Evaluation of long-heating kinetic process of edible oils using ATR–FTIR and chemometrics tools

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Abstract Long thermal oxidative kinetic and stability of four different edible oils (colza, corn, frying, sunflower) from various brands were surveyed with the use of attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) combined with multivariate curve resolution–alternative least square (MCR–ALS). Sampling from the heated oils (at 170 °C) was performed each 3 h during a 36-h period. Changes in the ATR–FTIR spectra of the oil samples in the range of 4000–550 cm^{−1} were followed as a function of heating time. MCR–ALS was utilized to resolve the concentration and spectral profiles of three detected kinetic components. Three variations in resolved concentration profiles were related to the thermal-deduction of triacylglycerol of unsaturated acid, appearance of hydroperoxides form of triacylglycerols and generation of secondary oxidation products. The kinetic profiles of these species were dependent on the type of oil. The proposed method can define a new way to monitor the oils' quality.

Keywords Edible oils · Heating process · Oxidative kinetic · ATR–FTIR · MCR–ALS

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Introduction

Checking the oil quality during heating is an important concern in food industries. It is well-known that, the edible oils mainly consist of triacylglycerols which are esters derived from glycerol and three saturated or unsaturated fatty acids (FAs) chain. The major FAs which characterize different oils generally consist of 14–18 carbon atoms. On the other hand, oxidation of oil induced by heating is an important degradation reaction and an undesirable chemical change with significant effect on the oil's flavour, aroma, and nutritional quality and also may cause side effects on human health (Le Dréau et al. 2009a; Ng et al. 2014; Gonçalves et al. 2014). Therefore, it is so important to make sure about the oils' quality after alterations accelerated by heating of edible oils.

Investigation of oil's oxidation processes is an approach for evaluation of its quality and thus lots of tests have been developed up to now for measuring oil oxidation's products. For example, iodometric titration has been used for measuring the peroxides and hydroperoxides, the acid number are measured by titration with a solution of potassium hydroxide, saturated and unsaturated fatty acids are determined by gas chromatography and gas chromatography–mass spectrometry, etc. (Armenta et al. 2007; Le Dréau et al. 2009a, b).

All of these tests are applicable to evaluate the oil quality but most of these official methods, such as titrations for the determination of acidity and peroxide content are time-consuming, laborious and are environmentally hazardous because of involving organic solvents. To increase analytical performance in these measurements, different analytical methods such as gas chromatography (GC) (Mannina et al. 1999), high performance liquid chromatography (HPLC) (Hein and Isengard 1997) and

vibrational spectroscopy (Muik et al. 2003; Christy and Egeberg 2006; Armenta et al. 2007) have been used in order to check the stability of edible oils, control of their possible denaturations or adulterations. However, in comparison to GC and HPLC, Fourier transform infrared spectroscopy (FTIR) is simpler and less expensive. Thus FTIR has been utilized as an acceptable technique in control of edible oil quality and monitoring its heating process (Armenta et al. 2007; Le Dréau et al. 2009a, b). In this work, we used the attenuated total reflectance–FTIR (ATR–FTIR) to analyze the heating kinetics of oil samples. Non-destructive, need minimal or no sample preparation, ease-of-use, and speed of operation can be stated as the bold characteristics of FTIR method. Because of the complex matrix of foods, their analysis with FTIR methods has been limited in some cases, but great advances in the application of FTIR techniques for food analysis have been occurred with the aid of chemometrics methods (Karoui et al. 2010).

Although lots of reports have been published on the coupling the infrared spectroscopy with chemometrics for analysis of oils (Moros et al. 2009; Le Dréau et al. 2009a; Karoui et al. 2010; Pinto et al. 2010; Javidnia et al. 2013; Luna et al. 2015), limited researches have been done with IR on the heating oxidative products of edible oils (Le Dréau et al. 2009a). Le Dréau et al. heated some edible oils for 3 h at 130 °C and the presence of four components in the oxidation process of the oils was proposed in their work with the aid of MCR-ALS as a chemometrics treatment (Le Dréau et al. 2009a).

