Talanta 88 (2012) 358–368

Contents lists available at SciVerse ScienceDirect

Talanta

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

A multiway chemometric and kinetic study for evaluating the thermal stability of edible oils by ^{1}H NMR analysis: Comparison of methods

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ARTICLE INFO

Article history:
Received 27 June 2011
Received in revised form 24 October 2011
Accepted 1 November 2011
Available online 6 November 2011

Keywords:
Edible oils
NMR
Chemometrics
Kinetics
Thermal stability
Principal component analysis
N-way PCA
Tucker3

ABSTRACT

The degradation process of edible oils of different nature, submitted to heating at 170 °C, 190 °C and 210 °C with aeration, was studied by means of ^{1}H nuclear magnetic resonance spectroscopy (NMR). In this study, secondary products such as aldehydes were detected and monitored over time. Two complementary analytical approaches were adopted to characterize the kinetics of the appearance of aldehydes in the heated oils. This first was a classical kinetic approach based on the assumption that the overall degradation reaction to form aldehydes follows a rate law of order 1. This approach allowed us to calculate a thermal stability criterion for classifying the oils according to their heat stability. A second approach was to use the spectral fingerprint corresponding to aldehydes in a multivariate data analysis procedure in order to give the major trend in the studied phenomena, taking into account the multiway nature of recorded data. The application of different 3-way and 4-way Tucker3 models led to a better understanding of the chemical stability of the oils studied and was used to determine the order of stability of these oils. This multiway approach provides additional information that 2-way processing (PCA) does not provide clearly, such as the overall contribution of the heating time factor on the chemical evolution of oils. In conclusion, this work shows that a fully chemometric study of NMR spectra allows to order the oils according to their thermal stability and to achieve a result in good agreement with existing analytical and kinetic studies in the literature.

1. Introduction

This study deals with the controlled heating of edible oils (rapeseed, sunflower and virgin olive) at high temperatures. Numerous chemical reactions contribute to the chemical and physical aging of oils. During heating, the oils undergo degradation and their functional and organoleptic features are significantly modified. The heating induces chemical reactions such as oxidation, polymerization, hydrolysis and *cis*/*trans* isomerization, which have an impact not only on the nutritional value of oils but may also generate toxic compounds damaging to health [1,2].

The most important cause of deterioration of oils is oxidation. Among the oxidation products, our interest has focused particularly on secondary oxidation products such as aldehydes because they are rarely present in natural unheated oil, as described by Choe et al. [3] from the study of secondary oxidation products proposed by Frankel [4].

The oxidation, thermal stability, chemical composition, and quality of edible oils under various conditions have previously been studied using various techniques such as infrared [5,6] and Raman spectroscopy [7–9], 1D and 2D NMR [10–16], differential scanning calorimetry [17–22] and front-face fluorescence spectroscopy [23,24]. Among these reports, few showed any tools or methods to determine the thermal stability of samples on the basis of a ^{1}H NMR kinetic measurements and chemometric treatment of NMR spectra.

In this work, an analytical approach was first adopted to calculate a new semi-quantitative criterion of thermal stability of oils. This new test is based on the assumption that by focusing on a selected portion of the spectra and for a relatively short time, we can model the appearance of aldehydes by a kinetic law of order 1, knowing that the mechanisms actually at work are more complex and associated with radical reactions. In a second part of this work, we compare the conclusion drawn from the kinetic approach and the conclusion provided by N-way principal component analysis. The N-way approach is used here as a descriptive and qualitative

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doi:10.1016/j.talanta.2011.11.001

Table 1
Chemical shift assignment of the ^{1}H NMR signals of the products generated in the oxidation process of virgin olive, rapeseed and sunflower oils during oven heating and their multiplicities.

Compounds	Chemical shift (ppm)	Functional group
Trans-2-alkenals	9.480 and 9.506 (d)	–CHO (aldehydic group)
Trans, trans-2,4-alkadienals	9.507 and 9.533 (d)	
Cis; trans-2,4-alkadienals	9.580 and 9.606	
N-alkanals	9.748 (t)	
4-hydroxy-trans-2-alkenals	9.560 and 9.586 (d)	
4,5-epoxy-trans-2-alkenals	9.538 and 9.564 (d)	
Short chain alkanals or oxo-alkanals	9.778 (t)	

d: doublet; t: triplet.

tool and for providing a rapid way for ordering the thermal stability of oils.

2. Materials and methods

2.1. Materials

Three types of edible oils were analyzed. Rapeseed, sunflower and virgin olive oils were purchased at a local supermarket and used in a thermal oxidation study. Approximately 12 mL of oil were placed in 10 cm diameter glass dishes and were subjected to heating in a laboratory oven with temperature control. Each of the three types of oil was heated at 170 °C, 190 °C and 210 °C, which are close to home-cooking temperatures. Three samples of 1 g were collected every 30 min until the end of the heating process, fixed at 180 min, resulting in a total of 189 samples to be analyzed. Samples were cooled in an ice-water bath for 4 min in order to stop thermal-oxidative reactions and then directly analyzed.

2.2. ^{1}H NMR analysis

Between 0.3 and 0.5 g of oil was introduced into an NMR tube (I.D. 5 mm) with 700 μL of deuterated chloroform for the sample to reach a filling height of approximately 5 cm. The proton NMR spectrum was acquired at 300.13 MHz on a Bruker 300 Advance Ultrashield spectrometer with a 7.05 T magnetic field. A basic spin echo sequence was applied. The acquisition parameters were: spectral width 6172.8 Hz; pulse angle 90–180°; pulse delay of 4.4 μs; relaxation delay 3 s; number of scans 64; plus 2 dummy scans, acquisition time 5.308 s, with a total acquisition time of about 9 min. The experiment was carried out at 25 °C. Spectra were acquired periodically throughout the thermal oxidation process. The assignments of the signals were done following recommendations proposed by Johnson et al. [25]; Guillén et al. [11,14,26]; Sacchi et al. [27], and are given in Table 1. The area of the signals was determined using the instrument manufacturer's software and integrations were performed in triplicates to obtain average values. All plots of ^{1}H NMR spectra or spectral regions were plotted with a fixed value of absolute intensity for comparison.

2.3. Data processing and statistical analysis

The computations were performed using the MATLAB environment, version R2007b (Mathworks, Natick, MA, USA) and with the N-way Toolbox [28].

2.4. Data

The initial matrix (189 samples × 1001 variables) contains ^{1}H NMR spectra of three oils at three heating temperatures and seven heating times.

