

Analytical Methods

Preliminary studies about thermal degradation of edible oils through attenuated total reflectance mid-infrared spectrometry

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ABSTRACT

Degradation of edible oils during their heating process has been evaluated through the determination of *cis*-unsaturation and *trans*-fatty acids together with free fatty acids as a function of time and temperature heating.

Two types of cooking oils, sunflower and seed (mixture of different seeds non-detailed), were heated at three different temperatures (147, 171 and 189 °C) during a total time of 1920 min (32 h) shared out in four sessions of 8 h each one, and samples were studied from their spectra obtained by Fourier transform infrared spectrometry using attenuated total reflectance measurements.

A critical comparison between different multivariate calibration models built based on full spectra or selected wavenumbers, using both PLS1 and PLS2 algorithms, was carried out for a preliminary evaluation of the heating conditions (temperature and time) of oil samples.

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1. Introduction

Fourier transform infrared (FT-IR) spectroscopy plays an increasingly important role in the analysis of edible oils by providing simple, non-destructive and rapid techniques to determine common oil quality parameters without any sample pre-treatment (Van de Voort, Ghetler, García-González, & Li, 2008; Van de Voort, Sedman, & Russin, 2001). As it is well known, this technique allows us qualitative information on molecular compounds, and quantitative data from the relationship between bands intensity and the concentration of major and minor oil constituents (Guillen & Cabo, 1997, 1999).

The characteristic flavour of fried foods derives from the formation of products corresponding to the frying fat alteration. Fried products absorb a high quantity of fat, which constitutes the frying media thus cumulating some alteration products. This kind of products comes from hydrolysis due to the food humidity, from oxidation of fats carried out by dissolved oxygen and from the thermal polymerisation, being the aforementioned processes temperature dependent. For this fact, stability of oils is conditioned by the presence of alteration products, which, over certain conditions, can attempt food quality and present harmful features for humans.

Lipids from oils and edible fats suffer from thermal degradation, when they are subjected to high temperatures in a persistent way, and because of that it is interesting to evaluate the heating conditions applied to edible oils.

Fat oxidation is developed in three phases: initialisation, propagation and completion. Initialisation phase takes place joint to the first free radical formation due to the heating of unsaturated molecules in the presence of oxygen. Propagation phase refers to chain reaction for free radical formation. In the presence of oxygen, the first formed free radical turns into peroxide, a free radical, which attacks another fat molecule. This last molecule, after losing a hydrogen atom, generates a hydroperoxide joint to another free radical. During the completion phase, the product degradation takes place, thus generating changes on smell and colour, as a consequence of the formation of molecules which affect the acidic, aldehydic, alcoholic or ketonic sensorial features due to the presence of peroxide and hydroperoxide compounds.

The use of edible oils in cooking involves the need of monitoring the evolution of frying oils in order to guarantee that they maintain appropriate parameters, which can be drastically modified during the heating process.

Methods to determine the rate at which the oil oxidation process advances are related to the measurement of the concentration of primary or secondary oxidation products or both, or to the amount of oxygen consumed during the process.

In the past few years, FT-IR spectroscopy has been successfully used to evaluate oxidative deterioration of culinary oils during frying, through univariate measurements of changes observed in the frequency data of some bands and also in the ratio of absorbance bands in the IR spectra, which have been correlated with changes in the unsaturation percentage (Moya-Moreno, Mendoza-Olivares, Amezcua-Lopez, Gimeno-Adelantado, & Bosch-Reig, 1999a), to the increase in *trans*-isomers (Moya-Moreno, Mendoza-Olivares,

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Amezquita-Lopez, Gimeno-Adelantado, & Bosch-Reig, 1999b), through the formation of carbonyl compounds (Moya-Moreno, Mendoza-Olivares, Amezquita-Lopez, Peris-Martínez, & Bosch-Reig, 1999c) or by changes in the free fatty acids (FFAs) level (Al-Alawi, Van de Voort, & Sedman, 2004), dielectric constant, colour, and viscosity, and by an increase in the number of polar molecules (Innawong, Mallikarjunan, Irudayaraj, & Marcy, 2004).

On the other hand, as stated by Vlachos et al. (2006) the resistance of oils to the oxidation process depends on the composition of the sample and on the conditions to which samples were subjected, as for example the flow of air or oxygen, the heating temperature and time, the presence or absence of light and catalysers and the exposure of the sample to a specific light frequency, amongst others (Guillen & Cabo, 2002).

To our knowledge, there are no precedents on the evaluation of heating conditions of edible oils through their IR spectra, and because of that we have developed a methodology to evaluate the heating time and temperature at which samples of oil were submitted. These studies were made by using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra combined with chemometrics, and could be of interest for the evaluation of fried edible oil quality.