In the current research, the focus was on the kinetics of long-time severe heating treatment of edible oils. We surveyed the oxidation kinetic of four types of oils including colza (canola), corn, frying and sunflower oils, which were heated for 36 h at 170 °C. MCR-ALS was utilized to resolve spectral and concentration pattern of the main produced/degraded species. It is worthy to mention that this work tried to include both variation of oil type and their brands in the investigation of thermal stability. The proposed approach could be applied in monitoring of the oils' quality and comparing their thermal stability during the heating oxidative process.

Materials and methods

Samples and reagents

Four commercially-available edible oils, i.e. colza (canola), corn, frying (a mixture of palm oil, sunflower and soybean or cottonseed oil) and Sunflower were purchased from Shiraz marketplace. From each kind of oil, 3 or 4 samples of different producing companies were supplied. All the

chemicals utilized for analysis such as KOH, methanol and n-hexane were obtained from Merck Chemical Company (Darmstadt, Germany).

Heating procedure of oils

A beaker containing 250 mL of oil samples was put over a heater thermostated at 170 °C. When the sample's temperature reach to the heater temperature, sampling was started; each 3 h for a duration of 36 h. The samples were immediately transferred to a vial of low temperature (4 °C) to damp the reaction. Therefore, in addition to sampling before the heating, 12 samples were taken for each of oils. Each sample was stored in sealed vials at the temperature of 4–6 °C in dark until the analysis and finally their spectra were recorded at room temperature. This heating and sampling procedure was independently repeated 3 times for each oil sample.

Fatty acid (FA) determination

For identification of the FA composition of each type of oil, their fatty acid methyl esters (%) were determined using gas chromatography–mass spectroscopy (GC–MS). The derivation of FA to their methyl ester was done according to ISO 5509:1978 (http://www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_detail_ics.htm?csnumber=11559). To do that, 0.5 mL methanolic KOH (1 M) was added to the methanolic solution of oil (0.1 g/40 mL) and the methylation of FA were performed under the reflux condition for 10 min; afterwards the decantation of methylated FAs were accomplished by adding 40 mL water to the mixture of the reaction products in n-heptane.

GC–MS analysis of the obtained fatty acid methyl esters was performed using an Agilent 7890A chromatograph, coupled with Agilent 5975C mass spectrometer (Agilent Technologies, USA), operating at 70 eV ionization energy, 0.5 s/scan and the mass range: 30–300, equipped with a DBWAX capillary column (polyethylene glycol, 30 m × 0.32 mm; 0.25 µm film thickness) programmed by increasing the oven temperature from 180 to 220 °C at a rate of 4 °C/min for 10 min, the injector and detector temperatures were 210 and 230 °C, respectively with helium as the carrier gas and a flow rate of 0.75 mL/min and a split ratio of 1:60. Chemstation software was utilized to handle mass spectra and chromatograms.

FT-IR spectroscopy

IR spectra of the oil samples were collected in absorption mode, with a Perkin Elmer RX1 FT-IR spectrometer equipped with an ATR cell (ZnSe Flat plate, 01873, PerkinElmer). The spectra were collected in the range

4000–550 cm^{-1} . Each spectral measurement was repeated five times and average of these five scans was utilized for future analysis. A background spectrum was recorded at the beginning of each sample measurement and was used for background correction.

Data analysis

Data were analyzed in MATLAB environment (version 7.12.0.635 Mathwork, Inc., <http://www.mathworks.com>, USA) using MCR-ALS toolbox (Jaumot et al. 2005), freely available from the home page of MCR (<http://www.mcrals.info/>).

Data set

The set of 13 ATR–FTIR runs for each oil type (one sample before heating procedure and 12 samples which were collected every 3 h during 36 h heating for each oil sample) gave a matrix, sized 13×3450 . After appending of these matrices of the same source oils one on top of each other (column wise augmentation), another matrix formed for each type of oils. In this augmentation, for corn oil we had a matrix with the size of 52×3450 , and for sunflower, colza and frying oil, matrices of 39×3450 dimensions were formed. The rows of each of these matrices contain oils' spectra and the columns include the wavelength variables.