A well known problem in NMR spectroscopy results from variations in proton chemical shifts due, for instance, to small instabilities in the magnetic field from one day to another, making it difficult to directly superimpose the recorded spectra. Thus, it is imperative to correct these shifts in each spectrum before applying a comprehensive approach for data processing. To facilitate this preprocessing, a procedure based on correlation optimized warping was applied. This warping algorithm is widely used in the field of spectroscopy and chromatography [29–31]. To complete the preprocessing, the baselines were corrected using a cubic spline interpolation procedure. The realigned matrix was then analyzed by PCA and N-way algorithms.

2.5. Kinetics

The first treatment applied on the spectra was the integration of each peak of interest between δ 9.0 and 9.8, corresponding to aldehydic protons of the components produced during the heating. The ratio between this surface value and that of the peak at δ 7.25, corresponding to traces of chloroform ($CHCl_3$) in the deuterated solvent ($CDCl_3$), was used as input data for the kinetic calculations. Small variations in the quantities of oil and $CDCl_3$ introduced into the NMR tube were corrected for by adjusting the calculated surface ratios using the corresponding masses of $CDCl_3$ and oil.

2.6. Principal component analysis

NMR signals between δ 9.0–9.8 were treated using principal component analysis (PCA), an unsupervised data analysis tool oriented towards decomposing the variance/co-variance matrix calculated from the data matrix into combinations of the original variables (principal components) containing the maximum variability. PCA is useful to monitor samples during a process. Briefly, PCA produces orthogonal components by decomposing the initial data matrix $\mathbf{X}$ into a matrix product $\boldsymbol{T}\cdot\boldsymbol{P}^{\boldsymbol{T}}$ (the "$\mathbf{T}$" in $\boldsymbol{P}^{\boldsymbol{T}}$ means "transposed matrix"). $\boldsymbol{T}$ (or T-matrix) is commonly named the ***scores*** matrix. In the T-matrix. The matrix $\boldsymbol{P}$ called *loadings* shows which variables are responsible for patterns found in scores T.

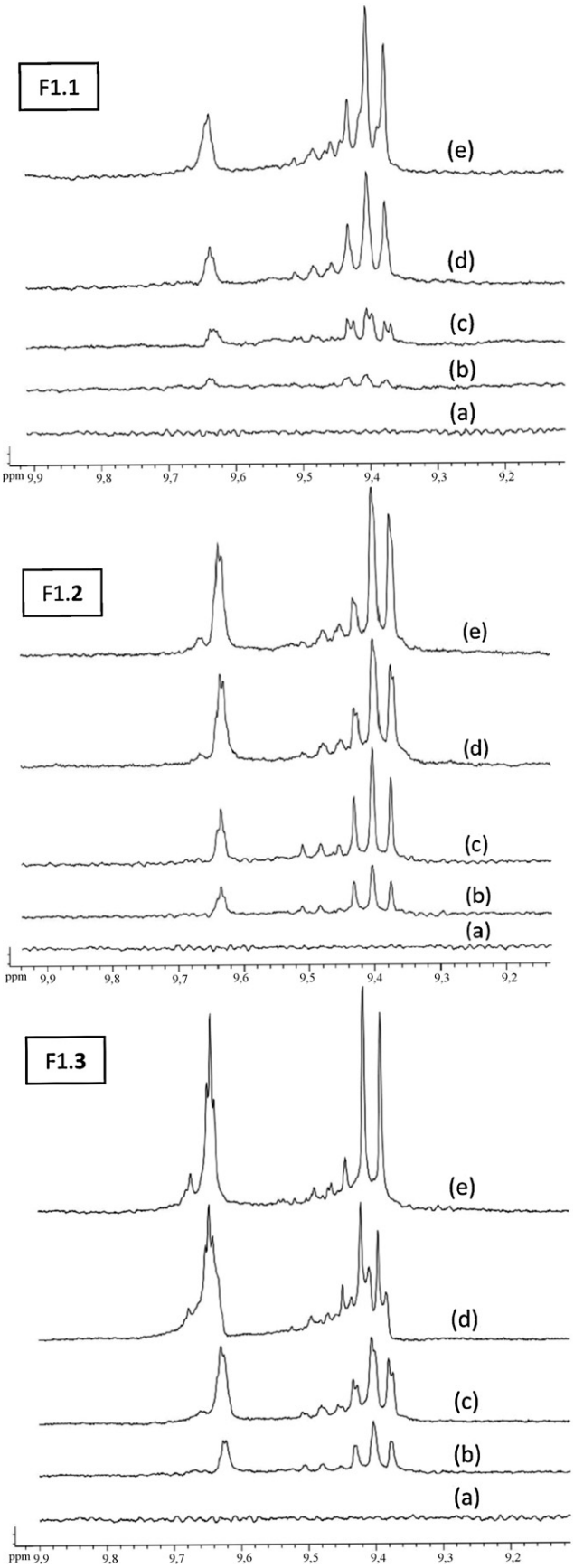
2.7. Tucker3

A Tucker3 analysis was also applied to the data to take advantage of its multiway structure. Conceptually, the Tucker3 model [32] is a generalization of two-way data decomposition methods such as PCA or singular value decomposition (SVD) to higher order arrays or tensors [8,9]. In such multiway methods, scores and loadings are not distinguishable and are commonly treated as numerically equivalent.

Being a generalization of principal component analysis to multiway data arrays, the Tucker3 model has for its objective to represent the measured data as a linear combination of a small number of optimal, orthogonal factors. For a 3-way data array, the Tucker3 model takes the following form:

$$x_{ijk} = \sum_{u=1}^{r}\sum_{v=1}^{s}\sum_{w=1}^{t} g_{iu}h_{jv}e_{kw}c_{uvw} + \varepsilon_{ijk}$$

where, x_{ijk} are the measured data, g_{iu}, h_{jv} and e_{kw} are the elements of the loading matrices for each the three ways (with r, s and t factors, respectively) and c_{uvw} are the elements of the core array (of size $r \times s \times t$), while ε_{ijk} are the elements of the array of the residuals. The core array in the Tucker3 model allows the extraction of different numbers of factors for each of the three modes. A tutorial on chemical applications of Tucker3 was proposed by



	Heating Conditions (min)
(a)	Not heated
(b)	30
(c)	60
(d)	120
(e)	180

Fig. 1. Expanded region between δ 9 and δ 10 of the ^{1}H NMR spectra of rapeseed oil at different times during heating (F1.1) at 170 °C, (F1.2) at 190 °C, (F1.3) at 210 °C.

