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Chemical monitoring of canola, corn, olive, soybean and sunflower oils after thermal treatment at conventional temperatures in domestic stoves

Monitoramento químico dos óleos de canola, milho, oliva, soja e girassol após tratamento térmico em temperaturas alcançadas por fogões domésticos

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ABSTRACT

The frying by immersion is a widely used cooking process and it improves the food texture and flavor. This study analyzed the initial thermal oxidation in five edible vegetable oils used for frying. Oils samples were heated twice for 30 minutes, at 180 °C and then at 240 °C simulating the domestic stoves temperatures. The oils decomposition temperatures were determined by TG, being all of them > 250 °C. The FA profile was analyzed by GC-FID and a slight decrease of UFA was found in corn and soybean oils. In canola, olive and sunflower oils, UFA was stable after heating treatment. Minor FA decomposition was found in canola oil, and followed by corn, olive, sunflower and soybean oils. NIR spectroscopy analyzes resulted in an extensive bands overlapping. The spectra were modeled by PCA and the oils were classified into two groups: fresh oil and heated oil, mainly by differing in 1900 nm region, associated with the carboxyl signal decrease, which might be related to the initial FA degradation in samples. It could partially understand what occurs to the vegetable oil in the beginning of its thermo-decomposition. These information are useful to consumers, food industry and health surveillance agency.

Keywords. vegetable oils, fatty acids, TG/DTA, GC-FID, NIR.

RESUMO

A fritura por imersão é um processo de cocção utilizado pela inclusão de textura e sabor aos alimentos. Foi analisada a oxidação térmica inicial de cinco óleos vegetais comestíveis utilizados para fritura de imersão. Amostras de óleos foram aquecidas duas vezes por 30 minutos, a 180 ºC e depois a 240 ºC, simulando-se as temperaturas de fogões domésticos. As temperaturas de decomposição dos óleos foram determinadas por TG, sendo > 250 ºC. O perfil de FA foi analisado por GC-FID, detectando-se pequeno decréscimo dos UFA nos óleos de milho e soja. Nos óleos de canola, oliva e girassol, os UFA foram estáveis após o tratamento térmico. A menor decomposição dos FA foi detectado no óleo de canola, seguido de milho, oliva, soja e girassol. Análises por espectroscopia NIR resultaram em grande sobreposição das bandas. Os espectros foram modelados por PCA, classificando-se os óleos em dois grupos: óleo fresco e óleo aquecido, principalmente pelas diferenças na região de 1900 nm, relacionadas ao decréscimo do sinal de carboxilas, e associadas à degradação inicial dos FA nas amostras. Ainda que parcialmente, pode-se entender o que ocorre com os óleos vegetais no início de termo-decomposição, abrangências que são úteis para consumidores, indústria alimentícia e órgão de vigilância sanitária.

Palavras-chave. óleos vegetais, ácidos graxos, TG/DTA, GC-FID, NIR.

INTRODUCTION

The use of frying provides convenience and speed in food preparation, as well as texture and pleasant flavor to the taste. However, the frying process can cause physical and chemical changes in the oil, which involve loss of nutritional value. The thermo-oxidative degradation leads to the formation of dimers and polymers originating from triacylglycerols of unsaturated acyl groups, sometimes more polar than the original triacylglycerol molecule[1,2].

The analyzes reported in the literature to evaluate the thermal stability of vegetable oils are diverse, using different techniques: differential scanning calorimetry (DSC)[3-11], high performance liquid chromatography (HPLC)[12,13], capillary electrophoresis (CE)[14], infrared[15,16], UV-Vis[17,18] and Raman spectroscopy[19], 1H nuclear magnetic resonance[20,21], rancimat[22], electron spin resonance spectroscopy[23], AOCS official methods[24] and gas chromatography[25,26]. In these work the extra virgin olive oil (EVOO) is the most analyzed and are mostly evaluated their antioxidant capacity[2,9-15].

There are some papers about thermal oxidation in vegetable oils when these oils are exposed to heating to critical levels of use, but usually the domestic oil is not reused so often. Martínez-Yusta and Guillén[2] heated EVOO to 190 °C, 8h/day, for 4 days. Gómez-Alonso et al[13] heated virgin olive oil and refined olive oil twelve times at 180 °C for 6 days. Tena et al[15] heated virgin olive oil to 190 °C for 94 hours. Zribi et al[16] heated four refined vegetable oils for ten consecutive times at 160 and 190 °C. Andrikopoulos et al[17] used virgin olive oil and vegetable shortening during domestic deep-frying and pan-frying for ten consecutive times. Takeoka et al[24] heated seven commonly used frying oils and fats at 190 and 204 °C for 8 h/day until they reached a critical level of polar constituents.

