Taylor & Francis
Taylor & Francis Group

Food Reviews International

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lfri20

Application of Raman Spectroscopy and Chemometrics for Quality Controls of Fats and Oils: A Review

Anjar Windarsih, Lily Arsanti Lestari, Yuny Erwanto, Anggita Rosiana Putri, Irnawati, Nurrulhidayah Ahmad Fadzillah, Nuning Rahmawati & Abdul Rohman

To cite this article: Anjar Windarsih, Lily Arsanti Lestari, Yuny Erwanto, Anggita Rosiana Putri, Irnawati, Nurrulhidayah Ahmad Fadzillah, Nuning Rahmawati & Abdul Rohman (2021): Application of Raman Spectroscopy and Chemometrics for Quality Controls of Fats and Oils: A Review, Food Reviews International, DOI: 10.1080/87559129.2021.2014860

To link to this article: https://doi.org/10.1080/87559129.2021.2014860

Published online: 22 Dec 2021.

Submit your article to this journal

Article views: 362

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=lfri20

FOOD REVIEWS INTERNATIONAL
https://doi.org/10.1080/87559129.2021.2014860

Taylor & Francis
Taylor & Francis Group

Check for updates

Application of Raman Spectroscopy and Chemometrics for Quality Controls of Fats and Oils: A Review

Anjar Windarsih[a,b], Lily Arsanti Lestari[b], Yuny Erwanto[b,c], Anggita Rosiana Putri[d], Irnawati[e], Nurrulhidayah Ahmad Fadzillah[f], Nuning Rahmawati[g], and Abdul Rohman[b,d]

[a]Research Division for Natural Product Technology (BPTBA), National Research and Innovation Agency (BRIN), Yogyakarta, 55861, Indonesia; [b]Center of Excellence Institute for Halal Industry & Systems (IHIS), Universitas Gadjah Mada, Yogyakarta, Indonesia; [c]Division of Animal Products Technology, Faculty of Animal Science, Universitas Gadjah Mada, Yogyakarta, Indonesia; [d]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Universitas Gadjah Mada, Yogyakarta, Indonesia; [e]Study Program of Pharmacy, Faculty of Pharmacy, Halu Oleo University, Kendari, Indonesia; [f]International Institute for Halal Research and Training (INHART), International Islamic University Malaysia (IIUM), Malaysia; [g]Medicinal Plant and Traditional Medicine, Research and Development Centre, Karanganyar, Indonesia

ABSTRACT

Edible fats and oils, composed of triacylglycerols (TAG) and some minor components having beneficial effects to human health such as lipid-soluble vitamins, carotenoids, and phenolics compounds, are essential to human diets because they are good energy sources. Some edible fats and oils had high price in the market which are lucrative to be adulterated with lower priced ones to gain the economical profits. Therefore, it is essential to assure the quality of edible fats and oils to fulfill the requirements and to detect the possibility of adulterated products using reliable analytical methods. Vibrational spectroscopies consisting of infrared and Raman are widely applied for analysis of edible fats and oils. In this review, Raman spectroscopy combined with chemometrics has been highlighted for quality control and authentication analysis of edible fats and oils either in raw materials or in food products.

KEYWORDS

Chemometrics; edible fats and oils; oxidative stability; Raman spectroscopy; quality control

Introduction

Edible fats and oils are considered as essential for the human diet, along with carbohydrates and proteins, due to its nutritional compositions especially fatty acids. Edible fats and oils also contained some minor components such as vitamins, sterols, carotenes and phenolics compounds having beneficial effects to human health.[1] Edible oils (olive oil, palm oil, soybean, corn oils, etc.), edible animal fats (beef fat and mutton fat) and fish oils (cod liver oil and tuna oils) are often supplemented in processed foods like chocolates, cream and bakery. These edible fats and oils are also used as food components in salad dressing and mayonnaise as well as vehicles and carriers in pharmaceutical products.

In daily applications, edible fats and oils are used for deep-frying which are subjected to high temperature, so that the thermal degradation can occur to yield off-flavors. Fats and oils contained high energy (about 9 kcal/g) and essential fatty acids needed for human health such as omega-fatty acids (EPA and DHA), linoleic acid and linolenic acid. Physical and chemical properties of fats and oils can affect the sensory attributes and nutritional quality of foods.[2,3] Therefore, the quality of edible

CONTACT Abdul Rohman abdulkimfar@gmail.com Centre of Excellence Institute for Halal Industry & Systems (IHIS), Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

© 2021 Taylor & Francis

fats and oils must be monitored regularly from the presence of harmful components occurring during incorrect treatment and storage such as peroxides or from the addition of foreign components having negative effects on human health.

The quality of edible fats and oils must be assured because they are prone to quality deterioration through oxidation and microbial degradation which resulted in the formation of off-flavor and loss in nutritional value. The degradation of edible fats and oils may contribute in the formation of some toxic and reactive compounds which are harmful to human health.[4] In quality control of edible fats and oils, several parameters were determined such as iodine value to evaluate the degree of unsaturation in which unsaturated oils are better to be consumed than the saturated ones, peroxide value to assess the primary oxidation products including peroxides, moisture content in which the presence of water could catalyze the hydrolytic degradation, specific gravity (purity), and acid value for the evaluation of fats and oils hydrolysis. These parameters determine the shelf-life quality of edible fats and oils, therefore, the evaluation of these parameters is needed.[3]

The reduced quality of edible fats and oils may also occur by adulteration practice by substituting high-quality fats and oils with lower ones.[5] Authentication of edible fats and oils is of paramount importance in the food industry in which raw materials and fats and oils-based foods must be tested for compliance with regulatory and health specifications.[1] According to FFDCA (Federal Food, Drug and Cosmetic Act), Food and Drug Administration (FDA), food including edible fats and oils can be declared as "adulterated" due to (a) the chemicals or substances are added which are harmful to human health, (b) the addition of cheaper or inferior quality of fats and oils into high-quality ones, (c) the extraction of any valuable components from the main fats and oils, (d) the reduced quality of fats and oils which is below the required standards, and (e) the addition of any substances in order to increase bulk or weight.[6]

In order to evaluate the quality of edible fats and oils and to assess the authenticity, some analytical techniques based on chemical and biological principles have been continuously developed and validated. Some reviews regarding the use of instrumental methods in combination with chemometrics for the quality control and authentication analysis of edible fats and oils existed, including near infrared spectroscopy,[7] Fourier transform infrared (FTIR) spectroscopy,[8,9] ^{1}H-NMR spectroscopy,[10] chromatographic-based techniques,[11] electronic noses and electronic tongues.[12] In this review, Raman spectroscopy combined with chemometrics were highlighted for analysis of some parameters related to the quality control and authenticity of edible fats and oils. The objective of this review was to highlight the use of Raman spectroscopy combined with chemometrics for the quality control and authentication analysis of edible fats and oils either in raw materials or in food products.

Methods

While preparing this narrative review, some articles appearing in several databases including Scopus, PubMed, Web of Science, and Google Scholar were retrieved. The literature search was carried using keywords "Raman" or "Fourier transform Raman spectroscopy", "vibrational spectroscopy", "quality control or oxidation products or acid value or iodine value or peroxide value", "authentication analysis or adulteration", "chemometrics" or "multivariate data analysis", and "fats and oils". To select the suitable papers for writing this review, the abstracts of the papers were selected. The inclusion criteria of selected papers were (1) studies regarding analysis and authentication of fats and oils using Raman spectroscopy between 2005–2021; (2) studies on analysis and authentication of fats in food products and fats-based products using Raman spectroscopy between 2005–2021; (3) studies on chemometrics for authentication of fats and oils using Raman spectroscopy; (4) all papers written in English language.

Raman spectroscopy

Raman spectroscopy (RS), based on Raman scattering effects, is one of the vibrational spectroscopic methods widely applied for food composition analysis, including edible fats and oils.[13] As other spectroscopic techniques, RS related to the interaction between electromagnetic radiations (laser beam) with the analyzed samples.[14] Owing to its non-destructive, high sensitivity, and on-line detection, RS is now increasingly being applied in various fields including in food safety evaluation, quality control and monitoring the adulteration practice of edible fats and oils.[15,16] Moreover, compared to other analytical techniques, Raman spectroscopy has benefits for analysis of fats and oils such as simple in sample preparation because the sample can be placed directly in to the sample pan. RS also supports green analytical chemistry because it does not require extensive solvents and reagents with short analysis time providing high efficiency.[17] RS in combination with chemometrics has main limitation in which the calibration model for one type of sample cannot be applied for different types of samples, so that the samples with different matrix required new calibration model.[18] For analysis of edible fats and oils, RS offers higher reproducibility and sensitivity because Raman spectra provide vibrational bands of many important oil constituents. For example, RS had useful fingerprint region at wavenumbers of 945–1600 cm^{-1} for determination of free fatty acids (FFA) which is important indicator for edible fats and oils quality.[19]

As other spectroscopic techniques, RS involved the interaction between analyte(s) and electromagnetic radiation at infrared region. The incident laser beam, used as energy source, is absorbed by analyzed samples. After that, the beam is released by emitting a photon having the same frequency with incident beam providing elastic scattering known as "Rayleigh scattering" or having the different frequency to give inelastic scattering known as "Raman scattering". The energy sources (laser) from the light particle with a known frequency and polarization is also transferred to analyte(s) and the remaining power is emitted to give inelastic light scattering known as *Raman effect*, as shown in Fig. 1. During this interaction, an inelastic collision between the incident photon from monochromatic laser beam and analyte(s) occurs which resulted in the changes in the vibrational or rotational energies, and the scattered radiation in all directions is shifted toward a different frequency (or different wavenumbers) known as *Raman shift*.[20,21] Raman spectra, typically a correlation between the intensity of the scattered light (*y-axis*) and the Raman shift (*x-axis*).

