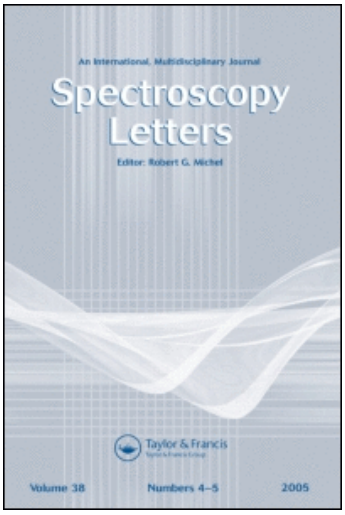

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Partial Least Squares Processing of Near-Infrared Spectra for Discrimination and Quantification of Adulterated Olive Oils

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Abstract: A new processing based on partial least squares (PLS) algorithm for the discrimination and determination of adulterants in pure olive oil using near-infrared (NIR) spectroscopy has been introduced. The 280 adulterations of olive oil with corn oil ($n = 70$), hazelnut oil ($n = 70$), soya oil ($n = 70$), and sunflower oil ($n = 70$) were prepared, and their NIR spectra in the region 12,000–4550 cm^{-1} were collected. The 70 spectra of each adulteration of olive oil were divided into

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two sets, 50 spectra for a calibration set and 20 spectra for a prediction set. The spectra of a total calibration set (n = 200) were separated into individual adulterant calibration sets (n_i = 50, i = corn, hazelnut, soya, sunflower) by using discriminant PLS (DPLS) analysis, and PLS calibration models for the quantification of adulterants with corn oil, hazelnut oil, soya oil, or sunflower oil were developed separately. A variety of wavelength ranges and data pretreatments were examined for obtaining optimal results for the discrimination and quantification objects. Four PLS models for differentiating the adulterant types were evaluated by classifying the NIR spectra of a total prediction set (n = 80) into known adulterant types. Then, these known adulterant spectra were analyzed by the PLS calibration models developed for each type to determine the content of an adulterant in pure olive oil. The results of evaluation revealed that the processing reported in this article works excellently for the discrimination and quantification of the adulterations of olive oil.

Keywords: Adulterated olive oil, discriminant partial least squares, discrimination, near-infrared spectroscopy, partial least squares regression, quantification

INTRODUCTION

There are three types of fats, saturated, polyunsaturated, and mono-unsaturated fats, in which different types of fatty acid functional groups are involved.[1] Only the polyunsaturated and mono-unsaturated fats have the excellent potential to reduce the blood cholesterol levels by preventing the oxidation of low-density lipoprotein cholesterol (LDL). LDL is considered as the bad cholesterol that leads to coronary heart disease.[1] Because olive oil is a mono-unsaturated fat and has the above potential, highly pure olive oil is desired. High-purity olive oil is very expensive in comparison with the low-purity oil. However, the most serious problem for consumers originates from the illegal activity of greedy suppliers who attempt to profit by producing adulteration in olive oil. The adulteration involves the dilution of pure olive oil with less expensive oil, such as seed oils and vegetable oils.[2–9] It is not easy to identify the adulterant type and determine the adulteration level for the final product of an olive oil blend. Consequently, ensuring the authenticity for olive oil has long been a subject of considerable importance in food analysis.

Generally, methods of measuring physical properties of oil samples such as refractive index, density, viscosity, and iodine value test have been used for classifying the adulterant types in olive oil.[10] These methods may result in feasible oil classification but are less accurate than chromatographic and spectroscopic techniques.[5] Therefore, high-performance liquid chromatography (HPLC),[11] gas chromatography (GC),[12,13] ultraviolet spectroscopy, and fluorescence spectroscopy have been employed to detect more precisely the adulterations in olive oil.[10] However, these techniques are costly and time consuming. For these reasons, the use of mid-infrared (MIR) spectroscopy

