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Analytical Methods

Application of partial least square regression to differential scanning calorimetry data for fatty acid quantitation in olive oil

Lorenzo Cerretani [a], Rubén M. Maggio [b], Carlo Barnaba [c], Tullia Gallina Toschi [a], Emma Chiavaro [c,*]

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

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ABSTRACT

A chemometric approach based on partial least (PLS) square methodology was applied to unfolded differential scanning calorimetry data obtained by 63 samples of different vegetable oils (58 extra virgin olive oils, one olive and one pomace olive oil, three seed oils) to evaluate fatty acid composition (palmitic, stearic, oleic and linoleic acids, saturated (SFA), mono (MUFA) and polysaturated (PUFA) percentages, oleic/linoleic and unsaturated/saturated ratios).

All calibration models exhibited satisfactory figures of merit. Palmitic and oleic acids, as well as SFA showed very good correlation coefficients and low root mean square error values in both calibration and validation sets. Satisfactory results were also obtained for MUFA, PUFA, stearic and linoleic acids, O/L ratio in terms of percentage recoveries and relative standard deviations. No systematic and bias errors were detected in the prediction of validation samples.

This novel approach could provide statistically similar results to those given by traditional official procedures, with the advantages of a very rapid and environmentally friendly methodology.

1. Introduction

Olive oil is the primary source of fat in the Mediterranean diet. It is consume has been associated with a reduced risk of overall and cardiovascular mortality, cancer frequency and incidence of Parkinson and Alzheimer disease, leading to an improved life quality (Covas, Konstantinidou, & Fitó, 2009). These health benefits are largely related to the high content of monosaturated fatty acids and oleic acid in particular, although it is now largely recognised the additional effect of other minor components having biological properties (Bendini et al., 2007). In addition, both the high content of oleic acid and low amounts of linoleic and linolenic acids, give an important contribution to the high oxidative stability to this type of vegetable oil (Aparicio, Roda, Albi, & Gutiérrez 1999).

Fatty acid composition of different commercial categories of olive oil, legally defined by the European Community (EC) Council of Regulation (EC, 2007) and also reported on the recently amended Current Official Standard of Codex Alimentarius (2009), is well recognised to largely vary. In particular, content of oleic acid ranges from 55% to 83%, as it is influenced by many agronomical factors (olive variety, climatic conditions during growth, degree of maturation) and practices related to irrigation treatment (Baccouri et al., 2007).

Differential scanning calorimetry (DSC) is widely employed in the field of vegetable oils (Aboul-Gheit, Abd-el-Moghny, & Al-Eseimi, 1997). Thermal properties obtained by cooling and heating thermograms are well recognised to be related to chemical composition for different vegetable oils (Che Man & Tan, 2002; Tan & Che Man, 2002) and a mathematical model based on a simple regression procedure was also developed to correlate melting parameters of several oils to mass fractions of mono and polyunsaturated fatty acids (Fasina, Craig-Schmidt, Colley, & Hallman, 2008). Relations have been also recently studied and established for extra virgin olive oil (Chiavaro et al., 2007) and commercial categories of olive oil (Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008) as well as, more deeply, statistical correlations were found among thermal properties upon cooling and both major and minor components of this vegetable oil (Chiavaro, Rodriguez-Estrada, Bendini, & Cerretani, 2010).

DSC is a very well established technique with several advantages for its application, as it does not require chemical treatments or time-consuming manipulation practices before each measurement leading to an easy data collection. Otherwise, the chemometric processing of digitised DSC curves is not commonly employed in literature although this approach seems to be an attractive alternative to the classical chemical methods due to the

* Corresponding author. Tel.: +39 0521 905888; fax: +39 0521 905705.
E-mail address: emma.chiavaro@unipr.it (E. Chiavaro).

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advantages obtained by DSC application above discussed. Some examples are reported in the fields of pharmaceuticals and chemicals (Miltyk, Antonowicz, & Komsta, 2010; Smidt & Tintner, 2007) and a lower number on food matrices such as meat (Bertram, Wu, van den Berg, & Andersen, 2006; Nedenskov Jensen & Jørgensen, 2003).