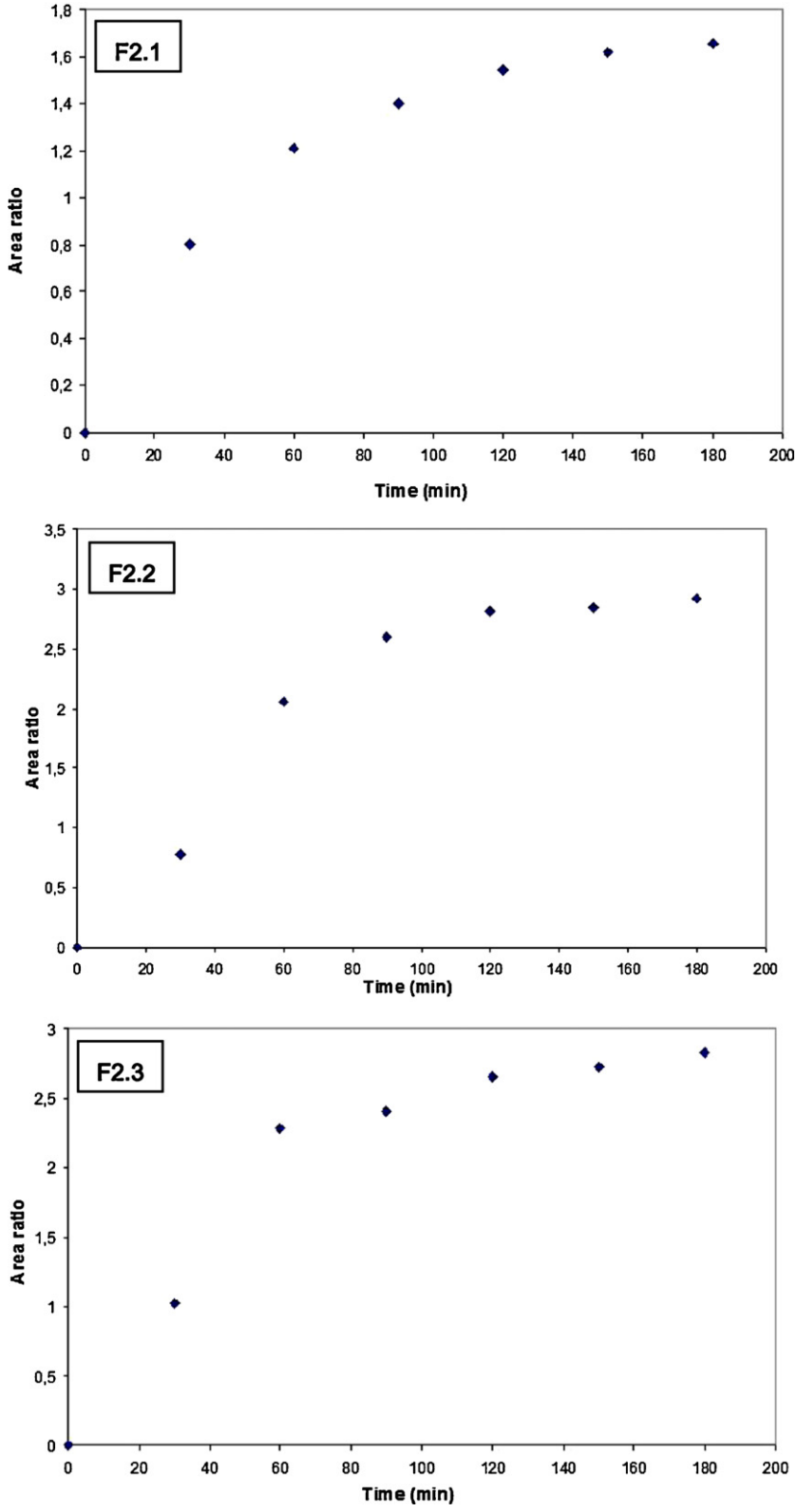


Fig. 2. Kinetics curves obtained for (F2.1) olive, (F2.2) sunflower, (F2.3) and rapeseed oils during 0 and 180 min of heating at 210 °C. Data represented are the ratios between the area under the peak of aldehydic protons (δ 9.4) and the area under the $CDCl_3$ peak (δ 7.25).

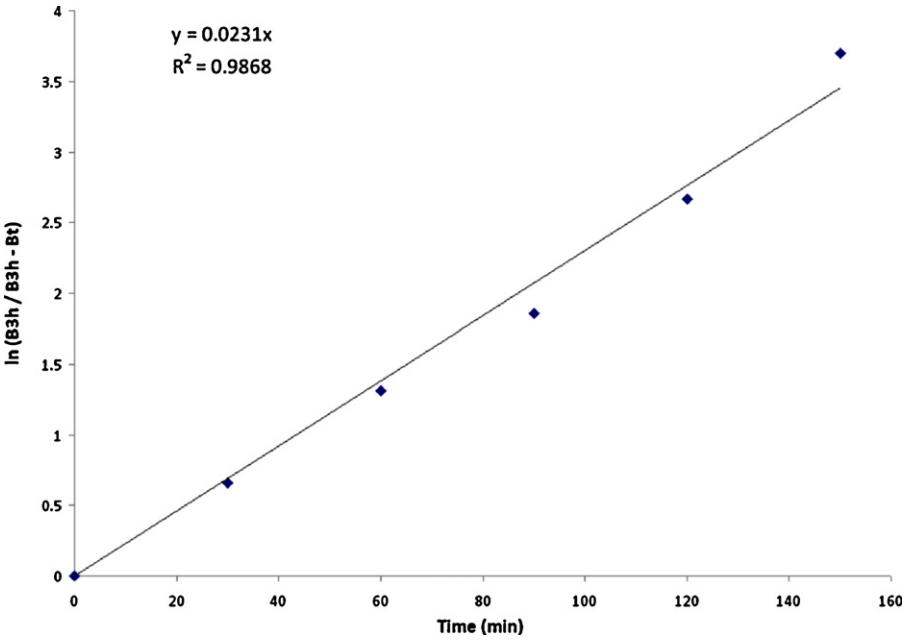


Fig. 3. Kinetics curves calculated from Eq. (5) for olive oils during 180 min of heating at 210 °C. Data shown are ratios between area of peak of aldehydic protons (9.4 ppm) and area under $CDCl_3$ peak (7.25 ppm). Similar curves are obtained for rapeseed and sunflower oils.

Henrion [33], while Kroonenberg [34] gives a detailed mathematical description of the model and discusses advanced issues such as data preparation/scaling and core rotation. For a complete and very pedagogical comparison of Tucker3 with PARAFAC, another multiway procedure, see Jiang [35].

3. Results and discussion

3.1. General observations

The chemical changes taking place in the oils over time and at different temperatures, were monitored by ^{1}H nuclear magnetic resonance spectroscopy.