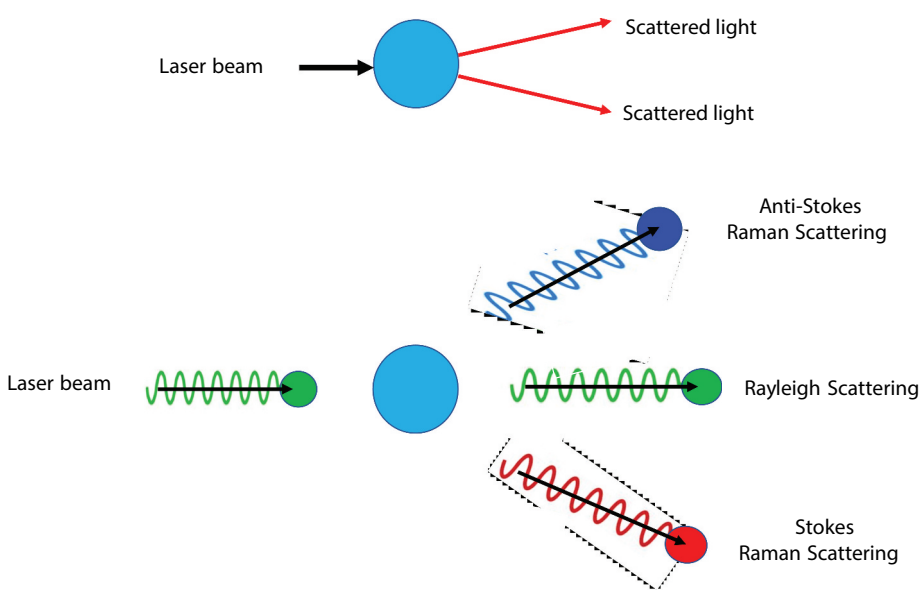

Figure 1. Simple diagram of Rayleigh scattering and Raman scattering (Stokes and anti-Stokes). Adapted from Ozaki and Šašić.[20]

Figure 2 exhibits an energy level diagram for illustrating Stokes (SRS) and anti-Stokes (ASRS) Raman scattering. SRS occurs from the interaction between the photon coming from laser beam and molecule in the ground state, while ASRS arises from the interaction between a photon and molecule in the excited state. Because the molecules are typically in the ground vibrational state, SRS occurs far more easily than ASRS, and this is why Stokes Raman scattering is usually measured.[19] According to the Boltzmann distribution, ASRS has lower intensity than SRS, and both ARSS and SRS are much weaker than Rayleigh scattering.[20]

Spectral bands in Raman spectra represent vibrational characteristics for chemical bonds and functional groups related to molecules in the analyzed samples. Raman spectra are unique for each individual substance and can be used as fingerprinting spectra. Therefore, it is possible to make the identification of molecule and to study its structure. RS is also widely used for the quantitative determination, because the intensity (peak width, half-width, and half-height and de-biasing ratio) of specific bands is linearly proportional to the analyte(s) concentration.[23] The relationship between peak intensity and analyte concentration is generally used for calibration procedure. An example of Raman spectra of olive oil was depicted in Fig. 3. Each peak corresponded to functional groups present in evaluated samples, as compiled in Table 1.

Combined with chemometrics techniques, several RS methods are widely applied in quality assessment and authentication of edible fats and oils.[14,27–31] Chemometrics is the use of statistical and mathematical to extract Raman spectra to provide analytical information. The chemometrics techniques commonly used for RS are (1) pre-processing spectra such as mean centering, spectra derivatization, standard normal variate, and baseline corrections, (2) unsupervised pattern recognition such as cluster analysis and principal component analysis known as exploratory data analysis, (3) supervised pattern recognition such as discriminant analysis, and multivariate calibrations like partial least square (PLS) and principle component regression (PCR).[5,13,32,33]

Determination the quality of fats and oils quality using Raman spectroscopy

Edible fats and oils were characterized by several parameters which are specific to them such as saponification value and iodine value. The quality of edible fats and oils can be evaluated from the oxidative stabilities. During processing and storage, the oxidative rancidity and oxidation reactions of fats and oils may occur resulting in the primary oxidation products of peroxides, which can be

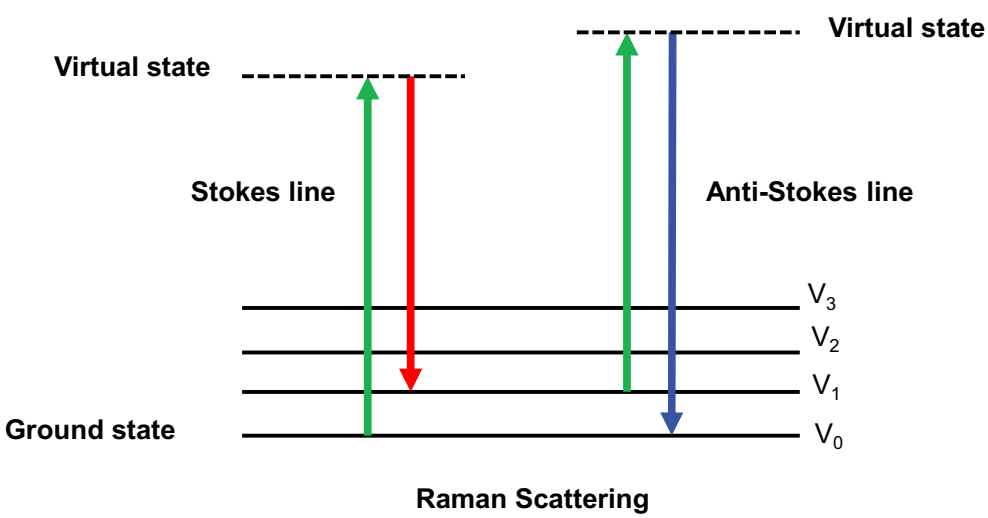

Figure 2. Energy level diagram for Raman scattering which illustrates Stokes Raman scattering and anti-Stokes Raman scattering. Adapted from Musa et al.[22]

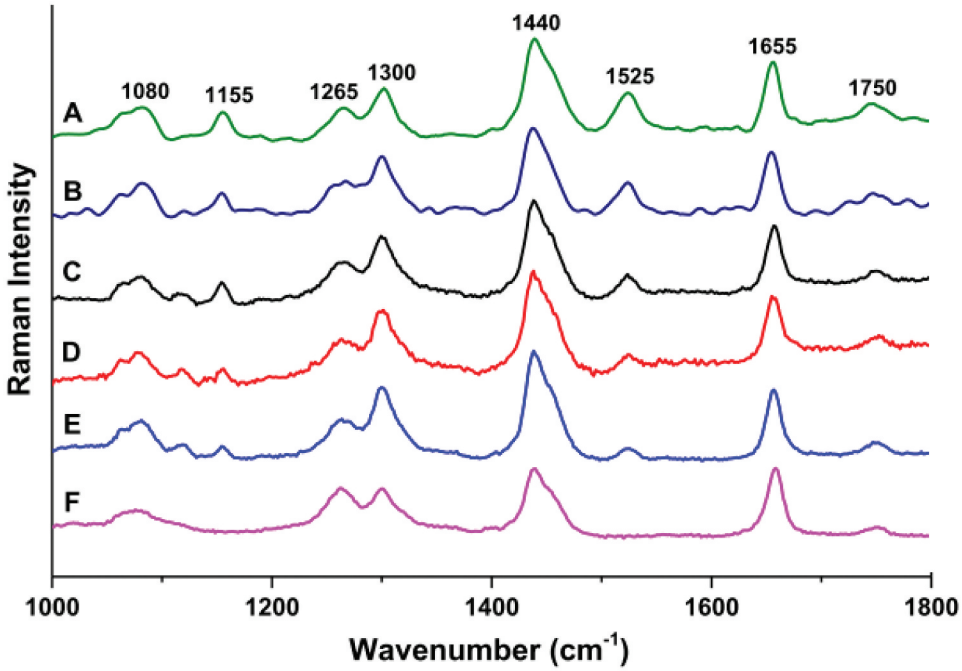

Figure 3. Raman spectra of olive oil samples assigned with A, B, C, D, E, and F from different origins. Taken from Qiu et al.[24] with license from Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Table 1. The functional groups along with vibrational modes of Raman scattering of edible oil (olive oil).[25,26].

Wavenumbers (cm^{-1})	Functional groups	Mode of vibration
1080	C-C (CH_2)n	Stretching vibration
1155	C-O	Stretching vibration
1265	=C-H (cis (R-HC = CH-R))	Bending vibration
1300	C-H (-CH_2)	Bending vibration
1440	C-H (-CH_2)	Scissoring vibration
1525	Difficult to assign	
1655	C = C (cis (R-HC = CH-R))	Stretching vibration
1750	C = O (R-C = OOR)	Stretching vibration

evaluated by peroxide value and conjugated dienes (K_{232}), and secondary oxidation products evaluated by conjugated triene (K_{270}) and thiobarbituric reactive substances (TBARS) such as malonaldehyde.[9] The higher PV, K_{232}, K_{270} and TBARS indicated the lower quality of edible fats and oils.[34] Oils with high PV, K_{232} and K_{270} indicate the presence of peroxides, diene- and triene-conjugated systems.[35] Table 2 compiled the use of Raman spectroscopy in combination with chemometrics for the determination of some parameters related to the quality of edible fats and oils such as free fatty acids, acid (AV), saponification (SV), peroxide (PV), and iodine (IV) values.

The formation of lipid peroxidation in fats and oils could have harmful effects on human health. Lipid peroxidation generates oxidation products which potentially have some risks for human health. There are two types of lipid peroxidation products, namely primary lipid peroxidation products and secondary lipid peroxidation products. The main primary lipid peroxidation product is lipid hydroperoxides. Meanwhile, the main secondary lipid peroxidation product is malondialdehyde (MDA), a kind of aldehyde compound. In addition, the adulteration practice of high-quality edible oils and fats with lower ones significantly affect its quality. High amount of lipid peroxidation products can be

Table 2. The application of Raman spectroscopy for the determination of some parameters related to the quality of edible fats and oils.