2. Experimental

2.1. Apparatus and reagents

To obtain attenuated total reflectance (ATR) spectra, approximately 100 μL of each sample were deposited on a DuraSamplIR outfitted accessory (SensIR Europe Ltd., Birchwood, UK) with a nine reflection diamond/KRS-5 composite DiComp™ DuraDisk™ installed on a FTIR spectrometer model Tensor 27 from Bruker GmbH (Bremen, Germany) equipped with a KBr beamsplitter and a DLaTGS detector.

For instrument control and data acquisition, OPUS® program Version 4.1 for Windows® software from Bruker GmbH was also employed.

For oil heating, a 1 L volume deep fryer with concealed heating element, model Professional 1 (1000 W) from Taurus (Lleida, Spain) equipped with a stainless steel body and non-stick, die-cast oil tank with optimal heat transmission were used.

Temperature applied for oil heating in the different studies was measured and controlled by using a thermocouple with electrically controlled heater, model AKO (Barcelona, Spain).

2.2. Samples

For this study, two vegetable edible oil samples belonging to frequently used oils in Spain for food frying were employed. Sunflower-refined oil and seeds-refined oil samples (this later a mixture of different seeds non-detailed) were directly purchased from the Spanish market and treated as follows.

2.3. Thermal treatment

Approximately, 1 L of oil was placed in the fryer and was subjected to heating. A thermocouple was also introduced in the fryer and was used to measure and control sample temperature. To follow the edible oil degradation process during the heating period, one of each sample was subjected to three individual different heating processes at 147 ± 2 , 171 ± 2 and 189 ± 2 °C during a total time of 1920 min (32 h) shared out in four sessions of 8 h each one.

During the heating study, 2 mL sample aliquots were collected in the glass vials at 60 min intervals and were stored at room temperature until infrared measurements. ATR-FTIR spectra were ob-

tained directly from 100 μL of collected oil fractions, previously tempered by placing them in the same temperature controlled room where the spectrometer was located before to carry out the analysis. Moreover, the sample compartment temperature was monitored, and it remained stable at 26 ± 1 °C during the acquisition of IR spectra of all analysed samples.

2.4. Obtaining of ATR-FTIR spectra

ATR-FTIR spectra of heated oils were recorded by triplicate with a nominal resolution of 4 cm^{-1} , accumulating 32 scans per spectra taking 28 s for collecting each average spectrum.

Different strategies for cleaning the cell were evaluated in order to avoid cross-contamination between samples, and finally the crystal surface was cleaned using soft paper slightly wetted in acetone for assessing that the accessory was ready to collect additional replicates or new samples.

2.5. Quantitative univariate evaluation of chemical parameters of oils

cis-Unsaturation, *trans*-fatty acids content and free fatty acids were evaluated by means of univariate measurements made on ATR-FTIR spectra following vibrational methods previously described in the literature.

The *cis*-unsaturation degree of oils was determined from the quotient between the peak height of the C–H stretching vibration bands at 3010 and 2854 cm^{-1} from ATR-FTIR spectra (Afran & Newbery, 1991).

The *trans*-fatty acids content was established from the experimental procedure described in the Association of Analytical Communities (AOAC) Official Method (2000) and Adam, Mossoba, and Lee (2000). *Trans*-fatty acids were evaluated based on the peak area of the band located between 1007 and 930 cm^{-1} , after subtraction of the absorbance spectra of heated and untreated samples.

Free fatty acids (FFAs) were determined by measuring the C=O peak area between 1740 and 1685 cm^{-1} using one fixed point baseline correction located at 1650 cm^{-1} after rationing the sample spectrum against that of untreated oil (Ismail, Van de Voort, Emo, & Sedman, 1993).

2.6. Chemometric analysis

Spectra treatment and data manipulation were carried out using Omnic 6.1 and OmnicMacros 6.1 software from Nicolet (Madison, WI, USA). PLS calibration models were obtained by using TurboQuant Analyst 6.0 software developed by Thermo Nicolet Corp. (Madison, WI, USA). OPUS® for Windows® 4.2 software from Bruker GmbH (Bremen, Germany). This software was also used for hierarchical cluster analysis in order to evaluate the similarity of samples in terms of their ATR-FTIR spectra and to assess the number of characteristic subsets, in which samples could be divided. Similar criteria to that already published for oil and milk samples classification were used (Iñón, Garrigues, & de la Guardia, 2004; Iñón, Garrigues, Garrigues, Molina, & de la Guardia, 2003).

Root-mean-square error of calibration (RMSEC), root mean square error of cross-validation (RMSECV) and root mean square error of prediction (RMSEP) were used through the text to evaluate the ability of the models to fit the calibration data and to estimate the average deviation of the model from experimental data (Mark & Workman, 2007; Miller & Miller, 2000).