On the other hand, the coupling of quantitative chemometrics strategies, partial least square (PLS) in particular, to evaluate the quality of edible oils by physical methods, such as spectrometric ones, are extensively reported in literature (Al-Alawi, Van de Voort & Sedman, 2004; Iñón, Garrigues, Garrigues, Molina, & de la Guardia, 2003). This combination allowed to merge spectral and analytical information leading to the construction of very useful predictive models for properties of interest generally based on concentration values. In particular, Maggio et al. (2009) has been recently applied coupled FTIR-PLS procedures to evaluate fatty acid composition and other quality parameters of virgin olive oil and to discover the adulteration of extra virgin olive oil added with other edible oils (Maggio, Cerretani, Chiavaro, Kaufman, & Bendini, 2010).

The DSC–PLS approach here proposed to quantify fatty acids represents an easy and convenient means for monitoring olive oil and, to the authors best knowledge, no works are present in literature on this application. Thus, the aim of this work was to develop and validate an analytical method based on DSC data, in combination with multivariate calibration methodologies, for the evaluation of important features of the olive oil's fatty acids composition. Palmitic, stearic, oleic and linoleic acids as well as total saturated, monosaturated and polyunsaturated percentages and some important ratios commonly employed to define olive oil quality were considered (oleic/linoleic acid and unsaturated/saturated).

2. Material and methods

2.1. Sampling

A series of 189 (63 by triplicate) samples of vegetable oils were analysed. Fifty-eight of them were extra virgin olive oils and differed in terms of cultivar, ripening degree, area of growth and extraction system (type, productive capacity and manufacturer), one was olive oil, one was obtained from pomace, while three were from other botanical origins (hazelnut, high oleic sunflower, canola oils). All Italian and Spanish extra virgin olive oils were obtained from olives hand-picked in the season 2008–2009 whereas Tunisian extra virgin olive oils, pomace olive oil, olive and all seed oils, were obtained from crop season 2007–2008. Samples were all stored in dark bottles without headspace at room temperature before being analysed within six months from production.

2.2. GC determination of total fatty acid

Fatty acid composition was determined according to Bendini, Cerretani, Vecchi, Carrasco-Pancorbo, and Lercker (2006), as methyl esters by capillary gas chromatography (GC), equipped with a flame ionisation detector (FID), after alkaline treatment. The results were expressed as area normalisation in percent (%). Fatty acids were also reported according to their unsaturation degree, as saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids. All solvents used were analytical or HPLC grade (Merck, Darmstadt, Germany). Reagents were purchased from Sigma–Aldrich (St. Louis, MO). The standard mixture of fatty acid methyl esters (GLC 463) was supplied by Nu-Chek (Elysian, MN). Three replicates were prepared and analysed *per* sample.

2.3. DSC

Oil samples (8–10 mg) were weighed into aluminium pans, covers were sealed into place and the whole analysed with a DSC Q100 (TA Instruments, New Castle, DE). Indium (melting temperature 156.6 °C, $\Delta H_f = 28.45$ J g^{-1}) and *n*-dodecane (melting temperature −9.65 °C, $\Delta H_f = 216.73$ J g^{-1}) were used to calibrate the instrument and an empty pan was used as reference. Oil samples were equilibrated at 30 °C for 3 min and then cooled at −80 °C at the rate of 2 °C min^{-1}, equilibrated at −80 °C for 3 min and then heated from −80 to 30 °C at 2 °C min^{-1}. Dry nitrogen was purged in the DSC cell at 50 cm^3 min^{-1}. Thermograms were analysed with Universal Analysis Software (Version 3.9A, TA Instruments) to be exported in an ASCII compatible format. Three replicates were analysed *per* sample.

2.4. Data processing and calibration models

Data were processed employing MVC1 (multivariate calibration 1) routines written for Matlab (Mathworks Inc., Natick, MA, USA), as previously reported (Olivieri, Goicoechea, & Iñón, 2004). PLS models were computed over an overall calibration set of samples for all parameter. Data were mean-centred (MC) before all calculations. Multiplicative signal correction (MSC) pre-treatment was used when necessary considering that MSC performs best if an offset correction is carried out first, as already reported (Isaksson & Næs, 1988). The signal correction was done considering the whole thermogram and providing that all the samples appear to have the same signal level as the ideal. As an estimate of the ideal sample, the average of the calibration was used.

About 30% of the samples was randomly selected as an external validation set for parameter determination, whilst the rest were used to build up the calibration model. The replicates were individually used to take account the sample-to-sample variation in the calibration model.