Edible fats and oils	Quality parameters	FTIR spectra and Chemometrics	Results	Ref.
Olive oils and oxidized olive oils	Peroxide values	Raman spectra at 200 to 2700 cm^{-1}	The correlation between actual values of PV and Raman-predicted values revealed R^2 of 0.91 with RMSECV of 2.36 and RMSEP of 2.57. RPD was relatively low (4.11%).	[36]
Olive oil	Peroxide values	PLS using the first derivative spectra at 1600–1800 cm^{-1}	The relationship between actual and predicted values of IV resulted R^2 of 0.986 and 0.971 in calibration and validation models. RMSEC and RMSEP were 0.68 and 0.72 meq O_2/kg respectively.	[37]
Olive oils and oxidized olive oils	Conjugated dienes (K232)	Raman spectra at 200 to 2700 cm^{-1}	The correlation between actual values K232 and predicted values gave R^2, RMSEC, RMSEP and RPD of 0.88, 0.36, 0,37 and 2.00%, respectively.	[36]
Olive oils and oxidized olive oils	Conjugated trienes (K232)	Raman spectra at 200 to 2700 cm^{-1}	The prediction K270 resulted R^2, RMSEC, RMSEP and RPD of 0.90, 0.05, 0.08 and 2.50, respectively.	[36]
Extra virgin olive oil	Free fatty acids	Normal Raman spectra at 945–1600 cm^{-1}	The correlation between actual values of FFA as determined using AOCS reference method and predicted values yielded R^2 of 0.963167, RMSEC of 0.01193 and RMSEP of 0.034114.	[38]
Olive oil	Free fatty acids	The ratio of peak intensity at 1525 cm^{-1} and 1655 cm^{-1}	Raman spectra could predict FFAs in olive oils with good linearity between actual and predicted values.	[26]
Vegetable oils	Iodine values	Peak ratio of (1600–1700 cm^{-1}/ peak at 1400–1500 cm^{-1}).	Iodine value can be predicted by equation of $y = 51142x10^{-3}x - 39553x10^{-2}$, with y = intensity ratio, x = iodine value having R^2 of 0.995.	[39]
Olive oil	Acidity, calculated as % oleic acid	PLS using the first derivative spectra at 1600–1800 cm^{-1}	The relationship between actual and predicted values of free acidity (%oleic acid) resulted good accuracy and precision performances with R^2 of 0.994 and 0.988 in calibration and validation models. RMSEC and RMSEP were 0.01 and 0.02%.	[37]
Mono-varietal olive oils	Determination of Fatty acids	Prediction of fatty acids using Raman spectra at 750–3050 cm^{-1} using PLSR.	The levels of fatty acids determined with Raman spectroscopy are comparable with those using reference method of GC-FID. The statistical results of PLSR revealed R^2 of 0.80–0.92, DRMSEC of < 0.08% and DRMSECV < 0.16%.	[40]
Edible oils and others	Determination of iodine value (IV)	Peak intensities of Raman spectra at 1655 cm^{-1} and 2852 cm^{-1} (I_{1655}/I_{2852})	The relationships between intensities ratio I_{1655}/I_{2852} (y) and actual IV resulted the equation of $y = 0.0009299 \times IV - 0.023$ The R^2 value was 0.976.	[25]
Edible oil	Peroxide values	PLS using Raman spectra at 1265 and 1436 cm^{-1}	The relative Raman intensity ($I_{1265/1436}$) has a good correlation with peroxide value.	[41]
Extra virgin olive oil	Free fatty acid	PLSR using Raman spectra at 200–185 cm^{-1}	Free fatty acids can be predicted using Raman model with correlation coefficient of 0.94 for validation and 0.93 for validation with standard error cross validation of 0.55 and standard error prediction of 0.52.	[42]
Extra virgin olive oil	Peroxide values	PLSR using Raman spectra at 200–185 cm^{-1}	Raman spectra using PLSR gave good performance for prediction of peroxide value with coefficient correlation for validation dan calibration of 0.92 and 0.92 respectively with standard error cross validation of 1.31 and standard error prediction of 1.11.	[42]

R^2 = coefficient of determination; DRMSEC = dimensionless root mean square error of calibration; DRMSECV = dimensionless root mean square error cross validation; RMSEC = root mean square error of calibration; RMSEP = root mean square error of prediction; RMSECV = root mean square error of cross validation; RPD = relative percentage difference.

correlated with pathological effects such pro-inflammatory activity and inflammation-related chronic diseases of organs, cytotoxicity, mutagenicity, aging process, genotoxicity, atherosclerosis, heart disease, neurodegenerative, metabolic and cancer diseases.[43–48]

RS can be used for evaluation of PV as primary oxidation products by selecting certain peaks in Raman spectra which corresponded to actual value of PV as determined by titrimetric method. When the calibration model of PV using variable of absorbance values of Raman spectra is valid, the developed model could be used to predict PV in the unknown edible fats and oils. However,

RS cannot be used for detail differentiation between harmful and non-harmful compounds, because some functional groups in harmful compounds are similar to non-harmful compounds.[13]

The study on the application of surface enhanced Raman spectroscopy (SERS) in the oxidation of edible oils was performed by Li et al.[49] The temperature used for canola oil oxidation was set 55°C for 5, 7, and 30 days. There are significant changes in SERS spectra in which the significant decrease was found at day 7 in major lipid, especially at peaks 2950–2850 cm^{-1}, 1665 cm^{-1} and 1450 cm^{-1}. This decrease in peak intensities at selected wavenumbers was caused by the reactant losses. The study confirmed that SERS provided more sensitive results to lipid oxidation in edible oils compared to the conventional Raman method.

RS along with gas chromatography-mass spectrometry (GC-MS) and chemometrics has also been used to study the quality of *Pistacia vera* (Greek variety "Aegina") oil obtained from two consecutive harvest periods in 2017 and 2018. GCMS in combination with OPLS-DA (orthogonal projections to latent structures-discriminant analysis) can be used to differentiate samples harvested in 2017 and in 2018. The variables used for differentiation were fatty acid compositions. Determination using variable important projections (VIP) value found five variables important for differentiation, namely palmitic acid, stearic acid, linoleic acid, behenic acid, and palmitoleic acid. Meanwhile, RS in combination with chemometrics was successful for the differentiation between Pistacia oil harvested in 2017 and 2018. The whole Raman spectra were used as variables to build OPLS-DA model. Result showed that 22 samples that could not be clearly classified. Only 59.1% of original and cross-validated samples were correctly classified. The low predictive capacity was demonstrated in its low R^2 value (0.644) and Q^2 value (0.270). From this study, GCMS combined with chemometrics showed better result for classification oil *Pistacia vera* oil harvested in two consecutive times.[50] However, analysis using GCMS requires longer time analysis and more preparation steps including derivatization procedure which involved some reagents and solvents. To obtain better classification model, the wavenumber region of Raman spectra used for chemometrics modelling should be optimized. Moreover, the processing technique such as spectra normalization and derivatization will also provide better classification model. Therefore, more in-depth study on the data processing of RS is highly needed to obtain comparable classification result obtained from GCMS measurement.

Determination of free fatty acids

During processing, TAG could be hydrolyzed to get free fatty acids (FFAs) and glycerol. FFA can reduce the quality of fats and oils, therefore, FFAs are considered as one of the main quality parameters of edible fats and oils. The official method for determination of FFAs is Ca 5a-40 method set by the American Oil Chemists' Society (AOCS) using titrimetric method which is time consuming and involving chemical reagents, therefore RS was proposed as an alternative method for prediction of FFAs.[51] FFAs in extra virgin olive oil (EVOO) has been determined using Raman spectra and multivariate calibration of PLS. Three regions namely 700–3050 cm^{-1}, the combined region of 2800–3,050 and 1650 cm^{-1}, and region of 945–1600 cm^{-1} were optimized for providing the best calibration model. Finally, based on the capability of Raman regions to give highest R^2 and lowest errors (RMSEC and RMSEP), FFA's was analyzed at 945–1600 cm^{-1}. The equation correlating the actual values and predicted values based on PLS model can be expressed as:

$FFAs_{Predicted} = 0.96 \times FFA_{actual} + 0.0031$ (with R^2 of 0.963167, RMSEC of 0.01193 and RMSEP of 0.034114). $FFAs_{Predicted}$ is FFA predicted using Raman spectra at 945–1600 cm^{-1} and FFA_{actual} is FFA obtained using AOCS method. High R^2 values and low RMSEC and RMSEP indicated that Raman spectra and PLS offered accurate and precise method for prediction FFAs in EVOO (El-Abassy et al. 2009).[38]

Analysis of iodine value

The levels of unsaturation degree in edible fats and oils were evaluated with specific iodine value (IV), therefore, IV can be used as characteristic parameter for characterization of certain edible fats and oils. Raman spectra of plant oils including sunflower, avocado oil, etc., were correlated for IV using specific bands.[25] The ratio of peak intensities of Raman spectra at 1655 cm^{-1} corresponding to ν(C = C) and 2852 cm^{-1} due to ν(CH_2) (I_{1655}/I_{2852}) was used for constructing the relationship between Raman spectra and iodine value. Table 3 revealed the correlation between I_{1655}/I_{2852} and iodine value of some oils having the coefficient of determination (r^2-value) of 0.976. There is an inverse correlation between the actual value of IV and I_{1655}/I_{2852} as indicated by negative value of correlation coefficient (R of −0.987) as shown in Fig. 4.

Determination of peroxide values

Low-resolution RS at 200 to 2700 cm^{-1} in combined PLSR has been successfully applied for prediction PV, K_{232}, and K_{270} in a set of 126 oxidized virgin olive oil samples. The correlation between actual values of PV as determined by reference method (titrimetric) and Raman-predicted values revealed R^2 of 0.91 with RMSECV of 2.36 and RMSEP of 2.57. Relative percentage difference (RPD) was 4.11%. The low value of RPD indicated that the model could be useful for initial screening purposes of PV values. In addition, the low errors in cross-validation (RMSECV) and in external validation set (RMSEP) indicated that the developed model is consistent and precise with good prediction models for a validation sample set. Meanwhile, the prediction of K_{232} and K_{270} gave R^2, RMSEC, RMSEP and RPD of 0.88, 0.36, 0.37, and 2.00% (K_{232}) and 0.90, 0.05, 0.08 and 2.50 (K_{270}), respectively. These results demonstrated that RS could be rapid and reliable technique for evaluating the oxidation status of olive oils because the oxidation products can be precisely and accurately determined in a non-destructive way.[36]

Raman spectra in combination with multivariate calibrations of PLS and PCR using normal and derivative spectra (first and second) was used for determination of PV in olive oils. Based on highest R^2 and lowest errors, the first derivative spectra at 1600–1800 cm^{-1} were used for prediction of IV. Using PLS with four latent variables, the relationship between actual (x-axis) and predicted values of IV (y-axis) yielded the equation of $y = 1.01x - 0.02$ (in calibration model, R^2 value of 0.986) and $y = 1.04x + 0.01$ (R^2 of 0.971 in validation model). The values of RMSEC and RMSEP were 0.68 and 0.72 meq O_2/kg respectively. This result indicated that PV in olive oil could be accurately and precisely predicted using Raman spectra offering direct and rapid analysis.[37]

Table 3. The Raman intensity due to vibration of CH_2 (~ 2852 cm^{-1}) and C = C (~ 1655 cm^{-1}) along with ratio value (I_{1655}/I_{2852}) and iodine value (IV) of studied fats and oils.