2.7. Cluster analysis

Cluster analysis classifies a set of observations into different *unknown* groups based on combinations of interval variables. The purpose of cluster analysis is to discover a system of organising

observations into groups, where objects of the groups share properties in common. It is cognitively easier to predict the behaviour or properties of objects based on group membership, all of which share similar characteristics.

In hierarchical cluster analysis, the similarity between samples is evaluated using the distance concept, calculated using a mathematical relationship (i.e., Euclidian norm) of numerical properties of the samples (i.e., absorbance at different wavelengths), and throughout this study cluster analysis was used to correctly select the different samples for calibration and prediction data sets (Everitt, Landau, & Leese, 2001).

3. Results and discussions

3.1. IR spectra of edible oils

Fig. 1 shows that infrared spectra of sunflower oil present differences after heating during 1920 min, especially in the regions around 3500, 1700, 1300–1200, 1050–800 and 575 cm^{-1} , due to changes in its composition.

As it can be seen, spectra in the mid-infrared region have well-resolved bands that can be assigned to different functional groups present in the oil (Guillen & Cabo, 1999). The small differences between spectra obtained before and after heating correspond to differences in the degree and form of unsaturation of the acyl groups and their length, and from the figure we can conclude that these differences, mainly located at the frequencies of the characteristic bands assigned to C=C, CH_2 and CH_3 , are related to the evolution of oil during the heating step.

3.2. Evolution of chemical parameters of oil during the heating process

On increasing the heating time of oils, the *cis*-unsaturation diminishes, and both the *trans*-fatty acids and the FFA content increases (see Fig. 2).

Using the recommended univariate procedures indicated in Section 2.5 to evaluate the *cis*-unsaturation, the *trans*-fatty acids and FFA content from ATR-FTIR spectra data reported in Fig. 2 were obtained for the heating process of both sunflower and seeds oil; as it can be seen a comparable behaviour was found for the two types of oil. However, the effect of temperature on *cis*–*trans* transformation for sunflower oil seems to be different than that

observed for seed oil (see Fig. 2A and B), and thus the general trend of these oils to reduce *cis*-unsaturation and to increase *trans*-fatty acids tends to follow a general model in the case of seeds oil for different temperature values and provides clearly differentiate theoretical models for each temperature in the case of sunflower oil.

On the contrary, for free fatty acids content, data found at 147 and 171 °C are closely similar for heating sunflower oil and provide different evolution lines in the case of seed oil.

A general conclusion from data shown in Fig. 2 indicates the difficulties to estimate the heating conditions of an oil sample from the aforementioned parameters, because close similar values of the evaluated indexes were obtained for different time–temperature conditions. So, it was decided to use a multivariate method to estimate the heating conditions of samples from the ATR-FTIR spectra based on the use of partial least squares (PLS) approaches.

3.3. Clustering of thermal-treated edible oil samples from their ATR-FTIR spectra

In order to evaluate possible classes amongst samples submitted to different thermal treatments, the ATR-FTIR spectra, obtained after different time and temperature heating of sunflower and seeds oil samples, were analysed by a clustering method based on the Euclidean distance after vector normalisation as pre-processing of data for the wavenumbers between 3996 and 519 cm^{-1} .

As it can be seen in Fig. 3, sunflower- and seeds-heated oils have a different behaviour evidenced by differences in groups classification based on ATR-FTIR spectra. However, a common guideline between both dendrograms is the evolution of groups from low to high temperature and from short to large heating times.

However, from the aforementioned tendency, it is not easy to identify the two main groups established from the Euclidean distance between spectra in separate terms of temperature or time, but it is quite evident that group A corresponds to soft heating conditions being group B mainly integrated by samples heated at 189 °C and for a time between 1500 and 1920 min.

In the case of seeds oil samples, group A1 (both A1a and A1b) corresponds to 147 °C and B2b to 189 °C, and the middle groups were integrated by samples heated at low temperatures and increasing time or at high temperature but during short periods of time.

