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Prediction of chemical parameters and authentication of various cold pressed oils with fluorescence and mid-infrared spectroscopic methods

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ABSTRACT

It was aimed to compare the performances of two spectroscopic methods, fluorescence and mid-infrared spectroscopy, in terms of their adulteration detection and estimation of several chemical properties for various cold pressed seed oils. Spectroscopic profiles, fatty acid, free fatty acid and total phenol contents of pumpkin seed, grape seed, black cumin oil, and sesame seed oils were determined and these oils were mixed with sunflower oil at 1–50% (v/v). Both spectroscopic techniques provided comparable results for determination of adulteration of each oil type and the most successful prediction was obtained for pumpkin seed oil at levels >%1. Combined data set of oils resulted in successful quantification of their free fatty acid value, total phenol and major fatty acids contents with both spectroscopic methods regardless of oil type. Both techniques could be used as reliable, fast and environmentally friendly alternatives in the analyses of different types of seed oils.

1. Introduction

Various health benefits such as anti-diabetic, anti-hypertensive, anti-inflammatory properties of different types of cold pressed oils from plants and oilseeds have been reported in the literature (Ibrahim, Attia, Maklad, Ahmed, & Ramadan, 2017). These oils are generally quite rich sources of phenolic compounds, phytosterols, carotenoids and tocopherols (Bjelica, Vujasinović, Rabrenović, & Dimić, 2019). Due to their productions in lower amounts and reported health benefits, there is an increased demand that causes higher prices for these products in the market. Hence, they are good candidates for mixing with cheaper oils. Cold pressed seed oils obtained from grape, nigella (black cumin), pomegranate, pumpkin and sesame have been getting more attention due to their ease of availability and prominent health benefits preserved perfectly due to niche manufacturing.

Authentication studies of cold pressed oils through the utilization of different methods such as the determination of fatty acid composition, lipid fractions, sterols and polycylic aromatic hydrocarbons based on wet chemical methods are available in the literature (Aparicio, García González, & Aparicio-Ruiz, 2018). As an alternative, fast spectroscopic methods have been also providing successful results for the authentication of different types of oils (de Lima, Musso, & Menezes, 2020). Pomegranate seed oils have been recently authenticated with mid-infrared (mid-IR), UV–visible and fluorescence spectroscopic methods (Uncu, Napiórkowska, Szajna, & Ozen, 2020). There are also studies regarding adulteration of grapeseed, black cumin and sesame oils with different individual spectroscopic methods (Akin, Elmas, Arslan, Yılmaz, & Kenar, 2019; Elmas, Arslan, Akin, Kenar, Janssen, & Yilmaz, 2019; Fadzlillah, Che Man, & Rohman, 2014; Rohman & Ariani, 2013; Yuan, Wang, Wang, Cheng, Wu, & Kong, 2020). Whereas any authentication study for pumpkin seed oil using spectroscopic methods was not found in the literature except a very recent study of pumpkin seed-sesame oil mixture (Irnawati, Riyanto, Martono, & Rohman, 2020). In addition, limited studies exist in the literature comparing different spectroscopic techniques in cold pressed seed oil authentication (Arslan, Akin, Elmas, Yilmaz, Janssen, & Kenar, 2019) and most of the authentication studies are only focusing on one type of pure seed oil at a time (Deng, Xu, Ye, Cui, Cai, & Yu, 2012; Ozulku, Yildirim, Toker, Karasu, & Durak, 2017; Zhao, Dong, Zheng, Jiao, & Lang, 2015). In the present study, both mid-IR and fluorescence spectroscopy were used and compared in authentication of various seed oils. To the best of our knowledge, these techniques have not been compared thoroughly in authentication of the various cold pressed oils in a single study.

These spectroscopic methods also allow estimation of compositional parameters of the analyzed samples; so that, it is possible to predict several parameters with a single measurement. Examples of these types of studies are more common especially for the determination of chemical constituents of olive oil such as fatty acid, phenolic and pigment

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composition with mid-IR spectroscopy (Uncu, Ozen, & Tokatli, 2019; Uncu & Ozen, 2015). Limited studies are available regarding the prediction of chemical indices and constituents with fluorescence spectroscopy. Saturated fatty acid profile of butterfat and total fat and fatty acid composition of beef were determined with front face fluorescence spectroscopy (Aït-Kaddour, Thomas, Mardon, Jacquot, Ferlay, & Gruffat, 2016; Ntakatsane, Liu, Zhou, Mothibe, Adegoke, & Odenya, 2014). In addition, quality indices of olive and cold pressed rapeseed oils were predicted from fluorescence spectra (Guzmán, Baeten, Pierna, & García-Mesa, 2015; Sikorska et al., 2019). However, data sets in these prediction studies, in general, were consisted of a single type of oil or product. It was intended to combine the chemical data of several cold pressed oils together in a single data set and to estimate the several parameters both from mid-IR and fluorescence spectral data in the current investigation. Therefore, it was aimed to construct a reliable multivariate statistical model that can be valid in screening quality parameters of different oil types as well as to provide a comparison of the efficiency of these two spectroscopic methods in the same type of application which have not been done before.

It is hypothesized that mixing of lower priced sunflower oil with cold pressed pumpkin seed, grape seed, black cumin, and sesame oils could be determined with both fluorescence and mid-IR spectroscopy. Another hypothesis is that it could be possible to predict the several chemical parameters (free fatty acid value, fatty acid profile and total phenolic content) of importance for pure cold pressed oils with a single chemometric model from these two spectral data.

2. Materials and methods

2.1. Oil samples

Cold pressed pumpkin seed, grape seed, black cumin and sesame oils were used in the investigation of adulteration and 15 pure oils from each oil type were obtained from reliable producers possessing a certification from a research center of a public university and applying Good Manufacturing (GMP), Good Agricultural (GAP) and Good Laboratory (GLP) Practices. Regular (linoleic type) commercial refined sunflower oil with free fatty acid content of 0.08% and major fatty acid profile as linoleic acid 56.90% and oleic acid 31.90% was used as an adulterant. Randomly chosen 7 samples from each oil were blended with sunflower oil, at 1, 5, 10, 15, 20, 30, 40 and 50% (v/v) ratio. The rest of the pure samples (8 oils) not involved in adulteration practice were used independently in statistical evaluation to increase diversity of the data set. As a result, 56 adulterated and 15 pure samples of each type of seed oils were used in authentication studies.

In prediction part, in addition to the four types of pure samples (4 × 15) used in authentication studies, two other edible oils as 15 cold pressed pomegranate seed oils and 15 olive oils were also analyzed in order to add more different types of oils and also to increase the number of the samples. Therefore, a total of 90 pure samples belonging to six different types of edible oils were used in prediction of chemical parameters.

2.2. Free fatty acid content

Percent free fatty acid content of the pure samples was determined with a titrimetric method (EEC, 1991). The results are expressed in terms of % pucinic acid (for pomegranate seed oils) and oleic acid (for other oils) as an average of duplicated measurements.

2.3. Fatty acid content

After the methyl esterification reaction, fatty acid contents of pure oils were determined with gas chromatography (GC). Analyses were performed with a GC device (Agilent 6890, Agilent Technologies, Santa Clara, CA, USA) having an auto-sampler (Agilent 7863&FID) and a split/splitless (1:50) injector. HP 88 capillary column (Agilent, USA) used in the analyses had dimensions of 100 m*0.25 mm ID*0.2 μm. Analyses were done using experimental conditions given in the literature (Uncu & Ozen, 2015). Results were expressed as averages of percentages of corresponding individual fatty acid methyl esters for the samples repeated twice. Total fatty acid compositions were also determined in terms of total saturated fatty acids (SFAs), total monounsaturated fatty acids (MUFAs), and total polyunsaturated fatty acids (PUFAs) contents.

2.4. Total phenolic content

Folin-Ciocalteu spectrophotometric method from the literature was used for the determination of total phenolic content of pure oils (Montedoro, Servili, Baldioli & Miniati, 1992). Results were calculated with respect to mg gallic acid equivalent (GAE)/kg oil. The measurements were repeated two times for each sample by using a UV–visible spectrophotometer (Shimadzu UV-2450 Spectrophotometer, Kyoto, Japan).

