Food Control 21 (2010) 890–895

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

A novel chemometric strategy for the estimation of extra virgin olive oil adulteration with edible oils

Rubén M. Maggio [a], Lorenzo Cerretani [b,*], Emma Chiavaro [c], Teodoro S. Kaufman [d], Alessandra Bendini [b]

[a] Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario and Instituto de Química Rosario, (CONICET-UNR), Suipacha 531, Rosario (S2002LRK), Argentina
[b] Dipartimento di Scienze degli Alimenti, Università di Bologna, p.zza Goidanich 60, I-47521 Cesena (FC), Italy
[c] Dipartimento di Ingegneria Industriale, Università degli Studi di Parma, viale Usberti 181/A, 43124 Parma, Italy
[d] Área Análisis de Medicamentos, Departamento de Química Orgánica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario and Instituto de Química Rosario (CONICET-UNR), Suipacha 531, Rosario S2002LRK, Argentina

ARTICLE INFO

Article history:
Received 1 September 2009
Received in revised form 22 November 2009
Accepted 4 December 2009

Keywords:
Virgin olive oil
Adulteration
FTIR
Partial least squares model

ABSTRACT

A useful procedure for the qualitative and quantitative determination of vegetable oils (canola, hazelnut, pomace and high linoleic/oleic sunflower) as adulterants in commercial samples of extra virgin olive oil, has been developed. Partial least squares (PLS) was employed for the analysis of Fourier transform infrared spectroscopy (FTIR) spectral data of the blend oil samples. Calibration models were constructed for extra virgin olive oil purity, with wavelength selection in the infrared region, according to their predictive ability, with first derivative and mean centering used as data pretreatment. PLS models were internally validated by the leave-one-out procedure. The method developed was very suitable for the determination of modeled adulterants but it may also reveal an adulteration even if it does not derive from the adulterants employed in this study.

1. Introduction

Olive oil is an economically important product in the Mediterranean countries. It has a fine aroma and a pleasant taste, and is internationally appreciated for its nutritional value and health benefits (Bendini et al., 2007; Harwood & Yaqoob, 2002). Costs of virgin olive oil are high when compared to other commonly used vegetable oils, making it prone to adulteration with less expensive oils in order to increase profits. Most common adulterants found in virgin olive oil are seed oils, such as sunflower, soy, corn and rapeseed oils as well as nut oils, including hazelnut and peanut oils (Firestone, 2001).

Several commercial categories of olive oil are legally defined by the European Community Council of Regulation (EC, 2001), which are marketed with different prices. Thus, there is also the possibility of mixing less expensive commercial categories such as refined olive oil and pomace oil with the highest quality product, extra virgin olive oil (EVOO), for economic reasons. Detection of these two types of adulteration is often complicated with no single test available that can accomplish the task, especially when oils with chemical compositions similar to EVOO are employed (García-González & Aparicio, 2006).

Detection and determination of the adulteration of EVOO are not simple tasks; efforts to detect and determine adulteration traditionally demand monitoring of several organic compounds to establish a comparison with typical unadulterated oils in order to identify change of composition that could be related to adulteration. In this respect, the detection of characteristic chemical components has been proposed as a suitable indication of the presence of other oils in EVOO (García-González & Aparicio, 2006; Ruiz, Caja, Herraiz, & Blanch, 1998), but the use of such compounds to discover adulteration, when refined oils are involved, is quite difficult. In addition, chemical methods traditionally employed for the control of authenticity of virgin olive oil as gas chromatography and high performance liquid chromatography are expensive, time-consuming, require skilled operators and have high environmental impact (Aparicio & Aparicio-Ruíz, 2000; Kamm, Dionisi, Hischenhuber, & Engel, 2001).

New and complementary analytical techniques devoid of such troubles, could act as supporting tools for currently used methods, being very helpful to improve the detection of EVOO adulteration. Among them, calorimetric techniques seem to be very promising and the application of differential scanning calorimetry to make evident the adulteration of EVOO was recently reported by Chiavaro and co-workers (Chiavaro, Vittadini, Rodriguez-Estrada, Cerretani, & Bendini, 2008; Chiavaro et al., 2009). On the other hand, nuclear magnetic resonance coupled with multivariate statistical analysis (Fragaki, Spyros, Siragakis, Salivaras, & Dais,

* Corresponding author. Tel.: +39 0547338121; fax: +39 0547382348.
E-mail address: lorenzo.cerretani@unibo.it (L. Cerretani).

0956-7135/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodcont.2009.12.006

2005) was successfully applied to detect EVOO adulteration with lampante olive oil and refined olive oil.