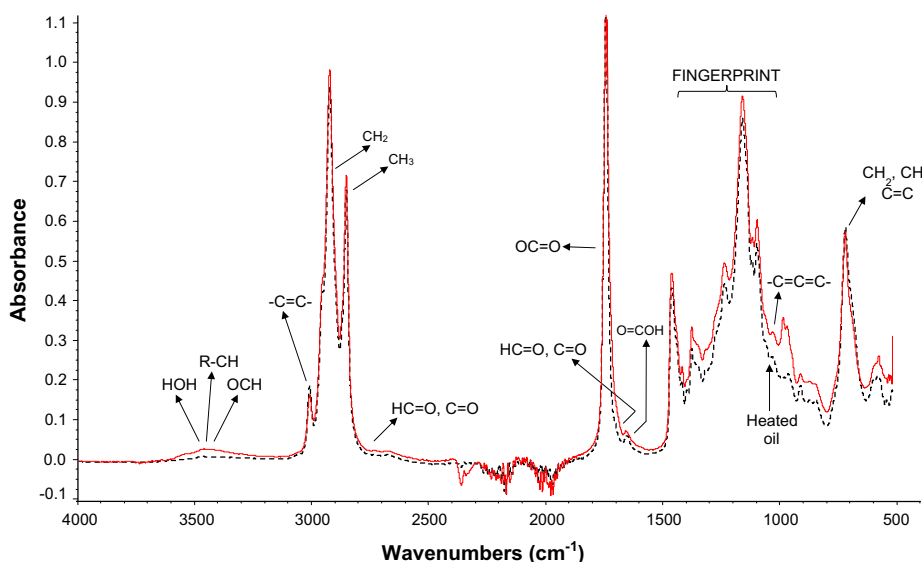
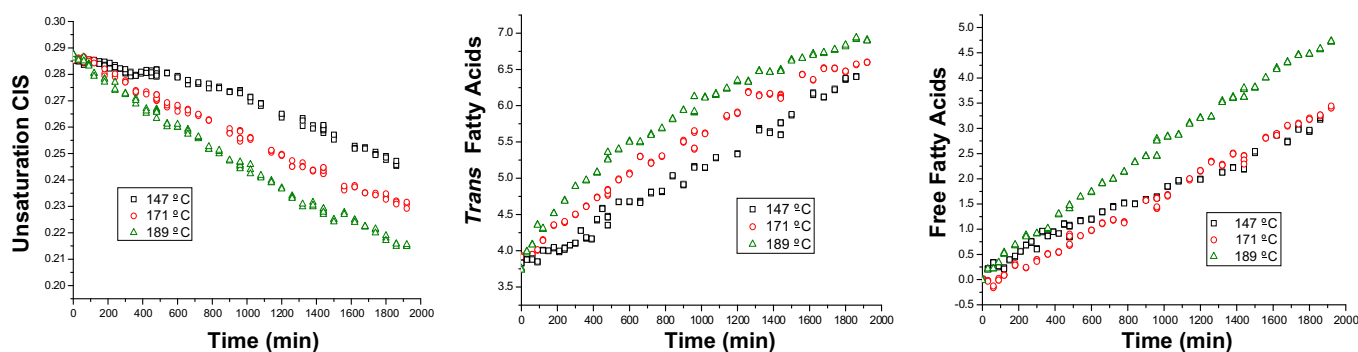


Fig. 1. ATR-FTIR spectra of untreated sunflower oil (—) and heated sunflower oil (---) at 147 °C during 1920 min.

A Sunflower edible oil



B Seeds edible oil

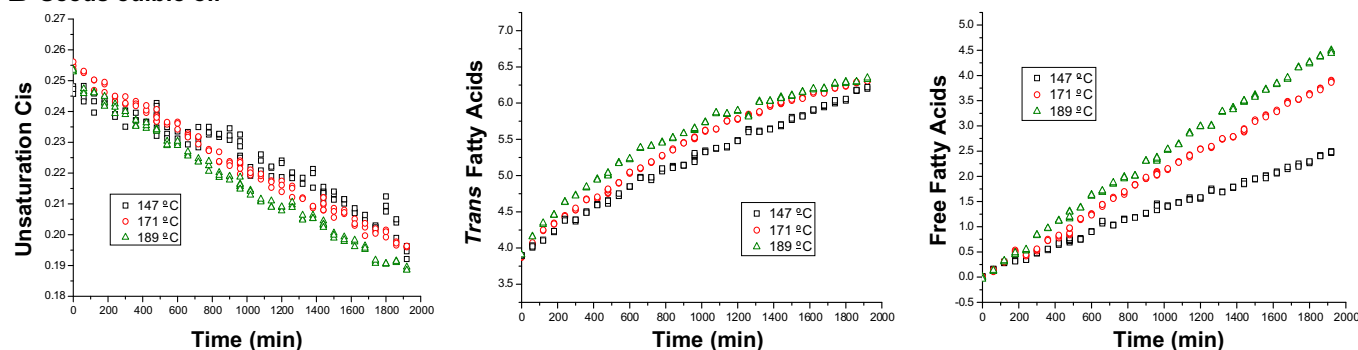


Fig. 2. Chemical parameters undergo evolution during heating process for sunflower (A) and seeds (B) oils.

In the case of sunflower-heated oils, differences in temperature treatment are not so clear as that for seeds oil, and thus group A is integrated by samples heated at three evaluated temperatures for short periods of time and only in the case of group B2b all samples classified in the group correspond to 189 °C.