	Raman intensity due to vibration of CH_2		Raman intensity due to vibration of C = C			
Oil	Frequency	Abs	Frequency	Abs	Ratio (I_{1655}/I_{2852})	IV (g/100 g fat)
Hazel	2853	28.67	1655	1.79	16.02	84.6
Sunflower	2852	20.81	1655	1.32	15.77	84.6
Avocado	2853	18.51	1656	1.23	15.05	89.47
Rice	2853	27.33	1656	1.91	14.31	105.96
Rapeseed	2853	20.66	1655	1.58	13.08	113.04
Roasted sesame	2854	23.99	1655	1.62	14.81	120.76
Pumpkin seed	2852	21.35	1656	2.04	10.47	122.2
Corn	2854	17.98	1657	1.81	9.93	129.8
Walnut	2854	21.00	1655	2.41	8.71	160.53
Safflower	2853	18.75	1657	2.19	8.56	161.34
Hemp	2852	18.14	1657	2.35	7.72	173.43
Low-linolenic flax	2852	12.46	1657	2.00	6.23	188.7
High-linolenic flax	2852	14.41	1655	2.71	5.32	212.1

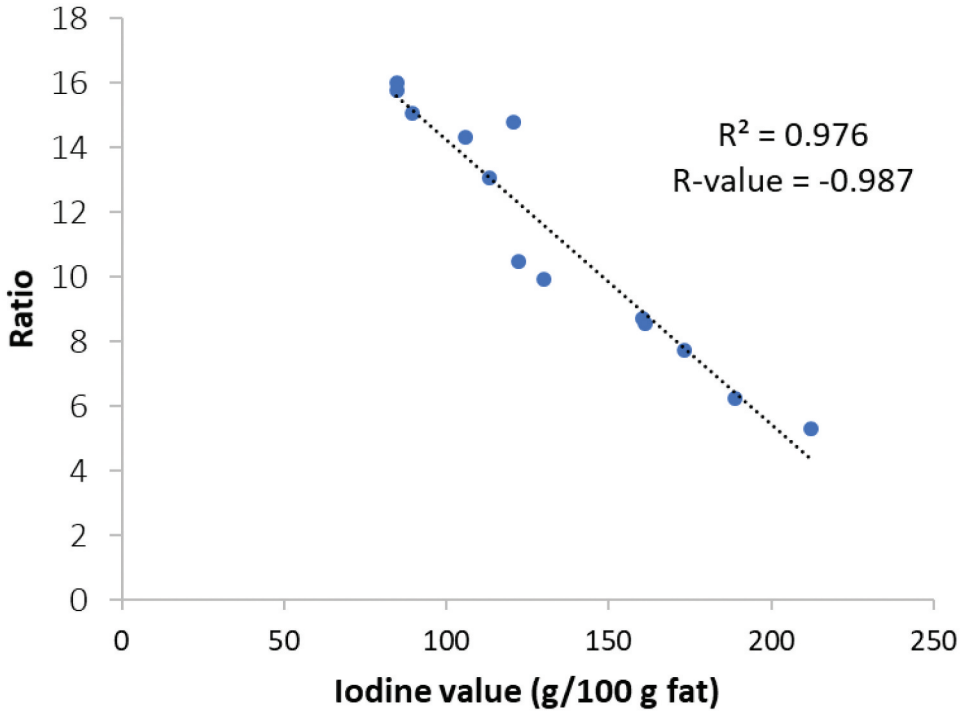

Figure 4. The inverse correlation between the actual value of iodine value (IV) and I_{1655}/I_{2852} of studied fats and oils with negative value of correlation coefficient (R of −0.987). See Table 2 for information of identification of fats and oils.

RS combined with multivariate analysis has also been used for edible oils authentication to determine the peroxide value (PV) which was obtained from iodometric titration according to AOAC method. The oil samples used for calibration model were rapeseed oil, soybean oil, sunflower oil, and peanut oil. Spectra acquisition was performed at the range of 1900–670 cm^{-1} using resolution of 16. Data were preprocessed using standard normal variate (SNV), smoothing and derivatization using Savitzky Golay method. PLS was used to build calibration model using Raman spectra to predict PV values in edible oil samples. PLS using successive projection algorithm (SPA) could be used for prediction of peroxide value in edible oils with R^2 of 0.858 and 0.757 for calibration and validation, respectively. The model had low error indicated by its RMSEC (0.065) and RMSEP (0.148) values.[52]

Application of Raman spectra for authentication of edible fats and oils

The adulteration practice of butter having high price in fats and oils industry with margarine has been analyzed using Raman spectra combined with chemometrics of PCA for classification and multivariate calibrations of PCR, PLS and artificial neural networks (ANNs) for prediction of adulteration levels. Table 4 compiled the use of RS combined with chemometrics for authentication of edible fats and oils. PCA using variables of absorbance values of the first derivative and mean centering Raman spectra at 200–2000 cm^{-1} was capable of classifying butters, margarines, and butter adulterated with 36–41% margarines, based on PC1 and PC2 accounting of 98.3% variances. PCR, PLS and ANN were compared for prediction of butter levels adulterated with margarine using the same conditions used in PCA. Based on R^2 for the relationship between actual values and Raman spectra-predicted values, PLSR offered better prediction performance than PCR and ANN. The values of R^2 using PLS obtained were of 0.992 and 0.987 in calibration and validation models, while RMSEC, RMSEP and RMSECV values for evaluation of precision method were of 2.98%, 4.94% and 8.83% respectively.[53]

Table 4. The use of Raman spectroscopy in combination with chemometrics for authentication of edible fats and oils.

Fats and Oils adulterated	The adulterants	Raman spectra	Chemometrics	Results	Ref.
Butter	Margarine	The first derivative and mean centering Raman spectra at 200–2000 cm^{-1}	PCA for classification as well as PCR, PLS and ANN for prediction the adulteration levels	PCA was capable of classifying butters, margarines, and butter adulterated with 36–41% margarines, based on PC1 and PC2 accounting of 98.3% variances. PLSR could predict the levels of butter with R^2 values of 0.992 and 0.987 in calibration and validation models, RMSEC of 2.98%, RMSEP of 4.94% and RMSECV of 8.83%.	[53]
Olive oil	Vegetable oils	Raman spectra at 1680–1800 cm^{-1}	kNN, PLS-DA, OCPLS, SVM and SIMCA for classification, PLSR for quantification	SIMCA offered the better models for classification of olive oils and others. The levels of olive oil could be predicted using PLSR with R^2 of 0.93 and RMSEC of 0.342	[54]
Olive oil	Olive pomace oil	Normal Raman spectra 400–4000 cm^{-1}	PLS regression for quantification of olive pomace oil	The close relationship between actual values and Raman predicted values resulted R^2 value of 0.995 and SECV = 2.23% for PLS calibration model, and R^2 value of 0.997 and SEP = 1.72% for the validation model.	[55]
Olive oil	Soybean oil, rapeseed oil, sunflower seed oil, or corn oil	Normal Raman spectra	PCA for classification	PCA using intensity ratio of the cis (=C-H) and cis (C = C) bonds normalized by the band at 1441 cm^{-1} (CH2) was capable of discriminating olive oils and others with good separation.	[56]
Virgin olive oil	Soybean, corn, and raw olive residue (olive pomace)	Normal spectra at 100–3250 cm^{-1}	PCR for prediction	The levels of virgin olive oil could be predicted by PCR using absorbance values at wavenumbers (3006, 2873, 1657, 1270 cm^{-1}) to reach an adjusted R^2 of 0.998 and R^2 of 0.999.	[57]
Olive oil	Hazelnut oil	Raman spectra at 1000–3000 cm^{-1}	PCA for classification and PLS for quantification	PCA could separate hazelnut oil, olive oil from different regions, and olive oil mixed with hazelnut oil using 2PCs accounting of 72.29% of the total explained variance. PLS could predict the levels of hazelnut oil with equation of: predicted value = 0.974 x actual values + 0.756 (R^2 of 0.979 and 0.94 in calibration and validation, and RMSEP of 4.16).	[58]
Cold pressed rapeseed oil (CPRO)	Refined sunflower oil (RFSO)	Raman spectra at 800.314–1800.22 cm^{-1}	SIMCA, PLSDA, LDA-KNN and LDA-SVM for classification and PLS-R for quantification	Chemometrics of SIMCA, PLS-DA, LDA-KNN, and LDA-SVM could classify CPRO and adulterated CPRO with RSFO with high sensitivity (93%). Chemometrics of PLS-R could be used to predict the concentration of RSFO in CPRO with minimum detection level value of 15%.	[59]
Macadamia oil (MaO)	Corn (CO) and sunflower oils (SFO)	Raman spectra at 1600–1700 cm^{-1} for MaO adulterated with CO and 1200–1400 cm^{-1} for MaO adulterated with SFO	PLS regression for quantification	The plots for correlation between actual and predicted values of CO and SFO in MaO yielded R^2 values of > 0.99.	[60]
Animal fats (chicken fat, beef tallow, duck oil)	lard	Raman spectra at 700–1800 cm^{-1}	PCA for differentiation	PCA perfectly differentiated chicken fat, beef tallow, duck oil, and lard based on the oil gauge (OG) values.	[61]

(*Continued*)

Table 4. (Continued).

Fats and Oils adulterated	The adulterants	Raman spectra	Chemometrics	Results	Ref.
Dairy cream	Sunflower oil (SFO), coconut oil (CO), palm oil (PO)	Raman spectra at 500–3100 cm^{-1}	PCA and PCA-DA for classification	Chemometrics of PCA could differentiate pure and adulterated dairy cream with SFO, CO, and PO. Chemometrics of PCA-DA successfully classified pure sample of dairy cream and adulterated dairy cream with SFO, CO, and PO with model sensitivity of 100%.	[62]
Butter	Margarine	Raman spectra at 800–1800 cm^{-1}	PCA for classification and PLS for quantification	PCA revealed clear differentiation between pure butter, pure margarine, and adulterated butter with margarine. PLS using three latent variables (LVs) resulted very good model performance for quantification of margarine in butter. The obtained R^2 value was 0.991 and 0.994 for calibration and validation model, respectively. The RMSEP was 2.754 while the RMSECV was 3.199.	[63]
Recycled frying oils	Pork	Raman spectra at 800–1800 cm^{-1}	PCA for classification	PCA using PC1 and PC2 could distinguish recycled frying oils, pork, and adulterated recycled frying oils with pork using several levels of adulterant concentrations.	[64]

ANN = artificial neural network; kNN = k-nearest neighbors; PCA = principal component analysis; LDA = linear discriminant analysis; PCR = principal component regression; PLS-DA = partial least squared-discriminant analysis; OCPLS = one-class partial least squares, SVM-C = support vector machine classification, SIMCA = soft independent modelling of class analogy.