Spectrofluorimetric methods are also emerging as an important alternative; in fact, excitation–emission fluorescence spectroscopy (Guillén & Cabo, 1999) was reported for detecting adulteration of olive oil. FTIR has been also successfully used to detect olive oil adulteration (Lerma-García, Ramis-Ramos, Herrero-Martínez, & Simó-Alfonso, 2009; Ozen & Mauer, 2002) and freshness (Sinelli, Cosio, Gigliotti, & Casiraghi, 2007). The latter technique is often coupled with chemometrics methods such as principal component analysis (PCA), linear discriminant analysis (LDA), support vector machine (SVM) and K-nearest neighbor (KNN) (Di, Shuijuan, Xiaojing, Haiqing, & Yong, 2008; Pravdova, Boucon, de Jong, Walczak, & Massart, 2002; Sikorska, Górecki, Khmelinskii, Sikorski, & De Keukeleire, 2006), that can be used to assign the measured spectrum to a category in a training set. In addition, quantitative chemometrics strategies are suitable for analysis of complex mixtures as they enable rapid and simultaneous determination of each component in a mixture without time-consuming separations and with minimum sample preparation. Among such methods, partial least squares (PLS) is a factorial multivariate calibration method that decomposes spectral data into loadings and scores, building the corresponding calibration models from these new variables (Geladi & Kowalski, 1986; Martens & Næs, 1989). This method, which requires analytes' compliance of Beer's Law, has been repeatedly coupled with FTIR spectroscopy and extensively used to obtain different quality parameters of edible oils (Al-Alawi, Van, de Voort, & Sedman, 2004; Bendini et al., 2007; Bertran et al., 1999; Iñón, Garrigues, Garrigues, Molina, & de la Guardia, 2003; Li, van de Voort, Ismail, & Cox, 2000; Li et al., 2000). Particularly, FTIR-PLS has been recently applied to the evaluation of the fatty acid composition and other quality parameters of virgin olive oil (Maggio et al., 2009).

The aim of the present work is to develop a new application of the FTIR-PLS association as a rapid, inexpensive and nondestructive authenticity measuring tool, useful to determine the adulteration of EVOO with other edible oils and also to identify and quantify the percentage of the ruining agent in the blend. This approach represents a facile and convenient means for monitoring olive oil quality with the advantage of ease of operation, high sample turnover and no sample pretreatment.

2. Materials and methods

2.1. Samples

Pure extra virgin olive oil (EVOO), high oleic sunflower oil (HOSO), pomace olive oil (POO), high linoleic sunflower oil (HLSO), canola oil (CO) and hazelnut oil (HO) samples used in this study were purchased in Italy. Samples were stored in dark bottles without headspace at room temperature before analysis.

A pure sample of each edible oil was analyzed. Different admixtures at various ratios (60:40, 70:30, 80:20, 90:10 and 95:5, EVOO: Adulterant, w/w) of these oils were prepared and used as calibration or prediction samples, as needed. All experiments and calculations were done in triplicate.

2.2. FTIR spectra

The FTIR spectra were acquired on a Tensor 27™ FTIR spectrometer system (Bruker Optics, Milan, Italy), fitted with a Rocksolid™ interferometer and a DigiTect™ detector system coupled to an attenuated total reflectance (ATR) accessory. The ATR accessory (Specac Inc., Woodstock, GA, USA) was equipped with a ZnSe 11 reflection crystal. Analyses were carried out at room temperature. Spectra were acquired (32 scans/sample or background) in the range of 4000–700 cm^{-1} at a resolution of 4 cm^{-1}, using OPUS *r.* 6.0 (Bruker Optics) software. For each sample (2 mL uniformly spread throughout the crystal surface), the absorbance spectrum was collected against a background, obtained with a dry and empty ATR cell. One spectrum per sample was recorded. Before acquiring each spectrum, the ATR crystal was cleaned with a cellulose tissue soaked in *n*-hexane and then rinsed with acetone.

2.3. Statistical analysis

Data were exported in ASCII compatible OPUS 6.0 format with the assistance of an OPUS macro script and processed employing MVC1 routines (Olivieri, Goicoechea, & Iñón, 2004) written for Matlab (Mathworks Inc., Natick, MA, USA).

For each adulterant a different set of samples containing three or four concentration levels of adulterant, was used for calibration; the corresponding admixtures were used for validation. Partial least squares models were computed for each blend with the respective training set samples. A moving-window strategy was also executed with the MVC1 program, setting the minimum window width to 10 sensors.

3. Results and discussion

The oils have different substitution patterns, also differing in the chain length of their acyl moieties, as well as in their unsaturation degree and position; these differences are reflected in the FTIR spectra. There are a close relationships between the frequency data of some specific bands and the composition of the oils: a list of IR bands and shoulders of some edible oils was published by Guillén and Cabo (1999), which also includes their tentative assignment to functional groups. The presence of small amounts of adulterant oil in virgin olive oil is evidenced by small variations in the values of the frequencies of specific bands in the spectra. ATR-FTIR spectra of the virgin olive oil samples are shown in Fig. 1. A two-instances procedure is proposed to detect the fraud. The first instance consists in the evaluation of the purity (%) of EVOO by a PLS model with the aim to determine if the sample was adulterated. For the second instance, a set of successive individuals PLS models for each adulterant are proposed, in order to determine the identity of the adulterant and its ratio.

