA was advantageously used for the discrimination of MO from MO adulterated with AGO at 1%-5%. LDA also clarified that the first discriminant function (DF1) and second discriminant function (DF2) accounted for 77.7% and 22.3% of the total variance, respectively. During quantitative analysis, the multivariate calibrations of PCR and PLS-R were optimised using the variable of absorbance values at three regions, namely (1) the absorbance values at wavenumbers 3050-2750 combined with absorbance values 1800-500 cm^{-1} , (2) absorbance values at 3050-2750 cm^{-1} and (3) absorbance values 1800-500 cm^{-1} using normal and derivative spectra (first and second derivative FTIR spectra). Finally, PLS-R using first derivative FTIR spectra at wavenumbers of 1800-500 cm^{-1} provided the best calibration model with RPD and RRE values of 52.230% and 0.033%, respectively. The R^2 value for the correlation between actual values of AGO and FTIR predicted values of 0.999 with RMSEP of 0.2% v/v. The lowest detected percentage of AGO in MO was 1% v/v. These results confirmed the feasibility of FTIR spectra- chemometrics as an effective and reliable technique for the detection of adulteration of AGO in MO (Jamwal *et al.*, 2020). Sota-Uba *et al.* (2021) reported that the combination of FTIR spectra and PLSR could detect EVOO adulterated by corn oil (CO) and canola oil (CaO) at 10% (v/v).

A new approach for the authentication study of virgin coconut oil (VCO) from potential adulterants of canola (CaO), corn (CO), sunflower (SFO) and soybean (SBO) using FTIR spectra and data driven SIMCA (DD-SIMCA) has been carried out. The authors scanned FTIR spectra of pure samples and samples adulterated with CaO, CO, SFO and SBO at wavenumbers of 4000-500 cm⁻¹. In DD-SIMCA, one class model was made in order to assess the authenticity of VCO. Two parameters (specificity and sensitivity) were used for the evaluation of correct identification. The mean sensitivity (%) for pure VCO, and VCO adulterated with CaO, CO, SFO and SBO was 88%-100%, while the mean specificity was in the range of 96%-100%. The results exhibited that FTIR spectra combined with DD-SIMCA offered a reliable and rapid technique to be implemented for the authentication of VCO (Neves and Poppi, 2020).

The authentication analysis of Babasu oil (BaO), an oil with 90% saturated fatty acids having similar composition to coconut oil and analogous applications in food products, from SBO has been carried out using FTIR spectra and chemometrics. FTIR spectra of all samples were scanned at 4000-600 cm⁻¹. Before chemometrics analysis, FTIR spectra were subjected to pre-processing of SNV, MSC, as well as the first derivative and second derivative. The selected FTIR spectra were used as a variable for classification between BaO and BaO adulterated with SBO at concentrations of 5%-50%. LDA associated with PCA revealed the efficient result during the classification of pure BaO and BaO adulterated with SBO from 5% to 50% of adulterant. The accuracy rates for correct classification in calibration and external validation samples were 99.88% and 97.06%, respectively (Pereira *et al.*, 2022).

FTIR spectra in conjunction with LDA for classification as well as PLSR and PCR has been validated for the detection of adulteration practice of milk fat (MF) from palm oil (PO) as MF's adulterant. After the optimisation, FTIR spectra using the first derivative mode at wavenumbers of 3033-692 cm⁻¹ were selected for the quantifying PO as an adulterant in MF as indicated by the high R² values of 0.9999 (in calibration) and 0.9998 (validation) models, respectively. Besides, the PLSR model also provided a low RMSEC of 0.154 and RMSEP of 0.743. In addition, PCR also exhibited a reliable method for the determination of PO levels in MF which resulted in R² values of 0.9998 (in the calibration model) and 0.9997 (in the validation model). The values of RMSEC and RMSEP were 0.671 of 0.905, respectively. LDA was capable of classifying MF and MF adulterated with PO samples with accuracy of 100%. The combination of FTIR spectra with LDA and multivariate calibrations (PLSR and PCR) is successfully applied for the authentication of MF with minimum use of solvents and without any sample preparation step (Windarsih *et al.*, 2021). A similar approach was also used successfully for the authentication of horse's milk from goat's milk and cow's milk (Arifah *et al.*, 2022). Table 1 compiled the employment of FTIR spectra-chemometrics for the authentication analysis of EFs and EOs.