More refined studies out of evaluation the effect of heating in vegetable oils simulating domestic use and with few uses of oils were not found. Also no studies were found that evaluated canola, corn, olive, soybean and sunflower oils submitted to usual thermal treatments using thermogravimetric analysis, gas chromatography and near infrared spectroscopy (NIR) concomitantly. Thus, a comparative study about the thermal oxidation for these household oils, mainly after little use, can be interesting.

In this context, a comparative study about the thermal oxidation for the household oils main after little use can be interesting. This study evaluated five vegetable oils commonly used in the human food: canola, corn, olive, soybean and sunflower oil. These oils were evaluated in three stages of heat. The experimental conditions were selected in order to simulate heating oils in the minimum and maximum temperatures recorded in domestic stoves. A thermogravimetric analysis was performed to determine the decomposition temperature for each oil sample. Besides, a comparative evaluation of the fatty acid profile in different heating stages of vegetable oils by gas chromatography with flame ionization detector (GC-FID) was performed. Finally, an exploratory study by NIR allied to multivariate analysis of data by Principal Component Analysis (PCA) was able to discriminate between different types of oils and different thermal treatments. The real understanding of the evolution of these effects during frying is still a challenge to researchers, consumers, food industry and health surveillance agencies.

MATERIAL AND METHODS

Reagents and solutions

All reagents used were of analytical grade. Water was purified by a deionization (Milli-Q system: Millipore®, Bedford, MA). Methanol, hexane, acetic acid, anhydrous sodium sulfate (Na_2SO_4), and sodium hydroxide (NaOH) were purchased from Vetec® (Rio de Janeiro, RJ, Brazil) and sodium methoxide solution were purchased from Fluka® (St. Louis, MO, USA).

Standards of fatty acid methyl esther (FAME) to GC analysis methyl palmitate (C16:0ME), methyl elaidate (C18:1ME), methyl oleate (C18:1ME), methyl linoleate (C18:2ME), methyl linolenate (C18:3ME), and Supelco 37 Component FAME Mix were purchased from Sigma Aldrich® (St. Louis, MO, USA). Individual FAME stock solutions were prepared at the 5.0 mmol L^{-1} by

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dissolving in hexane. All solutions were stored in a freezer at – 20 ºC.

Samples

The five main vegetable oils used in the Brazilian meal were chosen for analysis: namely extra virgin olive oil, canola oil, sunflower, corn and soybean. The samples were purchased at the local market and, in order to avoid the influence of a single batch, five packages were bought of each type of oil, prioritizing to different brands. A mixture was prepared of each oil using 100.0 mL of each of the brands obtained, totaling five different mixes. These stock solutions, 500.0 mL of each oil, were used in thermal, spectroscopic and chromatographic studies.

Thermal treatment

From 500.0 mL of samples stock solution, 10.0 mL of the samples were transferred into the glass beakers (with capacity for 80.0 mL) and placed on a heating plate inside the fume hood. Before heating (here denoted by time T_1 samples) 600.0 µL of aliquots of each oil sample were collected and transferred to glass vials. These vials were capped and stored on the fridge at – 20 °C until the time of analysis. The samples were then heated to 180 °C for 30 minutes (here denoted by T_2 samples), and again 600.0 µL samples were collected onto glass vials. Then, the temperature was raised to 240 °C for 30 minutes (here denoted by T_3 samples), and finally 600.0 µL of samples were collected onto glass vials. In both heating T_2 and T_3 the temperature was measured directly in oils with analog thermometer. The heaters were performed without agitation of the samples.

These temperatures were chosen because they are used in food cooking processes in domestic stoves. The first aliquot was taken at T_1, at room temperature and evaluated fresh oil. The second aliquot, T_2, tests a bland heating, simulating the minimum temperatures reached by domestic stoves, and the third aliquot, T_3, tests a hard heating, simulating the maximum temperatures.

Thermogravimetric analysis

In order to check the temperatures of decomposition of each vegetable oil only T_1 samples were analyzed in duplicate. Approximately 5 mg of each sample were weighed directly into aluminum crucibles previously allocated on the sample thermocouple and analyzes were performed without any sample preparation.

The TG / DTA curves of vegetable oils were obtained in a Thermogravimetric and Differential Thermal Analysis equipment, model DTG - 60 Shimadzu (Kyoto, Japan). The analyzes were performed using a heating rate of 10 °C/min between 25 and 550 °C under an atmosphere of synthetic air with a flow rate of 50 mL/min.