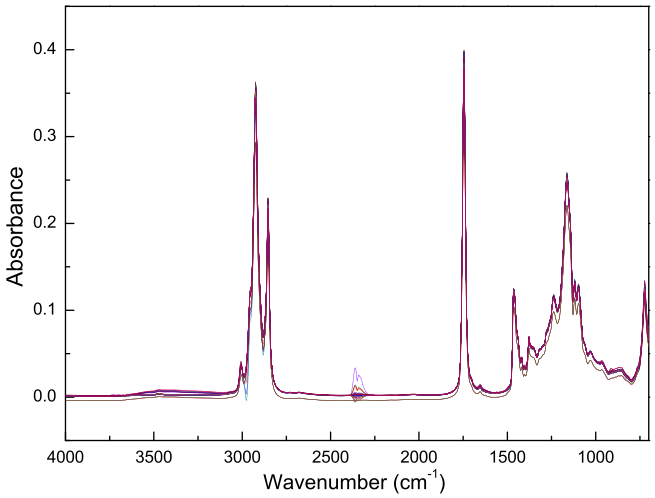

Fig. 1. FTIR spectra of the extra virgin olive oil (EVOO) purity calibration set. EVOO samples with 0, 10, 20 and 40% of high linoleic sunflower oil (HLSO), canola oil (CO), pomace olive oil (POO) and high oleic sunflower oil (HOSO).

3.1. PLS model for the EVOO purity (%)

In order to predict the purity (%) of EVOO, a multivariate calibration model was built by the PLS regression algorithm, using the first derivate of the mean centered spectral data. PLS is a simple and convenient calibration method for resolving mixtures, suitable for the current system resolution. The optimum number of factors (h) should be selected in order to avoid overfitting when using PLS. This can be done by applying the leave-one-out cross validation procedure as developed by Haaland and Thomas (1988). Using this procedure, the concentration (% purity) of the sample left out during the calibration is predicted. This process was repeated n times, until each one of n calibration samples has been left out once. The concentration (% purity) predicted for each sample is then compared with its actual concentration and the sum of squared prediction residual errors for all calibration samples (PRESS) is calculated (Eq. (1)).

$$\mathrm{PRESS} = \sum \left(\mathrm{C_{i,predicted}} - \mathrm{C_{i,actual}}\right)^2 \quad (1)$$

Simultaneous optimization of factor number and spectral interval was carried out using the mobile windows algorithm with the minimum PRESS criteria, as previously reported by Maggio, Castellano, Vignaduzzo, and Kaufman (2007). Additionally, the optimum number of factors on a determined spectral interval was obtained by computing the F-ratio PRESS ($h < h^*$)/PRESS (h) where h^* corresponds to the minimum PRESS, and selecting the number of factors leading to a probability of less than 75% (Haaland & Thomas, 1988); both criteria were in agreement.

The calibration set for the determination of EVOO purity was constituted by 49 samples, including pure samples of EVOO and mixtures containing 10%, 20% and 40% of HLSO, CO, HO, POO and HOSO.

The PLS model exhibited high predictive power for the determination of the presence of adulterant oils in the calibration and prediction sets. Fig. 2 shows the plots between the actual and predicted purity values of the calibration and validation mixtures.

The figures of merit of the PLS model (Table 1), were calculated as suggested by IUPAC (IUPAC, 2006). The intercept and the slope of the actual vs. predicted results for calibration data contain the values 0 and 1, respectively, in their confidence intervals. In addition, acceptable figures of dispersion (PRESS, RMSD and REP) were obtained for the calibration set, confirming the goodness of fitting of the model. Good analytical sensitivity and selectivity, and low spectral residues were also found, showing the good performance of the model.

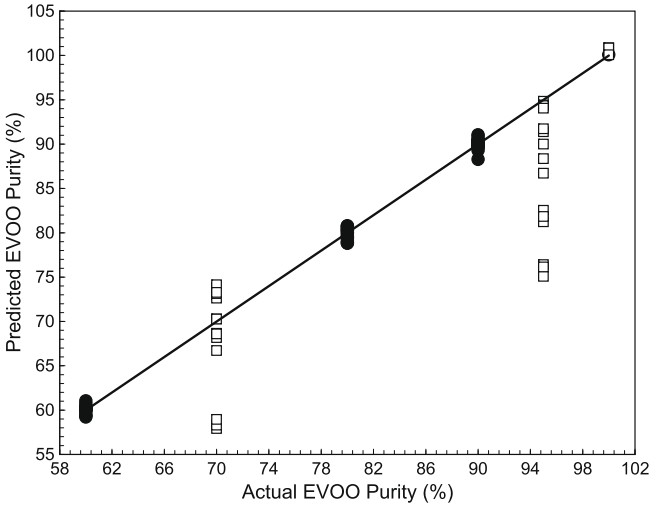

Fig. 2. Actual extra virgin olive oil (EVOO) purity percentage vs. FTIR-PLS predicted values in the calibration (●) and validation (□) sets. The equation of the curve for the calibration set is [Predicted] = (0.0 ± 0.5) + (1.000 ± 0.006) [Actual]; R^2 = 0.9979 ($p < 0.05$).