In general, FTIR spectroscopy is the most feasible method for the authentication and quality control of EOFs. This method is attractive as a good alternative technique for EOFs analysis due to its simplicity, effectivity, low cost, non-destructive, robustness, and minimum chemical reagents. In addition, it offers fast analysis and can be used for onsite and real-time monitoring. Despite the advantages of FTIR spectroscopy, there are also several challenges

TABLE 1. THE LIST OF PUBLISHED PAPERS REPORTING THE EMPLOYMENT OF FTIR SPECTRA- CHEMOMETRICS FOR THE AUTHENTICATION ANALYSIS OF EF_s AND EO_s

Issues	Methods	Chemometrics	Results	References
Authentication analysis of Camellia oil (CMO) from oil adulterants (soybean, palm, corn oils, <i>etc.</i>)	ATR-FTIR LDA: Spectra at 4 000-650 cm ⁻¹ Bi-PLS: Combination wavenumbers of 3100-2900, 1800-1700, 1500-1400 and 1200-1100 cm ⁻¹	LDA and Backward interval PLS (Bi-PLS)	LDA could classify edible oil samples with accuracy levels of 100%. The recognition rates during external validation were 100% (pure CMO) and 92.6% (CMO adulterated with other oils). BiPLS-34 model could provide R ² of > 0.99 and low values of RMSEC, RMSEP and RMSECV.	Ye and Meng (2022)
Authentication of edible oils (extra virgin olive oil or EVOO with almond oils, <i>etc.</i>)	ATR-FTIR at 4 000-400 cm ⁻¹	HCA and LDA	HCA and LDA could correctly classify and discriminate 20 samples of vegetable EOs. The adulteration of EVOO by CO or CaO could be detected at levels of 10% (v/v).	Sota-Uba <i>et al.</i> (2021)

TABLE 1. THE LIST OF PUBLISHED PAPERS REPORTING THE EMPLOYMENT OF FTIR SPECTRA- CHEMOMETRICS FOR THE AUTHENTICATION ANALYSIS OF EFs AND EOs (continued)

Issues	Methods	Chemometrics	Results	References
Detection of EVOO adulteration with safflower oil (SFO), canola oil (CaO) and hazelnut oil (HaO)	ATR-FTIR at 4 000-650 cm ⁻¹	PCA, PLS-DA and one class-SIMCA	<p>The second derivative ATR-FTIR spectra were applied. PLS-DA and SIMCA provided 100% sensitivity, in which as low as levels of 5% CaO and 15% HaO could be detected.</p> <p>The overall predictive power of every resulting model was found >92% indicating the high accuracy classification model for authentic and adulterated EVOO samples.</p>	Ordoudi <i>et al.</i> (2022)
Authentication of EOs (31 samples, including blended oil and oil from olive oil <i>etc.</i>) from frying oils	The oil sample was dissolved in isooctane, and the sample was scanned using ATR-FTIR at 6 000-400 cm ⁻¹	LDA and PLSR	<p>LDA using FTIR spectra at 1550-650 cm⁻¹ could discriminate the authentic and adulterated edible oils with minimum adulteration of 1% and could be qualitatively analysed with the recognition rate reach 100%.</p> <p>PLS using the same variables used in LDA could predict the level of adulterants down to 1.5%.</p>	Kou <i>et al.</i> (2018)
Authentication of sesame oil (SeO) from the adulterants of HAO, CaO, and SFO in different concentrations of 1%-50%	ATR-FTIR spectra at wavenumbers of 3 800-600 cm ⁻¹	HCA, PCA and PLSR	<p>FTIR spectra at the combined region of 1267-1209, 1121-1045 and 876-814 cm⁻¹ was selected to establish the HCA dendrogram for the authentication of SeO from hazelnut and canola oil.</p> <p>PCA was efficaciously applied for the grouping of pure SeO and mixed with others.</p> <p>PLSR provide reliable technique for prediction of oil adulterant levels with acceptable accuracy and precisions, as indicated by high R² and low RMSEC and RMSEP.</p>	Ozulku <i>et al.</i> (2017)
Discrimination of olive oils with different varieties in pure and adulterated with other oils	ATR-FTIR spectra at 3 800-600 cm ⁻¹	Some pre-processing treatments use derivatisation, smoothing and mean centering. HCA, PCA, PLS-DA, and PLSR	<p>FTIR in the mode first derivative spectra using the Savitzky-Golay was used. Spectra were normalised and mean centered for PCA, PLS-DA and PLSR models.</p> <p>Using HCA, three clusters were obtained. Cluster I comprised all olive oil samples, cluster II consisted of two peanut, one safflower and one high oleic sunflower oils, cluster III consisted of flaxseed oils.</p> <p>PCA was used for determination of PCs used for next discrimination in PLS-DA in which PLS-DA could discriminate olive oils and those adulterated with other oils with an accuracy rate of 100%.</p> <p>PLSR could predict the levels of olive oils blended with others with acceptable accuracy and precision.</p>	de la Mata <i>et al.</i> (2012)