Chemometrics methods

MCR-ALS is a bilinear model of resolving the contribution of pure-components coexisted in a samples. The details of MCR-ALS theory could be found elsewhere in literature (Jaumot et al. 2005; de Juan and Tauler 2006; De Oliveira et al. 2014). Briefly, this curve resolution method decomposes the data matrix (here the infrared spectroscopic data matrix of edible oils during heating process) into two absolute parts i.e. score, and loading in the direction of rows and columns of the original data, respectively. However during the decomposition process, some chemical/physical constraints (e.g., non-negativity, closure, unimodality, etc.) should be utilized in an iterative process to give logical and meaningful results.

If the IR spectroscopic information of edible oils in different heating times is collected in matrix **D**, then the decomposition of this matrix could be defined as: $\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$; where, **C** is the concentration profile (contained variation of each thermal product of oils during heating time) and **S** is the pure spectral profile. The superscript 'T' indicates the transpose of spectral profile. Also, **E** is the residual matrix with the same size of

D contained non-model information and ideally should be near zero after a converged run.

To have a successful iterative ALS algorithm for the decomposition of **D** to **C** and **S**, two points are vital: (1) the accurate estimation of number of chemical component in **D** and (2) calculating an initial estimate of **C** or $\mathbf{S}^T$ to start the iteration. In this work, the initial $\mathbf{S}^T$ was determined using SIMPLS-to-use Interactive Self-modeling Mixture Analysis (SIMPLISMA) method (Bogomolov and Hachey 2007) and initial estimation of **C** was performed by Evolving Factor Analyses (EFA) (Gemperline 2006).

Results and discussion

Fatty acid (FA) content of oil samples

GC–MS was utilized to determine different FAs composition in the oil samples. The details of utilized samples and the results of GC–MS are represented in Table 1. As seen in Table 1, the major FA compositions in all kinds of the tested oils are generally had 14, 16, and 18 carbon atoms. The GC–MS analysis of all different brands in each kind of oil displays approximately close percentage of FA compositions. However, due to the fact that different oil producing companies use various sources and, it is logical to see a few differences in FAs composition of certain oil of different brands. The saturated FA (SFA) chain with 14 carbon atom was observed only in frying oils and the percentage of SFA with 16 carbon atoms in the frying oils were larger than other kinds of oils. Thus, frying oils had the most percentage of SFA (and consequently less percentage of PUFA (Poly Unsaturated FA) in compare with the other kinds of oils (see Table 1).

ATR–FTIR spectra

The ATR–FTIR spectra of corn 1 oil (Table 1) heated to different interval are shown in Fig. 1. The spectra of oil heated for 6 h are represented. As it is clear from this figure, in spite of the variation in their chemical composition during the time, their spectra were very similar. All the spectra show bands specific to esters at 1743 and 1162 cm^{-1} and also display characteristic bands of aliphatic hydrocarbons generated from stretching, bending and rocking vibrations at 3000–2800, 1465–1377 and 720 cm^{-1} , respectively. The bands at 3008 and 970 cm^{-1} arise from the C–H stretching and C–H out of plan bending of olefins, while those at 1238, 1162, 1114, 1099 cm^{-1} are associated with the C–O stretching vibration (Sinelli et al. 2007; Le Dréau et al. 2009a, b).

Table 1 The characteristics of oil samples under study (type, number of samples and FA composition obtained by GC–MS)

Oil types	Number of samples	The oil name	FA composition of oils %							
			C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	%SFA ^a	%PUFA ^a
Colza	3	Colza 1	–	4.5	1.6	69.7	15.8	8.3	6.1	24.1
		Colza 2	–	4.5	1.9	67.0	21.6	4.9	6.4	26.5
		Colza 3	–	5.1	1.3	68.8	18.7	6	6.4	24.7
Corn	4	Corn 1	–	9.9	1.2	25.6	62.9	0.4	11.1	63.3
		Corn 2	–	10.5	0.1	27.6	61.3	0.5	10.6	61.8
		Corn 3	–	11.9	1.6	27.4	58.4	0.6	13.5	59.0
		Corn 4	–	9.7	1.2	25.7	62.9	0.5	10.9	63.4
Frying	3	Frying 1	0.9	33.7	3.1	43.6	18.2	0.3	37.7	18.5
		Frying 2	0.9	42.4	3.2	42.7	10.8	0	46.5	10.8
		Frying 3	0.8	23.3	2.8	55.7	17.1	0.1	26.9	17.2
Sunflower	3	Sunflower 1	–	7.1	3.1	31.8	57.3	0.8	10.2	58.1
		Sunflower 2	–	6.8	3.0	27.9	62.3	–	9.8	62.3
		Sunflower 3	–	6.8	3.1	26.3	62.7	1.0	9.9	63.7