In short, from the dendrographic classification of ATR-FTIR spectra of heated oils, it can be concluded that both oil types under study could be considered as different sample population and that for prediction of heating conditions calibration sets must include a pool of samples heated in different conditions to cover, at least, all the big sample groups from A1a to B2b.

3.4. Selection of the calibration set

The determination of an adequate number of samples to be used for calibration and their selection is always a critical factor in multivariate analysis. In this case, as in previous works, the selection was done based on the hierarchical cluster analysis results, using dendrograms depicted in Fig. 3 for selecting the calibration and validation datasets.

The sample selection criterion was based on the following principles: at least one sample of each cluster was selected for calibration. If the cluster is comprised more than one sample, the number of samples selected for calibration was approximately the root square of the total number of samples included in the cluster, whilst the remaining samples were integrated in the validation data set. Samples within a given cluster were selected randomly. So, for sunflower oil it used a calibration set of three replicates for 48 samples (144 spectra) and three replicates of 60 samples (180 spectra) for validation. In the case of seeds oil, 153 spectra (triplicates for 51 samples) were employed for calibration, and 162 spectra (triplicates for 54 samples) for validation. Additionally, an overall model was tried incorporating to the calibration set the sum of sunflower and seed oils samples selected before.

3.5. Partial least square modelling of ATR-FTIR data for time and temperature estimation

The most widely employed multivariate calibration method, partial least squares (PLS), was directly applied to evaluate the ATR-FTIR spectra of heated oils. Several spectral treatments and several algorithms (PLS1 and PLS2) were tested and different models were built and compared in terms of RMSEP values in order to evaluate their prediction capabilities for heated samples. Only the most significant results have been summarised in this paper.

3.6. Estimation of the heating time

Table 1 shows the experimental variables and features of PLS-ATR-FTIR models created for the estimation of heating time using either full spectra (except region displayed between 2402 and 1801 cm^{-1} as it was considered non-informative due to the high noise corresponding to the ATR element) or a selected spectral regions (in which samples presented significant differences), when PLS1 or PLS2 algorithms were employed. Mean centring spectral data pre-treatment was employed to eliminate common spectral information in both the cases.

As it can be seen, for PLS1 algorithm, the lowest calibration (RMSEC) and prediction (RRMSEP) errors were obtained for the separated consideration of each type of oil using both full spectra and selected wavenumbers data. However, when both the edible oils were processed together, lowest errors were found on using full spectra. For building the best calibration model, the adequate number of factors (selected based on the criterion of Haaland and Thomas (1988), which minimises the root mean square error of cross-validation) was similar for both strategies.

On the other hand, after application of PLS2 algorithm similar RRMSEP values were obtained for both full spectra and selected region data treatment. Nevertheless, in this case, the number of em-