The spectral region between δ 0 and δ 7.2 was not used in this work because the changes observed were not exclusively specific to heating by-products, as were those in the spectral region between δ 9 and δ 10. Figs. 1.1–1.3 present this spectral region for rapeseed oil for different heating times at 170 °C, 190 °C and 210 °C. The increase in the aldehydic protons peaks over time and as a function of temperature is clearly visible. It is to be noted that the temperature has a similar effect in this spectral region for sunflower oil but with a different patterns of peaks. This reflects differences in the structure of the aldehydes formed in the two oils. The effect of temperature is much smaller for olive oil due to the composition of the fatty acids and a higher concentration in natural antioxidants such as tocopherols. The aldehydic peak pattern observed for the olive oil used in this study is similar at 170 °C, 60 min from those observed by Guillèn et al. [26] after 240 min of heating under microwave conditions (see Fig. 8). In their study, Guillèn and coworkers produced samples under a microwave heating and record spectra every 10 min up to 240 min. They stopped the heating in order to insure the sample temperature remains lower than 190 °C. In our case, we observed different peaks patterns over 60 min heating. This is probably due to differences in the heating modes, the initial composition of the oils and/or to a small extent, the characteristics of the NMR spectrometers. Guillèn et al. used a microwave oven to heat samples and a 500 MHz NMR spectrometer whereas we used a classical oven to produce thermal oxidative conditions and a 300 MHz spectrometer.

3.2. Kinetic approach

Based on the evolution of aldehyde peaks over time, it was assumed that they follow first order kinetics. Fig. 2 shows the kinetics curves obtained from integration of the aldehydic peaks between δ 9.0 and 9.8. A sharp increase is observed during the first 100 min of heating, followed by a stabilization leading to a plateau. This type of curve can be modeled by the following simplified global schematic reaction:

$$A \xrightarrow{k} B \tag{1}$$

where A corresponds to concentration of all the components consumed in the corresponding global thermal process, B corresponds to the concentration of all the aldehydic compounds formed during the heating, and k is the apparent rate constant of this global process, corresponding to a weighted average of each individual reaction rate constant.

Under these conditions, the rate of appearance of oxidation products (aldehydes) can be modeled using a classical first order law and its expression is given by Eq. (2):

$$v_{global\,process} = -\frac{dA}{dt} = +\frac{dB}{dt} = k[A]_t \tag{2}$$

where k is the apparent rate constant and represents the speed at which the aldehyde precursors are oxidized, and its inverse (Eq. (3)) can be interpreted as a constant characteristic of thermal stability of the oil, in so far as this reaction is concerned.

$$k_{thermal} = \frac{1}{K_{TS}} \tag{3}$$

(TS = thermal stability).

After integrating the rate equation, the concentration of B (aldehydes) with time is expressed as:

$$B_t = A_0(1 - e^{-kt}) \tag{4}$$

To evaluate B_t, it is first necessary to determine B at $t = \infty$. In our case B_t at 3 h $\approx A_0$, and $e^{-kt} = 0$ for $t = \infty$. Thus, substituting into Eq. (4), we obtain:

$$B_t - B_0 = -B_0 \cdot e^{-kt}$$

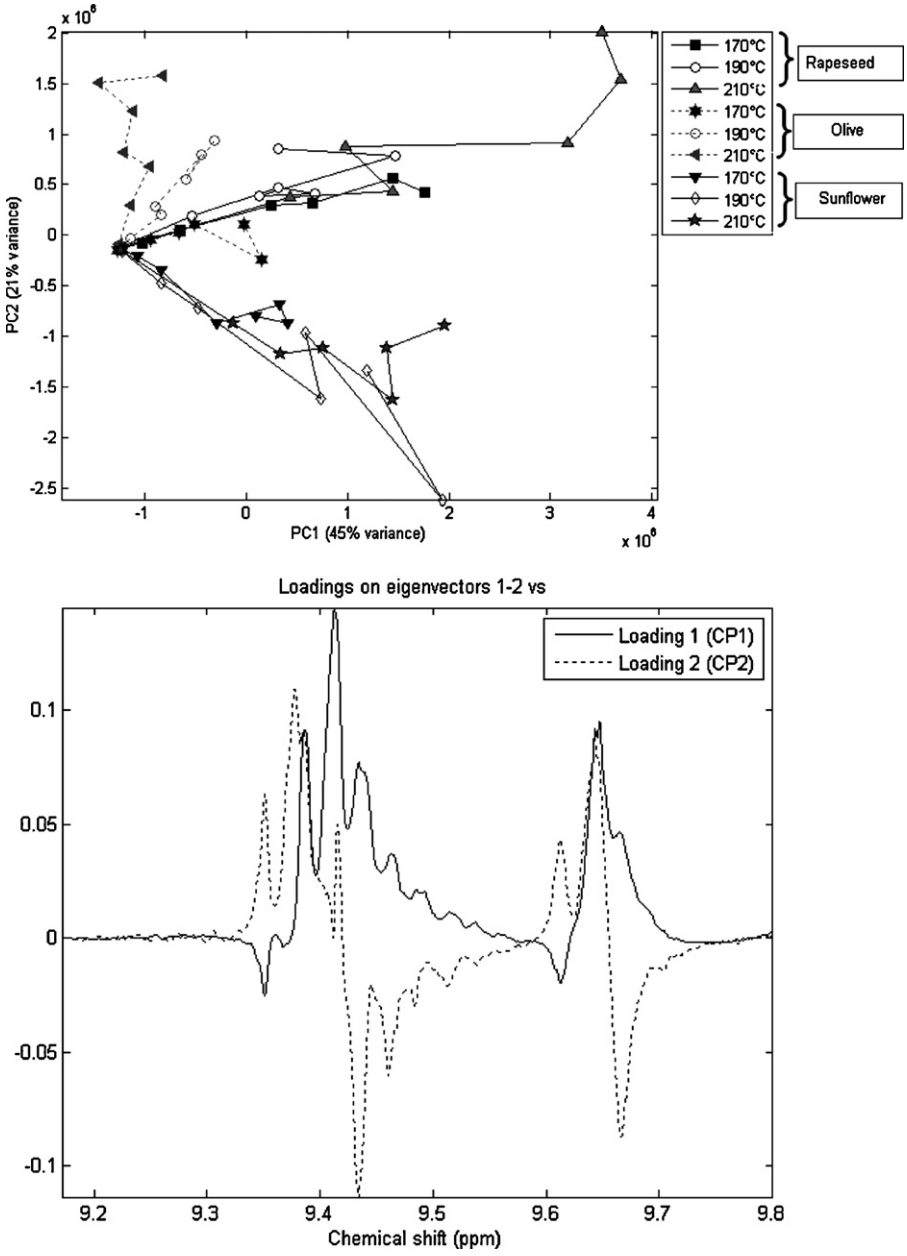


Fig. 4. PCA scores (up) and loadings (bottom) of (63 × 1001) data matrix for 3 types of oils and 3 heating temperatures. In both cases, only PC1 and PC2 are represented.