has been widely used in the examination of olive oil,[2–4,14] especially in the qualitative identification analysis. Unfortunately, all the above methods including some sampling techniques for MIR spectroscopy[14] are destructive techniques for olive oil samples. Moreover, it is often required to add some reagents into the samples for their experiments, and thus, the oil samples examined cannot be put up for sale after the detection.[2,14] Therefore, near-infrared (NIR) spectroscopy has recently received keen interest as a method for detecting the adulteration of olive oil nondestructively, rapidly, and inexpensively.[5–9,20] In addition, the NIR method can easily deal with the large number of samples with reasonable consuming time. It is also a very promising technique for inspecting oil samples at the on-market site because portable NIR spectrophotometers are available. In order to extract useful information from NIR spectra that consists of a number of overlapping bands due to overtones and combination modes, chemometric methods are usually employed for spectral analysis.

For the discrimination subject, principal component analysis (PCA) is generally used for classifying NIR spectra of adulteration of olive oil[5–9] and partial least squares (PLS) regression is a common method for the quantification of adulteration contents in olive oil.[8,9] These two methods have been employed for different subjects to detect the adulterations in olive oil samples. In our previous study, we reported the application of PCA and PLS methods for the detection and quantification of adulteration in olive oil by NIR spectroscopy, respectively. All the obtained results were satisfactory for the adulteration levels of 0–100% w/w.[9]

The purpose of the current study is to develop a new processing for discriminating and quantifying the adulterations in olive oil samples by using only PLS regression. PLS regression is not only employed for the quantitative analysis but also can be used for the discrimination analysis called discriminant PLS (DPLS) method.[15,16] DPLS is an alternative method for PCA in discrimination analysis. It optimizes the fitting and prediction to {0/1} coded membership indicating variables in the development of latent variables.[15,16] Many groups have evaluated the potential of DPLS for the classifications of various samples.[16–19] In the current study, we have developed a PLS process for identifying and quantifying the adulterations in olive oil samples. Four types of seed oils, corn oil, hazelnut oil, soya oil, and sunflower oil, were blended into pure olive oil with the adulteration levels of about 2–50% w/w. This adulteration levels are realistically more than the levels used in our previous study.[9] First, the DPLS is employed to develop DPLS1 models for each adulterant that will be used to identify unknown adulterant types in olive oil samples. Second, we transfer the spectral data of those identified samples into the PLS1 calibration models for those identical adulterant types that were developed for the prediction of adulterant contents in olive oil samples. This processing is straightforward because only

PLSR algorithm is used. We have evaluated this processing by identifying and quantifying a prediction set of adulterated olive oil samples, and excellent results have been obtained.

EXPERIMENTAL

Samples and Measurements

Pure olive oil was purchased from WAKO Pure Chemical Industries, Ltd. (Osaka, Japan). Hazelnut oil was purchased from Aarhus United UK Ltd., (Hull, England), and corn oil, soya oil, and sunflower oil were purchased from local supermarkets. The preparation of samples started from weighing olive oil in a 4-mm quartz cell quantitatively. Then, a small amount of the chosen adulterant was added to the oil, and the mixture was shaken well. The amount of added adulterant was determined by weighing a syringe containing the adulterant before and after injecting the adulterant in the cell. Then, an NIR spectrum in the region 12,000–4550 cm^{-1} was measured for a mixture sample in the measuring cell. All weighing was done by use of a Sartorius (Goettingen, Germany) analytic balance A200S that can measure mass with the accuracy of 0.0001 g. The addition of the chosen adulterant and the collection of NIR spectra were continued until the cell was nearly filled with the oil mixture. The same procedure was repeated for next adulterant type after cleaning and drying the used quartz cell. Totally, 280 adulterations of olive oil mixed with about 2–50% w/w of corn oil (n = 70), hazelnut oil (n = 70), soya oil (n = 70), or sunflower oil (n = 70) were prepared and their NIR spectra were collected. Table 1 summarizes the distribution of concentrations of adulterants in the samples thus prepared.