2.5. Fluorescence spectroscopy

Fluorescence spectra of the samples were collected with a fluorescence spectrometer (LS- 55, PerkinElmer Inc., Waltham, MA, USA) having a pulsed xenon lamp. All the studied samples were recorded two times under the emission spectra between 300 and 800 nm for each excitation wavelength (320, 330, 340, and 350 nm). Averaged spectra for each sample were used in the statistical model development. The constant measurement parameters were selected throughout the study for scanning as 0.5 nm data interval and 0.12 s integration time. Quartz sample cell (45 mm (H) × 12.5 mm (W) × 12.5 mm (D), PerkinElmer Inc., USA) having 10 mm light path was cleaned with hexane under the flow of nitrogen between each measurement.

In the authentication part of the study, different slit widths as well as excitation wavelengths for each type of seed oils were used to obtain the best resolution with optimal signal-to-noise ratio to avoid oversaturation. Trial and error method were applied to select the best parameters of interest to build statistical models. Slit widths were 15 and 10 nm for grape seed oils, 5 and 20 nm for black cumin seed oils, 15 and 5 nm for sesame seed oils, 10 and 20 nm for pumpkin seed oils for excitation and emission wavelengths, respectively. All seed oils except pumpkin seed oil (340 nm) were excited at 320 nm along with emission at 300–800 nm. Data from both scan types were used simultaneously in model building.

In prediction of chemical parameters, besides the four seed oils pomegranate seed and olive oils were also recorded with the slit widths of 10 and 20 nm, 5 and 5 nm, for excitation and emission, respectively. To sustain compatibility, excitation at 320 nm with full emission range of each seed oils were used in prediction model building.

2.6. Mid-infrared spectroscopy

Mid-IR spectra of pure and blended samples were obtained with a FTIR spectrometer (Spectrum 100 FTIR spectrometer, Perkin Elmer Inc., Waltham, MA, USA) having ZnSe-ATR acccessory and DTGS detector. Measurement range was 4000–650 cm^{-1} with two repetitions. Measurement parameters were 64 scans, 4 cm^{-1} resolution and 1 cm/s scan speed. The same parameters were used in examining samples in both part of the study.

2.7. Statistical analysis

SIMCA 14.1 software (Umetrics, Umeå, Sweden) was used in both authentication and prediction of chemical parameters of seed oils. Full spectra of FTIR (4000–650 cm^{-1}) and fluorescence (300–800 nm) scanning were used in statistical evaluation.

Prior to construction of the chemometric models, all the spectroscopic data were pre-processed to remove noise. First, basic pre-

processing methods such as mean-centering and unit variance scaling were applied for signal enhancement in construction of both authentication and prediction models. After that, further advanced pretreatment techniques as first derivative (FD), second derivative (SD), standard normal variate (SNV), wavelet denoising techniques (WDTs) and orthogonal signal correction (OSC) were used for signal correction as individually and/or in suitable combinations and these were selected with the trial and error method for the development of specific models (Uncu et al., 2019). Derivatives were applied by moving quadratic submodels of 15 data point long with a distance of 1 excluding the edge effects. WDTs were utilized in the form of wavelet function, Daubechies-10, with 99.5% confidence interval.

All the pre-treated data obtained with both spectral techniques were divided randomly into calibration and validation sets corresponding to 2/3 and 1/3 of total number of the samples, respectively. The optimum number of latent variables (LVs) to obtain OPLS-DA and PLS calibration models was calculated automatically by the SIMCA software internally with both 7-fold and leave-one-out cross validation (LOO-CV): samples were separated into 7 random subsets as well as LOO set. In detail, the strategy is based on dividing samples into *n* cancellation groups in which the first group included the first sample and one sample every n samples until their total number is reached. Process continues with the same logic, except the second group starts with sample 2 and the third group starts with sample 3 and goes like that in all the subsequent groups. As far as LOO-CV approach is concerned, the number of cancellation groups was the same with the number of samples (Pizarro, Rodríguez-Tecedor, Pérez-del-Notario, Esteban-Díez, & González-Sáiz, 2013). In this way, the corresponding models were protected from over and/or under fitting; otherwise, it would result in too optimistic or vice versa models.

In the authentication part, two chemometric techniques as orthogonal partial least square-discriminant analysis (OPLS-DA) and partial least squares (PLS) regression were used to differentiate pure and adulterated seed oil samples and quantify level of adulteration, respectively. OPLS-DA is a supervised data classification technique based on two main matrix block as X matrix (spectral data of FTIR and fluorescence) and an artificially constructed dummy Y variable matrix consisting of class 1 pure (non-adulterated) and as class 2 adulterated seed oil samples (Uncu et al., 2020). The results of OPLS-DA of each spectroscopic approach for each seed oils were given in terms of correct classification rate (%CC), sensitivity, specificity and precision. In OPLS-DA, any seed oil sample in classification list having a prediction value between 0.5 and 1.5 was accepted as correctly classified whereas out of range samples were considered as misclassified (Hirri, Bassbasi, Platikanov, Tauler, & Oussama, 2016). Another parameter in OPLS-DA, the %CC, also as known as accuracy, was based on the proportion of correctly classified samples to the total amount of calibration and/or validation set samples (Wang, Huang, & Wang, 2019). Sensitivity was determined by the ratio of true positive (TP) to the sum of TP and false negative (FN) samples whereas specificity was relying on proportion of true negative (TN) to the sum of TN and false positive (FP) samples. In addition, precision was formulated with ratio of TP to the sum of TP and FP samples. %CC, sensitivity, specificity and precision values were manually calculated based on the explained calculation methods while other statistical parameters such as LVs, coefficient of determination for calibration (R^2_{cal}) and coefficient of determination for cross validation (R^2_{cv}) were determined by automatic fitting function of the software for both OPLS-DA and PLS models. In addition, level of adulteration was quantified with PLS regression to see how well the ability of both spectroscopic methods in prediction of adulterant level is. With PLS regression, correlation of spectroscopic data of the seed oils as X matrix (adulterated and non-adulterated samples) with Y matrix consisting value of varying level of adulterated (1–50%) and non-adulterated (0%) pure seed oils were investigated (Gurdeniz & Ozen, 2009). The statistical information about PLS regression plot was given in terms of R^2 representing the goodness of fit in calibration (R^2_{cal}), cross-validation (R^2_{cv}) and external validation (R^2_{pred}). Root mean square error (RMSE) is an absolute value similar to the standard deviation for the calibration (RMSEC), cross-validation (RMSECV), and prediction (RMSEP). Residual predictive deviation (RPD) and the slope of the regression plot were the other parameters for evaluating the performance of PLS models. The threshold value for a robust prediction model is associated with R^2>0.90, RPD value>3.0 with a slope value 0.9–1.1 (Uncu & Ozen, 2015). Along with these criteria, a good model should have also comparable and low error values for RMSEC, REMSECV and RMSEP (Uncu & Ozen, 2015). The statistical parameters except RPD were calculated by the software whereas the RPD values were calculated based on the ratio of standard deviation of predicted values to RMSEP values to obtain more comprehensive idea about prediction ability of the corresponding models.

In the second part of the study, PLS regression was also used to quantify chemical parameters of the 6 types of oils. The same parameters for performance evaluation were also valid in prediction of chemical parameters of the edible oils.