TABLE 1. THE LIST OF PUBLISHED PAPERS REPORTING THE EMPLOYMENT OF FTIR SPECTRA- CHEMOMETRICS FOR THE AUTHENTICATION ANALYSIS OF EFs AND EOs (continued)

Issues	Methods	Chemometrics	Results	References
Authentication of grape seed oil (GSO) from refined soybean oil (SBO)	ATR-FTIR spectra at 4 000-650 cm ⁻¹	PCA, LDA, SIMCA and PLSR	PCA using PC1 of 64%, PC2 of 20% provides the separation of pure oils and those adulterated oils. SIMCA and LDA models provided good classification for pure GSO and GSO adulterated with SBO. PLSR could determine SBO at levels<0.59%.	Akin <i>et al.</i> (2019)
Authentication of cold pressed black cumin seed oil (BCSO) and quantification of soybean oil (SBO) as adulterant in BCSO	FTIR spectra at 4 000-650 cm ⁻¹	PCA, SIMCA and PLSR	PCA and SIMCA could classify BCSO and that adulterated with SBO. R ² and RMSEC of PLSR calibration model for FTIR spectra were of 0.9250-0.9998 and 0.1685-4.4762, respectively.	Arslan <i>et al.</i> (2019)
Authentication of Nigella sativa oil (NSO) from grape seed oil (GSO)	Absorbance values of ATR-FTIR spectra at 3 999-556 cm ⁻¹	PLSR	FTIR spectroscopy using full spectra and PLSR provide good accuracy during the quantification of NSO. PLSR offer good model with RMSEC of 0.0209 and RMSEP of 0.0173.	Zhu <i>et al.</i> (2022)

such as improving the spectra acquisition required. In addition, due to the variety of oils and fats, the developed methods must be examined for its reproducibility for various types of oils and fats.

Near Infrared Spectroscopy (NIRS) Employed for the Authentication Analysis of EOs

Data fusion using NIRS and Vis spectra at wavelength 1000-1700 nm (NIRS) and 500-1000 nm (Vis) has been optimised and validated for authentication of Argan oil (AO) from adulterants of cheap vegetable oils (designated by VO1 and VO2 respectively). Several pre-processing techniques were applied including smoothing, MSC, SNV, as well as first and second derivatives to provide the optimum chemometrics model. PCA using NIRS previously subjected to the first derivative at 1000-1700 nm could differentiate 112 AO samples (authentic and adulterated) clearly. NIRS offered a better calibration model than Vis spectra using PLS regression. The levels of AO adulterated with VO1 and VO2 were accurately predicted with R-value of 0.923; RMSEC of 3.220; SEC of 3.240 and bias of -0.018. The combination of NIRS-chemometric methods is effective technique for the detection of adulteration practice of AO from cheap vegetable oils with excellent predictive performance (Farres *et al.*, 2019).