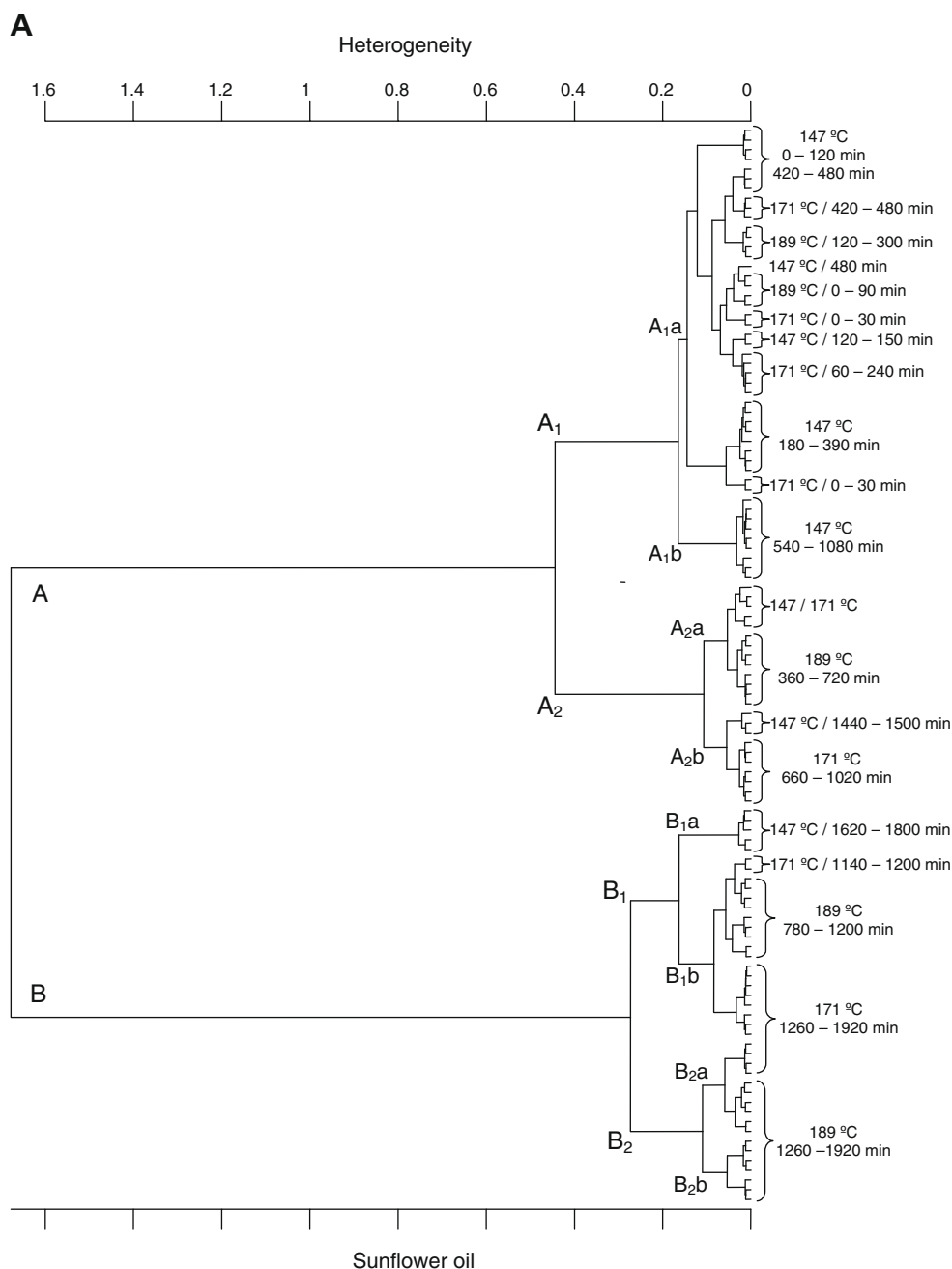


Fig. 3. Dendrographic classification of heated oil samples from their ATR-FTIR spectra for (A) sunflower and (B) seeds oils.

ployed factors is clearly lower on using full spectra than for selected wavenumbers.

It must be also noticed that the multiple correlation coefficient (r) of the calibration model provides similar values for all the situations assayed.

For both used algorithms, the quality coefficient (QC) values (Moros, Iñón, Garrigues, & de la Guardia, 2007) obtained were in general better for models based on selected spectral range than for full spectra models.

In short, the behaviour of seeds oil samples seems to be better modelled by processing the ATR-FTIR data than that of sunflower oil samples. However, the use of a common model provides acceptable errors with a little bit excessive number of factors but with a QC of around 30%.

However, the prediction capability of ATR-FTIR spectra to evaluate the heating time of fried edible oils is rather limited and could be used only for screening purposes.

3.7. Estimation of the heating temperature

A similar procedure to that followed for heating time estimation was made for building calibration-prediction models to evaluate the heating temperature. In this case, (Table 2) shows the best prediction capabilities obtained for this parameter. On comparing data reported in Table 2 with those included in Table 1, it can be seen that the different PLS models assayed present a similar behaviour. However, as it can be seen, both PLS1 and PLS2 in this case provide QC values between 0.3% and 7%. So, it is clear that ATR-FTIR spectra