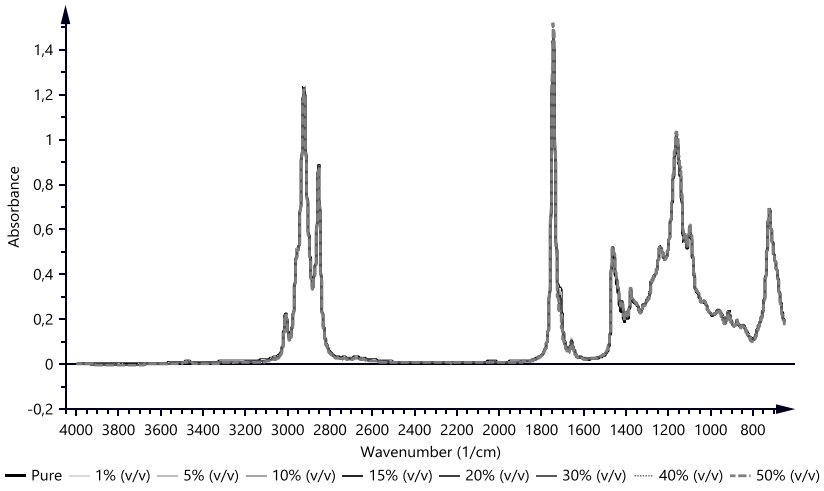
3. Results and discussions

3.1. Spectral evaluation of seed oils

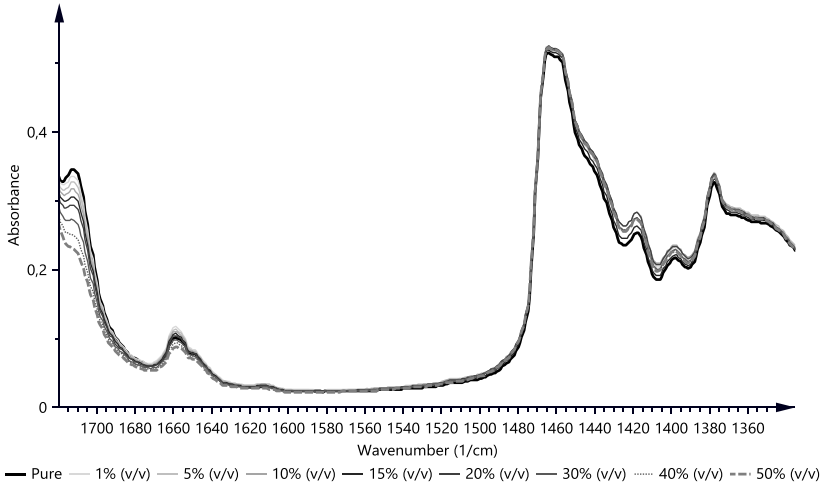
Typical spectra of all the seed oils including pure and adulterated ones recorded by mid-IR and fluorescence spectroscopy are given in Fig. 1 for black cumin seed oils and in Figs. S1–S3 for the rest of the oils. Quantitative differences exist in the mid-IR peaks of pure and adulterated samples in the regions of 2924 cm^{-1}, 2852 cm^{-1}, 1723 cm^{-1}, and 723 cm^{-1} and more significant differences could be also observed in the fingerprint regions (1464–983 cm^{-1}) of the pure vs adulterated samples of each seed oil (Fig. 1a and Figs. S1a–S3a). These differences are hard to see in whole scale mid-IR spectra; therefore, FTIR spectra of only black cumin seed oil samples (around 1723 cm^{-1} and part of the fingerprint region) are given in more detail (Fig. 1b) and the other seed oils have similar differences. Pure samples have higher and/or lower absorption at distinct wavelengths compared to increasing level of adulterant (sunflower oil) due to some significant chemical differences between pure and adulterated seed oils which are highly correlated with spectral information (Uncu et al., 2020). In detail, increasing adulteration level shows negative correlation for the peak at 1723 cm^{-1} with respect to pure black cumin seed oils (Fig. 1b). This could be associated with lower free fatty acid content of sunflower oil compared to black cumin seed oil since that wavelength is attributed to stretching of C=O groups (Hirri et al., 2016). Additional differences were also observed in the fingerprint region of the pure and adulterated samples due to their compositional differences. These differences are mainly based on minor components such as phenolics and individual and total fatty acid compositions as will be explained at the beginning of section 3.3. The same arguments are also valid for black cumin seed oils with higher noticeable differences in the fingerprint region (Fig. 1b). The other three types of cold pressed oils also have similar spectral patterns (Fig. S1a–3a).

Due to the nature of fluorescence spectra, differences between pure and adulterated samples are clearer compared to mid-IR spectra. The representative fluorescence spectra of each cold pressed oil samples with adulteration are shown in Fig. 1c and Fig. S1b-S3b. The spectral pattern was determined by characteristic bands of natural fluorophores which is highly affected by chemical compositions of the oil samples (Elmas et al., 2019). The emission bands between 400 and 500 nm are attributed to oxidation and degradation products (Milanez, Nóbrega, Nascimento, Insausti, Band, & Pontes, 2017), while the peaks from 500 to 550 nm and 660–690 nm are associated with vitamin E and fluorescent pigments, mainly chlorophylls and pheophytins, respectively (Yuan et al., 2020). All the pure cold pressed seed oils except sesame seed oils had higher fluorescence intensity with increasing level of adulteration due to the compositional differences (Fig. 1c and Fig. S1b-S3b).

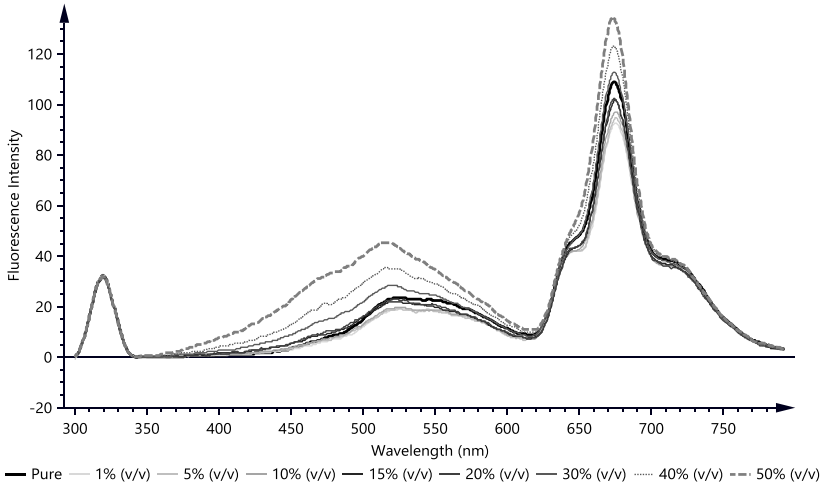
These differences are also investigated in more detail with the variable importance in projection (VIP) values obtained from multivariate



(a)



(b)



(c)

Fig. 1. Spectra of pure and adulterated black cumin seed oils with mid-IR (a), parts of mid-IR (b) and whole fluorescence (c) spectroscopy, respectively.

statistical analysis. VIP values>1 indicate significant wavelengths and wavenumbers in classification and/or prediction models (Fig. S4-S7).

3.2. Comparison of spectroscopic methods for authentication

In the first part of this study, performances of two common spectroscopic techniques, fluorescence and mid-IR, in authentication studies of oils are compared by using data sets from 4 cold pressed oils, pumpkin seed, grape seed, black cumin and sesame oils. Statistical parameters of OPLS-DA classification and PLS regression models are listed in Tables 1 and 2, respectively.

OPLS-DA models of all seed oil samples using both spectroscopic methods provided clear separation of pure and adulterated samples located in the left (negative) and right (positive) side of the first latent variable (LV1) of the score plots, respectively (Fig. 2).

In the present study, the most successful OPLS-DA and PLS regression models are obtained for pumpkin seed oil authentication with both spectroscopic methods compared to other seed oils. OPLS-DA model for each technique is constructed with similar statistical features as pre-processing SNV:FD, LVs: 1 + 4, R^2_{cal}: 0.98, R^2_{cv}: 0.44 for mid-IR spectroscopy and pre-processing FD, LVs:1 + 5, R^2_{cal}:0.87, R^2_{cv}: 0.48 for fluorescence spectroscopy. Moreover, their CC% as well as sensitivity, specificity, precision as shown in Table 1 are identical for both calibration (100%) and external validation models (96%, 100%, 95%, 80%), respectively. OPLS-DA score plots of each technique also provide clear differentiation between pure and adulterated pumpkin seed oil samples with respect to LV1 (Fig. 2a and e). The VIP values in the fingerprint region of the mid-IR (Fig. S4a) and 300–500 nm of fluorescence (Fig. S4b) are found significant for separation of pure and adulterated samples.

In the literature, only a recent study regarding the authentication of pumpkin seed oil with sesame seed oil was found and 100% accuracy level was obtained for differentiation of pumpkinseed and sesame oils (Irnawati et al., 2020). There is also another study that aimed to classify pumpkin seed oils in terms of quality rather than authentication with different spectroscopic techniques as UV–Vis, NIR and FTIR spectroscopy (Lankmayr et al., 2004).