The NIR measurements were performed using transmittance mode in the region 12,000–4550 cm^{-1} by means of a Bruker (Bruker Optics Inc., Germany) Vector 22/N FT-NIR spectrometer equipped with an InGaAs detector. All the spectral data were collected with a 4 cm^{-1} spectral resolution, and 32 scans were co-added to ensure a sufficient signal-to-noise ratio. The

Table 1. Distribution of contents of adulterants in olive oil samples

Adulterants	Mean (% w/w)	Standard deviation (% w/w)	Maximum (% w/w)	Minimum (% w/w)
Corn oil	24.63	14.29	49.23	2.39
Hazelnut oil	26.83	13.70	49.64	2.08
Soya oil	28.54	12.98	49.57	1.87
Sunflower oil	25.32	12.65	49.70	2.77

temperature of samples was kept at $25 \pm 0.2^{\circ}C$ by using a NESLAB (Karlsruhe, Germany) RTE-111 temperature controller that was connected to a cuvette cell holder.

Data Analysis

The OPUS (ver. 3.1; Bruker Optik GmbH, Germany) program was employed for the spectral data collection. The spectral data obtained were converted into files for the Unscrambler (ver. 7.08; CAMO AS, Trondheim, Norway) program. Discriminant PLS and PLS regression analyses were performed using the Unscrambler. For the discriminant PLS analysis, a value of 1.0 was given to the NIR spectra of an examined adulterant arbitrarily for the dummy variable "species," while a value of 0.0 was yielded to the spectra of other adulterants.[17,18] Next, the PLS1 model was developed for an examined adulterant and tested by identifying the adulterant types for a separated sample set (a prediction set). All samples with a predicted value more than or equal to 0.5 were classified as being members of the examined adulterant type. On the other hand, those with a predicted value lower than 0.5 were classified as not being members of the adulterant type. After the discrimination analysis, separated PLS calibration models for determining the content of each adulterant type in olive oil were developed.

The NIR spectra were subjected to multiplicative scatter correction (MSC), first derivative (5-point Savitsky-Golay filter), and second derivative (5-point Savitsky-Golay filter) before developing PLS models for the discrimination and quntification. Four wavenumber regions (i.e., the 9000–7700, 7700–6000, 6000–4550, and 9000–4550 cm^{-1} regions) were used for building the PLS models. Seventy NIR spectra for each adulterant (i.e., that with corn oil, hazelnut oil, soya oil, or sunflower oil) were divided into two sets, 50 spectra for the calibration set and 20 spectra for the prediction set. All the calibration sets were gathered ($n = 200$) and discriminated into each adulterant type by the discriminant PLS. The PLS calibration models for the quantification of adulterant contents in olive oil were built separately. When four PLS models for discriminating the adulterant types were obtained, these models were evaluated by classifying the NIR spectra of the total prediction set ($n = 80$) into four types of adulterated olive oils. Following the classification of adulterants, the type of adulterants in pure olive oil were revealed, and the concentrations of adulterants can be calculated by using the PLS calibration models developed for each adulterant type. Note that the segment cross-validation was used to validate and find the optimum number of PLS factors for the models used for the discrimination and quantification. The optimum number of PLS factors was selected by considering the factor number at which the lowest root mean squares error of validation (RMSEV) was obtained, and it increased from the next number.

RESULTS AND DISCUSSION

NIR Spectra of Olive Oils Adulterated by Corn Oil, Hazelnut Oil, Soya Oil, or Sunflower Oil

Figure 1 shows four mean NIR spectra in the 12,000–4550 cm^{-1} region of olive oils adulterated by corn oil, hazelnut oil, soya oil, or sunflower oil. The spectra show three major band groups at around 8300, 7100, and 5800 cm^{-1}. The first group consists of bands due to the second overtone of CH stretching modes of the CH_3 and CH_2 groups.[9,14,15] The second one contains bands assigned to the combination modes of the CH stretching and CH deformation vibration modes.[9,14,15] The last band group around 5800 cm^{-1} is composed of bands attributable to the first overtone of CH stretching modes.[9,14,15] It is noted in Fig. 1 that those mean NIR spectra are very similar to each other, and it is not easy to classify the spectra into each adulterant type. Therefore, the discriminant PLS method is applied in the current study to identify unknown adulterations in olive oil samples.