Table 1
Calibration parameters and statistical data for the FTIR-PLS analysis of EVOO purity.

PLS parameter	Value
Number of latent variables	13
Spectral region (cm^{-1})	3805.3–2840.9 plus 1876.6–1105.1
Spectral pretreatment	Mean centering and first derivative
Calibration interval (% EVOO)	60–100
PRESS	182.14
RMSD (%)	14.1
REP (%)	18.1
Slope (±SD)	1.000 ± 0.006
Intercept (±SD)	0.0 ± 0.5
R^2 (N = 49)	0.9979
Analytical sensitivity	49
Selectivity	0.049
Mean spectral residue	8.20×10^{-07}

RMSD $= (\mathrm{PRESS}/N)^{0.5}$; REP (%) $= 100 * \mathrm{RMSD}/\bar{y}$.

As indicated in Fig. 2, the PLS method has good predictive ability for the determination EVOO purity in the pure validation samples, yielding values near 100% purity for all of them. In addition, adulterated samples exhibited purities lower than 95%, with high dispersion. This can be explained taking into account the differences among the adulterants and their consequences on the corresponding FTIR spectra. These results evidenced that this instance was useful for distinguishing between adulterated and pure EVOO samples, regardless the nature of the adulterant.

3.2. PLS models for predicting the ratio of adulterant

In order to predict the ratio of adulterant in the EVOO, various multivariate calibration models were built by the PLS algorithm, using FTIR spectral data. A specific PLS model was prepared for each adulterant.

The different calibration conditions needed for each oil adulterant are shown in Table 2; mean centering and first derivate spectral pretreatment were needed in order to obtain good calibrations. Simultaneous optimization of factor number and spectral interval using the mobile window algorithm was required only for the POO model. In the other models, selection of the optimum spectral region did not evidence predictive performance improvement over the use of the full FTIR spectra. This may occur because POO and EVOO exhibited a very similar chemical composition and in this case, mobile window algorithm could improve the performance of the method selecting the spectral region where the difference is more evident. For all calibrated adulterants, low values were obtained for both RMSD and PRESS, which measure the average error in the analysis and evaluate the goodness of fit of the calibration data to the models developed during calibration. Low LOQs as well as good sensitivities and selectivities, demonstrated the quality of the models and their suitability for the proposed determinations.

The overall effectiveness of the PLS models for predicting the adulterant oils in the validation set was determined by calculating the relative error of prediction (REP) values, shown in Table 3. Almost quantitative recoveries were obtained for HLSO, CO and HOSO. In addition, acceptable recovery rates were obtained for HO and POO from their validation sets (Table 3). In all cases, the plots of actual vs. predicted values exhibited slopes close to 1, intercepts close to 0 and R^2 values higher than 0.9, showing the good performance of the models (Fig. 3). Regarding the spectral residues, values no higher than 10^{-4} absorbance units were found for the adulterants in their corresponding validation sets.

Table 2
Statistical data and figures of merit of the FTIR-PLS calibration models for HLSO, CO, HO, POO and HOSO.

Parameter	HLSO	CO	HO	POO	HOSO
Spectral range (cm^{-1})				1876–912	
Spectral pretreatment	Mean center and D′				
			0.0		
	0.05	0.05		0.00	0.05
Concentration levels			0.05		
	0.3	0.3		0.05	0.3
(Ratio in EVOO)			0.3		
	1.0	1.0		0.30	1.0
			1.0		
Number of factors (LVs)	3	3	4	4	4
Number of training samples (N)	10	9	12	9	9
PRESS	2.78×10^{-3}	6.18×10^{-2}	3.12×10^{-3}	2.51×10^{-3}	1.14×10^{-2}
Root mean square deviation (RMSD)	1.67×10^{-2}	8.29×10^{-2}	1.61×10^{-2}	1.67×10^{-2}	3.56×10^{-2}
Sensitivity	0.011	0.01	0.85	0.0015	0.0043
Analytical sensitivity	220	280	76	34	110
Selectivity based on total signal	0.4	0.68	0.054	0.6	0.42
Limit of detection (LOD)	0.016	0.007	0.001	0.001	0.04
Limit of quantification (LOQ)	0.048	0.021	0.003	0.003	0.12

Table 3
Results of the determination of accuracy and precision of the FTIR-PLS method for HLSO, CO, HO, POO and HOSO.