^a SFA saturated fatty acid(=C14:0 + C16:0 + C18:0), PUFA poly unsaturated fatty acid (=C18:2 + C18:3)

Fig. 1 The ATR–FTIR spectra of corn 1 oil during 36 h heating with 6 h intervals, **a** 4000–550 cm^{-1} **b** 1700–650 cm^{-1} **c** 2800–1800 cm^{-1} **d** 3800–2950 cm^{-1} . 1 corn 1–0 h, 2 corn 1–6 h, 3 corn 1–12 h, 4 corn 1–18 h, 5 corn 1–24 h, 6 corn 1–30 h, 7 corn 1–36 h

As it can be seen in Fig. 1, the maximum differences on the infrared spectra of the oil during 36 h heating procedure are in the regions around 1050–800, 3450, 2700 and 1650 cm^{-1} due to changes in their composition. It seems that these differences correspond to variation in the unsaturation degree and type of the acyl groups and their chain length (Moros et al. 2009), and also assign to

oxidation products such as hydroperoxydes, acids, aldehydes or ketones (Le Dréau et al. 2009a). The infrared spectra of other oil samples are shown in Fig S1–S13 (Supplementary information).

The spectral region between 3000 and 3600 cm^{-1} needs special attention. The whole region is changed in intensity uniformly without any evidence of peak except at

3450 cm^{-1} which is weak and broad. The general trend looks much more like a baseline shift than any real chemically originated change. However, as it was explained in the experimental section, the spectra were subjected to background correction for baseline drift. Moreover, each reported spectrum is the average of five replicate independent measurements. To ensure that the observed spectral changes in the mentioned wavenumber region are not primarily to baseline drift, the spectra of the repeated experiments of one oil sample before heating and 36 h after heating are given in the supplementary section Fig S4. As it is observed, the degree of spectral changes during heating is larger than of baseline variation.

One may assume that the peak at 3450 cm^{-1} might also originate from water since the samples were heated in air. However, the amount of water dissolved in oil is not enough high to produce clear observable changes in the IR spectra. On the other hand, as it will be explained in the MCR-ALS section, the resolved pure spectra of different oil types are different for different oil types whereas if one assume that the observed spectral changes around 3450 cm^{-1} are related to water, at least one of the resolved spectra should be similar for all studied oil types.

Rank analysis and initial estimation

Rank analysis for estimating the number of components in the data matrix is the first step before MCR-ALS optimization. Herein, the number of chemical components in each time-derived spectra set was determined using the singular value decomposition (SVD) method. To estimate the number of chemical rank, Eigen value of first five principle components (logarithmic scale), percent of cumulative variance of components and RSD were checked and are represented in Table S1 (Supplementary information). Using these criteria, the existence of three components was verified in spectroscopic data of all kinds of oils recorded in different time of heating treatment.

The variations of Eigen values extracted from total spectral range of different oil samples in different number of factors are represented in Fig S14 (Supplementary information). Evolving factor analysis (EFA) was another chemometrics tool that was applied to estimate the number of components in the matrix of spectra. The forward and backward EFA profiles are plotted in Fig S14 (Supplementary information). This Figure suggests the presence of 3–5 components. However the presence of three components in spectra of heating process was indispensable, but in some case the probability of existence of more components (4 or 5) could not be neglected. Thus for more carefulness, we have performed MCR-ALS for 2–5 compounds.