Discriminant PLS Analysis for the Classification of Adulterants in Olive Oil

The statistical results for the discriminant PLS regressions are summarized in Table 2. The discrimination models were developed by use of the four selected spectral ranges and the four spectra types: original and three pretreatment

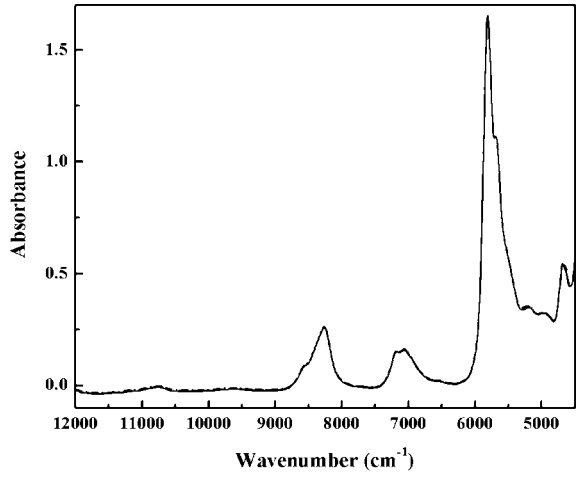

Figure 1. Four mean NIR spectra in the 12,000–4550 cm^{-1} region of olive oils adulterated by corn oil, hazelnut oil, soya oil, or sunflower oil.

Table 2. The statistical results of discriminant PLS regression for classifying the adulterant types in olive oil samples

		Wavenumber regions (cm^{-1})							
		9000–7700		7700–6000		6000–4550		9000–4550	
Adulterants	Data pretreatment	No.[a]	CP%[b]	No.	CP%	No.	CP%	No.	CP%
Corn oil	None	9	98.8	9	98.8	9	98.8	9	97.5
	MSC	8	98.8	8	97.5	9	98.8	9	97.5
	First derivative	7	100.0	8	100.0	8	98.8	7	97.5
	Second derivative	4	100.0	6	100.0	6	100.0	4	98.8
Hazelnut oil	None	6	98.3	9	100.0	9	98.8	9	100.0
	MSC	6	98.3	9	100.0	9	100.0	6	96.7
	First derivative	5	100.0	6	100.0	9	100.0	9	100.0
	Second derivative	4	100.0	7	100.0	8	100.0	7	100.0
Soya oil	None	6	100.0	6	100.0	4	100.0	6	100.0
	MSC	6	100.0	7	100.0	4	100.0	7	100.0
	First derivative	3	100.0	3	100.0	2	100.0	2	100.0
	Second derivative	3	100.0	3	100.0	2	100.0	2	100.0
Sunflower oil	None	6	95.0	6	97.5	5	98.8	6	97.5
	MSC	10	97.5	9	100.0	9	98.8	9	98.8
	First derivative	4	100.0	5	98.8	7	98.8	6	98.8
	Second derivative	5	100.0	7	100.0	7	100.0	6	98.8

PLS, partial least squares; MSC, multiplicative scatter correction.
[a]No. = the number of PLS factors used.
[b]CP% = %correct classification for prediction set.