Analysis by GC-FID

For GC analysis the oil samples were directly esterificated by basic catalysis with sodium metoxide[27,28]. For each sample at times T_1, T_2 and T_3 were performed experimental trial under duplicate, totaling thirty analyses. Approximately 12 mg of each sample were weighed and transferred into glass tubes and submitted to esterification reaction using 2.0 mL of methanol solution containing sodium methoxide. Then, the flask was heated in a water bath at 50 °C with reflux during 10 minutes. The bath was turned off and the solution was cooled. After, 100 µL of glacial acetic acid was added to neutralize the extract, followed by 5.0 mL of deionized water and 3.0 mL of hexane. After agitation in vortex by 1.0 min and phase separation in an ice bath, the organic phase (upper part) was transferred to 10.0 mL Pyrex tube and an additional 3.0 mL of hexane was added to the first mixture. After agitation and phase separation, the organic phase was placed in the same 10.0 mL Pyrex tube and 1.0 g of anhydrous Na_2SO_4 was added to dry the FAME solution. The solution was transferred to volumetric flask of 5.0 mL and volume completed with hexane, the solution was stored in a capped vial at -20 °C. Before injection into the GC equipment, the solution was transferred to a vial and analyzed without dilution.

FAME analysis was performed on Shimadzu gas chromatograph equipment (GC 2010-Plus, Shimadzu, Kyoto, Japan), with split-splitless injector type, AOC-20-i autoinjector and flame ionization detection. A fused silica capillary column was used (CP-SIL 88 for FAME; 100 m x 0.25 mm x 0.2 µm,

Agilent Technologies, Palo Alto, USA). The chromatographic conditions were: injection volume of 1.0 µL and mode split with flow rate of 20 mL min^{-1} at 250 °C; the FID detector temperature was fixed at 270 °C; the oven programmed temperatures were initially 80 °C, then an increase of 4 °C min^{-1} up to 220 °C and was held for 5 min; after that, the temperature increased by 4 °C min^{-1} up to 240 °C and was held for 10 min. The carrier gas was hydrogen with a flow rate of 1.0 mL min^{-1} and the pressure was 140.3 kPa. The compounds were identified by standard co-injection and retention time relative to the Supelco 37 Component FAME Mix. FA were determined by area normalization and expressed in g per 100g of FA[29].

Analysis by NIR spectroscopy

Aliquots taken at times T_1, T_2 and T_3 were transferred to glass vials with i.d. 8.0 mm and placed directly into the equipment compartment for the acquisition of the spectra, without sample preparation. The analyzes by NIR were performed with the Fourier-Transform spectrometer (FT) equipment model FT-NIR MPA from Bruker equipped with a Te-InGaAs detector and quartz optics. The spectra were collected in the transmittance mode, in the region between 1200 to 4000 cm^{-1} with a resolution of 4 cm^{-1} with 32 scans accumulated by sample.

Software

In this work the spectra were acquired with the OPUS 6.5 software from Bruker Optik GmbH (Ettlingen, Germany), chromatograms were obtained with the GC Solution software from Shimadzu (Kyoto, Japan), TG and DTA curves were obtained from the software TA-60 WS Shimadzu (Kyoto, Japan) and the multivariate statistical analysis was performed with SIMCA P+ 12.0.1 software from Umetrics (Umeå, Sweden).

RESULTS AND DISCUSSION

To evaluate the decomposition temperature of each vegetable oil thermal analyzes were performed in five samples (canola, corn, olive, soybean and sunflower oils) by TG-DTA, however, because they have similar profiles, only two are shown, the remainder can be seen in the supplementary material. **Figures 1a** and **1b** highlight the thermal behavior of the olive and sunflower oils respectively, both in an oxidant atmosphere. As can be seen from the DTA curve in **Figure 1a** presents four exothermic events attributed to transitions and volatilization processes and/or decomposition of the triacylglycerols. The TG curve shows the first stage of decomposition between 220 and 370 °C and DTA curve shows an exothermic peak between 254 and 355 °C. Based on extrapolation of the TG curve, it can be seen that the onset temperature for the first stage of decomposition is approximately 258 °C. The second weight loss step occurs between 375 and 408 °C, with an exothermic peak between 380 and 408 °C[30]. The presence of an exothermic peak at 410 °C indicates a third step of weight loss between 410 and 454 °C. Finally, between 454 and 550 °C is observed a small weight loss and an exothermic peak of low intensity attributed to burning of organic waste matter from the previous stages of the heat treatment.