MCR-ALS

MCR-ALS analysis was applied to all data of all oil samples. Models with 2–5 components have been computed. Just as seen in Table 2, three approaches were used for making initial estimate to use in ALS process. SIMPLISMA was utilized to estimate the pure spectra and EFA was applied in two different ways for construction of the pure concentration. In the first approach of EFA, the spectroscopic data of 3 or 4 different brands of each edible oil sample were augmented in a column-wised manner and were analyzed by EFA. In the second approach, EFA was run on spectroscopic data of each brand separately and the extracted concentration profiles were augmented to make our initial concentration estimate (E_{total} , Table 2).

The MCR-ALS optimization program was applied on all the recorded data during 36 h heating of the colza, corn, frying and sunflower oil samples. It is worthy to mention that MCR-ALS was utilized on the column-wised augmented data of different brands of each oil sample. In ALS run, non-negativity constraint was applied on spectra (**S**) and concentration (**C**); and unimodality and closure constraints were applied only on the concentration (Jaumot et al. 2005). This process was done for all kind of oil samples by considering 2–5 components as the optimum number of factors and some statistics related to results are abstracted in Table 2. According to this Table (% LOF and squared correlation coefficient) and also the logical extracted profiles (spectral and concentration), the existence of three components was confirmed even with different initial estimates. Therefore in the following, the results of MCR-ALS containing three active components will be presented.

Here, the resolved profiles belong to the run related to the initial estimate from EFA on augmented data (**E**), but two other initial estimates (E_{total} and pure) led to similar profiles (results not shown); which indicate the capability of MCR-ALS for monitoring the chemical compounds in oxidation kinetic of oils. Spectral profile of three components resolved by MCR-ALS, for the range of 1730–900 and 3650–2900 cm^{-1} is shown in Fig. 2. The main differences between the three detected compounds (different line style in Fig. 2) in all types of oils can be observed around 970, 1465, 1650, 3008 and 3450 cm^{-1} (Fig. 2), due to changes in their composition. It is clear that the differences are mainly located at the frequencies of the characteristic bands correspond to trans ($-\text{CH}=\text{CH}-$), aliphatic ($-\text{CH}_2-$), the ($\text{C}=\text{O}$) group, cis ($-\text{CH}=\text{CH}-$) and OH intermolecular bendings, respectively (Moros et al. 2009; Le Dréau et al. 2009a; Pinto et al. 2010).

The extracted concentration profiles of three detected compounds of all kind of oils resolved by MCR-ALS are displayed in Fig. 3a–c. Based on the changes which were

Table 2 The quality parameters of the MCR-ALS optimization for the oils with three distinct initial estimation methods

Oils	Initial estimation method		Number of compounds			
			2	3	4	5
Corn	Pure	%LOF	3.282	2.746	2.368	2.071
		%R ²	99.892	99.925	99.944	99.957
	E	%LOF	3.283	2.734	2.501	2.061
		%R ²	99.892	99.925	99.937	99.957
	E _{total}	%LOF	3.282	2.899	2.415	2.178
		%R ²	99.892	99.916	99.942	99.953
Sunflower	Pure	%LOF	NC ^a	2.636	2.064	1.925
		%R ²	NC ^a	99.930	99.9574	99.963
	E	%LOF	2.648	2.510	2.051	1.932
		%R ²	99.929	99.937	99.958	99.963
	E _{total}	%LOF	2.648	2.444	2.0499	1.958
		%R ²	99.929	99.9403	99.958	99.962
Colza	Pure	%LOF	1.546	1.143	0.925	0.9202
		%R ²	99.976	99.987	99.991	99.991
	E	%LOF	1.567	1.158	0.968	0.910
		%R ²	99.975	99.986	99.991	99.992
	E _{total}	%LOF	1.5637	3.3229	0.9243	0.896
		%R ²	99.975	99.990	99.991	99.992
Frying	Pure	%LOF	2.339	1.327	1.042	1.026
		%R ²	99.945	99.982	99.989	99.989
	E	%LOF	2.341	1.467	1.059	0.978
		%R ²	99.945	99.978	99.989	99.990
	E _{total}	%LOF	2.341	1.359	1.105	1.005
		%R ²	99.945	99.981	99.988	99.989

^a NC Convergence was not achieved

$\%LOF = 100 \sqrt{\frac{\sum_{ij} d_{ij} \hat{d}_{ij}}{\sum_{ij} d_{ij}^2}}$, where d_{ij} are the elements of the original FTIR data matrix and $\hat{d}_{ij}$ those reproduced by the utilized MCR-ALS method

observed in the extracted concentration profile during the time and the resolved pure spectra of each compound with the aid of MCR-ALS, the interpretation of three proposed compounds will be described below.