Reflectance NIRS in combination with chemometrics has been applied for the authentication analysis of Camellia oil (CMO) from

the adulterants of CO, rapeseed oil (RPO), and SFO in the market. LDA using absorbance values of NIRS in the first derivative mode at 9000-4500 cm⁻¹ was successfully used for the identification of cheap oils' types (CO, RPO, and SFO) as adulterants in CMO with accuracy rates of 96.7%. PLSR using the same variable provides good modelling during this study (authentication of CMO from CO, RPO, and SFO) after the spectral optimisation using some different pretreatment methods with R²-values higher than 0.995, RMSEC and RMSEP lower than 6.79 and 4.98 respectively (Du *et al.*, 2021). The combination of NIRS-chemometrics offered reliable tools for the authentication analysis of CMO from adulterants of CO, RPO and SFO, therefore, the developed methods are suitable for routine monitoring of high-quality edible oils from the potential adulterants. *Table 2* exemplifies the application of NIR spectroscopy in combination with chemometrics for authentication analysis of EOFs.

In general, NIR spectroscopy can be used for rapid and accurate screening of various types of EOFs. The extension of spectral range in NIR compared to FTIR is advantageous in a more comprehensive analysis of EOFs. In addition, NIR spectroscopy provides lower limit of detection than FTIR resulting in the detection of lower levels of adulterants. Despite its benefits, several limitations of NIR spectroscopy are also important to be considered. The combination of bands and overtone superposition could affect the spectra interpretation becoming more complicated. It

TABLE 2. THE LIST OF PUBLISHED PAPERS REPORTING THE EMPLOYMENT OF RAMAN SPECTRA- CHEMOMETRICS FOR THE AUTHENTICATION ANALYSIS OF EFs AND EOs

Issues	Methods	Chemometrics	Results	References
Butter adulterated with soybean oil	NIR spectra at 12 000-4 000 cm^{-1}	PCA and PLS	PCA could differentiate butter and butter adulterated with soybean oil. PLS could predict soybean oil in butter with R^2 of 0.999 for both calibration and validation model, with RMSEC of 0.89 and RMSEP of 1.26.	Pereira <i>et al.</i> (2019)
Butter adulterated with palm kernel oil, bean oil, sunflower oil, linseed oil, and fish oil	NIR spectra at 6 400-5 100 cm^{-1}	PCA, PLS-DA, and PLS	PCA could differentiate butter from adulterants. PLS-DA could discriminate and classify butter and adulterated butter. PLS could predict adulterant levels in butter with high accuracy and high precision.	Heussen <i>et al.</i> (2007)
Virgin olive oil adulterated with peanut oil, sunflower oil, soybean oil, sesame oil, and maize oil	NIR spectra at 1 000-2 500 cm^{-1}	BOSS (bootstrapping soft shrinkage)-PLS	PLS could predict all adulterants in virgin olive oil with $R^2=0.992$ and RMSEP=1.49%.	Jiang and Chen (2019)
Copaiba oil adulterated with soybean oil	NIR spectra at 906-1 676 cm^{-1}	PLS	PLS successfully predicted soybean oil in copaiba oil with $R^2=0.991$ and RMSEP=1.5%.	Oliveira-Moreira <i>et al.</i> (2018)
Differentiation of transgenic and non-transgenic soybean oil	NIR spectra at 1 100-2 500 cm^{-1}	SVM-DA and PLS-DA	Correct classification between transgenic and non-transgenic soybean oil (>80%).	Luna <i>et al.</i> (2013)
Virgin olive oil adulterated with soybean oil	NIR spectra at 833-2 500 cm^{-1}	PLS	PLS successfully predicted soybean oil with $R^2>0.98$ and RMSEP=1.76%.	Mendes <i>et al.</i> (2015)

also has lower structural selectivity compared to FTIR. In addition, it also has the same drawback as FTIR spectroscopy such as the reproducibility for different types of EOFs must be examined and verified.