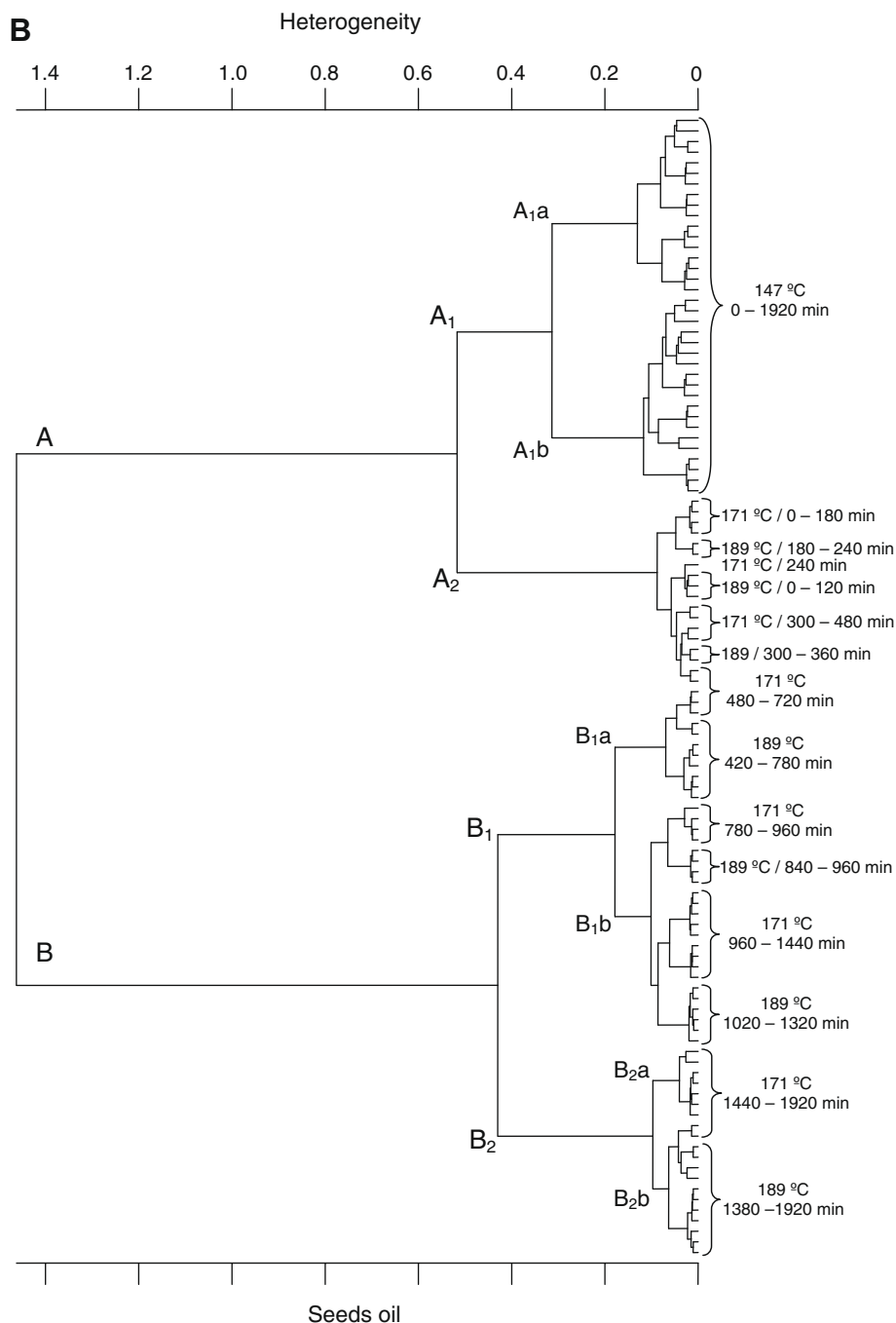


Fig. 3 (continued)

of processed samples offer an excellent way for the accurate prediction of the heating temperature at which samples were submitted. However, these excellent results must be considered just as a preliminary estimation because of the high number of calibration items used for only three values of heating temperature, which could justify the small errors found for new samples estimated by the model.

3.8. Evaluation of heating conditions on oils used for frying

In order to evaluate the developed models heated sunflower samples used to fry potatoes and other foods were evaluated from their ATR-FTIR spectra.

Data found for different samples heated at 170 ± 10 °C for periods between 150 and 600 min using the PLS1 model based on selected wavenumbers provided estimated data between 157 and 160 °C and time heating values, which varied from 500 to 1440 min thus evidenced that the model developed seems to work very well for heating temperature estimations in any condition (presence or absence of food) and fails for time estimation when oil was heated in the presence of food.

These data could be interpreted by the presence of water and other oxidative compounds (such as starch) in potatoes and other fried foods, which could either undergo an acceleration of the oil thermal degradation or modify the intensity of some characteristic bands used for the time prediction model performance. So, new

Table 1

Prediction capabilities of PLS-ATR-FTIR models for heating time estimation of vegetable edible oils.

	Full spectra			Selected wavenumbers		
	Sunflower oil	Seed oil	Overall	Sunflower oil	Seed oil	Overall
<i>PLS1</i>						
Calibration set	144	153	297	144	153	297
Validation set	180	162	342	180	162	342
Spectral region (cm ⁻¹)	3882–2402/1801–554			1768–1654/1508–939		
Factors	9	4	9	10	5	10
RMSEC (min)	59	66	74	48	39	102
<i>r</i>	0.995	0.993	0.992	0.997	0.998	0.98
RMSECV (min)	130	98	166	82	61	122
RMSEP (min)	116	69	105	57	48	131
RRMSEP (%)	13	7	8	6	5	14
<i>s</i> _{trip} (min)	80	14	35	27	20	49
QC (%)	82	24	26	18	12	30
<i>d</i> _{x–y} (min)	–5	–11	–18	–7	3	–20
<i>s</i> _{x–y} (min)	116	69	103	56	48	130
<i>PLS2</i>						
Calibration set	144	153	297	144	153	297
Validation set	180	162	342	180	162	342
Spectral region (cm ⁻¹)	3882–2402/1801–554			1768–939		
Factors	4	4	4	10	9	10
RMSEC (min)	43	75	63	44	29	73
<i>r</i>	0.998	0.991	0.994	0.997	0.999	0.98
RMSECV (min)	170	99	180	84	48	98
RMSEP (min)	65	70	101	55	47	83
RRMSEP (%)	7	7	10	6	5	9
<i>s</i> _{trip} (min)	38	12	38	26	19	33
QC (%)	12	58	58	14	9	27
<i>d</i> _{x–y} (min)	–4	–4	–16	–6	–0.6	–12
<i>s</i> _{x–y} (min)	65	70	99	54	47	82