Raman spectra in combination with PCA and classical least square (CLS) has been successfully used for classification of four animal fats namely lard, beef tallow, duck oil, chicken fat and for quantification of lard in binary mixtures with other animal fats and oils. PCA using variable of 6 intensities at 968 cm^{-1} corresponding to functional group of -C = C bending, 1268 cm^{-1} (=CH bending), 1300 cm^{-1} and 1442 cm^{-1} (C-H bending), 1655 cm^{-1} (C = C stretching) and 1744 cm^{-1} (RC = OOR, C = O stretching) was capable of animal fats. In addition, CLS using intensities calculated from ratio of absorbance values at 1655, 1968 and 1442 cm^{-1} $(I_{1655} \times I_{968})/(I_{1442} \times I_{1442})$ could predict the levels of lard with good correlation coefficients of 0.96674 (for lard in binary mixture with beef tallow) and 0.97148 (for lard in duck oil samples) with excellent linearity for lard contents ranging from 0 to 100% (v/v).[61]

FT-Raman spectra combined with linear discriminant analysis (LDA) and canonical variate analysis (CVA) were employed for the discrimination and classification of edible fats and oils namely butter, lard, cod liver oil, extra virgin olive oil, corn oil, peanut oil, canola oil, soybean oil, safflower oil and coconut oil using variable of absorbance values of 4000–3700 cm^{-1} and 1600–1700 cm^{-1} with accuracy rate of 94%.[65] The correlation between Raman spectra at peak ratios of 1654/1748 and 1654/1445 with lipid characteristics namely degree of unsaturation of animal fats existed with coefficients of determination of > 0.94. This phenomenon could be used for distinguishing animal fats which can be exploited for authentication of edible fats and oils. Furthermore, PLS-DA using variable of absorbance values at 1850–1200 cm^{-1} could discriminate animal fats with sensitivity and specificity of > 0.85.[66]

One of authentication issues is related to geographical origins and cultivar types. Raman spectra combined with chemometrics of PCA and LDA was used for clustering and discrimination of monovarietal extra virgin olive oils (EVOOs) as a function of the cultivar (Arbequina, Leccino, Maurino and Moraiolo) at different four stages of harvesting. Using the first nine PCs, about 90% of the total variance could be explained, and the score plot of PC1 and PC2 revealed good clustering of the samples according to olive oil's cultivar at each harvesting steps. Based on loading plots, PC1 (contributed to 45.4% of the total variance) is mainly described by peaks at wavenumbers of 1004, 1156 and 1523 cm^{-1}, which can be related to the presence of carotenoid in olive oil.[67] Peaks at wavenumbers 1301, 1656, 1440 and 1081 cm^{-1} contributed to PC2 which can be attributed from the contents of fatty acids. Discrimination analysis of MVOO using three discriminant canonical variables (CVs) accounting for 100.0% of the variability could classify correctly with accuracy levels of 83.3–94.4% of EVOO samples.[40] The classification chemometrics of k-NN, PLS-DA, OCPLS, SVM classification, and SIMCA has been compared for classification of olive oils and other vegetable oils based on Raman spectra. These chemometrics using Raman spectra at 1680–1800 cm^{-1} could classify olive oils and others either in training sets or in validation sets, in which SIMCA offered the better models as indicated by higher sensibility levels. The prediction of olive oil levels in the other mixture with vegetable oils using PLSR at 1680–1800 cm^{-1} revealed good correlation with R^2 of 0.93 and RMSEC of 0.342.[54]

The adulteration of virgin olive oil with other vegetable oils has also been investigated using Raman spectroscopy combined with chemometrics of least square support vector machines (LS-SVM) improved with Bayesian framework. Raman spectra were recorded at the wavenumber range of 1800–800 cm^{-1}. Bayesian framework is aimed to obtain the best parameters for creating the model of LS-SVM and to obtain better adulteration prediction model compared to common PLS model. Result showed that LS-SVM employing Bayesian framework demonstrate high R^2 value (0.9976) and RMSEP value (0.0509). The model possessed better accuracy and computational efficiency compared to the PLS model and it is easy to operate and more lipid sensitive.[68]

Classification of olive oils as a function of harvest year, olive variety, geographical origin and Andalusian Protected Designations of Origin (PDO) for qualitative information has been done using Raman spectra and LDA.[69] Using whole Raman spectra at 100–3100 cm^{-1} which are previously subjected to Savitzky-Golay smoothing function for reducing spectral noise, LDA allowed a correct classification of olive samples based on harvest year, olive variety, geographical origin and PDO with accuracy levels of 94.3%, 84.0%, 89.0% and 86.6%, respectively. The combination of Raman

spectroscopy with PCA has been used for the discrimination of foreign fats and oils in the samples of milk cream and yogurt. In this study, the binary mixtures of cream and oils (corn and sunflower oil), and vegetable fat blends were prepared. The lipid fractions were extracted and subjected to RS. PCA using first derivative spectra at 800–1400 cm^{-1} could classify foreign oils namely corn oil, Sunflower oil, margarine, cream (milk fat) samples, vegetable fat blends and yogurt samples. Based on the loading plots, it can be informed that Raman spectral peaks at six regions (200–207, 812–829, 840–850, 950–1050, 1100–1120, and 1250–1300 cm^{-1}) explained the most contributing variables for classification of the evaluated samples.[70]

Classification of some vegetable oils namely palm oil, soybean, sunflower, corn, castor, and rapeseed oils having different IVs has been successfully performed using PCA and Raman spectra at 700–3000 cm^{-1}. PCA using Raman spectra offered better classification of these oils than infrared spectra. The plot of PC-1 and PC-2 against iodine values revealed linear trend with statistical $R^2 = 0.92$ (PC-1) or $R^2 = 0.82$ (PC-2) from FT- Raman spectra, and $R^2 = 0.80$ (PC-1) or $R^2 = 0.02$ (PC-2) from mid-IR spectra. This can be explained by high sensitivity of Raman spectra for absorption of C = C, which is related to iodine value. Besides, FT-Raman spectra also revealed the good signal-to-noise ratio allowing a good classification of studied oils.[39]

Due to its high price, milk fat is often adulterated with other lower price of fats by unethical players for economic reasons. RS has been studied for the authentication of milk fat in ultra-filtered white cheese replaced either partially or fully using foreign components such as corn oil, palm oil, and margarine. Fat was extracted using Folch method to obtain pure lipid from white cheese samples. Raman measurement was performed using a laser source of 785 nm and spectra acquisition was carried out at wavenumber of 200–2000 cm^{-1} at a resolution of 20 cm^{-1}. PLS-DA was used for samples classification while PLS was performed to quantify the level of adulterants in white cheese samples. Result showed that PLS-DA successfully classified between pure samples of white cheese, corn oil, palm oil, and margarine and adulterated samples of white cheese with good predictivity. In addition, PLS was successfully used for quantification of adulterants in white cheese samples. PLS using Raman spectra resulted good calibration and prediction models for detection and quantification of corn oil, palm oil, and margarine in white cheese samples with R^2 of calibration and prediction more than 0.9.[71]

The use of RS namely FT-Raman and Vis-Raman has been investigated for differentiation of animal fats such as lard, chicken, beef, and mutton. FT-Raman was performed using a laser source of 1064 nm and the animal fat samples were scanned at 400–3600 cm^{-1} at a resolution of 4 cm^{-1} and number of scans 128. On the other hand, Vis-Raman was carried out using custom built Raman equipped with a 532 nm laser excitation. Chemometrics of PCA, PLS-DA and SVM-DA was used for samples classification either in FT-Raman and Vis-Raman spectra of animal fat samples. PCA perfectly classified between lard, chicken, beef and mutton. Each fat appeared at different locations in the PCA score plot. PCA loading score provided information that the bands of 2800–2900 cm^{-1}, 1745 cm^{-1}, 1366 cm^{-1}, 1127 cm^{-1} and 1065 cm^{-1} correspond to the peak of ruminant fats, whereas the peak of 3007 cm^{-1}, 1654 cm^{-1}, 1438 cm^{-1}, 1258 cm^{-1}, and 967 cm^{-1} correspond to the non-ruminant fat samples. PLS-DA and SVM-DA were further used for classification of animal fat samples obtained using FT-Raman and Vis Raman. Moreover, Vis-Raman spectroscopy demonstrated better classification than FT-Raman obtained from PLS-DA and SVM-DA results.[72]

The employment of RS and chemometrics has been studied for the detection of butter adulteration with lard. The adulterated samples of butter with lard were prepared in binary mixtures with lard concentration range from 0% to 100%. Raman spectra were measured at wavenumber range of 200–2000 cm^{-1} using diode laser at 1064 nm. Chemometrics of Hierarchical Cluster Analysis (HCA) created using first derivative Raman spectra at 200–2000 cm^{-1} could differentiate pure butter, pure lard, and adulterated butter with lard appeared in separate clusters. In addition, chemometrics of PCA created using first derivative Raman spectra using the same wavenumber range in HCA perfectly differentiate between pure butter, pure lard, and adulterated butter with lard. Other chemometrics technique, namely PLS was also applied to create model for quantification of lard in butter. PLS was

created using wavenumber region of 1250–1285 cm^{-1}. The PLS models were evaluated using R^2, SECV, PRESS, and bias values. All developed models demonstrated high R^2 values either in normal or derivative spectra. The best model obtained using PLS providing R^2 of 0.9997 with the SECV of 1.9, PRESS of 0.5, and bias of 0.2.[73]

RS has been used for the detection of fat adulteration in bakery products especially in cake products. Lipid components was extracted using solvent extraction of n-hexane prior to Raman analysis. Raman spectra acquisition was performed using Raman spectrophotometer with a 785 nm laser source. Spectra were recorded from 200 cm^{-1} to 2000 cm^{-1} with a resolution of 2 cm^{-1}. The samples used for measurement were margarine, extracted margarine from cake, butter, extracted butter from cake, adulterated butter, and adulterated butter extracted from cake. The peaks at 1440, 1301, 1120, 1078, 1039, 888, 867, 602, and 460 cm^{-1} demonstrated specific changes for each type of samples. PCA using wavenumber of 200–2000 cm^{-1} was used to differentiate among samples. PCA using three principal components which explains 99.72% of the total variance could differentiate clearly between butter and butter extracted from cake samples. Spectra derivatization at first derivative were used for creating PCA model. On the other hand, PCA could not clearly differentiate between margarine samples and extracted margarine from cake samples.[24]

RS with temperature probing could be used for discrimination of adulteration in olive oil mixed with soybean oil. Authentication was focused on the spectra of oleic acid and linoleic acid since the main components of olive and soybean oils are oleic and linoleic acids. The concentration of soybean oil used for adulterated samples of olive oil was 5% v/v. The changes in temperature were expected to be analogous for oleic and linoleic acid. Temperature elevation was from −169.9°C to 13.8°C. For the spectra measured at room temperature, there were no differences between pure olive oil and adulterated olive oil with 5% of soybean oil. The spectra of adulterated olive oil overlapped with the spectra of pure olive oil. However, when there was a change in temperature, the differences could be investigated between authentic olive oil and adulterated olive oil with 5% of soybean oil. The differences of Raman spectra could be found at peak of 1600–1800 cm^{-1}, 1200–1520 cm^{-1}, and 800–1200 cm^{-1}. There were shifts of band position, band shape, and intensity change from the elevated temperature. PCA-LDA demonstrated the discrimination of pure olive oil and adulterated olive oil with 5% of soybean oil at the temperature of −36.4°C.[74]

Poiana *et al.*[75] have studied authentication of olive oil mixed with soybean oil using RS and ATR-FTIR spectroscopy. The presence of adulteration could be observed by the changes of absorbance value at wavenumber of 3006 cm^{-1}. In addition, the ratio of the maximum heights of peak at the bands of 3006 and 2925 cm^{-1} was also used to evaluate and investigate adulteration in olive oil. LDA successfully classified authentic olive oil and adulterated olive oil with soybean oil, grapeseed oil, and walnut oil using the combined region of 3018–3002 cm^{-1} and 1200–1000 cm^{-1} for olive oil adulterated with grapeseed oil and soybean oil as well as at combined region of 3029–2954 cm^{-1} and 1125–667 cm^{-1} for olive oil adulterated with walnut oil. Quantitative analysis using PLS could also successfully used for predicting the adulterant concentration in olive oil with high R^2 value and low value of RMSEC and RMSEC.[76] These results suggested that both Raman and FTIR spectroscopy method could be used for authentication of olive oil from other oil adulterants with good result. However, comparative study on the application of FTIR and Raman spectroscopy in combination with chemometrics for authentication analysis of olive oils from other oils has not been reported. Therefore, further study including the effects of data processing technique to the results of analysis and authentication of olive oil using FTIR and Raman spectroscopy should be carried out to obtain clear results.