Figure 1b shows a thermal behavior similar to that observed for the olive oil, i.e. four stages of thermal decomposition. Furthermore, the onset temperature of decomposition in the first stage for sunflower oil is equal to 283 °C, while the one for olive oil is 254 °C. The DTA curve also shows four exothermic peaks with different intensities compared to olive oil, i.e., the difference of exothermic peaks relating to the second (390-427 °C) and third (427-464 °C) decomposition steps of sunflower oil are probably due to the difference in composition of fatty acids present in the samples.

Figure 1c shows the comparison of TG curves of all oils and the thermal stability can be sorted in descending order as from the temperature of the first stage of thermal decomposition: corn (302 °C), soybean (300 °C), canola (298 °C), sunflower (283 °C) and olive oil (258 °C). In this case, the higher the onset temperature of thermal decomposition step of edible oil, the higher its thermal stability. It is observed that the decomposition temperatures of the edible vegetable oils tested are higher than

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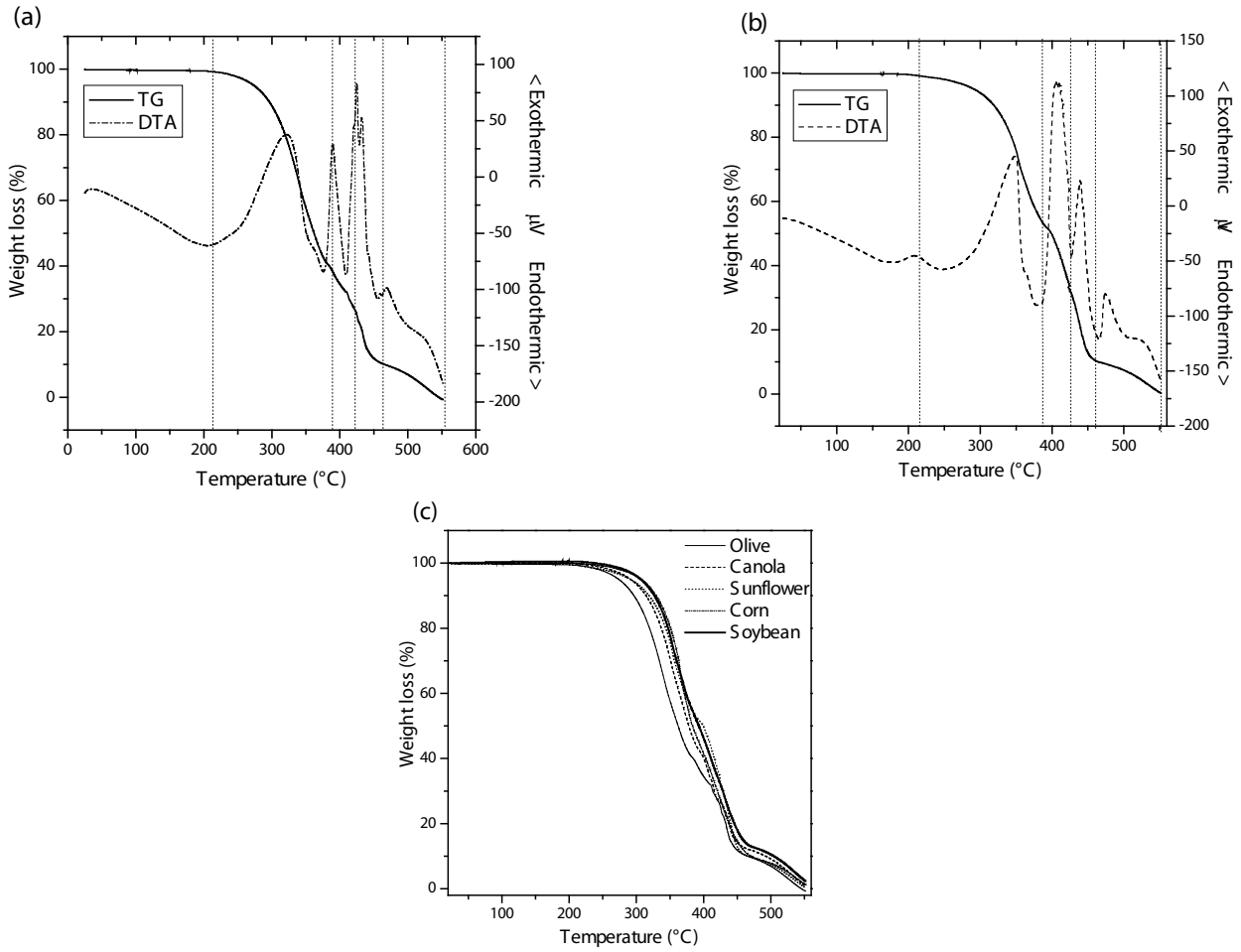

Figure 1. (a) TG and DTA curves of olive oil in air; (b) TG and DTA curves of sunflower oil in air; (c) TG curves of olive, canola, sunflower, corn and soybean oils in air

the temperatures commonly observed in domestic frying process by immersion.