3. Results and discussion

3.1. Fatty acid composition of oils

Main fatty acid ranges for vegetable oils analysed in this study are reported in Table 1. Among oil samples, 58 were extra virgin olive oil and they were achieved from the two major European country producers (Italy and Spain), whereas the others were obtained from olives growth in Tunisia, which is actually referred as the most important extra-European olive oil producer. All extra virgin olive oil fell within the main fatty acid range composition indicated by the Commission Regulation for this olive oil category (EC, 2007), with palmitic and oleic acids accounted for about 85% of the total fatty acid percentages. The amount of linolenic acid was always lower than 1%, as generally observed for olive oils, whereas content of other minor fatty acids as myristic, arachidic, behenic and lignoceric acids was in accordance with in the range indicated by Commission Regulation for this olive oil category (EC, 2007).

Among samples, Italian extra virgin olive oils were representative of the national oil market, coming from the most important fruit varieties (i.e. Leccino, Coratina) or from the local market. Fatty acid composition was in agreement with previous work (Chiavaro et al., 2010) and presented oleic acid content in the range 64–75% with linoleic acid from 7% to 14%, accounting an oleic/linoleic acid (O/L) ratio higher than seven in most of the samples; this last is considered as the limit value to be overcame for oil oxidative stability. Tunisian virgin olive oils, coming from the most important varieties widespread on the country (Chemlali and Chetoui), were characterised by significantly higher and lower value of linoleic

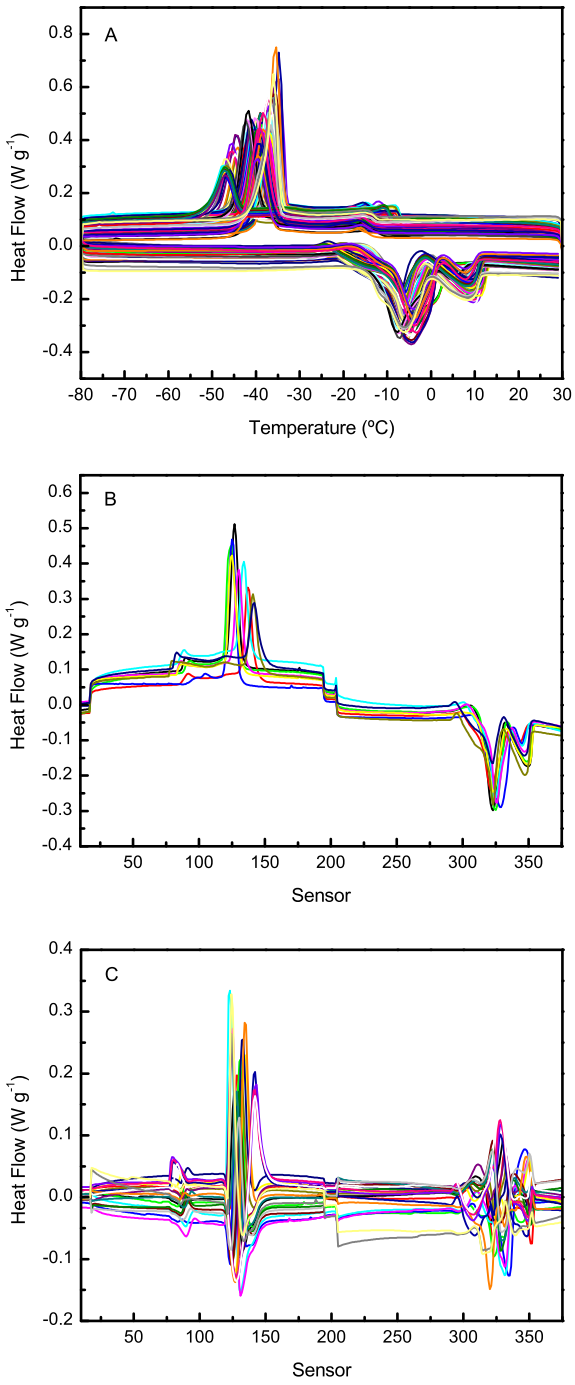

Fig. 1. DSC thermograms (A) obtained; (B) unfolded and (C) mean centred unfolded from selected oil samples.

(~16%) and oleic (~58%) acids, in comparison with the Italian samples, with Chemlali also presenting high palmitic acid amounts (~20%), as previously observed (Baccouri et al., 2008). Spanish samples were obtained from Picual and presented typical composition of oils obtained from this cultivar, similar to those of Italian samples (Allouche, Jiménez, Gaforio, Uceda, & Beltrán, 2007).