Adulteration of virgin coconut oil with other lower price fats and oils has been studied using Raman spectroscopy and chemometrics. The adulterants used were sunflower oil, canola oil, vaseline, palm kernel oil and babassu oil. The adulterated virgin coconut oil samples were prepared in binary mixtures with adulterant levels from 2% to 30%. Samples were heated at 40°C prior Raman measurement. Raman spectra of samples either pure or adulterated virgin coconut oil samples were acquired using Raman spectrometer equipped with a charge coupled device (CCD) detector with a diode laser

operated at 785 nm. The spectra were recorded from 200–3200 cm^{-1} using resolution of 2 cm^{-1} and number of scans 8. Chemometrics of MCR-ALS (multi curve resolution-alternating least squares) was used for quantitative analysis to predict the adulterants concentration in virgin coconut oil using absorbance values at wavenumbers of 800–1800 cm^{-1}. MCR-ALS model demonstrated good prediction model for detection and quantification of sunflower oil, canola oil, vaseline, palm kernel oil, and babassu oil in virgin coconut oil. All models resulted high R^2 values (> 0.9) indicating good model and low RMSEC (< 3%) and RMSEP (< 3.7%) values indicating low model errors. PCA was also used to study samples differentiation. Virgin coconut oil adulterated with canola oil and sunflower oil were more distinct and appeared far from pure virgin coconut oil in the PCA score plot. It suggested that RS combined with chemometrics is very potential for authentication of virgin coconut oil.[77]

The combination of RS and PLS has been used for rapid authentication of walnut oil and pumpkin oil adulterated with sunflower oil. Adulterated samples were prepared in binary mixtures of walnut oil and pumpkin oil with sunflower oil at the concentration of 2.5% to 50%. Raman spectra were acquired using a diode laser of 1064 nm at the range of 200–2000 cm^{-1}. PLS using nonlinear iterative partial least square (NIPAL) algorithm was successfully used for quantification of sunflower oil both in walnut oil and pumpkin oil. Result of PLS for the walnut oil demonstrated good model for predicting the concentration of sunflower oil with R^2 prediction of 97.29%. It means that the model could predict the adulterant concentration with high accuracy. Meanwhile, PLS for the pumpkin oil also resulted good prediction model for quantification of sunflower oil with R^2 prediction of 98.64%.[78]

The application of RS and chemometrics has been applied for authentication of virgin olive oil from waste cooking oil. The blend of olive oil and waste cooking oil samples was made using concentration of WCO from 2.5% to 50%. Raman measurements were performed using Raman spectrometer equipped with a diode laser of 785 nm at the range of 100–3500 cm^{-1} and resolution of 6 cm^{-1}. Chemometrics of iPLS (interval partial least square) and SiPLS (synergy interval partial least square) was used for the detection and quantification of WCO in olive oil. SiPLS is the development of iPLS which is superior to iPLS model. Before chemometrics modeling, the spectra were preprocessed using baseline fitting, normalization, standard normal transformation, first derivative, and second derivative. The best model obtained from iPLS was using spectra range of 1218–1262 cm^{-1} with R^2 of 0.775 for calibration and 0.902 for prediction. RMSEC value of 0.0841 and RMSECV value of 0.117 were obtained. Meanwhile, for SiPLS analysis, the model was created using 4 combination of interval number (11, 13, 18, and 23) with R^2 of 0.961 for calibration and 0.982 for prediction. The values of RMSEC and RMSECV were of 0.0485 and 0.0503, respectively. It can be concluded that SiPLS provided better model for quantification of WCO in olive oil than iPLS.[79]

Future application of Raman spectroscopy for quality control of fats and oils

RS offers chemical fingerprinting technique for analysis of edible fats and oils. Fingerprinting technique, when combined with chemometrics of multivariate analysis which is divided into two categories, namely pattern recognition and multivariate calibration becomes a powerful tool for quality control of edible fats and oils including the authentication of fats and oils as well as fats-based food products. RS provides fast time analysis, simple in sample preparation, green analytical chemistry because it does not require much solvent, and it provides high reliability. Many researches have been studied the use of Raman spectroscopy for quality control of fats and oils by determining the parameters for quality control of fats and oils such as free fatty acids, iodine value, and peroxide value. Results proved that Raman spectroscopy could be successfully used to measure these parameters with good accuracy and precision. Moreover, Raman spectroscopy has also been successfully applied for adulteration analysis in fats and oils for authentication purposes. The combination of Raman spectra with chemometrics of PCA, PLS-DA, OPLS-DA, SIMCA and cluster analysis was successfully used for classification of high quality and low quality of fats and oils as well as to differentiate authentic and adulterated fats and oils with other lower price and lower quality materials. In addition, RS and multivariate calibrations of PLS and PCR could be used to predict free fatty acids, iodine value,

peroxide value, and adulterant concentrations in fats and oils. These results demonstrate the potential application of Raman spectroscopy in combination with chemometrics for quality control of fats and oils. Raman spectroscopy combined with chemometrics is very promising because it can be used as a reliable method and rapid analytical method for quality control of many types of fats and oils as well as fats and oils-based food products.

Conclusion

The development of analytical methods for quality assurance and authentication analysis of fats and oils has grown rapidly. Raman spectroscopy (RS) in combination with several chemometrics techniques has emerged as a potential method for quality control of fats and oils analysis of adulteration of fats and oils in food products. By optimizing Raman spectral region, spectral processing and chemometrics techniques, RS has been successfully applied for analysis of free fatty acid, iodine value and some oxidation products including peroxide values, K232, K270 and TBARS. From these results, it can be concluded that RS combined with chemometrics could be developed as an alternative methods to reference methods which are typically applying titrimetric methods.

For authentication analysis, the combination of RS and chemometrics of pattern recognition and multivariate calibrations has been successfully reported for detection and quantification of adulteration practice of high price edible fats and oils with lower ones. Combined with chemometrics of multivariate analysis of pattern recognition techniques including PCA, LDA, SIMCA and PLS-DA as well as multivariate calibrations of PLS and PCR, RS using variables of absorbance values at the optimized wavenumber regions could be an ideal method for the authentication analysis of edible fats and oils. The combination of RS and chemometrics has been proved as accurate and reliable analytical method for quality control and authentication of edible fats and oils, as highlighted in this review. This method must be validated in order to be applied as the standard analytical method for quality control and routine analysis of fats and oils.

Acknowledgments

The authors acknowledged the Ministry of Research and Technology, Republic of Indonesia, Faculty of Pharmacy Universitas Gadjah Mada (UGM), and Integrated Laboratory of Research and Testing (LPPT-UGM) for facilities and supports needed for research activities.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The authors thanks to Universitas Gadjah Mada 2021 through Program Twin center between Center of Excellence, Institute for Halal Industry & Systems (PUI-PT IHIS UGM) and International Institute for Halal Research and Training (INHART), International Islamic University Malaysia (IIUM), Malaysia.

References

[1] Baeten, V.; Aparicio, R. Edible Oils and Fats Authentication by Fourier Transform Raman Spectrometry. *Biotechnol. Agron. Soc. Environ.* 2000, *4*, 196–203.
[2] Rohman, A. Infrared Spectroscopy for Quantitative Analysis and Oil Parameters of Olive Oil and Virgin Coconut Oil: A Review. *Int. J. Food Prop.* 2017, *20*, 1447–1456. DOI: 10.1080/10942912.2016.1213742.
[3] Endo, Y. Analytical Methods to Evaluate the Quality of Edible Fats and Oils: The JOCS Standard Methods for Analysis of Fats, Oils and Related Materials (2013) and Advanced Methods. *J. Oleo Sci.* 2018, *67*, 1–10. DOI: 10.5650/jos.ess17130.