As a quantitative approach, PLS regression was used with the data from both spectroscopic techniques to determine the limit of detection for adulteration. Quantification of adulterant level (0–50% v/v) of each sample was also accomplished with this analysis. PLS regression plots and statistical outputs are given in Fig. 3 and Table 2, respectively. In PLS regression, both models are pre-processed with the same statistical tool as OSC:SNV:FD and almost identical statistical performances such as R^2 of 0.99, and close RPD (9.14 and 9.28) and low error values of the techniques were obtained (Table 2). It could be also seen that both FTIR and fluorescence spectroscopy have the same limit of detection (%1 > v/v) according to Fig. 3a and e, respectively. In the light of these, it could be concluded that both techniques are successful in qualitative and quantitative authentication of pumpkin seed oils.

Grape seed oil samples were authenticated perfectly with 100% CC %, sensitivity specificity and precision with calibration models of both spectroscopic techniques (Table 1). For validation models, CC% for mid-IR (96%) was found higher than the one for fluorescence spectroscopy (83%). The OPLS-DA models for SD of FTIR and WDTs: SD of fluorescence were built with 1 predictive and 3 orthogonal components and 1 predictive and 6 orthogonal components, respectively. First LVs explained 58% and 14% of the total variations of OPLS-DA models of mid-IR data (Fig. 2b) and fluorescence spectroscopy (Fig. 2f), orderly. Other statistical parameters of grape seed oil for these models were similar in terms of R^2 values (Table 1). The VIP values of the models indicated that 2800–3000 cm^{-1} region and a peak around 1743 cm^{-1} along with fingerprint region of mid-IR spectra (Fig S5a) and 300–500 nm and 600–700 nm of fluorescence spectra (Fig. S5b) were the most influential wavelengths and wavenumbers which caused differentiation of pure and adulterated samples, respectively.

PLS regression models for grape seed oils were built by applying pre-treatments of OSC: FD and OSC: SNV to mid-IR and fluorescence spectral data, respectively. The PLS model of mid-IR data (Fig. 3b) were built with 4 LVs with high regression coefficient for both calibration (0.99) and validation (0.98) data sets with low error values as 1.61% and 2.87% for calibration and prediction, respectively (Table 2). In addition, limit of adulteration detection was found as ≥ 5% for grape seed oil by mid-IR spectroscopy (Fig. 3b) with a high RPD value (5.97) and robust slope (0.99) that show the validity of the PLS model (Table 2). Fluorescence spectroscopy was also used in quantification purposes. Three component PLS regression model for fluorescence spectral data pre-processed with OSC:SNV revealed robust prediction ability with R^2 value 0.96 for both calibration and external validation. However, higher error values with lower RPD value were obtained for fluorescence models of grape seed oils compared to mid-IR models (Table 2). This is also supported with the higher detection limit (≥10%) of the fluorescence PLS model (Fig. 3f). In the literature, there are quite limited number of studies about grape seed oil authentication with any of these spectroscopic methods and the studies use only single method focusing on different adulterants. In one study, adulteration of cold pressed grape seed oil with refined soybean oil was investigated by reflectance mid-IR spectroscopy with a detection limit < 0.59% and R^2 > 0.99 in cross-

Table 1
Statistical parameters of OPLS-DA calibration and validation models of pure and adulterated seed oils with spectroscopic methods.

Seed oils[1]	Techniques	Specifications[2]	Model[3]	%CC	Sensitivity	Specificity	Precision
PuSOs	Mid-IR	Pre-treatment: SNV:FD, LVs:1 + 4, R^2_{cal}:0.98, R^2_{cv}:0.44	Cal	100	100	100	100
			Val	96	100	95	80
	Fluorescence	Pre-treatment: FD, LVs:1 + 5, R^2_{cal}:0.87, R^2_{cv}:0.48	Cal	100	100	100	100
			Val	96	100	95	80
GSOs	Mid-IR	Pre-treatment: SD, LVs:1 + 3, R^2_{cal}:0.99, R^2_{cv}:0.33	Cal	100	100	100	100
			Val	96	100	95	80
	Fluorescence	Pre-treatment: WDTs:SD, LVs:1 + 6, R^2_{cal}:0.98, R^2_{cv}:0.53	Cal	100	100	100	100
			Val	83	57	94	80
BSOs	Mid-IR	Pre-treatment: FD, LVs:1 + 5, R^2_{cal}:0.99, R^2_{cv}:0.40	Cal	100	100	100	100
			Val	92	80	95	80
	Fluorescence	Pre-treatment: WDTs: FD, LVs:1 + 5, R^2_{cal}:0.98, R^2_{cv}:0.16	Cal	100	100	100	100
			Val	92	100	90	60
SSOs	Mid-IR	Pre-treatment: SD, LVs:1 + 3, R^2_{cal}:0.99, R^2_{cv}:0.42	Cal	100	100	100	100
			Val	92	80	95	80
	Fluorescence	Pre-treatment: WDTs: SD, LVs:1 + 7, R^2_{cal}:0.99, R^2_{cv}:0.31	Cal	100	100	100	100
			Val	92	80	95	80

[1] PuSOs: pumpkin seed oils, GSOs: grape seed oils, BSOs: black cumin seed oils, SSOs: sesame seed oils, [2]FD: first derivative, SD: second derivative, SNV:FD: combination of standard normal variate and first derivative, WDTs:FD: combination of wavelet denoising techniques and first derivative, WDTs:SD: combination of wavelet denoising techniques and second derivative [3]Models for each oil and each technique consist of 47 samples for calibration (Cal) and 24 samples for external validation (Val).

Table 2
Statistical parameters of PLS regression models for prediction of various seed oils adulteration with spectroscopic methods.

Seed oils[1]	Techniques	Pre-treatment[2]	LVs	R^2_{cal}	R^2_{cv}	R^2_{pred}	RMSEC	RMSECV	RMSEP	RPD	Slope
PuSOs	Mid-IR	OSC:SNV:FD	3	0.99	0.99	0.99	1.13	2.83	1.87	9.14	0.99
	Fluorescence	OSC:SNV:FD	3	0.99	0.99	0.99	1.25	1.70	1.90	9.28	0.99
GSOs	Mid-IR	OSC:FD	4	0.99	0.95	0.98	1.67	5.55	2.87	5.97	0.99
	Fluorescence	OSC:SNV	3	0.96	0.95	0.96	3.61	3.80	3.37	5.08	0.96
BSOs	Mid-IR	OSC:SNV:FD	2	0.99	0.98	0.99	1.27	2.94	2.08	8.21	0.99
	Fluorescence	OSC	4	0.99	0.99	0.99	0.96	3.73	1.21	14.11	0.99
SSOs	Mid-IR	OSC:FD	3	0.99	0.96	0.98	1.37	4.81	2.60	6.57	0.99
	Fluorescence	OSC:SNV	3	0.98	0.97	0.96	1.31	1.35	1.37	12.44	0.98

[1] PuSOs: pumpkin seed oils, GSOs: grape seed oils, BSOs: black cumin seed oils, SSOs: sesame seed oils, [2] OSC: orthogonal signal correction, OSC:FD: combination of orthogonal signal correction and first derivative, OSC:SNV: combination of orthogonal signal correction and standard normal variate, OSC:SNV:FD: combination of orthogonal signal correction, standard normal variate, and first derivative.

validation (Akin et al., 2019). In another study, synchronous fluorescence spectroscopy was used with a determination level < 0.55% for blending with refined soybean oil (Elmas et al., 2019).

Score plots of OPLS-DA models constructed with FD of FTIR and WDTs:FD of fluorescence spectra are shown in Fig. 2c and g, respectively for black cumin seed oils. In both techniques, pure vs adulterated samples are clearly separated from each other according to LV1. A clear separation is obtained between pure and adulterated samples as calibration set (100%) and external validation set (92%) in the same rate for both techniques (Table 1). The similar differentiation pattern for mid-IR and fluorescence spectral data is also visualized in the Fig. 2c and g, orderly. Both OPLS-DA models were constructed with the same number of LVs with similar R^2_{cal} values. The VIP values of the models revealed the significant contribution of the specific band patterns. For the mid-IR spectral differentiation (Fig. S6a), the highest VIP values are found around 1800–1700 cm^{-1} (carbonyl C═O stretching vibration) and approximately 1200–1000 cm^{-1} (C—O stretching vibration) regions. For fluorescence (Fig. S6b), the same parameters are determined between 450 and 700 nm.