Five different oil samples were considered in this work; two (olive oil and olive–pomace oil) were from other commercial categories than extra virgin olive oils, as legally defined by the EC Council of Regulation (2001). The other three (high oleic sunflower, hazelnut and canola oils), having a different botanical origin, were chosen on the basis of their composition rich in oleic and/or linoleic acid, as well as for their common employment in the sector of edible oils.

Olive oil exhibited a fatty acid composition similar to those of extra virgin olive oil samples. On the other hand, olive–pomace oil showed significantly greater linoleic and linolenic acid contents as well as PUFA amount, in comparison to oils directly obtained by olives. This is probably ascribable to their more efficient recovery from seeds due to the application of solvent extraction for oil production (Contiñas, Martínez, Carballo, & Franco, 2008). High oleic sunflower oil presented a higher oleic acid (~80%) and lower palmitic acid (~4.0%) contents that leads to lower SFA and higher MUFA than extra virgin olive oil samples (O'Brien, 2004). Canola oil showed lower oleic (~63%) and higher linoleic (~18%) and linolenic (~8%) acid contents than olive oils, with an higher content of PUFA, as consequence (O'Brien, 2004). Hazelnut oil exhibited a fatty acid composition similar to that of high oleic sunflower oil with an higher contents of palmitic (~6.0%) and linoleic (~11.5%) acids, as previously observed (Chiavaro, Vittadini, Rodriguez-Estrada, Cerretani, & Bendini, 2008).

3.2. DSC analysis of thermograms

DSC is a suitable technique to characterise such phase transitions as crystallisation and melting of vegetable oils that require the intake or release of thermal enthalpy. All DSC thermograms, obtained upon cooling and heating of oil samples, are reported in Fig. 1A. Generally, cooling curves are more interpretable than those obtained upon heating where the well known melting-re-crystallisation phenomenon, named polymorphism, could easily occur for the original oil crystals (Che Man & Tan, 2002; Tan & Che Man, 2002). In addition, crystallisation of oils was well known to be influenced by chemical composition whereas the initial crystalline state has no role in developing transition (Che Man & Tan, 2002).

Extra virgin olive oil samples exhibited two well defined exothermic events, a major one peaking at ~−40 °C and a minor at higher temperature (~13 °C), as previously reported (Chiavaro et al., 2007, 2008, 2010; Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008), with slight shifts of both peaks ascribable to differences of fatty acid composition for some samples (Chiavaro et al., 2010). Similar cooling profiles were also shown by olive and olive–pomace oils although the major peak shifted towards lower temperature, peaking at ~−45 °C, for this latter oil, as previously observed (Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008), due to higher unsaturation degree of lipids.

Otherwise, different cooling profiles than those of oils obtained by olive were shown by the seed oils analysed. High oleic sunflower oil, which phase transitions upon DSC were, for the first time, reported in literature in a previous work (Chiavaro et al., 2009), exhibited a single well defined exothermic event peaking at −34 °C with a small shoulder onsetting at ~−15 °C. Crystallisation also occurred over a narrower range of temperature than olive oils being highly cooperative, due to the high content of oleic acid (Chiavaro et al., 2009). Similar cooling profile was exhibited by hazelnut oil with a first, less defined shoulder peak, onsetting at −15 °C, followed by a more important event peaking at −37 °C (Che Man & Tan, 2002; Chiavaro et al., 2008) and by canola oil where a major exothermic event, sharp and tall, peaked at −45 °C and a minor shoulder event was distinguishable at higher temperature (−21 °C) (Che Man & Tan, 2002). These DSC profiles are characteristic of vegetable oils with higher content of oleic and/or linoleic acids than olive oils (Che Man & Tan, 2002; Chiavaro et al., 2008, 2009).

All oil samples exhibited multiple transitions as heated from −80 to 30 °C. Oils from olive showed, at first, a minor exothermic peak and, successively, a major endothermic event occurring over the −18/12 °C temperature range. A first exothermic event,

Table 1
Statistical summary and figures of merit from the DSC–PLS calibration for all oil parameters.