And then, $\ln(B_\infty/(B_\infty - B_t)) = kt$

i.e.

$$\ln\left(\frac{B_{3h}}{B_{3h} - B_t}\right) = f(t) \quad (5)$$

Fig. 3 shows the kinetics obtained by applying Eq. (5) to rapeseed sunflower and olive oils heated to 210 °C. The same type of results was obtained for 170 °C and 190 °C.

The slope of the straight lines obtained is the constant defined by Eq. (3). The smaller the rate constant k, the more stable the oil for the aldehyde peak at δ 9.4. Table 2 presents the results for K_{TS} values calculated for the oils from the slope values and for each temperature of heating. Based on these K_{TS} values, it is possible to propose a stability order for these oils at each heating temperature.

Table 2 shows the differences in thermal stability of the three oils at lower temperature and how this stability decreases as the temperature increases. We interpret this fact as a consequence of both direct thermal acceleration of the lipid oxidation reaction and the destruction of protective antioxidants. At 210 °C, the three types of oils have similar oxidation kinetics.

Table 2
K_{TS} values calculated from ^{1}H NMR data of aldehyde peaks at 9.4 ppm and thermal stability order proposed for comparing studied edible oils at three heating temperatures.

	170 °C	190 °C	210 °C
K_{TS} value (min^{-1})			
Rapeseed (RO)	75.75	54.05	44.25
Olive (OO)	163.93	67.11	43.29
Sunflower (SO)	109.89	70.92	40.16
Stability order			
	OO ≫ SO ≫ RO	SO ≈ OO > RO	OO ≈ RO ≈ SO

The stability order determined by this method is in good agreement with literature data on the thermal stability of rapeseed, olive and sunflower oils [26,36,37] carried out by NMR and Infrared spectroscopy. These studies have shown that olive oil is always more

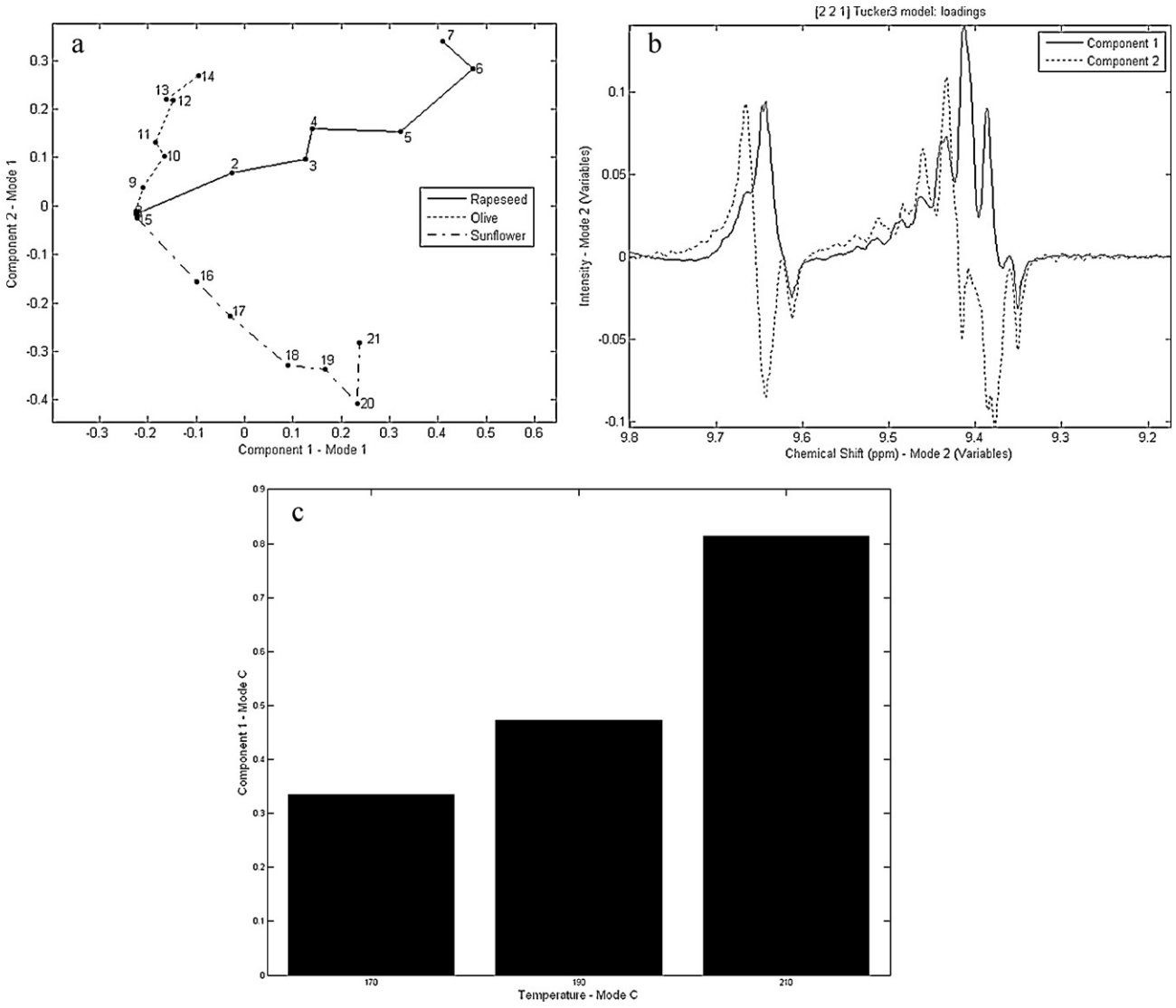


Fig. 5. Tucker3 procedure with [2 2 1] model performed on (21 × 1001 × 3) matrix; Rapeseed, sunflower and olive oils heated at 170, 190 and 210 °C from 0 to 180 min. (a) Loadings on mode A (samples); (b) loadings on mode B (NMR variables); (c) loadings on mode C (temperature).

stable than other types of oil due to its high content of antioxidants like tocopherols. And second, between rapeseed oil and sunflower oil, studies in oxidizing conditions have shown that sunflower oil is slightly more stable than rapeseed oil.

3.3. Chemometric approaches

A complementary approach was adopted using principal component analysis (PCA) and Tucker3 approaches (3-ways and 4-ways datasets). Our objective was to find an alternative way to evaluate the thermal stability of oils taking into account the multiway nature of the data.