PLS regression models of black cumin seed oils with mid-IR and fluorescence spectra are presented in Fig. 3c and g, respectively. Comparable statistical evaluation is shown in Table 2. It is found that fluorescence and mid-IR spectroscopy have similar performances for prediction of adulteration levels for black cumin oils. Statistical model (Table 2) developed with 2 LVs after 3 pre-treatment of FTIR spectral data (OSC:SNV:FD) whereas 4 LVs with single pre-treatment (OSC) are required for fluorescence data. R^2 values of each model are high and close to each other. With fluorescence data, lower error values except RMSECV are obtained compared to mid-IR data which also explain higher RPD value of fluorescence evaluation. Limit of detection was found as > 5% and ≥ 5% for FTIR and fluorescence, respectively. Few studies existing about black cumin seed oil authentication in literature used different adulterants than the current study. Authentication of black cumin seed oil in binary and ternary mixtures with corn oil and soybean oil was investigated by using FTIR with high R^2 (0.99) and low error values (0.47–1.34% v/v) (Rohman & Ariani, 2013). In another study, FTIR and synchronous fluorescence spectroscopy were used in detection of adulteration of cold pressed black cumin seed oil with soybean oil (Arslan et al., 2019). It was found that fluorescence spectroscopy (below 5%) was more successful than mid-IR (below 8.56%) in terms of limit of detection (Arslan et al., 2019). These results are in accordance with the findings of the present study using a different adulterant (sunflower).

Sesame seed oil samples were also authenticated with two spectroscopic techniques. OPLS-DA score plots reveal the similar and perfect differentiation pattern of both methods with respect to LV1 (Fig. 2d and h). This is also supported with the same classification ability between pure and adulterated sesame seed oil samples with 100% and 92% CC% of calibration and validation sets, respectively (Table 1). Sensitivity, specificity and precision for validation set for both techniques are calculated as 80%, 95% and 80%, in order. Other statistical parameters as R^2_{cal} and R^2_{cv} are also similar for both models. The VIP values (Fig. S7a) indicated that 1267–1209 cm^{-1} (stretching of -C—H, bending in CH_2), 1121–1045 cm^{-1} (-C—O esters, stretching) and 896–814 cm^{-1} (–CH_2 wagging) wavelengths are the most important in differentiation with respect to FTIR spectra (Guillén & Cabo, 1997; Ozulku et al., 2017). The same wavenumbers of fluorescence spectra (Fig. S7b) for the previous seed oils are also effective for sesame seed oil.

Fluorescence spectroscopy (Fig. 3h) is more successful than mid-IR (Fig. 3d) in determination of adulterant level of sesame seed oil according to PLS regression analysis. PLS model of OSC:FD mid-IR spectra consisted of 3 LVs along with high $R^2 \geq 0.96$ and relatively low error values (1.37–4.87% v/v) with approximate RPD value of 6.57 (Table 2). However, fluorescence spectroscopy possessed lower and close error values (1.31–1.37% v/v) with higher RPD value (12.44). These findings are also supported in favor of fluorescence spectroscopy (>1% v/v) with lower limit of detection than mid-IR (≥5% v/v) as can be seen in Fig. 3h and d, respectively. Scientific literature indicated that authentication studies about sesame oil mostly performed with mid-IR spectroscopy than fluorescence and relatively few studies exist in fluorescence about authentication of this oil. In addition, there is no comparable study in the literature about sesame oil by using these methods. Some studies aimed at detection of a single adulterant whereas some were performed with multiple. In one study, FTIR was used to determine corn oil adulteration of sesame seed oil successfully with high R^2 of 0.99 and low error values of 0.53% and 1.31% v/v (Fadzlillah et al., 2014). In another study, FTIR was used to detect adulteration with 3% (w/w) or more of various oils, including rapeseed, soybean, palm and peanut oils (Deng et al., 2012). Potential of mid-IR spectroscopy in authentication was also proven with detection of different adulterants mixed into sesame oil as three kinds of edible oils (corn, sunflower, blended oil), and sesame oil flavor (Zhao et al., 2015) as well as hazelnut, canola, and sunflower oils (Ozulku et al., 2017). In a recent work, mid-IR spectroscopy was used to determine presence of four possible adulterants as corn, peanut, soybean and sunflower oils in chia and sesame oils with acceptable prediction errors ranging between 1% and 5% (Rodríguez, Gagneten, Farroni, Percibaldi, & Buera, 2019). Recently, excitation-emission matrix fluorescence spectroscopy was used to determine the authenticity and adulteration of sesame oil (Yuan et al., 2020). 3D fluorescence spectroscopy and convolutional neural network was also applied for the same purpose (Wu, Zhao, Tian, Shang, & Liu, 2020).

For the most of the examined oils of this study, a comparison between the performances of mid-IR and fluorescence spectroscopy is provided for the first time in terms of their adulteration with sunflower oil. Overall, both spectroscopic methods provided quite close results for differentiation of adulterated and pure oils with similar detection levels. OPLS-DA and PLS regression methods are also quite effective in the analysis of all spectroscopic data.

3.3. Prediction of chemical parameters

Basic chemical characteristics of the studied seed oils were

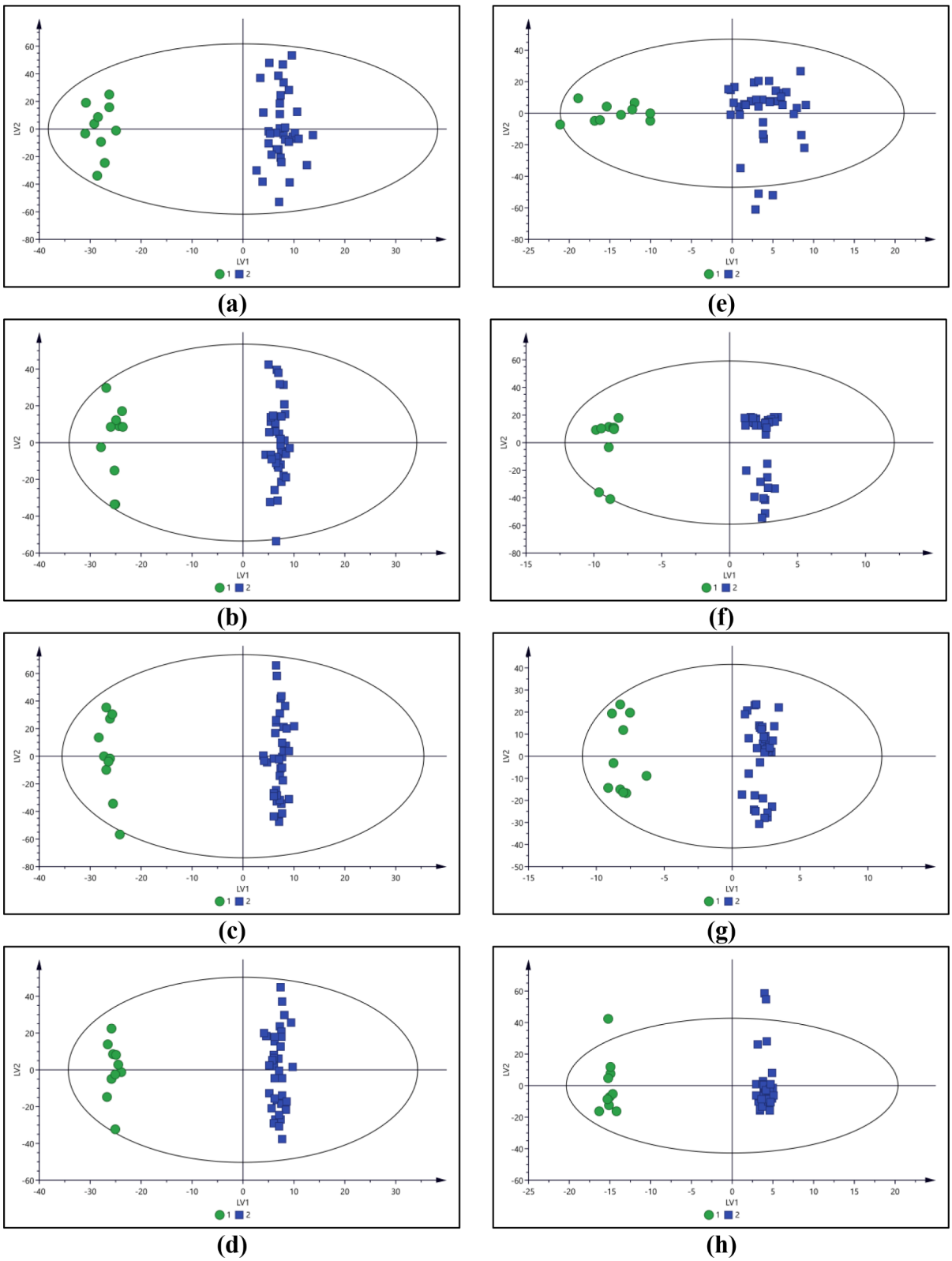


Fig. 2. OPLS-DA score plots of pure and adulterated pumpkin seed oil (a) and (e), grape seed oil (b) and (f), black cumin seed oil (c) and (g) and sesame seed oil (d) and (h) samples from mid-IR and fluorescence spectral data, respectively (class 1: pure seed oil samples class 2: adulterated seed oil samples (1–50% v/v)).