The extracted concentration profile of the first proposed component in the four types of tested oils are displayed in Fig. 3a (A–D) and the spectrum of this proposed component is that with the lowest height at 3450 cm^{-1} (“—” line style in Fig. 2a–d). From Fig. 2 the characteristic bands of this component’s spectra are attributed to triacylglycerol of unsaturated acid. The slight absorption which is observed in this part of spectrum relates to the overtone of the triacylglycerol carbonyl function (Le Dréau et al. 2009a). Other characteristic bands correspond to triacylglycerol of unsaturated acid are located at 3008, 2925, 2850, 1743, 1650 and 720 cm^{-1} . In corn and frying oil, the absorbance at 3008 is lower in this component’s spectra than the spectra of the other detected compounds and could be related to deduction of triacylglycerol of

unsaturated cis acid. The kinetic profiles (concentration variation during time) of this component in different brands of each kind of edible oil are shown in Fig. 3. As it is clear that the concentration of triacylglycerol of unsaturated acid is decreased during heating time in most cases. According to the data shown in Table 1, the decreasing slope of this component in the oil samples with lower ratio of PUFA to SFA, were less pronounced (for example compare this ratio for corn 3 with other corn samples and also compare fryings 1 and 2 with frying 3 in Table 1 and see their kinetic profile in Fig. 3).

However since the oil samples were procured from the market with different initial conditions (different brands with diverse production date, antioxidants, plastic packaging, form of storage and light exposure), the relative concentration of the detected compounds and their changing pattern, were different. As seen in Fig. 3a, the concentration profiles for colza 1 and corn 1 were distinct from the others, and after an initial decrease they display an

Fig. 2 The extracted spectra obtained by MCR-ALS (with the second estimation method in Table 2) for three compounds, obtained from the spectra of the long heating process of oils (**a** frying, **b** colza,

c corn, **d** sunflower), **A** 1730–900 cm^{-1} **B** 3650–2900 cm^{-1} . (—) triacylglycerol of unsaturated acid; (---) hydroperoxides form of triacylglycerols; (— · —) Secondary products of oxidation

induction period or abnormal period and then decreasing was started again.

The extracted concentration profile of the next component is shown in Fig. 3b and its corresponded spectra is the one with the middle height spectrum at 3450 cm^{-1} (“- - -”

line style in Fig. 2a–d). This compound could be related to the hydroperoxides form of unsaturated acid. According to Fig. 2, in addition to band at 3450, this component presents band at 970 cm^{-1} assigned to trans form of triacylglycerols. As it is clear from Fig. 3b, a decrease after an

Fig. 3 The concentration profiles of the detected components by MCR-ALS during 36 h heating process of different oils. **a** The first detected component (triacylglycerol of unsaturated acid); **b** the

second detected component (hydroperoxides form of triacylglycerols); **c** the third detected component (Secondary products of oxidation). (A colza, B frying, C sunflower, D corn)

Fig. 3 continued

increase in the concentration profile of this component in almost all the oil samples could be observed. However this is not an identity manner in all samples and the variation in this case was more depended on the brands and oil types. The changing pattern in the concentration profile of this compound for each type of oil was almost in opposite direction of the changing triacylglycerol of unsaturated acid, which express the close relationship between the increasing and decreasing of these two compounds.

Finally, the third detected compound is the secondary oxidation products, include carboxylic acid, aldehyde and ketone form of triacylglycerol which showed the highest band at 3450 cm^{-1} (“— —” line style in Fig. 2a–d). Due to the OH stretching vibration of acid and a band at 970 cm^{-1} attributed to trans double bond on acid. The associated kinetic profile of this component (secondary oxidation products) is represented in Fig. 3c which was increased during heating in almost all the oil samples.