Note: Factors were selected to obtain the best prediction capabilities of the model for the validation set. *r* is the multiple correlation coefficient for calibration. RMSEC is the root mean square error of calibration; RMSECV is the root mean square error of cross-validation, RMSEP is the root mean square error of prediction and RRMSEP is the RMSEP divided by the mean value of time in the validation dataset. *s*_{trip} is the standard deviation of three replicates. *d*_(x–y) and *s*_(x–y) are the mean difference and the standard deviation of mean differences between predicted vs. actual time values (min), respectively. QC is the quality coefficient.

Table 2

Prediction capabilities of PLS-ATR-FTIR models for the estimation of heating temperature of vegetable edible oils.

	Full spectra			Selected wavenumbers		
	Sunflower oil	Seed oil	Overall	Sunflower oil	Seed oil	Overall
<i>PLS1</i>						
Calibration set	144	153	297	144	153	297
Validation set	180	162	342	180	162	342
Spectral region (cm ⁻¹)	3882–2402/1801–554			1469–1126		
Factors	10	6	2	5	6	8
RMSEC (°C)	1.9	7	12	4	0.8	3
<i>r</i>	0.994	0.91	0.74	0.98	0.999	0.98
RMSECV (°C)	16	14	19	8	15	18
RMSEP (°C)	2.5	8	12	4	0.7	4
RRMSEP (%)	1.5	5	7	2	0.4	2
<i>s</i> _{trip} (°C)	1.7	0.08	0.08	1.6	0.7	1.7
QC (%)	1.3	5	7	2	0.3	2
<i>d</i> _{x–y} (°C)	0.06	–0.9	0.2	0.11	–0.19	0.3
<i>s</i> _{x–y} (°C)	3	8	12	4	0.7	4
<i>PLS2</i>						
Calibration set	144	153	297	144	153	297
Validation set	180	162	342	180	162	342
Spectral region (cm ⁻¹)	3882–2402/1801–554			1768–939		
Factors	4	8	10	10	5	10
RMSEC (°C)	1.8	0.5	3	1.7	1.1	3
<i>r</i>	0.994	0.9995	0.98	0.995	0.998	0.99
RMSECV (°C)	9	1.5	6	3	1.7	4
RMSEP (°C)	3	0.8	5	2	1.1	3
RRMSEP (%)	1.5	0.4	3	1.4	0.6	2
<i>s</i> _{trip} (°C)	1.7	0.7	2	1.2	0.8	4
QC (%)	1.4	0.3	3	1.4	0.6	1.9
<i>d</i> _{x–y} (°C)	0.11	–0.2	0.6	0.04	–0.4	0.4
<i>s</i> _{x–y} (°C)	3	0.7	5	2	1.0	3

Note: The meaning of the different evaluated parameters is the same as that indicated in Table 1.

future studies are in due course to evaluate these effects related with food cooking and particularly the influence of humidity and food composition in the thermal degradation of oil.

4. Conclusion

Attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) affords a lot of structural information in order to evaluate the degree of compositional changes of oils as a function of their heating process. In general, data reported in this study evidence the good capacity of the system to evaluate the heating temperature and the possibilities offered in the estimation of the heating time through the use of selected wavenumbers model built from the ATR-FTIR spectra of oil samples heated under controlled conditions.

On comparing both PLS1 and PLS2 models, the general rule can be confirmed. The use of PLS2 provides a common set of PLS factors for all analytes, and this fact simplifies the procedure and data interpretation and it enables a simultaneous graphical inspection. However, it is surprising that in spite of the fact that time and temperature heating conditions are strongly correlated and one may expect that the PLS2 model could be more robust than separated PLS1 models, practical experience in this case indicates that PLS1 calibration performs equally well or better than PLS2 in terms of predictive accuracy. Thus, when the ultimate requirement of the calibration study is to enable the best prediction, a separate PLS1 regression for each parameter could be advised. From results obtained in the present work PLS1 models could be recommended for the estimation of oil heating conditions.

On the other hand, it is interesting to notice that the use of hierarchical cluster analysis of ATR-FTIR spectra offers an excellent way to evaluate the prediction capabilities of the model for new samples by making a comparison of their cluster classification.

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