	HLSO	CO	HO	POO	HOSO
Concentration	0.10	0.10	0.10		0.10
				0.10	
Levels	0.20	0.20	0.20		0.20
				0.20	
(Ratio in VOO)	0.40	0.40	0.40		0.40
Number of validation samples	10	9	9	7	10
Recovery (%)	86	99	65	142	108
REP (%)	8.2	1.13	20.8	16.4	5.8
Slope (±SD)	−0.04 ± 0.02	−0.005 ± 0.003	1.1 ± 1	1.21 ± 0.1	0.03 ± 0.02
Intercept (±SD)	1.13 ± 0.09	1.03 ± 0.01	−0.09 ± 0.03	0.03 ± 0.01	0.88 ± 0.06
R^2	0.9448	0.9993	0.9351	0.9733	0.9647
Mean spectral residue	4.0×10^{-5}	3.8×10^{-5}	9.8×10^{-6}	6.0×10^{-5}	5.5×10^{-5}

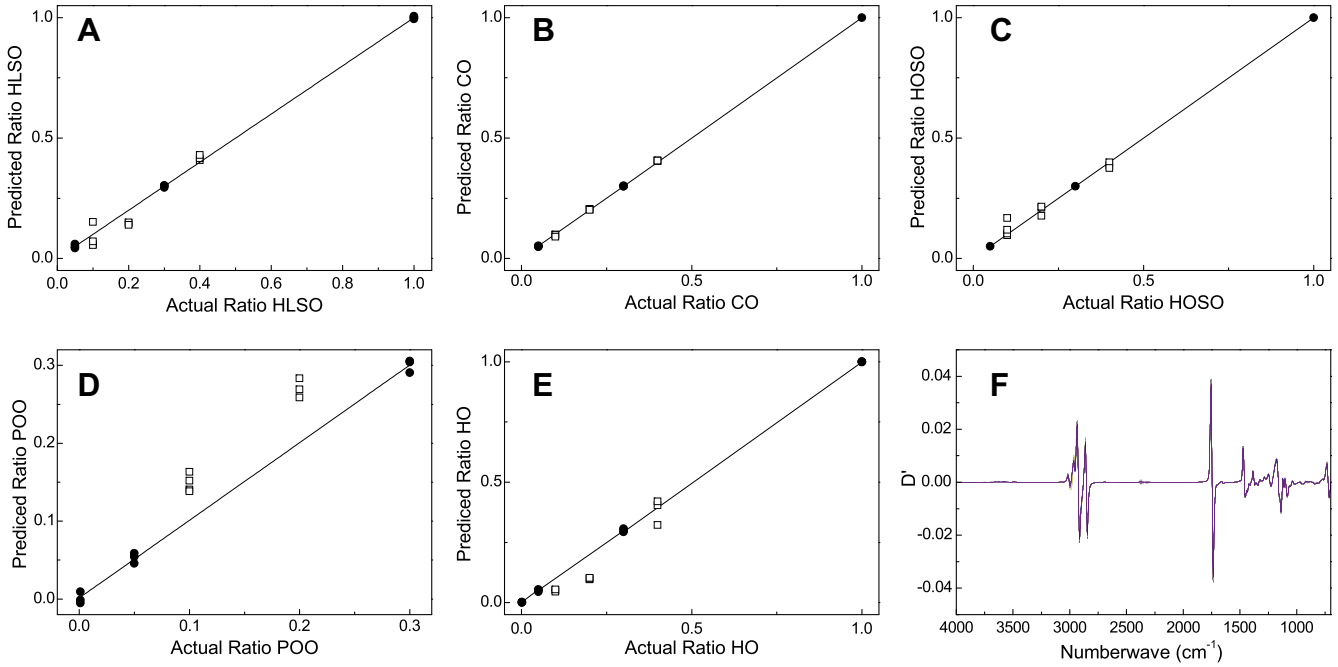

Fig. 3. Plot of actual vs. predicted ratios of (A) HLSO; (B) CO; (C) HOSO; (D) POO; (E) HO in EVOO for the calibration (●) and validation sets (□). (F) First derivative spectra of the adulterated EVOO samples.

3.3. Complete procedure for detecting adulteration of EVOO

A scheme containing the proposed two-instances multi-stage examination procedure for studying the adulteration of EVOO is shown in Fig. 4. In the first instance, the purity of EVOO is evaluated by means of a PLS model prepared with pure EVOO and mixtures containing different amounts of adulterants. If the level of EVOO is found to be lower than 99%, a second instance is proposed, where a set of adulterant-specific PLS models is used for the different adulterants, with the aim to identify the adulterant and determine its amount in the mixture, along successive stages.

When the spectral residues were analyzed, it was observed that for a given model unknown samples yielded significantly different values depending on whether the adulterant was modeled or not (Table 4), in avail of the use of spectral residues as a classification rule. This is an innovative utilization of the First Order Calibration Method Advantage (Olivieri, 2008) and the class by class comparison is analogous to the Soft Independent Modeling of Class Analogy (SIMCA) procedure (Candolfi, De Maesschalck, Massart, Hailey, & Harrington, 1999; Wold, 1976) with different classification rules.