spectra. In the cases of the discriminant models for corn oil and hazelnut oil adulterations in olive oil, the models using the second derivative spectra in the region 9000–7700 cm^{-1} yield 100% correct classification of the prediction set (%CP) for the lowest number of PLS factor 4 (Table 2). As for the discriminant model for the soya oil adulteration in olive oil, the first and second derivative spectra in the regions 6000–4550 and 9000–4550 cm^{-1} provide very good models (CP% = 100) with only PLS factor of 2. For the sunflower oil adulteration, the models developed by using the first and second derivative spectra in the 9000–7700 cm^{-1} region with the PLS factor of 4 and 5, respectively, show good classification performance. It is known that a small number of PLS factor required for developing a model that provides acceptable results indicates the stability and accuracy of such model.[15,18] It can be seen in Table 2 that when the spectral data are pretreated by second derivative, the models with high %CP are mostly obtained for a small number of PLS factor. Especially, when the second derivative spectra in the region 9000–7700 cm^{-1} are used to calculate a discriminant model, a superior classification model with a small number of PLS factor is obtained. Therefore, it seems that the second derivative pretreatment can enhance spectral differences in the region 9000–7700 cm^{-1} where bands due to the second overtone of CH stretching modes of CH_3 and CH_2 groups appear.[9,14,15] This result is in good agreement with the fact that the composition of the vegetable oils varies with the fatty acid component in the glycerides molecules. Different oils have different fatty acid components, and there must be differences in the intensities of peaks due to the second overtones of the CH stretching modes of CH_3 and CH_2 groups.[9,14,15] It is clear from the results in Table 2 that the discriminant PLS method is very powerful to identify adulterant types in the adulteration of olive oil samples. For most of the cases, the discriminant models provide the correct classification with the accuracy of 100%, and even at the worst case the %CP is still acceptable (95%) (Table 2).

PLS Calibration Models for the Quantification of Adulterant Contents in Olive Oil

Table 3 summarizes the statistical results for the prediction of the concentrations of adulterants contained in the olive oil samples. It is noted in Table 3 that the excellent prediction results are obtained mostly from the models built by using the region of 6000–4550 cm^{-1} for all the adulterants. This region contains bands arising from the first overtone of CH stretching modes of CH_2 and CH_3 groups and those due to the combination modes of CH vibrations.[9,14,15] A very good prediction result is obtained for corn oil adulterated in olive oil, when the model is generated by using the spectral range 6000–4550 cm^{-1} of every spectral data types. The three models for the quantitative determination of corn oil built by the using raw spectra,

Table 3. The prediction results of PLS calibration models for adulterant contents in olive oil samples

		Wavenumber regions (cm^{-1})							
		9000–7700		7700–6000		6000–4550		9000–4550	
Adulterants	Data pretreatment	No.[a]	RMSEP (% w/w)	No.	RMSEP (% w/w)	No.	RMSEP (% w/w)	No.	RMSEP (% w/w)
Corn oil	None	5	0.49	3	0.59	2	0.33	3	0.40
	MSC	4	0.49	6	0.50	2	0.40	3	0.40
	First derivative	3	0.44	4	0.44	2	0.32	3	0.32
	Second derivative	4	0.33	3	0.37	2	0.33	3	0.34
Hazelnut oil	None	3	1.15	5	0.90	3	0.60	4	0.50
	MSC	4	0.95	6	0.93	4	0.62	4	0.62
	First derivative	3	0.86	3	0.53	3	0.58	3	0.65
	Second derivative	2	1.60	5	0.46	4	0.44	4	0.46
Soya oil	None	5	3.14	5	0.54	6	0.49	6	0.55

(*continued*)

Table 3. Continued

		Wavenumber regions (cm^{-1})							
		9000–7700		7700–6000		6000–4550		9000–4550	
Adulterants	Data pretreatment	No.[a]	RMSEP (% w/w)	No.	RMSEP (% w/w)	No.	RMSEP (% w/w)	No.	RMSEP (% w/w)
	MSC	5	4.16	5	0.70	5	0.54	5	0.62
	First derivative	4	3.42	4	0.61	5	0.47	6	0.48
	Second derivative	6	3.44	5	1.51	7	0.72	7	0.73
Sunflower oil	None	10	4.34	6	1.28	5	1.05	5	1.05
	MSC	5	4.12	6	1.74	4	1.50	5	1.38
	First derivative	6	4.25	7	1.36	4	1.34	5	1.14
	Second derivative	8	3.02	6	1.35	5	1.50	5	1.70

PLS, partial least squares; MSC, multiplicative scatter correction.
[a]No. = the number of PLS factors used.