[4] Negash, Y. A.; Amare, D. E.; Bitew, B. D.; Dagne, H. Assessment of Quality of Edible Vegetable Oils Accessed in Gondar City, Northwest Ethiopia. *BMC Res. Notes*. 2019, *12*, 1–5. DOI: 10.1186/s13104-019-4831-x.
[5] Nunes, C. A. Vibrational Spectroscopy and Chemometrics to Assess Authenticity, Adulteration and Intrinsic Quality Parameters of Edible Oils and Fats. *Food Res. Int.* 2014, *60*, 255–261. DOI: 10.1016/j.foodres.2013.08.041.
[6] Bansal, S.; Singh, A.; Mangal, M.; Mangal, A. K.; Kumar, S. Food Adulteration: Sources, Health Risks, and Detection Methods. *Crit. Rev. Food Sci. Nutr.* 2017, *57*, 1174–1189. DOI: 10.1080/10408398.2014.967834.
[7] Li, X.; Zhang, L.; Zhang, Y.; Wang, D.; Wang, X.; Yu, L.; Zhang, W.; Li, P. Review of NIR Spectroscopy Methods for Nondestructive Quality Analysis of Oilseeds and Edible Oils. *Trends Food Sci. Technol.* 2020, *101*, 172–181. DOI: 10.1016/j.tifs.2020.05.002.
[8] Rohman, A.; Man, Y. B. C. Application of Fourier Transform Infrared Spectroscopy for Authentication of Functional Food Oils. *Appl. Spectrosc. Rev*. 2012, *47*, 1–13. DOI: 10.1080/05704928.2011.619020.
[9] Rohman, A. The Use of Infrared Spectroscopy in Combination with Chemometrics for Quality Control and Authentication of Edible Fats and Oils: A Review. *Appl. Spectrosc. Rev*. 2017, *52*, 589–604. DOI: 10.1080/05704928.2016.1266493.
[10] Santos, J. S.; Escher, G. B.; Pereira, J. M. D. S.; Marinho, M. T.; Prado-Silva, L. D.; Sant'Ana, A. S.; Dutra, L. M.; Barison, A.; Granato, D. ^{1}H NMR Combined with Chemometrics Tools for Rapid Characterization of Edible Oils and Their Biological Properties. *Ind. Crop Prod.* 2018, *116*, 191–200. DOI: 10.1016/j.indcrop.2018.02.063.
[11] Esteki, M.; Simal-Gandara, J.; Shahsavari, Z.; Zandbaaf, S.; Dashtaki, E.; Vander Heyden, Y. A Review on the Application of Chromatographic Methods, Coupled to Chemometrics, for Food Authentication. *Food Control*. 2018, *93*, 165–182. DOI: 10.1016/j.foodcont.2018.06.015.
[12] Peris, M.; Escuder-Gilabert, L. Electronic Noses and Tongues to Assess Food Authenticity and Adulteration. *Trends Food Sci. Technol.* 2016, *58*, 40–54. DOI: 10.1016/j.tifs.2016.10.014.
[13] Berghian-Grosan, C.; Magdas, D. A. Raman Spectroscopy and Machine-learning for Edible Oils Evaluation. *Talanta*. 2020, *218*, 121176. DOI: 10.1016/j.talanta.2020.121176.
[14] Das, R. S.; Agrawal, Y. K. Raman Spectroscopy: Recent Advancements, Techniques and Applications. *Vib. Spectrosc.* 2011, *57*, 163–176. DOI: 10.1016/j.vibspec.2011.08.003.
[15] Hasanah, L.; Julian, C.; Mulyanti, B.; Aransa, A.; Sumatri, R.; Johari, M. H.; David, J. P. R.; Mohmad, A. R. Photoluminescence and Raman Scattering of $GaAs_{1-x}Bi_x$ Alloy. *Sains Malays.* 2020, *49*, 2559–2564. DOI: 10.17576/jsm-2020-4910-21.
[16] Hu, R.; He, T.; Zhang, Z.; Yang, Y.; Liu, M. Safety Analysis of Edible Oil Products via Raman Spectroscopy. *Talanta*. 2019, *191*, 324–332. DOI: 10.1016/j.talanta.2018.08.074.
[17] Carmona, M. A.; Lafont, F.; Jiménez-Sanchidrián, C.; Ruiz, J. R. Raman Spectroscopy Study of Edible Oils and Determination of the Oxidative Stability at Frying Temperature. *Eur. J. Lipid Sci. Technol.* 2014, *116*(11), 1451–1456. DOI: 10.1002/ejlt.201400127.
[18] Kwofie, F.; Lavine, B. K.; Ottaway, J.; Booksh, K. Incorporating Brand Variability into Classification of Edible Oils by Raman Spectroscopy. *J. Chemom.* 2019, *37*(7), 1–14.
[19] Jimenez-Sanchidrian, C.; Ruiz, J. R. Use of Raman Spectroscopy for Analysing Edible Vegetable Oils. *Appl. Spectrosc. Rev*. 2016, *51*(5), 417–430. DOI: 10.1080/05704928.2016.1141292.
[20] Ozaki, Y.; Šašić, S. *Introduction to Raman Spectroscopy. Pharmaceutical Applications of Raman Spectroscopy*; John Wiley & Sons, Inc, 2007. DOi: 10.1002/9780470225882.ch1.
[21] Yang, D.; Ying, Y. Applications of Raman Spectroscopy in Agricultural Products and Food Analysis: A Review. *Appl. Spectrosc. Rev*. 2011, *46*, 539–560. DOI: 10.1080/05704928.2011.593216.
[22] Handapangoda, C. C.; Nahavandi, S.; Premaratne, M. *Review of Nanoscale Spectroscopy in Medicine: Nanoscale Spectroscopy with Applications*; CRC Press. Monash University, 2013; pp 439–472. DOI: 10.1201/b15615-12.
[23] Li, Y. S.; Church, J. S. Raman Spectroscopy in the Analysis of Food and Pharmaceutical Nanomaterials. *J. Food Drug Anal.* 2014, *22*, 29–48. DOI: 10.1016/j.jfda.2014.01.003.
[24] Üçüncüoğlu, D.; Ilaslan, K.; Boyaci, I. H.; Özay, D. S. Rapid Detection of Fat Adulteration in Bakery Products Using Raman and Near-infrared Spectroscopies. *Eur. Food Res. Technol.* 2013, *237*, 703–710. DOI: 10.1007/s00217-013-2030-x.
[25] Dymińska, L.; Calik, M.; Albegar, A. M. M.; Zając, A.; Kostyń, K.; Lorenc, J.; Hanuza, J. Quantitative Determination of the Iodine Values of Unsaturated Plant Oils Using Infrared and Raman Spectroscopy Methods. *Int. J. Food Prop.* 2017, *20*, 2003–2015. DOI: 10.1080/10942912.2016.1230744.
[26] Qiu, J.; Hou, H. Y.; Yang, I. S.; Chen, X. B. Raman Spectroscopy Analysis of Free Fatty Acid in Olive Oil. *Appl. Sci. (Switzerland)*. 2019, *9*. DOI: 10.3390/app9214510.
[27] Bumbrah, G. S.; Sharma, R. M. Raman Spectroscopy – Basic Principle, Instrumentation and Selected Applications for the Characterization of Drugs of Abuse. *Egypt. J. Forensic Sci.* 2016, *6*, 209–215. DOI: 10.1016/j.ejfs.2015.06.001.
[28] Craig, A. P.; Franca, A. S.; Irudayaraj, J. Surface-Enhanced Raman Spectroscopy Applied to Food Safety. *Annu. Rev. Food Sci. Technol.* 2013, *4*, 369–380. DOI: 10.1146/annurev-food-022811-101227.
[29] Lohumi, S.; Lee, S.; Lee, H.; Cho, B. K. A Review of Vibrational Spectroscopic Techniques for the Detection of Food Authenticity and Adulteration. *Trends Food Sci. Technol.* 2015, *46*, 85–98. DOI: 10.1016/j.tifs.2015.08.003.

[30] Rohman, A.; Windarsih, A.; Lukitaningsih, E.; Rafi, M.; Betania, K.; Fadzillah, N. A. The Use of FTIR and Raman Spectroscopy in Combination with Chemometrics for Analysis of Biomolecules in Biomedical Fluids: A Review. *Biomed. Spectrosc. Imaging*. 2020, *8*, 55–71. DOI: 10.3233/bsi-200189.
[31] Zheng, J.; He, L. Surface-Enhanced Raman Spectroscopy for the Chemical Analysis of Food. *Compr. Rev. Food Sci. F.* 2014, *13*, 317–328. DOI: 10.1111/1541-4337.12062.
[32] Mazivila, S. J.; Olivieri, A. C. Chemometrics Coupled to Vibrational Spectroscopy and Spectroscopic Imaging for the Analysis of Solid-phase Pharmaceutical Products: A Brief Review on Non-destructive Analytical Methods. *Trac-Trends Anal. Chem.* 2018, *108*, 74–87. DOI: 10.1016/j.trac.2018.08.013.
[33] Rohman, A.; Windarsih, A.; Erwanto, Y.; Zakaria, Z. Review on Analytical Methods for Analysis of Porcine Gelatine in Food and Pharmaceutical Products for Halal Authentication. *Trends Food Sci. Technol.* 2020, *101*, 122–132. DOI: 10.1016/j.tifs.2020.05.008.
[34] Rohman, A.; Che Man, Y. B. Application of FTIR Spectroscopy for Monitoring the Stabilities of Selected Vegetable Oils during Thermal Oxidation. *Int. J. Food Prop.* 2013, *16*, 1594–1603. DOI: 10.1080/10942912.2011.603874.
[35] Li, Q.; Chen, J.; Huyan, Z.; Kou, Y.; Xu, L.; Yu, X.; Gao, J. M. Application of Fourier Transform Infrared Spectroscopy for the Quality and Safety Analysis of Fats and Oils: A Review. *Crit. Rev. Food Sci. Nutr.* 2019, *59*, 3597–3611. DOI: 10.1080/10408398.2018.1500441.
[36] Guzmán, E.; Baeten, V.; Fernández Pierna, J. A.; García-Mesa, J. A. Application of Low-resolution Raman Spectroscopy for the Analysis of Oxidized Olive Oil. *Food Control.* 2011, *22*(12), 2036–2040. DOI: 10.1016/j.foodcont.2011.05.025.
[37] 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. DOI: 10.1016/j.talanta.2014.10.042.
[38] El-Abassy, R. M.; Donfack, P.; Materny, A. Rapid Determination of Free Fatty Acid in Extra Virgin Olive Oil by Raman Spectroscopy and Multivariate Analysis. *J. Am. Oil Chem. Soc.* 2009, *86*(6), 507–511. DOI: 10.1007/s11746-009-1389-0.
[39] Samyn, P.; Van Nieuwkerke, D.; Schoukens, G.; Vonck, L.; Stanssens, D.; Van Den Abbeele, H. Quality and Statistical Classification of Brazilian Vegetable Oils Using Mid-infrared and Raman Spectroscopy. *Appl. Spectrosc.* 2012, *66*, 552–565. DOI: 10.1366/11-06484.
[40] Portarena, S.; Anselmi, C.; Zadra, C.; Farinelli, D.; Famiani, F.; Baldacchini, C.; Brugnoli, E. Cultivar Discrimination, Fatty Acid Profile and Carotenoid Characterization of Monovarietal Olive Oils by Raman Spectroscopy at a Single Glance. *Food Control.* 2019, *96*, 137–145. DOI: 10.1016/j.foodcont.2018.09.011.
[41] Jiang, Y.; Su, M.; Yu, T.; Du, S.; Liao, L. Quantitative Determination of Peroxide Value of Edible Oil by Algorithm-assisted Liquid Interfacial Surface Enhanced Raman Spectroscopy. *Food Chem.* 2020. DOI: 10.1016/j.foodchem.2020.128709.
[42] Aykas, D. P.; Karaman, A. D.; Keser, B.; Rodriguez-Saona, L. Non-targeted Authentication Approach for Extra Virgin Olive Oil. *Foods*. 2020, *9*, 1–17. DOI: 10.3390/foods9020221.
[43] Sottero, B.; Leonarduzzi, G.; Testa, G.; Gargiulo, S.; Poli, G.; Biasi, F. Lipid Oxidation Derived Aldehydes and Oxysterols between Health and Disease. *Eur. J. Lipid Sci. Technol.* 2018, *121*(1), 1700047. DOI: 10.1002/ejlt.201700047.
[44] Vieira, S. A.; Zhang, G.; Decker, E. A. Biological Implications of Lipid Oxidation Products. *J. Am. Oil Chem.' Soc.* 2017, *94*, 339–351. DOI: 10.1007/s11746-017-2958-2.
[45] Sultana, R.; Perluigi, M.; Butterfield, D. A. Lipid Peroxidation Triggers Neurodegeneration: A Redox Proteomics View into the Alzheimer Disease Brain. *Free Radic. Biol. Med.* 2012, *62*, 157–169. DOI: 10.1016/j.freeradbiomed.2012.09.027.
[46] Davi, G.; Falco, A.; Patrono, C. Lipid Peroxidation in Diabetes Mellitus. *Antioxid. Redox Signal.* 2005, *7*(1–2), 256–268. DOI: 10.1089/ars.2005.7.256.
[47] Zhong, S.; Li, L.; Shen, X.; Li, Q.; Xu, W.; Wang, X.; Tao, Y.; Yin, H. An Update on Lipid Oxidation and Inflammation in Cardiovascular Diseases. *Free Radic. Biol. Med.* 2019, *144*, 266–278. DOI: 10.1016/j.freeradbiomed.2019.03.036.
[48] Yee, T. P.; Tiu, T. K. Effects of Oxidized Oils on Inflammation-related Cancer Risk. *J. Oil Palm Res.* 2019, *31*(1), 1–13.
[49] Li, Y.; Driver, M.; Decker, E.; He, L. Lipid and Lipid Oxidation Analysis Using Surface Enhanced Raman Spectroscopy (SERS) Coupled with Silver Dendrites. *Food Res. Inter.* 2014, *58*, 1–6. DOI: 10.1016/j.foodres.2014.01.056.
[50] Valasi, L.; Kokotou, M. G.; Pappas, C. S. G. C.-M. S. FTIR and Raman Spectroscopic Analysis of Fatty Acids of *Pistacia Vera* (Greek Variety "Aegina") Oils from Two Consecutive Harvest Periods and Chemometric Differentiation of Oils Quality. *Food Res. Inter.* 2021, *148*, 110590. DOI: 10.1016/j.foodres.2021.110590.
[51] Rukunudin, I. H.; White, P. J.; Bern, C. J.; Bailey, T. B. A Modified Method for Determining Free Fatty Acids from Small Soybean Oil Sample Sizes. *J. Am. Oil Chem. Soc.* 1998, *75*, 563–568. DOI: 10.1007/s11746-998-0066-z.