According to the values of temperature of thermal decomposition of oils, the corn oil presents the higher thermal stability. This first decomposition step highlighted in the TG curves of the oils analyzed is a property of great practical importance, specially when frying foods, to avoid the deterioration process of the oils. On the other hand, the olive oil has a lower thermal stability between all samples analyzed by thermogravimetric analysis. As previously discussed, the difference in the onset temperature of ecomposition of the oils can be assigned the presence of different fatty acids. As will be discussed below, the results of the GC-FID presented in the **Table 1** show the quantification of FA majority, namely, palmitic, stearic, oleic, linoleic and linolenic acids, in oils analyzed.

After exposure of the samples to the heat treatment at times T_1, T_2 and T_3, each oil was analyzed by GC-FID in duplicate. The chromatograms for the analysis of oils at time T_1 are shown in **Figure 2**, while the chromatograms at times T_2 and T_3 were not shown since they are similar to the one at T_1.

Chromatographic conditions: column CP-SIL 88 for FAME with 100 m x 0.25 mm x 0.2 µm at 80 °C, 4 °C min^{-1} to 220 °C, 5 min, 4 °C min^{-1} to 240 °C, 10 min, the carrier gas was hydrogen with 1.0 mL min^{-1} and the pressure 140.3 kPa, injection with flow 20 mL min^{-1} at 250 °C, volume injection 1.0 µL and FID at 270 °C.