first and second derivative spectra give almost the same and very low values of root mean square error of prediction (RMSEP) of about 0.33% w/w with the PLS factor of 2 (Table 3). The superior prediction result for the content of hazelnut oil adulteration in olive oil has RMSEP of 0.44% w/w with the PLS factor of 4. This result was obtained from the model developed by use of the second derivative spectra in the 6000/4550 cm^{-1} region. As for the prediction result of soya oil content in the adulteration of olive oils, the quite good RMSEP value with a low number of PLS factor (0.47% w/w; PLS factor of 5) was obtained from the model developed by using the first derivative pretreatment in the region 6000–5500 cm^{-1} (Table 3). Two best calibration models for sunflower oil adulterated in olive oil yield the prediction result with the RMSEP of 1.05% w/w with the PLS factor of 5. These models were built by using the original spectra of the 6000–4550 and 9000–4550 cm^{-1} regions, respectively. Table 3 clearly shows that the models developed by use the region of 6000–4550 cm^{-1} are better than those developed by using the higher wavenumber regions of 9000–7700 and 7700–6000 cm^{-1}. Probably because the higher wavenumber regions contain inadequate information, they cannot produce an optimal model for the analyte. As for the comparison in the prediction results between models developed by using the regions 6000–4550 and 9000–4550 cm^{-1}, there is not so large a difference. However, when the wide spectral range is used, a larger number of PLS factor is required compared with the use of the region 6000–4550 cm^{-1}. This is probably because the wide spectral range includes regions that contain more noise than relevant information to the model development for the concentration of an analyte. Therefore, the optimal models were selected from the models giving the lowest RMSEP value with the smallest number of PLS factor. Note that when the spectral data were pretreated and then used to build models, the effects on predictive accuracy can be noticed (Table 3).

To simply understand the PLS processing for the discrimination and quantification of the adulteration of olive oil, the conclusions of the procedures were reported here. In the current study, only four adulterants in olive oil can be examined (i.e., corn oil, hazelnut oil, soya oil and corn oil). First, the original NIR spectra of unknown adulterations of olive oil were pretreated by using second derivative with the same pretreatment conditions as the optimal models applied. Next, the second derivative spectra of unknown adulterants are identified by the optimum discriminant PLS models for individual adulterant types. At this moment, the adulterant types in olive oil samples are revealed. Then, the content of adulteration in olive oil can be verified by using PLS calibration models for specific adulterant type. We transferred the previous second derivative pretreatment spectra of unknown adulterants classified into those of corn oil and hazelnut oil to the prediction process by using the optimum PLS calibration models for corn oil (PLS factor of 2) and hazelnut oil (PLS factor of 4), respectively. As for the unknown adulteration of olive oil samples identified as the adulterations

containing soya oil and sunflower oil, the first derivative pretreated spectra of the unknown adulterant identified as soya oil and the original spectra of the unknown adulterant identified as sunflower oil are transferred into the prediction process by using the optimum PLS calibration models for soya oil (PLS factor of 5) and sunflower oil (PLS factor of 5), respectively. Finally, the contents of adulterants in olive oil samples can be predicted.

CONCLUSIONS

The results obtained in the current study have demonstrated that NIR spectroscopy combined with the PLS processing is very powerful for discriminating adulterations in olive oil samples and for quantifing the contents of adulterants in them. The obtained results for the discrimination and the prediction of adulterant contents are quite good. For the discriminant PLS, the %CP for the prediction set was 100% for all optimum discrimination PLS models for the four adulterants. The optimum PLS calibration models yielded the prediction results for the adulterants of corn oil, hazelnut oil, soya oil, and sunflower oil with the error limits of $\pm 0.33\%, \pm 0.465\%, \pm 0.47\%$, and $\pm 1.05\%$w/w, respectively.

Generally, the operation of PLS regression is simple, and the meaning of the results is easy to understand. By using the processing reported above, the classification and quantitative determination of adulteration of olive oils would become practically simple and rapid. However, the current study has been carried out for only four adulterants. Several other kinds of adulterant types for olive oil should be investigated for the application of this processing under practical conditions.

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