3.4. Principal component analysis

PCA scores plots show classical trajectories with time and temperature of the three oils and 66% of the total variance are explained by the first 2 components (see Fig. 4). The scores plot shows that the thermal degradations are quite different, with that of olive oil being much less extensive and with that of rapeseed being more similar to olive oil than to sunflower oil. This observation makes sense because olive oil and rapeseed oil have approximately the same range of oleic acid (respectively 55.0–83.0% and 52.0–67.0% [38]) which is one of the three major unsaturated fatty acids of edible oils, along with linoleic and linolenic acids, while sunflower oil has a lower content (14.0–38.0%). The smaller spread of scores for olive oil at a given temperature indicates that chemical changes caused by heating over time are more pronounced in rapeseed and sunflower than in olive oil. Olive oil is also different from the other two oils in that the orientation of its scores trajectory is different for each temperature. The plot of the PC1 and PC2 loadings suggests that the chemical evolution of the sunflower oil and olive oil are not characterized by the formation of the same aldehyde protons. The scores for PC1 characterize the time factor for sunflower, rapeseed and olive oils at 170 °C, while the loadings for PC1 characterize the progressive appearance of trans-2-alkenals and E,E-2,4-dialkadienals associated with peaks at δ 9.534, 9.507 and 9.554 (see Fig. 4) and of the short chain alkanals associated with the peak at δ 9.766. The scores for PC2 are more related to the time factor for rapeseed oil and olive oil at 190 and 210 °C. The loadings for PC2 are characterized by several peaks: δ 9.497 and 9.506 (possibly related to the increase of trans-2-alkenals), δ 9.763 and δ 9.786 (N-alkanals and short chain alkanals or oxo-alkanals) and δ 9.553 (possibly 4,5-epoxy trans-2-alkenals). According to Guillén

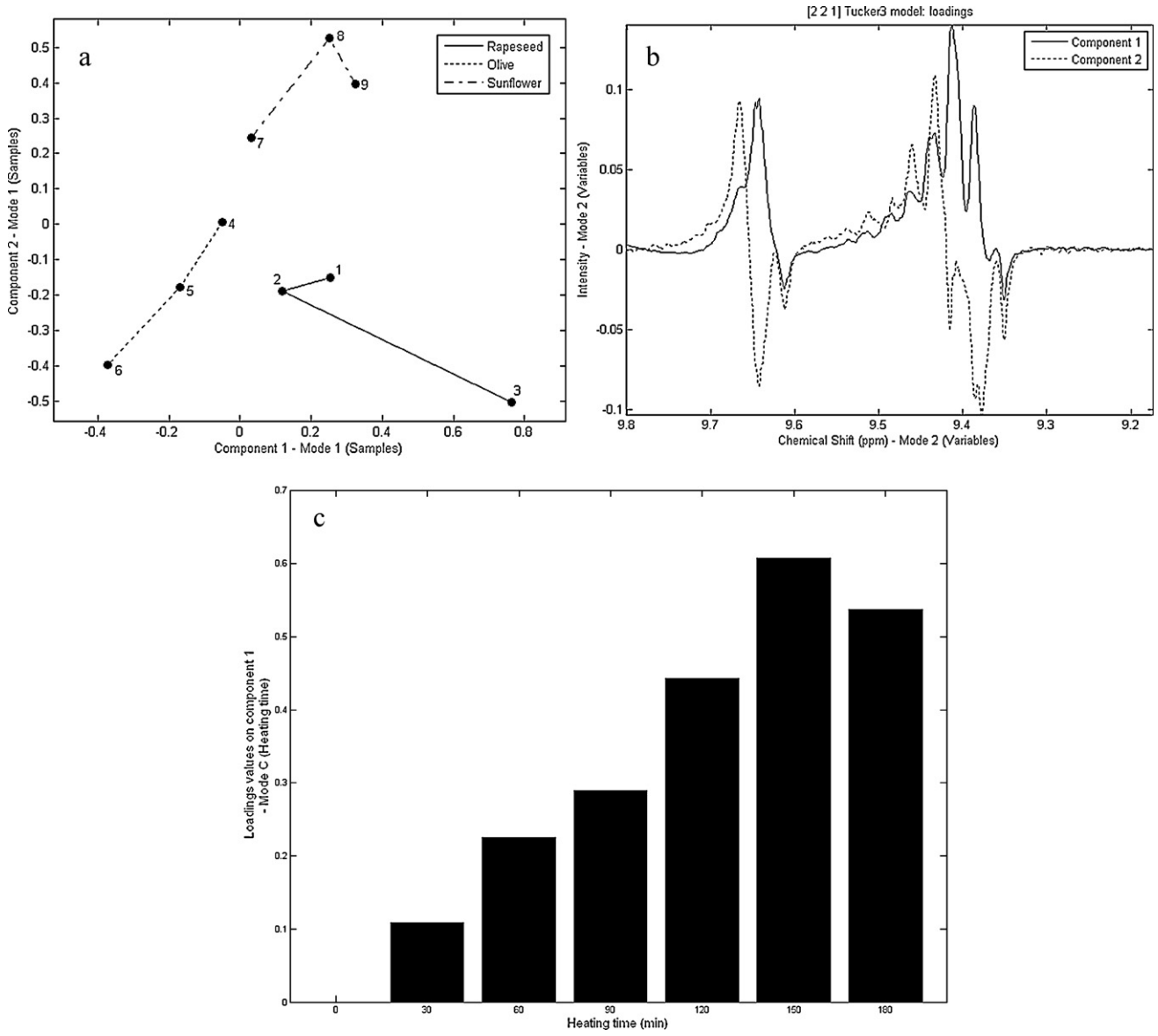


Fig. 6. Tucker3 procedure with [2 2 1] model performed on (9 × 1001 × 7) matrix; Rapeseed, sunflower and olive oils heated at 170, 190 and 210 °C from 0 to 180 min. (a) Loadings on mode A (samples); (b) loadings on mode B (NMR variables); (c) loadings on mode C (heating time).

et al. [11,39] these compounds are among the secondary oxidation products. The loadings of each PC give a clear idea of which peaks increase or decrease during the heating and allow a better understanding of what differentiates the oil samples from a chemical point of view. However, no other obvious information on the effects of the temperature and heating time is given by the 2-way PCA. A multiway approach was therefore tested.

3.5. N-way PCA: Tucker3

The data is initially in a 4 way array (3 Oils × 1001 variables × 3 temperatures × 7 heating times). Two additional rearrangements were performed for a multiway processing: (oils × heating times) × variables × temperatures (21 × 1001 × 3) and (oils × temperatures) × variables × heating times (9 × 1001 × 7). The pre-treatment used is *j*-scaling. According to the Tucktest which is a model selection procedure included in the N-way toolbox [28], in both 3-way cases, a [2 2 1] multiway-model is sufficient. In the 4-way data arrangement, the Tucktest gave a [2 2 1 1] model as the best choice. The recovered percentage of total variance is nearly 50% for all tested models and allows a simultaneous interpretation of the three or four modes in which we find clear and consistent results of the chemical kinetics and conventional PCA (see Table 3).