determined to obtain general information about the samples (Table S1). Average free fatty acid values of grape seed, black cumin, sesame seed and pumpkin seed oils were determined as 1.81%, 7.34% 0.79% and 0.72%, respectively. Grape seed, black cumin, sesame seed and pumpkin seed oils have average TPC content in terms of mg/kg as 76.35, 459.27, 63.00 and 71.80, in order. The major fatty acid profiles were similar in the studied oils except their quantity. In grape seed oil, average palmitic acid (8.63%), stearic acid (4.55%), oleic acid (19.79%), linoleic acid (66.01%), SFAs (13.49%), MUFAs (20.29%), PUFAs (66.22%) are found in accordance with the values from literature (Dabetic et al., 2020). The

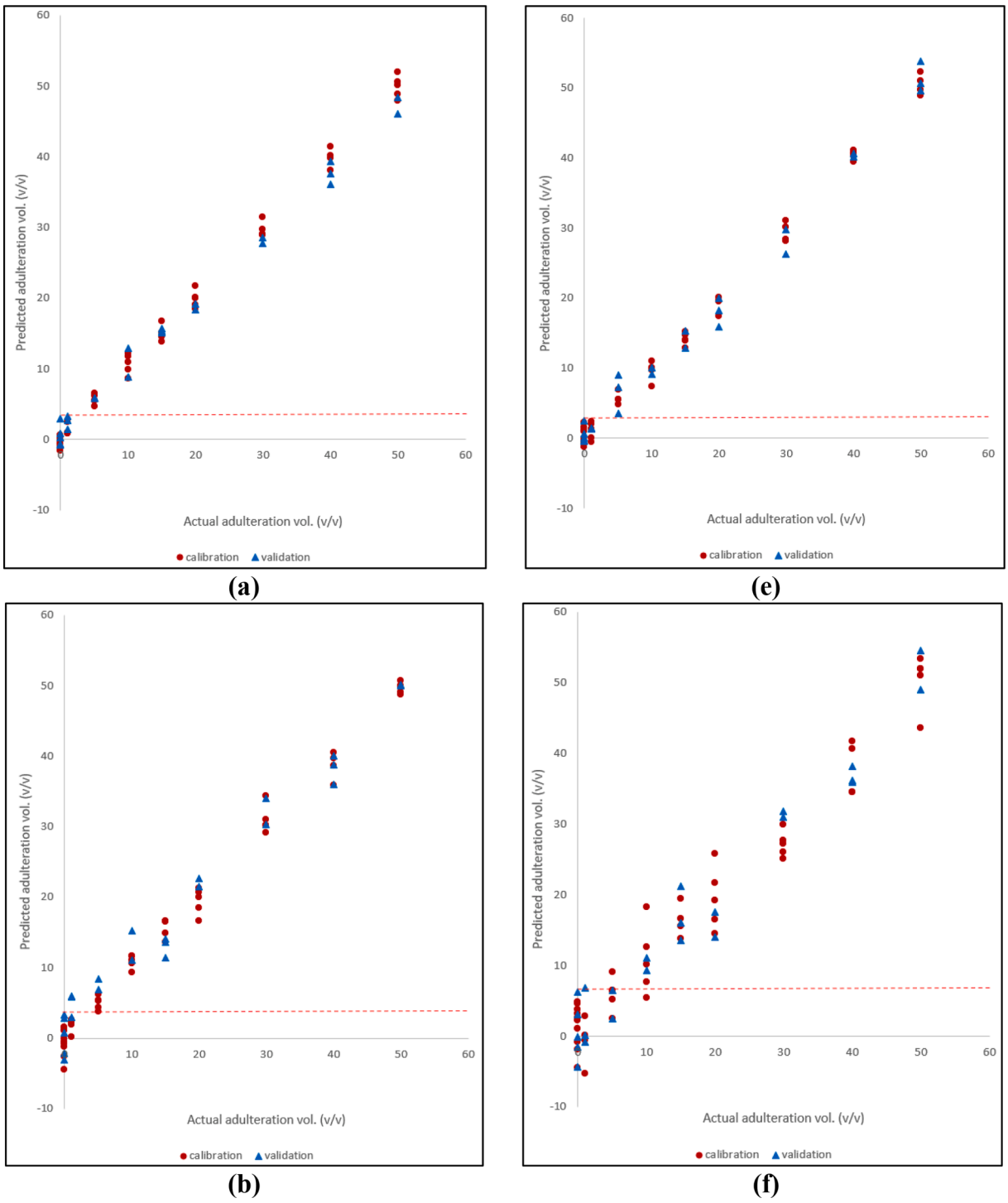


Fig. 3. PLS regression plots of actual versus predicted adulteration volume of pumpkin seed oil (a) and (e), grape seed oil (b) and (f), black cumin seed oil (c) and (g) and sesame seed oil (d) and (h) samples from mid-IR and fluorescence spectral data, respectively (red dashed line: the threshold line for limit of adulteration detection). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

same parameters for black cumin seed oil were determined as palmitic acid (11.95%), stearic acid (3.52%), oleic acid (25.36%), linoleic acid (55.01%), SFAs (15.98%), MUFAs (26.36%), PUFAs (57.66%) and this fatty acid profile is also similar to a previous study (Kiralan, Çalik, Kiralan, Özaydin, Özkan, & Ramadan, 2019). Other seed oils as sesame and pumpkin are found similar to each other with respect to fatty acid profiles and also free fatty acid and TPC values. Average SFAs, MUFAs, PUFAs for sesame and pumpkin seed oils were determined as 16.04% and 19.36%, 39.62% and 34.89%, 44.33% and 45.19%, respectively. The results for the sesame oil are in agreement with the literature (Hama, 2017). For pumpkin seed oils, results are comparable with a previous study (Neđeral, Škevin, Kraljić, Obranović, Papeša, & Batal-jaku, 2012).

The chemical characteristics of analyzed seed oils are predicted from mid-IR and fluorescence spectra of pure oils using multivariate statistical analysis, PLS regression, and the ranges of these chemical properties