Low LOD values of individual FTIR-PLS adulterant models support the good sensitivity of the global method, whereas low values of spectral residues convert the overall procedure in a selective tool for the assessment of EVOO adulteration.

The sequence of adulterant analysis was designed taking into account possible interferences produced among the adulterants. An exhaustive study was carried in this direction and the result is shown in Table 4. Percentage (%) of interference indicated how much the signal (predicted analyte concentration) increases respect to the concentration of a determined interferent. In addition, Spectral Residue (SR %), a typical chemometrics indicator, was evaluated. It should be compared with SR % of the calibrated samples. No interference was found for the HSLO-PLS model. On the other hand, HO, POO and HOSO did not interfere in the CO-PLS model. Therefore, a non-modeled adulterant can be detected by an inspection of the SR % of the PLS models. The complete procedure, useful for a routinary assessment of EVOO purity, is

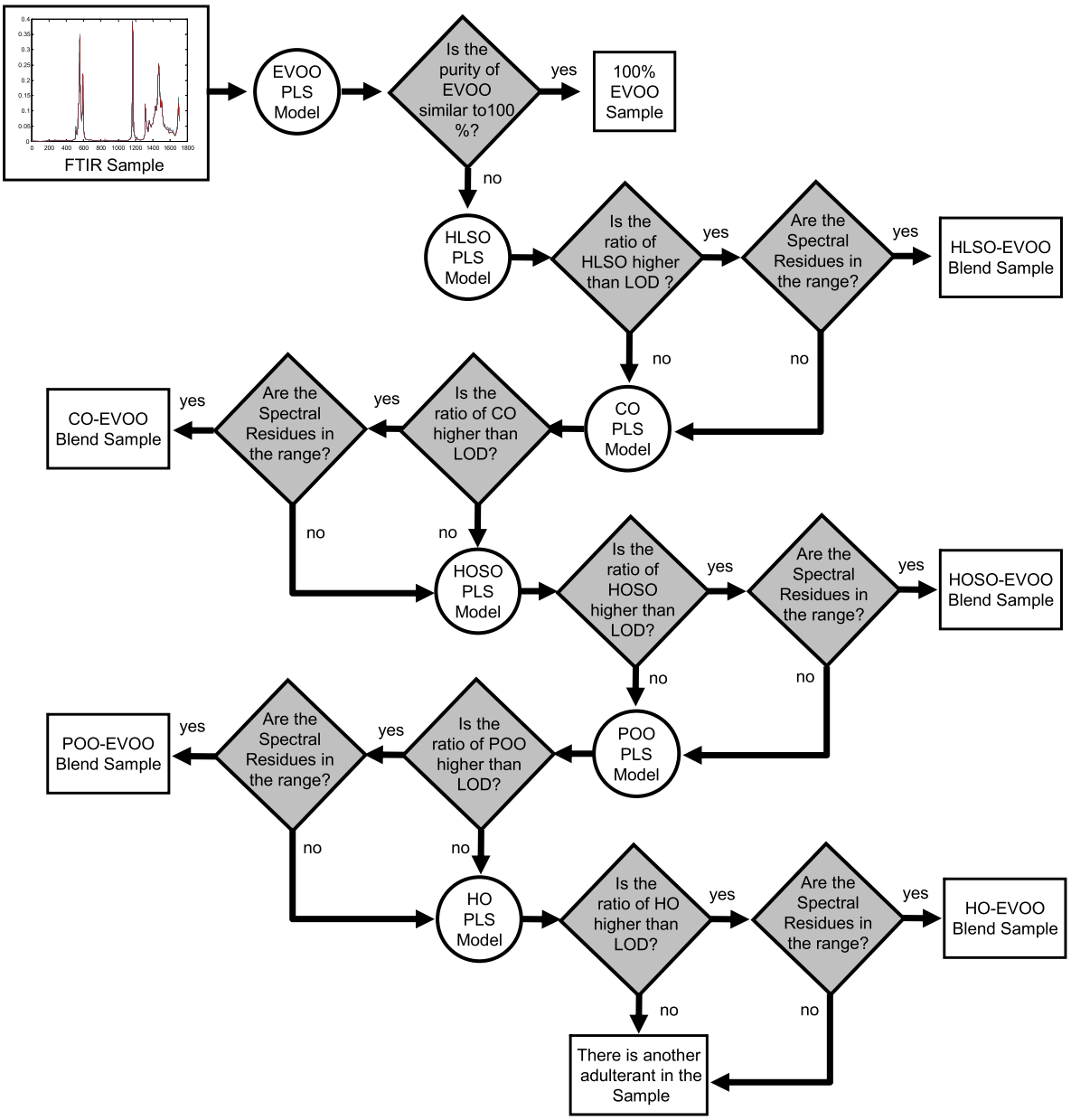

Fig. 4. Overall procedure for the qualitative and quantitative determination of EVOO adulteration.