Raman Spectroscopy

Raman spectra in combination with chemometrics of support vector regression (SVR) have been reported to authenticate EVOO from SFO through the determination of β -carotene in synthetic EVOOs. In this study, confocal Raman technique was applied for the identification of molecular differences between EVOO and SFO, by exploring the differences in Raman spectra of β -carotene, oleic acids and linoleic acids. Three peaks of Raman spectra in SFO exhibited higher intensity than those in EVOO, namely peaks at 1112, 1265 and 1658 cm^{-1} respectively. Peak at 1112 cm^{-1} is practically invisible between EVOOs and SFO due to the low Raman active of aliphatic *all-trans* C–C stretch. The intensity of Raman scattering at peaks 1161 and 1526 cm^{-1} in SFO is lower than that

in EVOO. These two Raman bands are coming from the vibration of C–C stretching and C=C stretching in β -carotene, respectively. Furthermore, SVR was used to predict the levels of β -carotene intended to authenticate EVOO from SSO. The linear kernel of SVR provide good correlation between actual value and predicted values of β -carotene with R^2 of 0.9868 and RMSE of 0.0653 (Fang *et al.*, 2022). The results indicated that laser confocal Raman technique combined with chemometrics could be effective tools for authentication of EVOO.

The combination of Raman spectra and chemometrics of PCA and PLS-DA was applied for the authentication of cold-pressed black cumin oil (CPBCO), cold-pressed almond oil (CPAO) and cold-pressed walnut oil (CPWO) from the adulterants of commercial SFO and corn oil (CO). PCA score plot models for the discrimination of CPBCO, CPAO, and CPWO from the adulterated samples (these oils adulterated with SFO and CO) accounted for 93.35%, 96.24% and 94.25% of the cumulative variances, respectively. Using PLS-DA for the classification of CPBCO, CPAO and CPWO from the adulterated samples (SFO and CO) provides RMSEC, RMSECV,

and RMSEP values of 0.06-0.21, 0.03-0.11, and 0.05-0.21; 0.08-0.24, 0.06-0.15, and 0.08-0.25; and 0.05-0.18, 0.03-0.10 and 0.09-0.20, respectively. These results showed that Raman spectra in combination with chemometrics of PCA and PLS-DA could be effective tools either for the discrimination of cold-pressed oils or for the rapid determination of the adulteration of these cold pressed oils with cheaper oils (Temiz *et al.*, 2021). Table 3 shows the application of Raman spectroscopy and chemometrics for the authentication analysis of EOFs.

Two vibrational spectroscopies namely Raman spectroscopy and FTIR spectroscopy were compared in terms of characteristics performance during authentication analysis of olive oils with different qualities and for discriminating olive oils from other vegetable edible oils such as SBO, SFO, RPO, CO, *etc.* The classification chemometrics used were kNN, PLS-DA, OCPLS, SVM-C and SIMCA, while the quantification of adulterant oil models was PLS-R. PLS-DA or SVM-C techniques are capable of discriminating 100% of EVOO samples and 92% of other vegetable EOs. For

quantitative analysis, FTIR spectroscopy is also more preferred than Raman spectra as indicated by low errors obtained using FTIR spectra. The reliability of the two methods was established based on R²-values and the errors of quantification in calibration and validation errors as evaluated by RMSEV, mean absolute error of validation (MAEV) and median absolute error of validation (MdAEV). FTIR spectroscopy provide the values of R² of 0.86, RMSEV of 17.6, MAEV of 14.6 and MdAEV of 16.0, while the Raman spectroscopy showed values of 0.93, 34.2, 27.8 and 29.6, respectively. Although the R² values obtained from FTIR are not sufficiently good (0.86) compared to Raman spectroscopy (R² of 0.93), the validation errors of FTIR spectroscopy (about 15%-17%) are lower than those using Raman spectroscopy (about 28%-34%), therefore, FTIR spectroscopy provides precise method than Raman spectroscopy (Jiménez-Carvelo *et al.*, 2017).

In general, Raman spectroscopy is a well-suited technique for the analysis of EOFs. It provides high specificity for multicomponent measurement of

TABLE 3. THE LIST OF PUBLISHED PAPERS REPORTING THE EMPLOYMENT OF RAMAN SPECTRA- CHEMOMETRICS FOR THE AUTHENTICATION ANALYSIS OF EFs AND EOs