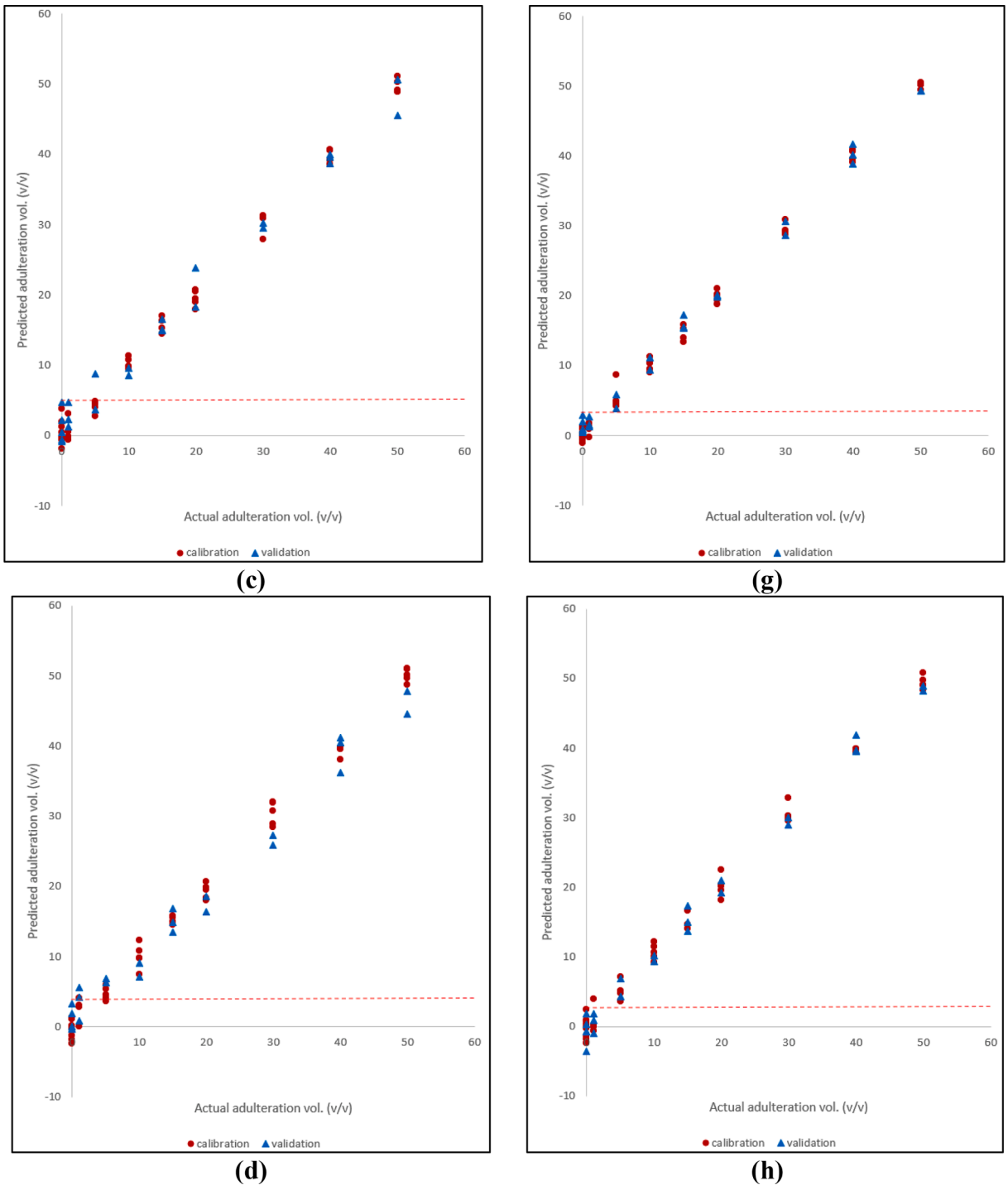


Fig. 3. (*continued*).

are listed in Table 3. Since it is essential to use a large data set as much as possible to obtain accurate prediction models, two additional oil types, pomegranate seed and olive oils, from our previous studies are also included to the data set to increase the number of the samples so that the capacity, validity and inclusiveness of prediction models could be enhanced. Number of the samples for each oil is 15; therefore, a data set containing 90 samples were used in generating the PLS prediction models. 2/3 of these samples are used as calibration data set and the rest are included to external validation set. While prediction studies in the literature are mostly based on the statistical models for a single type of oil (Karunathilaka, Mossoba, Chung, Haile, & Srigley, 2017; Uncu et al., 2019; Uncu & Ozen, 2015) data from different types of oils are combined here to test if it is possible to obtain a model that can estimate these chemical parameters regardless of the type of the oil. While prediction studies are more common with mid-IR spectroscopy, fluorescence spectroscopy has been used less for this purpose (Aït-Kaddour et al., 2016; Guzmán et al., 2015; Ntakatsane et al., 2014; Sikorska et al., 2019). In addition, it was not encountered any study in the literature regarding the comparison of these two techniques in any prediction study. Statistical measures of developed PLS regression models from mid-IR and fluorescence spectral data are shown in Table 3. Models having high R^2 (R^2_{cal}, R^2_{cv}, R^2_{pred}) values with low RMSE (RMSEC,

Table 3
Comparison of statistical parameters for PLS regression models of chemical parameters with fluorescence and mid-IR spectroscopy.

Parameter	Range	Techniques	Pre-treatment	LVs	$R^2_{cal.}$	$R^2_{cv.}$	$R^2_{pred.}$	RMSEC	RMSECV	RMSEP	RPD	Slope
FFA[1]	0.27–11.70	Fluorescence	OSC	3	0.98	0.96	0.92	0.47	0.65	0.61	3.33	0.98
		Mid-IR	FD	3	0.97	0.95	0.96	0.48	0.61	0.58	4.78	0.97
TPC[2]	38.46–653.81	Fluorescence	OSC	3	0.97	0.93	0.96	29.92	45.75	30.20	4.70	0.97
		Mid-IR	OSC	4	0.96	0.93	0.92	34.94	37.90	40.14	3.46	0.96
C14:0[3]	0.00–0.17	Fluorescence	OSC	3	0.98	0.97	0.98	0.01	0.01	0.01	6.44	0.98
		Mid-IR	OSC	3	0.97	0.95	0.99	0.01	0.01	0.01	8.19	0.97
C16:0[4]	2.52–15.85	Fluorescence	OSC	6	0.96	0.94	0.94	0.77	0.92	0.91	3.96	0.94
		Mid-IR	SD	4	0.99	0.98	0.96	0.77	0.92	0.68	5.29	0.99
C16:1[5]	0.00–1.16	Fluorescence	OSC	5	0.99	0.99	0.99	0.03	0.04	0.02	11.28	0.99
		Mid-IR	SD	4	0.99	0.92	0.95	0.03	0.09	0.06	4.30	0.99
C17:0[6]	0.04–0.19	Fluorescence	OSC	8	0.98	0.94	0.97	0.01	0.01	0.01	5.58	0.98
		Mid-IR	FD	8	0.99	0.76	0.56	0.01	0.02	0.02	1.51	0.99
C17:1[7]	0.00–0.29	Fluorescence	OSC	4	0.99	0.99	0.99	0.01	0.01	0.01	10.49	0.99
		Mid-IR	SD	5	0.99	0.89	0.87	0.01	0.03	0.05	1.90	0.99
C18:0[8]	1.88–7.38	Fluorescence	OSC	6	0.98	0.96	0.96	0.26	0.34	0.36	4.62	0.98
		Mid-IR	FD	5	0.98	0.94	0.95	0.21	0.45	0.37	4.34	0.98
C18:1n9c[9]	4.06–72.47	Fluorescence	OSC	4	0.98	0.98	0.99	2.80	3.28	2.44	8.32	0.98
		Mid-IR	FD	3	0.99	0.99	0.99	1.64	2.28	2.01	10.22	0.99
C18:2n6c[10]	4.14–67.90	Fluorescence	OSC	4	0.97	0.94	0.97	4.15	6.39	4.28	5.30	0.97
		Mid-IR	SD	3	0.99	0.99	0.99	1.22	2.90	2.37	9.51	0.99
C20:0[11]	0.15–0.65	Fluorescence	OSC	3	0.97	0.95	0.93	0.03	0.03	0.04	3.94	0.97
		Mid-IR	SD	5	0.99	0.95	0.94	0.01	0.05	0.04	3.45	0.99
C18:3n3[12]	0.14–2.55	Fluorescence	OSC	8	0.94	0.89	0.87	0.07	0.11	0.10	2.81	0.94
		Mid-IR	OSC	4	0.94	0.80	0.88	0.10	0.25	0.10	2.73	0.94
C20:1[13]	0.00–0.35	Fluorescence	OSC	6	0.97	0.95	0.96	0.02	0.03	0.02	5.14	0.97
		Mid-IR	SD	4	0.99	0.96	0.95	0.01	0.03	0.02	4.64	0.99
C20:2[14]	0.00–2.62	Fluorescence	OSC	3	0.98	0.97	0.97	0.13	0.17	0.14	5.92	0.98
		Mid-IR	FD	4	0.96	0.89	0.97	0.18	0.27	0.16	5.68	0.96
C22:0[15]	0.00–0.20	Fluorescence	OSC	4	0.92	0.86	0.84	0.02	0.02	0.02	2.49	0.92
		Mid-IR	SD	5	0.98	0.71	0.72	0.01	0.04	0.03	1.91	0.98
C20:3n6[16]	0.00–0.11	Fluorescence	OSC	6	0.98	0.97	0.96	0.01	0.01	0.01	4.79	0.98
		Mid-IR	FD	1	0.99	0.98	0.99	0.01	0.01	0.01	7.60	0.99
C20:4n6[17]	0.00–0.71	Fluorescence	OSC	3	0.99	0.98	0.97	0.03	0.03	0.04	5.44	0.98
		Mid-IR	OSC	3	0.92	0.89	0.90	0.03	0.03	0.06	3.27	0.92
C18:3n5(c, t, c)[18]	0.00–81.12	Fluorescence	OSC	6	0.97	0.96	0.95	5.01	6.18	6.92	4.15	0.97
		Mid-IR	SD	1	0.99	0.99	0.99	1.14	1.34	1.29	21.60	0.99
C18:3n5(c, t, t)[19]	0.00–10.42	Fluorescence	OSC	6	0.95	0.93	0.96	0.61	0.78	0.45	4.36	0.95
		Mid-IR	SD	3	0.99	0.96	0.98	0.28	0.68	0.36	5.55	0.99
C18:3n5(t, t, c)[20]	0.00–4.07	Fluorescence	OSC	6	0.86	0.78	0.82	0.32	0.38	0.24	1.92	0.86
		Mid-IR	FD	6	0.98	0.89	0.94	0.11	0.25	0.18	3.80	0.98
SFAs[21]	4.87–19.99	Fluorescence	OSC	6	0.97	0.96	0.96	0.79	0.93	1.05	4.41	0.97
		Mid-IR	FD	4	0.99	0.98	0.99	0.47	0.68	0.40	11.49	0.99
MUFAs[22]	4.06–74.18	Fluorescence	OSC	4	0.98	0.98	0.99	2.90	3.39	2.51	8.22	0.98
		Mid-IR	FD	3	0.99	0.99	0.99	1.85	2.51	1.69	12.21	0.99
PUFAs[23]	8.72–90.80	Fluorescence	OSC	4	0.98	0.97	0.99	3.53	4.11	3.19	7.55	0.98
		Mid-IR	FD	3	0.99	0.99	0.99	1.42	2.22	1.43	16.83	0.99