Table 3
Total variance recovered in terms of chemometric model used.

Chemometric technique	Model type	Model description	%Explained variance
Classical PCA	2PCs	–	66.0 (PC1 + PC2)
Tucker3	[2 2 1]	(3 Oils × 7t) × 1001V × 3 T	56.7
Tucker3	[2 2 1]	(3 Oils × 3 T) × 1001 V × 7t	52.9
Tucker3	[2 2 1 1]	3 Oils × 1001 V × 3 T × 7t	47.9

3.5.1. 3-way Tucker3 [2 2 1] with data cube (21 × 1001 × 3)

The *mode A* of this data arrangement shows the evolution of each type of oil over time (Fig. 5a). One can note that the distance between two points of curves is not equal, indicating that the kinetics of the changes is not constant for each time lapse. A possible interpretation is that between two sampling intervals

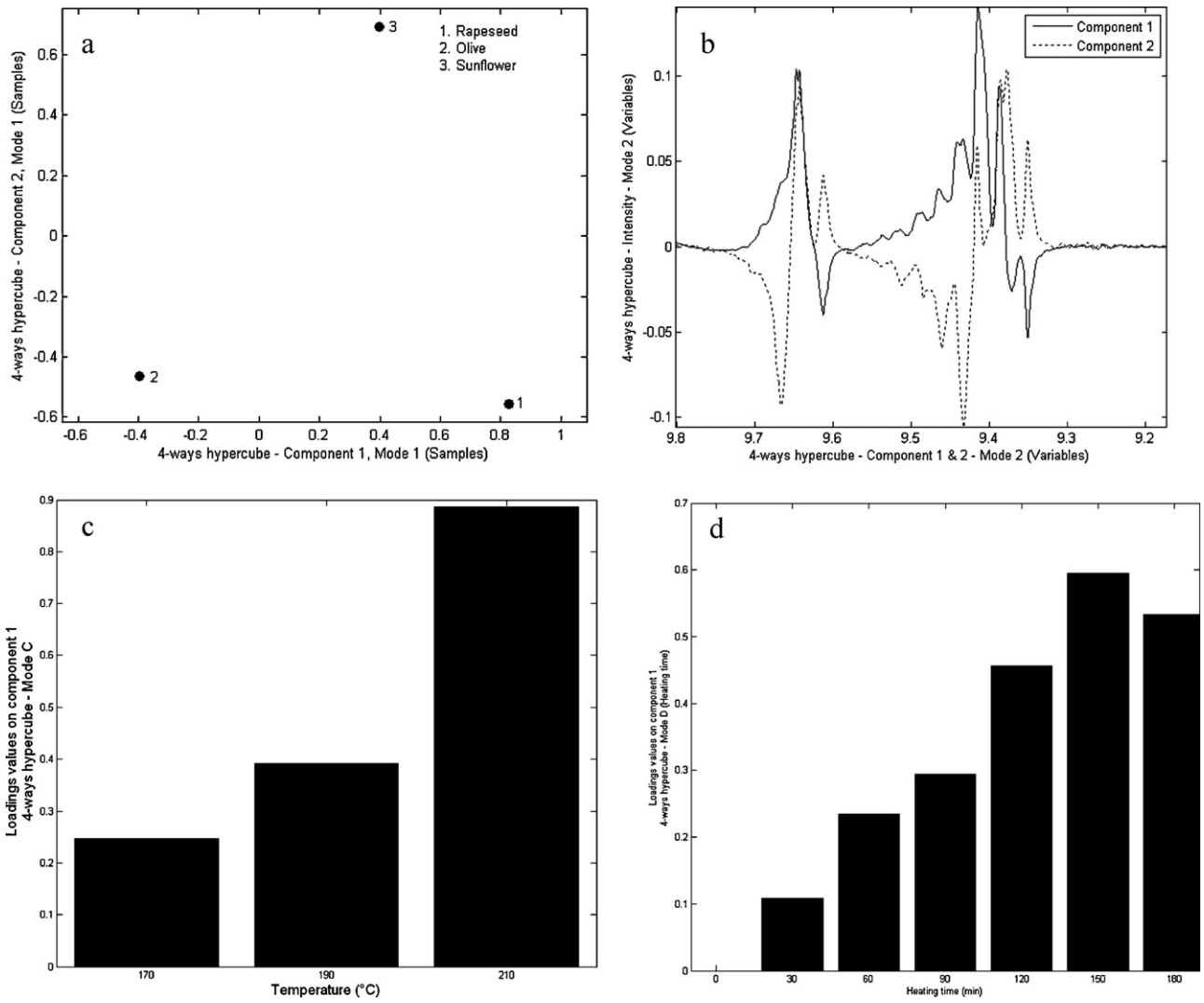


Fig. 7. 4-way Tucker3 procedure with [2 2 1 1] model performed on (3 × 1001 × 3 × 7) data hypercube; rapeseed, sunflower and olive oils heated at 170, 190 and 210 °C from 0 to 180 min. (a) Loadings on mode A (samples); (b) loadings on mode B (NMR variables); (c) loadings on mode C (temperature); (d) loadings on mode D (heating time).

(e.g. 60–90 min), chemical changes due to heating are not similar between each oil and do not occur with the same rate. *Mode A* is very similar to the scores-plot of 2-way PCA. The curve related to the olive oil samples is shorter than the other curves, indicating that olive oil is more stable than rapeseed and sunflower oil.

Mode B (Fig. 5b) is the same as the 2-way PCA loadings and does not give any new information. The main result is provided by *Mode C* (Fig. 5c), which shows the contribution of the temperature to the global kinetics. Particularly, it can be seen that the difference between 210 °C and 190 °C is much greater than the difference between 190 °C and 170 °C.

3.5.2. 3-way Tucker3 [2 2 1] with data cube (9 × 1001 × 7)

In this data arrangement, *Mode A* (Fig. 6a) shows the contribution of the temperature in distinguishing between the oil samples. *Mode A* shows the effects of oil types and temperatures. This loadings plot confirms *Mode C*, the loadings-plot of the previous Tucker3 model computed on the (21 × 1001 × 3) data cube. Along Factor 1, one observes a greater distance between the points for 190 °C and 210 °C (i.e. Rapeseed oil: distance between points 2–3 vs. distance between points 1–2 or for olive: distance between points 5–6 vs. distance between points 4–5) than between 170 °C and 190 °C. This difference is not as great for olive oil as for the other oils and is greatest for rapeseed oil. This provides a concrete point of view on the relative thermal stability of these oils. *Mode B* (Fig. 6b) is the same as for PCA and the previous Tucker3. *Mode C* (see Fig. 6c) shows the global contribution of the heating time factor on the chemical evolution of the oils. From a general point of view, this loadings plot presents the general evolution (increasing) of aldehydic components in samples over time. Here we find the general shape of the kinetics curves obtained in the first part of this work.