Calibration	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	O/L	U/S	SFA	MUFA	PUFA
Concentration range (%)	3.9–20.0	1.7–4.1	53.8–80.4	4.7–19.3	2.8–17.5	3.2–40.1	8.2–23.8	56.4–82.8	5.2–26.8
Statistical summary									
PLS factors	13	11	16	10	13	11	10	12	11
Pre-treatment	MC	MC	MC	MC	MC	MC	MC	MC	MC
	–	MSC	–	–	–	–	–	–	–
RMSE	0.92	0.25	1.50	1.05	0.92	0.67	1.03	1.85	1.06
REC	7.21	9.15	2.10	10.80	10.87	11.06	6.35	2.53	10.15
R^2	0.92	0.78	0.94	0.92	0.91	0.98	0.89	0.91	0.94
Figures of merit									
Sensitivity	0.41	1.6	0.15	0.62	0.46	0.4	0.63	0.26	0.53
Analytical sensitivity	9.8	31	4.5	9.9	11	7.5	9.9	5.8	10
Selectivity	0.25	0.31	0.13	0.32	0.2	0.5	0.37	0.23	0.31
LOD (3.3*SD)	0.96	0.24	1.95	1.08	1.01	0.72	0.75	1.96	11.92

Abbreviations used: O/L, ratio between oleic and linoleic acid percentages; U/S, ratio between unsaturated and saturated fatty acid percentages; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; MC, mean-centre; MSC, multiplicative scatter correction; RMS, root mean square; REC, relative error in calibration; LOD, limit of detection.

occurring in the −30 to −15 °C temperature range, was distinguishable for extra virgin oils and olive oil sample but less evident in olive–pomace oil, as it was spread over a larger temperature range (from −40 to −15 °C) (Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008). It was previously attributed to an exothermic molecular rearrangement of crystals into more stable polymorphic forms (Tan & Che Man, 2002). On the other hand, the complex endothermic events occurring at higher temperatures were related to the melting of crystallised lipids and characterised by multiple overlapping contributions (Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008; Tan & Che Man, 2002). In particular, two endothermic events were more distinguishable. The major peaked at lower temperature, in the range −3.5/−7.0 °C for oil samples from olive, probably in relation with the unsaturation degree of lipid (Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008). Additional endothermic events were possibly observed in some samples, displaying themselves as shoulder peaks embedded in the major event at lower or higher temperature (at ∼−14 and ∼−3 °C).

The minor endotherm peaking at higher temperature (in the range 6.0/8.0 °C), showed different peak profiles among samples, being more evident and wider, with a maximum skewed towards higher temperature, or sharper and more symmetric or still hardly distinguishable. These differences were previously observed for extra virgin olive oil samples of different lipid composition in relation to cultivar and/or commercial categories (Chiavaro, Rodriguez-Estrada, Barnaba et al., 2008).

High oleic sunflower oil exhibited a heating profile with a well distinct endothermic event peaking at about −7 °C and a shoulder peak embedded in the major one peaking at higher temperature (about −2.5 °C), as previously reported (Chiavaro et al., 2009). Heating thermogram of hazelnut oil sample showed an endothermic event peaking at −7.0 °C, with two less distinct shoulder peaks, at lower (∼−15 °C) and higher temperatures (∼−2 °C) (Chiavaro et al., 2008; Tan & Che Man, 2002). Heating transition of canola oil displayed itself with a broad endotherm formed by four overlapping transitions; the major one peaked at about −16 °C, whereas the minor transitions were set at lower (about −26 and −22 °C, respectively) and higher (about −9 °C) temperatures, as previously observed (Tan & Che Man, 2002). All these profiles are related to the melting of different polymorphic forms of lipid crystals probably due to the kind of acyl moieties linked to glyceride skeleton.

3.3. PLS model construction for calibration and validation

The vegetable oils analysed in this study exhibited different substitution patterns, also differing in the chain length and position of the acyl moieties, as well as in their unsaturation degree, as above described. Thus, samples of oils from other botanical origin as well from different commercial categories were added to extra virgin olive oils to construct a more robust model for calibration, enlarging ranges of fatty acid composition.

A multivariate approach was used to obtain practical information to quantitatively approach DSC data, as differences in the DSC thermograms ascribable to fatty acid composition are not easily and always detectable by univariate analysis. In particular, PLS, a full data method, was proposed as possible solution, and it was applied to unfolded DSC data (Fig. 1B).

In order to predict the main fatty acids (palmitic, stearic, oleic and linoleic acids) and their percentage sums, (SFA, MUFA and PUFA) as well as quality ratios (O/L and U/S ratios) in olive oil, several multivariate calibration models were built by the PLS algorithm, using the pre-processed spectral data reported in Table 1 where the statistical summary and figures of merit from the DSC–PLS calibration for all oil parameters are also reported. The appropriate number of model dimensions, which was individually found out for each quality parameter, was determined applying the Haaland and Thomas statistical criterion ($\alpha = 0.75$) (Haaland & Thomas, 1988).