[1] free fatty acid,[2]total phenolic content,[3]mystric acid, [4]palmitic acid, [5]palmitoleic acid, [6]heptadecanoic acid, [7]*cis*-10-heptadecanoic acid, [8]stearic acid, [9]oleic acid, [10]linoleic acid, [11]arachidic acid, [12]linolenic acid, [13]*cis*-11-eicosenoic acid, [14]*cis*-11,14-eicosadienoic acid, [15]behenic acid, [16]*cis*-8,11,14-eicosatrienoic acid, [17]arachidonic acid, [18]punicic acid, [19]α-eleostearic acid, [20]catalpic acid, [21]saturated fatty acids, [22]monounsaturated fatty acids, [23]polyunsaturated fatty acids.

RMSECV, RMSEP) with respect to measured concentration ranges, high RPD values and slopes close to 1 show the reliability and the robustness of the constructed models (Munawar, von Hörsten, Wegener, Pawelzik, & Mörlein, 2016).

The best transformation for all PLS regression models of fluorescence spectral data is OSC. FFA and TPC are predicted from fluorescence spectra with models having 3 LVs. R^2 values are quite high for these models and their ranges are 0.92–0.98 for FFA and 0.93–0.97 for TPC. Slopes (0.97 and 0.98) of the calibration curves for these parameters are very close to 1. While FFA range of the samples are in 0.27–11.70%, RMSE values vary between 0.47 and 0.61. RMSE values for TPC are 29.92–45.75 for a measurement range of 38.5–653.5 mg/kg. These measures are indications of very good prediction models for FFA and TPC obtained from fluorescence spectra. In a study from the literature, acidity and oxidation indices (peroxide value, K values) of the olive oils were estimated from fluorescence spectral data with PLS and the best result was obtained for K270 value (Guzmán et al., 2015). Front face fluorescence spectroscopy was also used in prediction of some oxidation parameters along with tocopherol, carotenoid and pheophytin content of cold pressed rapeseed oil (Sikorska et al., 2019).

In general, accurate estimations of individual fatty acids and total saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA) are also acquired with the analysis of fluorescence spectroscopy data with PLS (Table 3). The worst models are obtained for linolenic (R^2 values of 0.87–0.94, RPD: 2.81), catalpic (R^2 values of 0.78–0.86, RPD: 1.92) and behenic (R^2 values of 0.84–0.92, RPD: 2.49) acids. Studied oils have relatively lower amounts of these fatty acids with a narrow concentration range. As our experience indicates, PLS regression models, in general, result in more accurate models when the measured concentration ranges of the constituents are wide. According to studies in the literature, SFA compositions of butterfat and beef were successfully determined using front face fluorescence spectroscopy while the same success was not obtained for UFA in both studies (Aït-Kaddour et al., 2016; Ntakatsane et al., 2014). However, prediction of both SFA and UFA were achieved with reliable and robust models in the current study.

Good PLS prediction model with high R^2 values (0.95–0.97) and low RMSE of 0.48–0.61% was obtained for FFA using mid-IR spectra. RPD value (4.78) of this model is high enough for reliability. Same conclusion could be also reached for TPC model having R^2 of 0.92–0.96 and RPD of 3.46 with a slope of 0.97. Calibration R^2 values of the models for all fatty

acids are quite high and R^2 0.94 of linoleic acid is the lowest one. However, external validation R^2_{pred} of heptadecanoic (0.56) and behenic (0.72) acids are lower than 0.8 and *cis*-10-heptadecenoic acid and linolenic acids have R^2_{pred} of lower than 0.9. R^2 values of 0.8–0.9 provide approximate predictions and are still acceptable. RPD values of the models having R^2_{pred} lower than 0.8 is also lower compared to others. Successful estimation of FFA, TPC and fatty acid profiles of olive oils (Gurdeniz, Ozen, & Tokatli, 2010; Uncu & Ozen, 2015) and PUFA composition of marine oils (Vongsvivut, Heraud, Zhang, Kralovec, McNaughton, & Barrow, 2012) are the several examples of the use of mid-IR spectroscopy in prediction studies from the literature. More could be also found in the literature; however, it was not encountered any investigation regarding the application of this technique in determination of chemical measures as FFA, TPC and fatty acid profile for the combination of various cold pressed oils.

It could be concluded that prediction models constructed using mid-IR and fluorescence data provide, in general, comparable results. Models are especially very good at estimating the amounts of fatty acids with higher concentrations and having large concentration variations such as palmitic, oleic and linolenic acids. Less success was obtained with linolenic, behenic and catalpic acid predictions with both spectroscopic techniques. Although PLS regression models of both mid-IR and fluorescence spectroscopy resulted in good predictions for *cis*-10-heptadecanoic, *cis* 11, 14 eicosadienoic, *cis* 8, 11, 14 eicosatrienoic, punicic, α-eleostearic and catalpic acids, these fatty acids exist in only one type of oil. Consequently, models for them should be used with caution. However, high prediction power of these models are still the indications of the capacity of these spectroscopic methods in prediction of the amounts of these fatty acids.

4. Conclusions

In the first part of the present study, it could be concluded that both mid-IR and fluorescence techniques are quite successful and comparable in determination of mixtures of sunflower oil with different cold pressed seed oils. Among the studied oils, it was found that adulteration of pumpkin seed oil could be detected with the lowest threshold (>%1 v/v) for both spectroscopic techniques followed by sesame seed oils with fluorescence (>1%) and mid-IR spectroscopy (≥5%). However, mid-IR spectroscopy (≥5%) worked better than fluorescence (≥10%) for grape seed oils and limit of detection for black cumin seed oil was found quite similar for both mid-IR (>5%) and fluorescence (≥5%) techniques.

In the second part, predictability of some important chemical parameters of different edible oils in a single comprehensive model was tested by both spectroscopic approaches. The outputs of the PLS regression models for each technique revealed that FFA, TPC and major fatty acid profile could be determined robustly with these techniques. As a result, both spectroscopic techniques have similar advantages of rapid analysis, cost and ease of use and they could be used in quick detection of adulterated minor oils and quantification of important chemical characters of these oils regardless of oil type. Therefore, one or the other could be used for authentication and prediction purposes as an alternative to tedious wet chemical techniques.

CRediT authorship contribution statement

Ilgin Dogruer: Formal analysis, Investigation, Methodology, Writing - original draft. **H. Hilal Uyar:** Formal analysis, Investigation, Methodology, Writing - original draft. **Oguz Uncu:** Data curation, Formal analysis, Investigation, Methodology, Supervision, Writing - original draft, Writing - review & editing. **Banu Ozen:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2020.128815.

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