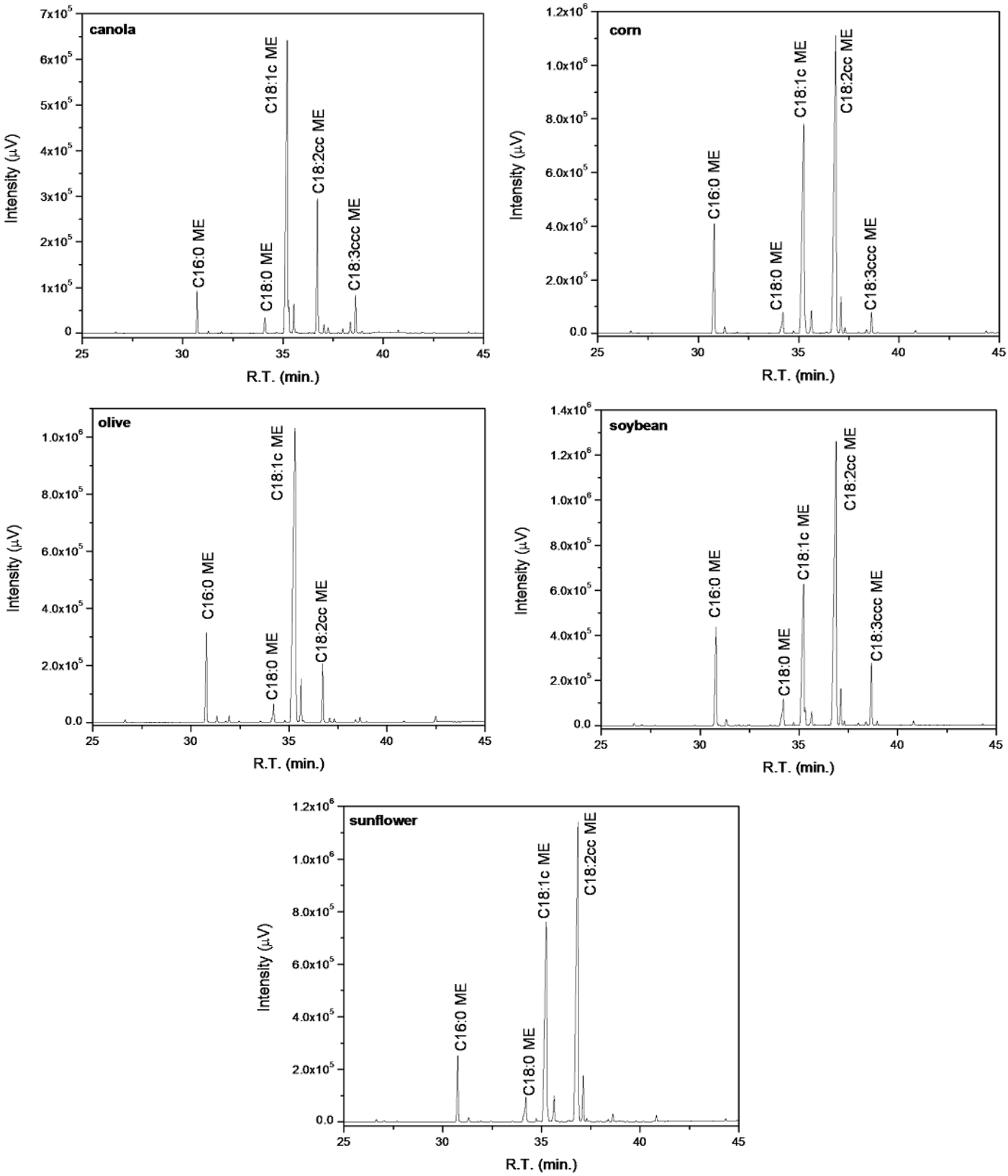

Figure 2. GC chromatograms of each raw vegetable oil analyzed in T1. Chromatographic conditions: column CP-SIL 88 for FAME with 100 m x 0.25 mm x 0.2 μm at 80 °C, 4 °C min^{-1} to 220 °C, 5 min, 4 °C min^{-1} to 240 °C, 10 min, the carrier gas was hydrogen with 1.0 mL min^{-1} and the pressure 140.3 kPa, injection with flow 20 mL min^{-1} at 250 °C, volume injection 1.0 μL and FID at 270 °C

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The quantification of FA majority, namely, palmitic, stearic, oleic, linoleic and linolenic acids, in oils tested is presented in Table 1. It can be seen that the sum of these five FA majority represent about 90 % of FA present in all analyzed oils (last column of **Table 1**, named total fatty acids – TFA). The results shown in **Table 1** are mean values of authentic duplicate analyzes for each oil and relative standard deviations of all measures was less than 3 %.

It can be seen also in **Table 1**, there was an increase of 6 units of oleic acid (monounsaturated) in sunflower oil, as well as the decrease of 5 units of linoleic acid (polyunsaturated) in the same oil. This may be related to the first desaturation signs of oil, in which the polyunsaturated acids is hidrogenated and pass to monounsaturated. Keszler et al[31] present in their work an interesting mechanism for decomposition of unsaturated fatty acids (UFA), with different products.

The results of the Tukey test presented in **Table 1** show that palmitic acid, stearic and oleic acid no significant variations at 95 % confidence in any of the analyzed oils. This test also shows that canola oil presented less decomposition after heat treatments applied here, with a slight variation only in the composition of linoleic acid in the second heating (240 °C). Corn oil also showed low decomposition into FA majority, showing only small variation of linoleic acid throughout warming. The other oils analyzed (olive, soybean and sunflower) showed significant differences at 95 % confidence mainly in linoleic acid and linolenic acid with heat treatment in which they were submitted.

For a better interpretation of results presented in **Table 1**, the **Figure 3** shows a graph of the variation of saturated fatty acid (SFA) and UFA as a function of heat treatment. It can be seen that the amount of SFA remains constant for the five types of vegetable oil analyzed. The UFA show a slightly larger dispersion compared to

Table 1. FA quantification results by GC in g of FA per 100g of FA*

Sample	TT	Palmitic	Stearic	SFA	Oleic	Linoleic	Linolenic	UFA	TFA
Canola	1	4.5a	2.2a	6.7	62.5a	17.3a	4.5a	84.3	91.1
	2	4.7a	2.3a	7.0	63.2a	16.6a	4.2a	84.0	90.9
	3	4.5a	2.3a	6.8	62.9a	16.0a	3.6b	82.5	89.4
Corn	1	10.6a	2.4a	13.0	33.3a	45.2a	1.6a	80.1	93.1
	2	10.1a	2.6a	12.7	33.4a	42.6b	1.8a	77.7	90.5
	3	10.5a	2.6a	13.2	33.9a	42.0c	1.6a	77.5	90.7
Olive	1	11.0a	2.4a	13.4	71.8a	5.7a	0.5a	77.9	91.3
	2	11.0a	2.5a	13.5	71.9a	6.2a,b	0.4b	78.6	92.1
	3	10.7a	2.4a	13.1	71.4a	6.4b	0.3c	78.3	91.4
Soybean	1	10.7a	3.5a	14.2	22.8a	50.0a	5.6a	78.4	92.6
	2	10.5a	3.4a	13.9	22.6a	48.1b	5.1b	75.8	89.7
	3	10.6a	3.4a	14.1	22.6a	46.7c	4.4c	73.7	87.8
Sunflower	1	5.8a	3.1a	8.9	32.4a	49.5a	0.6a	82.5	91.4
	2	5.6a	3.1a	8.6	37.0a	46.2b	0.4b	83.6	92.3
	3	5.5a	3.1a	8.6	38.2b	44.5b	0.4c	83.1	91.6