Table 4
Interferences and spectral residues (SR) for non-modeled adulterants analyzed by adulterant-specific PLS models.

Adulterant	PLS model									
	HLSO		CO		HOSO		POO		HO	
	Interf. (%)	SR (%)	Interf. (%)	SR (%)	Interf. (%)	SR (%)	Interf. (%)	SR (%)	Interf. (%)	SR (%)
HLSO	–	76	163	128	334	219	−8	119	363	176
CO	34	134	–	85	221	123	252	132	306	361
HOSO	−4.9	109	35	155	–	86	148	126	−8	176
POO	2.24	150	31.1	92	72	157	–	79	57	99
HO	19.6	216	31	258	108	264	150	110	–	156

amenable for automatization employing a series of Matlab routines (Fig. 4).

4. Conclusions

A multi-stage strategy combining infrared spectrometry with PLS as a multivariate method was developed as a powerful tool for monitoring the purity of EVOO and performing qualitative and quantitative determinations of adulterants in its commercial samples. PLS calibration models constructed for the evaluation of EVOO purity and for the adulterants HLSO, CO, HO, POO and HOSO were internally validated by the leave-one-out procedure and their predictive ability was assessed by independent external validation sets. The described calibration models were linear, accurate and precise when the contents of all adulterants were assayed in synthetic samples. The general operating procedure represents an improvement toward adulterant assessment in EVOO, using the prediction of adulterant ratio and the spectral residues to determine sample composition. The obtained results also confirm that the method is highly suitable for the intended purpose.

References

Al-Alawi, A., van de Voort, F. R., & Sedman, J. (2004). New FTIR method for the determination of FFA in oils. *Journal of the American Oil Chemists' Society, 81*, 441–446.

Aparicio, R., & Aparicio-Ruíz, R. (2000). Authentication of vegetable oils by chromatographic techniques. *Journal of Chromatography A, 881*, 93–104.

Bendini, A., Cerretani, L., Carrasco-Pancorbo, A., Gómez-Caravaca, A. M., Segura-Carretero, A., Fernández-Gutiérrez, A., et al. (2007). Phenolic molecules in virgin olive oils: a survey of their sensory properties, health effects, antioxidant activity and analytical methods. An overview of the last decade. *Molecules, 12*, 1679–1719.

Bendini, A., Cerretani, L., Di Virgilio, F., Belloni, P., Bonoli-Carbognin, M., & Lercker, G. (2007). Preliminary evaluation of the application of the FTIR spectroscopy to control the geographic origin and quality of virgin olive oils. *Journal of Food Quality, 30*, 424–437.

Bertran, E., Blanco, M., Coello, J., Iturriaga, H., Maspoch, S., & Montoliu, I. (1999). Determination of olive oil free fatty acid by Fourier transform infrared spectroscopy. *Journal of the American Oil Chemists' Society, 76*, 611–616.

Candolfi, A., De Maesschalck, R., Massart, D. L., Hailey, P. A., & Harrington, A. C. E. (1999). Identification of pharmaceutical excipients using NIR spectroscopy and SIMCA. *Journal of Pharmaceutical and Biomedical Analysis, 19*, 923–935.

Chiavaro, E., Vittadini, E., Rodriguez-Estrada, M. T., Cerretani, L., & Bendini, A. (2008). Differential scanning calorimeter application to the detection of refined hazelnut oil in extra virgin olive oil. *Food Chemistry, 110*, 248–256.

Chiavaro, E., Vittadini, E., Rodriguez-Estrada, M. T., Cerretani, L., Capelli, L., & Bendini, A. (2009). Differential scanning calorimetry detection of high oleic sunflower oil as adulterant in extra virgin olive oil. *Journal of Food Lipids, 16*, 227–244.

Di, W., Shuijuan, F., Xiaojing, C., Haiqing, Y., & Yong, H. (2008). Independent component analysis and support vector machine combined for brands identification of milk powder based on visible and short-wave near-infrared spectroscopy. *Image and Signal Processing, Congress on, 5*, 456–459.

European Community, Commission Regulation (EC, 2001). No. 1513/2001 July 23 amending Regulations No. 136/66/EEC and No. 1638/98 as regards the extension of the period of validity of the aid scheme and the quality strategy for olive oil. *Official Journal of European Communities, L201*, 4–7.

Firestone, D. (2001). Assuring the integrity of olive oil products. *Journal of AOAC International, 84*, 176–180.

Fragaki, G., Spyros, A., Siragakis, G., Salivaras, E., & Dais, P. (2005). Detection of extra virgin olive oil adulteration with lampante olive oil and refined olive oil using nuclear magnetic resonance spectroscopy and multivariate statistical analysis. *Journal of Agriculture and Food Chemistry, 53*, 2810–2816.