It is worth mentioning that based on Table 1, the percentage of double bonds in the aliphatic chain of FAs are not the same in different kinds of oils. For example, the samples of frying oil has the least percentage of PUFA compared to the other types of oil and it can be said that by decreasing the percentage of unsaturation, higher resistance to oxidation is observed (Le Dréau et al. 2009a). On the other hand, the percentage of monounsaturated fatty acids

is also partially responsible for resistance to oxidative process and the greater percentage of monounsaturated FAs led to the less sensitivity to oxidation (Gonçalves et al. 2014). It seems that the slope of the concentration profile of these proposed components in different oils is related to their oxidative stability and may be related to the additional antioxidants and their amount in the oil samples.

Conclusion

Long oxidative kinetic and stability of various edible oils (colza, corn, frying and sunflower) during a 36-h heating process was surveyed with the use of ATR-FTIR coupled with MCR-ALS as a feasible tool to monitor oils quality.

In this research the concentration and spectra of three main formed/degraded compounds during long heating process were detected utilizing MCR-ALS method. The use of different initial estimate methods in MCR-ALS end to approximately similar concentration profiles for each type of oils. So, MCR-ALS could be used to monitor the chemical compounds in kinetics of oils' oxidation and can led to a way to compare the oils' thermal stability.

Description of results showed that these three compounds were related to the decrease in triacylglycerol of

unsaturated acid, appearance of hydroperoxides form of triacylglycerols and secondary oxidation products during the 36-h oxidation process of oils. Due to differences which existed in the oil samples, the changing in the concentration profile of the detected compounds was different. So it should be emphasized that in addition to types of oils, the condition of production in different brands and also form of storage in diverse samples from a single brand could be effective on the thermal stability of edible oils.

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Authors' contribution M. Mahboubifar did most of the work including collecting the data and running software. B. Hemmateenejad supervised the work and prepared the final edited version of the manuscript. K. Javidnia was the co-supervisor of the work. S. Yousefinad did parts of data analysis and prepared the initial version of the manuscript.

Compliance with ethical standards

Conflict of interest The authors have nothing to disclose.