Issues	Methods	Chemometrics	Results	References
Olive oil adulterated with pomace oil	Raman spectra at 400-4 000 cm ⁻¹	PLS	PLS could predict pomace oil in olive oil with R ² calibration=0.995 and SECV=2.23%, and R ² validation=0.997 and SEP=1.72%.	Yang and Irudayaraj (2001)
Olive oil adulterated with soybean oil, rapeseed oil, sunflower seed oil and corn oil	Raman spectra at 400-4 000 cm ⁻¹	PCA	PCA was capable of separating olive oils from adulterants with good separation.	Zou <i>et al.</i> (2009)
Macadamia oil (MaO) adulterated with corn oil (CO) and sunflower oil (SFO)	Raman spectra at 1 600-1 700 cm ⁻¹ for MaO-CO and 1 200-1 400 cm ⁻¹ for MaO-SFO	PLS	PLS model for both MaO-CO and MaO-SFO yielded R ² >0.99.	Carmona <i>et al.</i> (2015)
Olive oil adulterated with hazelnut oil	Raman spectra at 1 000-3 000 cm ⁻¹	PCA and PLS	PCA could differentiate olive oil from hazelnut oil, clearly. The level of hazelnut could be predicted using PLS with R ² calibration=0.979, R ² validation=0.940, and RMSEP=4.16.	Lopez-Diez <i>et al.</i> (2003)
Animal fats (chicken fat, beef tallow, duck oil) adulterated with lard	Raman spectra at 100-1 800 cm ⁻¹	PCA	PCA based on the oil gauge values successfully differentiated animal fats from lard.	Lee <i>et al.</i> (2018)
Butter adulterated with margarine	Raman spectra at 200-2 000 cm ⁻¹	PCA and PLS	PCA could differentiate butter from margarine and butter adulterated with margarine. PLS could predict margarine in butter with R ² calibration=0.992, RMSEC=2.98%, R ² validation=0.987, and RMSEP=4.94%.	Uysal <i>et al.</i> (2013)

samples in a process. It is also a non-destructive technique with rapid acquisition time and gives a spectral fingerprint of the molecules contained in EOs and EFs. However, Raman techniques also have limitations such as higher cost compared to FTIR and NIR spectroscopy and has low signal-to-noise ratio. In addition, the application of Raman spectroscopy on various types of EOs must be checked to ensure its reproducibility.

CONCLUSION AND FUTURE PERSPECTIVES

Edible fats and oils are export commodities for some countries, which attract unethical producers to adulterate or substitute high priced fats and oils with lower priced oils to get economic profits. Due to its property as a fingerprinting analytical technique, vibrational spectra (near infrared, mid infrared, Raman) are widely developed and validated for the authentication of edible fats and oils. Vibrational spectra contain big data analysis, so the employment of chemometrics is inevitable to treat these data. The combination of vibrational spectra, previously subjected to preprocessing spectral treatments and pattern recognition models is proven to be an accurate and precise method for the classification of authentic and adulterated edible fats and oils. Furthermore, by selecting the appropriate variables and multivariate calibrations, vibrational spectroscopy is fast and reliable technique for the prediction of adulterant levels in edible fats and oils. FTIR, NIR and Raman spectroscopy combined with chemometrics provides a rapid analysis, non-destructive and green analytical method for the analysis of edible oils and fats. Most of the chemometrics used were PCA, DA, PLS-DA and HCA for qualitative analysis and PLS for quantitative analysis. Among these vibrational spectroscopy techniques, FTIR spectroscopy is widely chosen and applied for the authentication of oils and fats due to its high reliability. It can be used to identify many functional groups contained in oils and fats samples. In terms of sensitivity, NIR spectroscopy offers higher sensitivity in detecting adulterants shown by the lower limit of detection compared to the FTIR spectroscopy technique. In addition, NIR spectroscopy provides an extended spectral range which is useful for authentication purposes. On the other hand, Raman spectroscopy allows high specificity for multicomponent analysis of complex samples. However, Raman spectroscopy is the most expensive compared to FTIR and NIR spectroscopy techniques. It also has low signal to noise ratio. Therefore, the consideration in choosing the method for authentication analysis of edible fats and oils, depends on the purpose and target of analysis referring to the advantages

and drawbacks of each technique. In the future, this developed method should be subjected to collaborative study through proficiency testing among the competent laboratories to become a standard analytical method with the scope of fats and oils authentication.

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