3.5.3. 4-way Tucker3 [2 2 1 1] with data hypercube (3 × 1001 × 3 × 7)

Treatment with the 4-way [2 2 1 1] model can find all the previous results, while recovering nearly 50% of the total variance (Table 3). The 4-way approach allows an easy visualization of the relationships between the factors studied. *Modes A* and *B* (Fig. 7a and b) clearly show which NMR variables are responsible for the differentiation of the samples from a chemical point of view by Factor 1 and Factor 2. As previously with the 3-ways models, rapeseed and olive oils are distinguished by Factor 1 mainly by the NMR peaks at δ 9.471 and δ 9.534, which are associated with *trans*-2-alkenals and *trans,trans*-2,4-dialkadienals, while Factor 2 allows a good separation of sunflower oil. Sunflower oil is therefore richer in *trans*-2-alkenals (peaks at δ 9.506 and δ 9.498) with lower

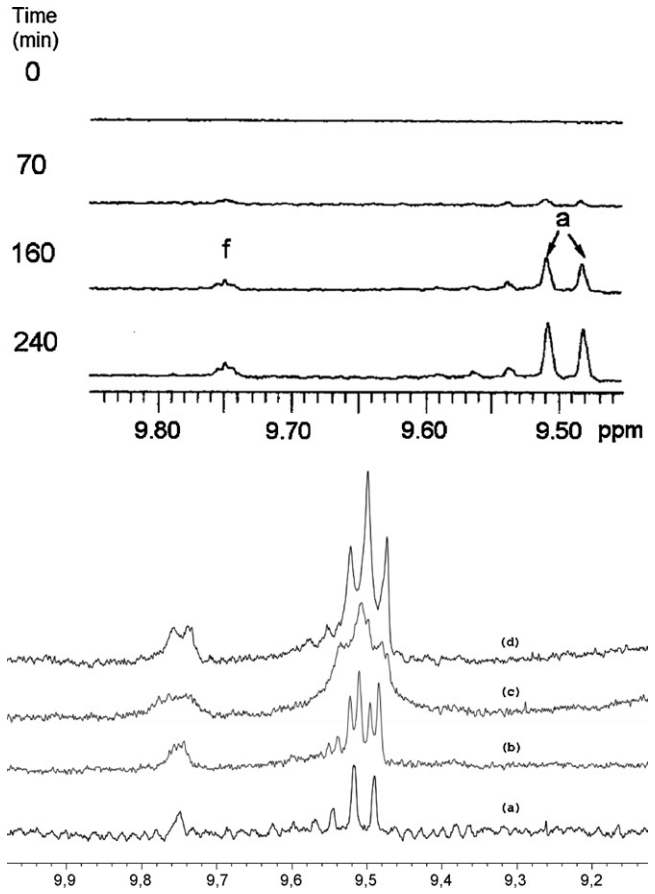


Fig. 8. ^{1}H NMR spectra for olive oil submitted to 170 °C during (a) 60 min, (b) 90 min, (c) 150 min, and (d) 180 min, obtained with a 300 MHz spectrometer and classical heating (drying oven). On top: NMR spectra obtained by Guillèn et al. on 500 MHz NMR spectrometer and microwave heating.

Source: Illustration from Guillèn et al., Food Chem. 96 (2006) 665–674.

Table 4
Thermal stability order of the studied oils given by chemometric methods OO: olive oil, RO: rapeseed oil, SO: sunflower oil.

	Observed thermal stability order		
	Temperature		
	170 °C	190 °C	210 °C
2-way PCA	OO > SO >= RO	OO > RO >= SO	OO > SO ≫ RO
N-way PCA		OO ≫ SO >= RO	

contents in short chain alkanals or oxo-alkanals and *trans,trans*-2,4-dialkadienals (peaks at δ 9.786 and δ 9.553, respectively), these latter therefore being more characteristic of olive and rapeseed oils.

Mode C (Fig. 7c) presents the contribution of the temperature on the global kinetics as previously illustrated by the *Mode C* of the Tucker3 procedure applied to the $(9 \times 1001 \times 7)$ data cube. And finally, *Mode D* (see Fig. 7d) is identical to the *Mode C* of the Tucker3 procedure applied to the $(21 \times 1001 \times 3)$ data cube showing the global contribution of the heating-time factor on the chemical evolution of the oils studied.

3.5.4. Thermal stability ordering by chemometric results

Table 4 resumes the thermal stability order based on the interpretation of chemometric results including 2-way PCA and N-way PCA (Tucker3). This qualitative stability order was determine using the scores plots of 2-way PCA and the samples loadings of N-way PCA by evaluating the multivariate distance (Euclidean) of sample points for each temperature in the case of 2-way PCA and for overall temperatures in the case of N-way PCA. The result is presented as qualitative inequalities.

4. Conclusion

Using NMR spectra, we adopted an analytical approach to calculate a new quantitative criterion for thermal stability of oils. Based on the assumption of first-order kinetics, a simple model allows monitoring of the appearance of aldehydes in heated oils with good approximation. The differential equations expressing the rate law can lead to the constant *K*, corresponding to the inverse of a rate constant, which we call the constant of thermal stability. Its calculation for the three kinds of oils (rapeseed, olive, sunflower) at 170, 190 and 210 °C can provide an order of stability of oils. Olive oil is more stable than sunflower oil and rapeseed oil, regardless of the heating temperature. Sunflower oil appears generally more stable than rapeseed oil. The order of thermal stability observed at each temperature by the kinetic approach is very similar to that given by the use of the 2-way (simple PCA) and N-way chemometric methods (Tucker3). These multiway tools give complementary information about the effects of temperature and heating time on chemical evolution in the samples and allow a better understanding on the differences observed experimentally. These results are in good agreement with the literature data concerning the thermal stability of these oils and show that this chemometric point of view well reflects the underlying chemical oxidation reactions under the conditions of this study.

Further work could lead to a tool for assessing the quality and stability of oil solely from spectral data using a basic chemometric method and a carefully constructed database for controlling quality and thermal stability of different varieties of edible oil.

Acknowledgements

We thank Dr. Marcia B. France from the Washington and Lee University (Department of Chemistry, Science Center, Lexington, VA) for reviewing the manuscript, and Dr. Luc Eveleigh (From Analytical Chemistry Laboratory, UMR1145 INRA/AgroParisTech, Paris, France) for his tips and discussion on the kinetics of oils.

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