TT – Thermal treatment; SFA – Saturated fatty acids; UFA – Unsaturated fatty acids; TFA – Total fatty acids FA concentration values marked with the same letter to different times analyzed have no significant differences by Tukey test with 95 % confidence, since the values marked with different letters are significant differences by Tukey test with 95 % confidence

*All measurements were made in duplicate and relative standard deviations were all below 3.0 %

SFA. In this case corn and soybean oils exhibit a small decrease in the amount of UFA, while canola, olive and sunflower oils remained constant.

In these GC analyzes are quantified FA that were initially linked to triacylglycerol, not being analyzed, therefore, free fatty acids, because transesterification was carried out by basic catalysis[27,28]. The results indicate that there was

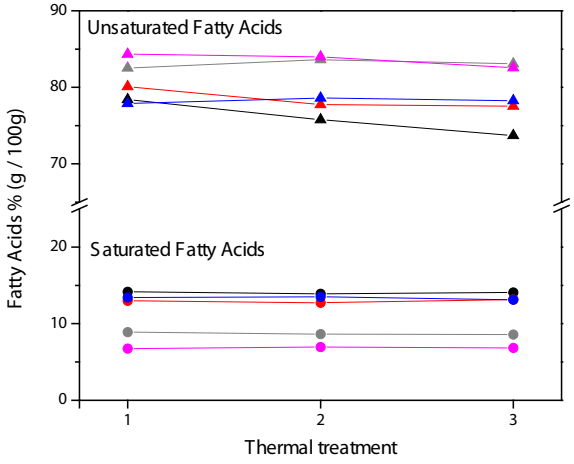

Figure 3. Variation of SFA and UFA with applied heat treatment with legends: (—) canola, (—) corn, (—) olive, (—) soybean and (—) sunflower

no big change in the FA present in vegetable oils for the thermal treatment applied, though these are its main constituents. This is a positive result when thinking about food quality and safety. This avoids the consumption of degradation products of vegetable oils.

For a more comprehensive investigation of the FA, the same set of samples was analyzed by NIR spectroscopy. The approach used was the multivariate analysis of data from the full spectrum of all samples by Principal Component Analysis (PCA)[32]. The motivation for using this approach is due to the overlapping of the spectra of different vegetable oils as well as the different thermal treatment and the failure to provide a vibrational marker easily identifiable to discriminate different oil origins or thermal treatment. The results obtained by NIR spectroscopy are summarized in **Figure 4**.

Figure 4a shows the complete collection of the spectra of all analyzed samples with the highlight for the region near 1900 nm, which will be discussed later. **Figure 4b** shows a PCA analysis, based on the NIR spectra of all edible oils analyzed. The score diagram for PCA, **Figure 4b**, shows a separation, in the horizontal axes (PC1), for different species of vegetable oils, in this case, four groups are formed in which sunflower and corn oils are in the same group. This result corroborates with the measurements carried out by GC analysis, as sunflower and corn oils have more similar distribution most similar of fatty acids than other oils. In summary, the direction of PC1, which represents 84 % of the total variance explained (R^2) by the PCA model, is responsible for the discrimination of different types of oils analyzed, and such separation occurs because the distribution of fatty acids.

The most important regions of the NIR spectrum for this separation along the horizontal axis are presented in a loading plot, shown in **Figure 4c**, for PC1. The assignments of these regions are the following: 1160 nm corresponds to the second overtone of CH stretching of the CH_3 groups, the stretching in 1660 nm is related to the vibration CH with cis unsaturation and the band at 1216 nm is attributed to the vibration of CH_2 groups associated with the second overtone of CH stretch[33].

Figure 4b evidenced that all analyzed samples at ambient temperature (denoted in this figure by '1') are located on the third and fourth quadrants, or negative vertical axis. This axis (PC2) represents 12 % of variance explained of the PCA model. This tendency of separation by thermal treatment may be related to the decrease for carboxyl groups present in oils, given that in 1900 nm occur the stretching due the second overtone of the carboxyl.

One hypothesis to explain the decrease in the signal of the carboxyl after heat treatments can be the thermo-oxidative degradation of FA, such as Keszler and collaborators[31] demonstrates in a mechanism proposal. The loading plot for PC2, **Figure 4c**, confirms that the most important region in the NIR spectrum to explain this separation is the band near to 1900 nm.