[52] Liu, H.; Chen, Y.; Shi, C.; Yang, X.; Han, D. FT-IR and Raman Spectroscopy Data Fusion with Chemometrics for Simultaneous Determination of Chemical Quality Indices of Edible Oils during Thermal Oxidation. *LWT*. 2020, *119*, 108906. DOI: 10.1016/j.lwt.2019.108906.
[53] Uysal, R. S.; Boyaci, I. H.; Genis, H. E.; Tamer, U. Determination of Butter Adulteration with Margarine Using Raman Spectroscopy. *Food Chem.* 2013, *141*, 4397–4403. DOI: 10.1016/j.foodchem.2013.06.061.
[54] Jiménez-Carvelo, A. M.; Osorio, M. T.; Koidis, A.; González-Casado, A.; Cuadros-Rodríguez, L. Chemometric Classification and Quantification of Olive Oil in Blends with Any Edible Vegetable Oils Using FTIR-ATR and Raman Spectroscopy. *Food Sci. Technol.* 2017, *86*, 174–184. DOI: 10.1016/j.lwt.2017.07.050.
[55] 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*, 889–895. DOI: 10.1007/s11746-001-0360-6.
[56] Zou, M. Q.; Xiao-Fang, Z.; Xiao-Hua, Q.; Han-Lu, M.; Dong, Y.; Chun-Wei, L.; Guo, X.; Wang, H. Rapid Authentication of Olive Oil Adulteration by Raman Spectrometry. *J. Agric. Food Chem.* 2009, *57*, 6001–6006. DOI: 10.1021/jf900217s.
[57] 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*, 2225–2230. DOI: 10.1021/jf9600115.
[58] 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*, 6145–6150. DOI: 10.1021/jf034493d.
[59] McDowell, D.; Osorio, M. T.; Elliott, C. T.; Koidis, A. Detection of Refined Sunflower and Rapeseed Oil Addition in Cold Pressed Rapeseed Oil Using Mid Infrared and Raman Spectroscopy. *Eur. J. Lipid Sci. Technol.* 2018, *120*, 1700472. DOI: 10.1002/ejlt.201700472.
[60] Nedeljkovic, A.; Tomasevic, I.; Miocinovic, J.; Pudja, P. Feasibility of Discrimination of Dairy Creams and Cream-like Analogues Using Raman Spectroscopy and Chemometric Analysis. *Food Chem.* 2017, *232*, 487–492. DOI: 10.1016/j.foodchem.2017.03.165.
[61] Lee, J. Y.; Park, J. H.; Mun, H.; Shim, W. B.; Lim, S. H.; Kim, M. G. Quantitative Analysis of Lard in Animal Fat Mixture Using Visible Raman Spectroscopy. *Food Chem.* 2018, *254*, 109–114. DOI: 10.1016/j.foodchem.2018.01.185.
[62] Carmona, M. A.; Lafont, F.; Jiménez-Sanchidrián, C.; Ruiz, J. R. Characterization of Macadamia and Pecan Oils and Detection of Mixtures with Other Edible Seed Oils by Raman Spectroscopy. *Grasas Y Aceites.* 2015, *66*. DOI: 10.3989/gya.1191142.
[63] Nedeljković, A.; Rösch, P.; Popp, J.; Miočinović, J.; Radovanović, M.; Pudja, P. Raman Spectroscopy as a Rapid Tool for Quantitative Analysis of Butter Adulterated with Margarine. *Food Anal. Methods*. 2016, *9*, 1315–1320. DOI: 10.1007/s12161-015-0317-1.
[64] Ghazali, H. H.; Tukiran, N. A. Analysis of Pork Adulteration in Recycled Frying Oils Using Raman Spectroscopy. *Malays. J. Halal Res.* 2021, *4*, 2021. DOI: 10.2478/mjhr-2021-0004.
[65] 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*, 25–32. DOI: 10.1016/j.foodchem.2004.08.039.
[66] Gao, F.; Xu, L.; Zhang, Y.; Yang, Z.; Han, L.; Liu, X. Analytical Raman Spectroscopic Study for Discriminant Analysis of Different Animal-derived Feedstuff: Understanding the High Correlation between Raman Spectroscopy and Lipid Characteristics. *Food Chem.* 2018, *240*, 989–996. DOI: 10.1016/j.foodchem.2017.07.143.
[67] Portarena, S.; Baldacchini, C.; Brugnoli, E. Geographical Discrimination of Extra-virgin Olive Oils from the Italian Coasts by Combining Stable Isotope Data and Carotenoid Content within a Multivariate Analysis. *Food Chem.* 2017, *215*, 1–6. DOI: 10.1016/j.foodchem.2016.07.135.
[68] 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*, 2772–2777. DOI: 10.1039/c2ay25431j.
[69] 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. DOI: 10.1016/j.talanta.2016.05.014.
[70] Yazgan, K. N. N.; Bulat, T.; Boyaci, I. H.; Topcu, A. Raman Spectroscopy Coupled with Chemometric Methods for the Discrimination of Foreign Fats and Oils in Cream and Yogurt. *J. Food Drug Anal.* 2019, *27*, 101–110. DOI: 10.1016/j.jfda.2018.06.008.
[71] Genis, D. O.; Sezer, B.; Durna, S.; Boyaci, I. H. Determination of Milk Fat Authenticity in Ultra-filtered White Cheese by Using Raman Spectroscopy with Multivariate Data Analysis. *Food Chem.* 2021, *336*, 127699. DOI: 10.1016/j.foodchem.2020.127699.
[72] Gao, F.; Ben-Amotz, D.; Zhou, S.; Yang, Z.; Han, L.; Liu, X. Comparison and Chemical Structure-related Basis of Species Discrimination of Animal Fats by Raman Spectroscopy Using Near-infrared and Visible Excitation Lasers. *LWT*. 2020, *134*, 110105. DOI: 10.1016/j.lwt.2020.110105.

[73] Taylan, O.; Cebi, N.; Tahsin, Y. M.; Sagdic, O.; Bakhsh, A. A. Detection of Lard in Butter Using Raman Spectroscopy Combined with Chemometrics. *Food Chem.* 2020, *332*, 127344. DOI: 10.1016/j.foodchem.2020.127344.

[74] Ryoo, D.; Hwang, J.; Chung, H. Probing Temperature Able to Improve Raman Spectroscopic Discrimination of Adulterated Olive Oils. *Microchem. J.* 2017, *134*, 224–229. DOI: 10.1016/j.microc.2017.06.002.

[75] 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*, 689–698. DOI: 10.1515/chem-2015-0110.

[76] Rohman, A.; Che-Man, Y. B.; Ismail, A.; Hashim, P. FTIR Spectroscopy Coupled with Chemometrics of Multivariate Calibration and Discriminant Analysis for Authentication of Extra Virgin Olive Oil. *Int. J. Food Prop.* 2017, *20*, S1173–S1181. DOI: 10.1080/10942912.2017.1336718.

[77] Neves, M. D. G.; Poppi, R. J. Authentication and Identification of Adulterants in Virgin Coconut Oil Using ATR/FTIR in Tandem with DD-SIMCA One Class Modeling. *Talanta*. 2020, 219. DOI: 10.1016/j.talanta.2020.121338.

[78] Becze, A.; Simedru, D. Rapid Detection of Walnut and Pumpkin Oil Adulteration Using Raman Spectroscopy and Partial Least Square Methodology. *Not. Bot. Horti Agrobot. Cluj-Napoca*. 2020, *48*, 1426–1438. DOI: 10.15835/nbha48312024.

[79] Li, Y.; Fang, T.; Zhu, S.; Huang, F.; Chen, Z.; Wang, Y. Detection of Olive Oil Adulteration with Waste Cooking Oil via Raman Spectroscopy Combined with iPLS and SiPLS. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2018, *189*, 37–43. DOI: 10.1016/j.saa.2017.06.049.