García-González, D. L., & Aparicio, R. (2006). Olive oil authenticity: The current analytical challenges. *Lipid Technology, 18*, 81–85.

Geladi, P., & Kowalski, B. R. (1986). Partial least-squares regression: A tutorial. *Analytica Chimica Acta, 185*, 1–17.

Guillén, M. D., & Cabo, N. (1999). Usefulness of the frequencies of some Fourier transform infrared spectroscopic bands for evaluating the composition of edible oil mixtures. *Fett/Lipid, 101*, 71–76.

Haaland, D. M., & Thomas, E. V. (1988). Partial least-squares methods for spectral analyses. Relation to other quantitative calibration methods and the extraction of qualitative information. *Analytical Chemistry, 60*, 1193–1198.

Harwood, J. L., & Yaqoob, P. (2002). Nutritional and health aspects of olive oil. *European Journal of Lipid Science and Technology, 104*, 685–697.

Iñón, F. A., Garrigues, J. M., Garrigues, S., Molina, A., & de la Guardia, M. (2003). Selection of calibration set samples in determination of olive oil acidity by partial least squares-attenuated total reflectance-Fourier transform infrared spectroscopy. *Analytica Chimica Acta, 489*, 59–75.

IUPAC, Analytical Chemistry Division Olivieri, A. C., Faber, N. M., Ferré, J., Boqué, R., Kalivas, J. H., & Mark, H. (PAC 2006). Uncertainty estimation and figures of merit for multivariate calibration. *Pure and Applied Chemistry, 78*, 633–661.

Kamm, W., Dionisi, F., Hischenhuber, C., & Engel, K. H. (2001). Authenticity assessment of fats and oils. *Food Reviews International, 17*, 249–290.

Lerma-García, M. J., Ramis-Ramos, G., Herrero-Martínez, J. M., & Simó-Alfonso, E. F. (2009). Authentication of extra virgin olive oils by Fourier-transform infrared spectroscopy. *Food Chemistry, 118*, 78–83.

Li, H., van de Voort, F. R., Ismail, A. A., Sedman, J., Cox, R., & Simard, C. (2000). Discrimination of edible oil products and quantitative determination of their iodine value by Fourier transform near-infrared spectroscopy. *Journal of the American Oil Chemists' Society, 77*, 29–36.

Li, H., van de Voort, F. R., Ismail, A. A., & Cox, R. (2000). Determination of peroxide value by Fourier transform near-infrared spectroscopy. *Journal of the American Oil Chemists' Society, 77*, 137–142.

Maggio, R. M., Castellano, P. M., Vignaduzzo, S. E., & Kaufman, T. S. (2007). Alternative and improved method for the simultaneous determination of fexofenadine and pseudoephedrine in their combined tablet formulation. *Journal of Pharmaceutical and Biomedical Analysis, 45*, 804–810.

Maggio, R. M., Kaufman, T. S., Del Carlo, M., Cerretani, L., Bendini, A., Cichelli, A., et al. (2009). Monitoring of fatty acid composition in virgin olive oil by Fourier transformed infrared spectroscopy coupled with partial least squares. *Food Chemistry, 114*, 1549–1554.

Martens, H., & Næs, T. (1989). *Multivariate calibration*. Chichester: Wiley.

Olivieri, A. C. (2008). Analytical advantages of multivariate data processing. One, two, three, infinity? *Analytical Chemistry, 80*, 5713–5720.

Olivieri, A. C., Goicoechea, H. C., & Iñón, F. A. (2004). MVC1: An integrated Matlab toolbox for first-order multivariate calibration. *Chemometrics and Intelligent Laboratory Systems, 73*, 189–197.

Ozen, B. F., & Mauer, L. J. (2002). Detection of hazelnut oil using FT-IR spectroscopy. *Journal of Agriculture and Food Chemistry, 50*, 3898–3901.

Pravdova, V., Boucon, C., de Jong, S., Walczak, B., & Massart, D. L. (2002). Three-way principal component analysis applied to food analysis: An example. *Analytica Chimica Acta, 462*, 133–148.

Ruiz, D. C., Caja, M. M., Herraiz, M., & Blanch, G. P. (1998). Rapid recognition of olive oil adulterated with hazelnut oil by direct analysis of the enantiomeric composition of filbertone. *Journal of Agriculture and Food Chemistry, 46*, 5128–5131.

Sikorska, E., Górecki, T., Khmelinskii, I. V., Sikorski, M., & De Keukeleire, D. (2006). Monitoring beer during storage by fluorescence spectroscopy. *Food Chemistry, 96*, 632–639.

Sinelli, N., Cosio, M. S., Gigliotti, C., & Casiraghi, E. (2007). Preliminary study on application of mid infrared spectroscopy for the evaluation of the virgin olive oil "freshness". *Analytica Chimica Acta, 598*, 128–134.

Wold, S. (1976). Pattern recognition by means of disjoint principal components models. *Pattern Recognition, 8*, 127–139.