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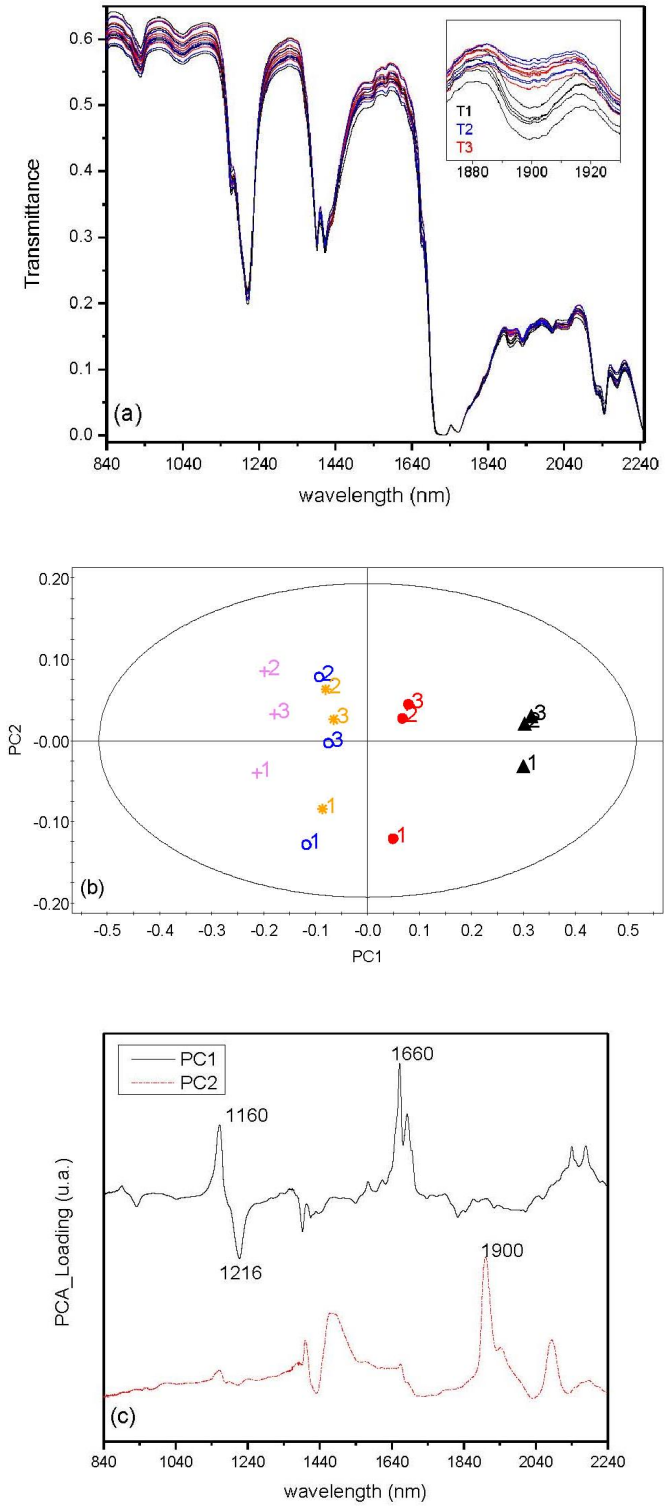

Figure 4. Near Infrared analysis. (a) NIR spectra of all edible oils analyzed with highlighting for the thermal treatment T1, T2 and T3 near to 1900 nm; (b) score plot of PCA model based NIR spectra with legends: canola (•), corn (✻), olive (▲), soybean (+) and sunflower (o), numbers representing the thermal treatment; (c) loading plot for PCA analysis

CONCLUSION

From the TG curves of edible oils analyzed in an oxidant atmosphere it is concluded that all oils have onset decomposition temperature above the temperatures obtained from household stoves. The TG curves obtained between 25-550 °C allowed the analyze complete of the thermal events of decomposition of all oils studied. However, for the FA composition, GC analysis showed that the canola, olive and sunflower oils were more stable for thermal treatments at 180 °C and 240 °C, while corn and soybean oils showed a small decrease in UFA.

Analyses by NIR spectroscopy showed that despite the differences in FA composition of each sample, all of them showed similar behavior when subjected to heat treatments. NIR spectroscopy indicated that the absorption at around 1900 nm, which can be attributed to degradation products of UFA, this is the main difference between the fresh oil (T1) of heated oils (T2 and T3). This study allowed the understanding of what happens to the vegetable oil in the beginning of his term-decomposition, such information is useful to consumers, food industry and health surveillance agency.

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