The best prediction ability was achieved when the PLS calibration was carried out on the mean centred (MC) unfolded DSC data of oil samples (Fig. 1C). In addition, for stearic acid also MSC pretreatment was necessary to achieve good results. Acceptable values were obtained for RMSE (root mean square error) and REC% (percentage relative error in calibration). These parameters measure the average error in the analysis and evaluate the goodness of fit of the calibration data to the models developed during calibration. LODs (limit of detection) under linear minimum calibration concentration were found, indicating that the linear range is able to quantification. R^2, which describes the goodness of fit of the predicted concentrations to their actual values, was higher than 0.90 for almost all parameters. A 0.78 R^2 value was found for stearic acid and this may be due to its narrow range of composition. The figures of merit demonstrated the quality of the models and the suitability of the method for the proposed determinations.

DSC–PLS statistical results for the prediction of selected parameters in the validation set are reported in Table 2. The validation set exhibited nearly quantitative recoveries (between 98.2% and 103.4%) for all calibrated parameters. Relative standard deviations below 7% were found for palmitic and oleic acids as well as for SFA whereas stearic and linoleic acids as well as MUFA and PUFA and U/S ratio exhibited relative standard deviations slightly higher but lower than 15%.

The yields obtained are illustrated in Fig. 2, showing a good agreement between predicted and actual levels on validation data

Table 2
DSC–PLS statistical results for the prediction of selected parameters in the validation set. Standard deviation is given in parentheses.

Validation	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	O/L	U/S	SFA	MUFA	PUFA
RMSE (conc. units)	0.878	0.248	2.232	0.995	1.263	0.584	0.986	1.753	1.040
REP (%)	6.89	9.15	3.13	10.25	14.87	9.63	6.07	2.39	9.95
R^2	0.936	0.776	0.901	0.947	0.843	0.838	0.906	0.939	0.944
Recovery (%)	100.0 (6.9)	103.0 (10.2)	100.6 (3.2)	100.1 (12.2)	103.4 (16.4)	100.9 (11.8)	99.6 (5.7)	98.2 (13.6)	100.4 (11.7)
Slope	0.94 (0.03)	0.80 (0.06)	0.93 (0.04)	0.95 (0.03)	0.91 (0.06)	0.95 (0.06)	0.91 (0.04)	0.91 (0.03)	0.93 (0.03)
Intercept	0.75 (0.46)	0.59 (0.16)	5.52 (2.99)	0.51 (0.34)	0.85 (0.50)	0.32 (0.32)	1.40 (0.70)	6.13 (2.38)	0.36 (0.36)

Abbreviations used: O/L, ratio between oleic and linoleic acid percentages; U/S, ratio between unsaturated and saturated fatty acid percentages; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; RMSE, root mean square error; REP, relative error in prediction.