References

- Armenta S, Garrigues S, de la Guardia M (2007) Determination of edible oil parameters by near infrared spectrometry. *Anal Chim Acta* 596:330–337. doi:[10.1016/j.aca.2007.06.028](https://doi.org/10.1016/j.aca.2007.06.028)
- Bogomolov A, Hachey M (2007) Application of SIMPLISMA purity function for variable selection in multivariate regression analysis: a case study of protein secondary structure determination from infrared spectra. *Chemom Intell Lab Syst* 88:132–142. doi:[10.1016/j.chemolab.2006.07.006](https://doi.org/10.1016/j.chemolab.2006.07.006)
- Christy AA, Egeberg PK (2006) Quantitative determination of saturated and unsaturated fatty acids in edible oils by infrared spectroscopy and chemometrics. *Chemom Intell Lab Syst* 82:130–136. doi:[10.1016/j.chemolab.2005.06.019](https://doi.org/10.1016/j.chemolab.2005.06.019)
- de Juan A, Tauler R (2006) Multivariate Curve Resolution (MCR) from 2000: progress in concepts and applications. *Crit Rev Anal Chem* 36:163–176. doi:[10.1080/10408340600970005](https://doi.org/10.1080/10408340600970005)
- De Oliveira RR, De Lima KMG, De Juan A, Tauler R (2014) Application of correlation constrained multivariate curve resolution alternating least-squares methods for determination of compounds of interest in biodiesel blends using NIR and UV–visible spectroscopic data. *Talanta* 125:233–241. doi:[10.1016/j.talanta.2014.02.073](https://doi.org/10.1016/j.talanta.2014.02.073)
- Gemperline P (2006) Practical guide to chemometrics, 2nd edn. Taylor & Francis Group, Boca Raton
- Gonçalves RP, Março PH, Valderrama P (2014) Thermal edible oil evaluation by UV–Vis spectroscopy and chemometrics. *Food Chem* 163:83–86. doi:[10.1016/j.foodchem.2014.04.109](https://doi.org/10.1016/j.foodchem.2014.04.109)
- Hein M, Isengard H (1997) Determination of underivatized fatty acids by HPLC. *Z Lebensm Unters Forsch A*. doi:[10.1007/s002170050105](https://doi.org/10.1007/s002170050105)
- Jaumot J, Gargallo R, de Juan A, Tauler R (2005) A graphical user-friendly interface for MCR-ALS: a new tool for multivariate curve resolution in MATLAB. *Chemom Intell Lab Syst* 76:101–110. doi:[10.1016/j.chemolab.2004.12.007](https://doi.org/10.1016/j.chemolab.2004.12.007)
- Javidnia K, Parish M, Karimi S, Hemmateenejad B (2013) Discrimination of edible oils and fats by combination of multivariate pattern recognition and FT-IR spectroscopy: a comparative study between different modeling methods. *Spectrochim Acta Part A Mol Biomol Spectrosc* 104:175–181. doi:[10.1016/j.saa.2012.11.067](https://doi.org/10.1016/j.saa.2012.11.067)
- Karoui R, Downey G, Blecker C (2010) Mid-infrared spectroscopy coupled with chemometrics: a tool for the analysis of intact food systems and the exploration of their molecular structure–quality relationships—a review. *Chem Rev* 110:6144–6168. doi:[10.1021/cr100090k](https://doi.org/10.1021/cr100090k)
- Le Dréau Y, Dupuy N, Artaud J et al (2009a) Infrared study of aging of edible oils by oxidative spectroscopic index and MCR-ALS chemometric method. *Talanta* 77:1748–1756. doi:[10.1016/j.talanta.2008.10.012](https://doi.org/10.1016/j.talanta.2008.10.012)
- Le Dréau Y, Dupuy N, Gaydou V et al (2009b) Study of jojoba oil aging by FTIR. *Anal Chim Acta* 642:163–170. doi:[10.1016/j.aca.2008.12.001](https://doi.org/10.1016/j.aca.2008.12.001)
- Luna AS, da Silva AP, Pinho JS et al (2015) A novel approach to discriminate transgenic from non-transgenic soybean oil using FT-MIR and chemometrics. *Food Res Int* 67:206–211. doi:[10.1016/j.foodres.2014.11.011](https://doi.org/10.1016/j.foodres.2014.11.011)
- Mannina L, Patumi M, Fiordiponti P et al (1999) Olive and hazelnut oils: a study by high-field ¹H NMR and gas chromatography. *Ital J Food Sci* 11:139–149
- Moros J, Roth M, Garrigues S, de la Guardia M (2009) Preliminary studies about thermal degradation of edible oils through attenuated total reflectance mid-infrared spectrometry. *Food Chem* 114:1529–1536. doi:[10.1016/j.foodchem.2008.11.040](https://doi.org/10.1016/j.foodchem.2008.11.040)
- Muik B, Lendl B, Molina-Díaz A, Ayora-Cañada MJ (2003) Direct, reagent-free determination of free fatty acid content in olive oil and olives by Fourier transform Raman spectrometry. *Anal Chim Acta* 487:211–220. doi:[10.1016/S0003-2670\(03\)00560-9](https://doi.org/10.1016/S0003-2670(03)00560-9)
- Ng C-Y, Leong X-F, Masbah N et al (2014) Heated vegetable oils and cardiovascular disease risk factors. *Vascul Pharmacol* 61:1–9. doi:[10.1016/j.vph.2014.02.004](https://doi.org/10.1016/j.vph.2014.02.004)
- Pinto RC, Locquet N, Eveleigh L, Rutledge DN (2010) Preliminary studies on the mid-infrared analysis of edible oils by direct heating on an ATR diamond crystal. *Food Chem* 120:1170–1177. doi:[10.1016/j.foodchem.2009.11.053](https://doi.org/10.1016/j.foodchem.2009.11.053)
- Sinelli N, Cosio MS, Gigliotti C, Casiraghi E (2007) Preliminary study on application of mid infrared spectroscopy for the evaluation of the virgin olive oil “freshness”. *Anal Chim Acta* 598:128–134. doi:[10.1016/j.aca.2007.07.024](https://doi.org/10.1016/j.aca.2007.07.024)