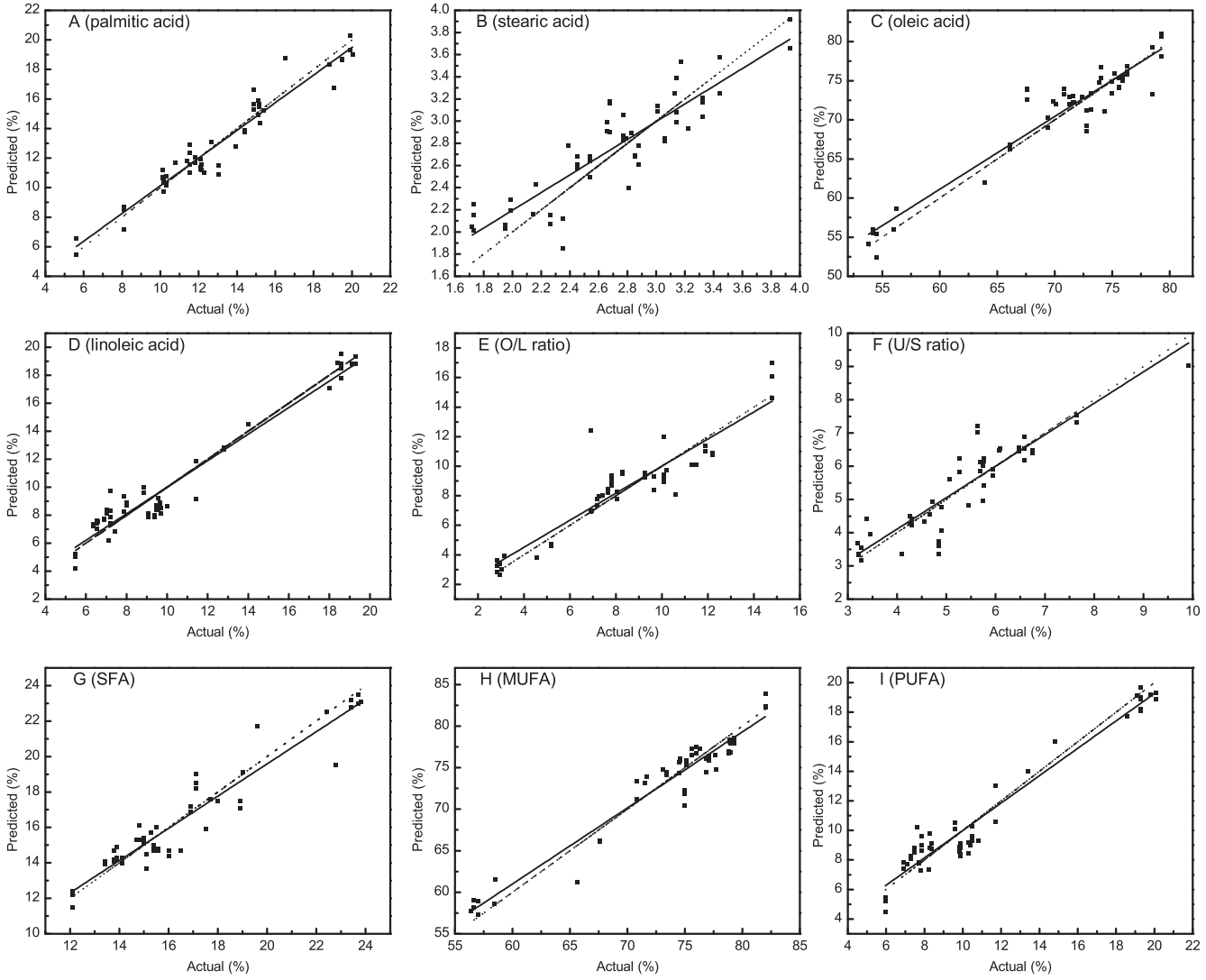

Fig. 2. Actual vs. DSC–PLS predicted values in the validation (■) sets for (A) palmitic acid, (B) stearic acid, (C) oleic acid, (D) linoleic acid, (E) O/L ratio, (F) U/S ratio, (G) SFA, (H) MUFA, (I) PUFA. Ideal fitting (intercept = 0, slope = 1, —) and actual fitting curves (- -) for predicted values of (A) palmitic acid, (B) stearic acid, (C) oleic acid, (D) linoleic acid, (E) O/L ratio, (F) U/S ratio, (G) SFA, (H) MUFA, (I) PUFA are shown.

sets. The fitting curves of actual vs predicted values are close to ideal fitting curve, slope and intercept equal to unity and zero, respectively, indicating low bias and absence of systematic regression errors (Table 2).

4. Conclusions

In this work, a novel strategy based on DSC–PLS for the determination of fatty acid composition of olive oil was developed, presenting an approach that was little or not present in literature jet and very suitable for the quality evaluation of the most precious vegetable oil. In particular, the model appeared to be suitable for the determination of overall, oleic acid content, which is related to oil health benefits. Results are also excellent for palmitic acid and SFA contents, showing very good correlation coefficients and low RMSE values in both calibration and validation sets. Satisfactory results were also obtained for MUFA, PUFA, stearic and linoleic acids, and O/L ratio in terms of percentage recoveries and relative

standard deviations. These good findings were obtained considering a large set of olive oil samples representative of the European market with the addition of few samples of different botanical provenience to enforce the robustness of the model, evidencing the capability of PLS based analytical procedures for simultaneously processing information obtained from different analytical signals as well as the discriminatory power resulted by DSC data.

In conclusion, this novel approach could provide results statistically similar to traditional official procedures in terms of analytical performance being very rapid and environmentally friendly and also proposing itself as a suitable tool for quality assurance besides than research purposes.

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