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COMPREHENSIVE INVESTIGATION OF THERMAL DEGRADATION CHARACTERISTICS AND PROPERTIES CHANGES OF PLANT EDIBLE OILS BY FTIR-SPECTROSCOPY

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Abstract: Structural characterization of edible oils after thermal treatment was made by (FTIR) spectroscopy. Olive, corn and sunflower oil samples were thermally treated at three consecutive cycles. Each cycle consisted of heating at the boiling point for 8 h, followed by cooling at room temperature for 16 h. At the end of each cycle the characteristics of oils were studied by FTIR spectroscopy and standard methods.

Study of FTIR spectra of the treated oils revealed that the heating of oils caused significant changes in the intensities of their bands and produced shifts in the position of specific bands such as 3008 cm^{-1} and 1745 cm^{-1}. The level of oil oxidation during different heating period was followed by the absorbance ratio at 3530/3472 cm^{-1}. Additionally, the absorbance ratio 2853/3008 cm^{-1} was used as a measure of degree of unsaturation. The thermal heating of oils produced an initial decrease in the specific absorbance ratios which could be attributed to the reduction of unsaturated fatty acid content due to oxidation process. The results in

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this study demonstrated that FTIR could be used for assessment of the state of oils by using specific absorbance ratios as indicators.

Keywords**:** FTIR, edible oils, thermal degradation, oxidation, absorbance ratio

Introduction

Nowadays, food safety and quality is in the focus of citizens' concerns and intensive research has been done on different issue in production, storage and use of food products and commodities. Consumer demands and their preoccupation for a rational and healthy diet determined the increased consumption of vegetable oils rich in unsaturated fatty acids. As a result, import rate of expensive oils, which are not usually produced in the Republic of Kosovo, has been increased recently. However, higher prices of these oils leaded to bad practices on the market: oil adulteration, repeated use in cocking, inappropriate storage, etc.

Olive oil (OO) is especially rich in monounsaturated fatty acids, like oleic acid (18:1) and palmitoleic acid (16:1) that are known to decrease the blood levels of LDL or “bad cholesterol” and increase the levels of HDL or “good cholesterol”. Sunflower oil (SFO) is rich in polyunsaturated fats. Moreover, it contains some fatty acids that our bodies cannot synthesize and thus become an essential part of our diet. Olive and sunflower oils contain triglycerides with fatty acids different in chain length, position of double bond, degree of saturation, etc. Most vegetable oils such as safflower oil, sunflower oil, soybean oil and corn oil consist of high percentage of polyunsaturated fatty acids which make them more susceptible to deterioration and thus less suitable for frying. Monounsaturated fatty acids, on the other hand, are more stable and less oxidisable than polyunsaturated ones.[1] Extra virgin olive oil is an excellent example of oil rich in oleic acid, a monounsaturated fatty acid. Its relatively high oxidative stability is also due to its high tocopherol and phenolic content.[2,3] During thermal processing of edible oils containing polyunsaturated lipid molecules, lipid oxidation is demonstrated to be the main deterioration process.[4,5] It is well known that edible oils used as cooking medium at high temperatures in the presence of oxygen are subject to isomerization, thermoxidation, polymerization, and hydrolysis, and the resulting decomposition products not only produce undesirable off-flavors, but can also decrease the nutritional quality of the fried product.[6,7]

Different quality parameters are proposed to monitor the quality of the oils: peroxide value (PV), iodine value (IV), absorbance at 270 nm and 232 nm (K270 and K232 indexes, respectively). The most commonly used indices which provide information about the early stage of the oil oxidation process is peroxide value based on determination of the concentration of hydroperoxide. However, PV is demonstrated not to be an appropriate indicator to follow polyunsaturated fatty acids oxidation because of the high instability of hydroperoxides issued from their degradation.[8] Iodine value provides information about number of double bonds in oil based on Wijs reagent. The iodine value is not the best indices for oil stability since it does not take into account the positions of the double bonds available for oxidation. However, it is still important in assessing the oil stability. These methods, which are time-consuming and needed different hazardous reagents, provide information about the oxidation stage of the oil at the moment of the analysis, but they cannot predict the “best before” date.

The polyunsaturated fatty acids oxidation results in formation of hydroperoxides. Immediately after peroxide formation, the non-conjugated double bonds presented in natural unsaturated lipids rearrange generating conjugated dienes, which absorb at 232 nm.[4] When polyunsaturated fatty acids containing three or more double bonds undergo oxidation, the conjugation can be extended including another double bond. As a result of this process conjugated trienes, absorbing at 270 nm, are formed. The changes in UV absorbance at 232 and 270 nm, quantified by K_{232} and K_{270} indices, are used as a relative measure of oil oxidation.[9] The presence of conjugated dienes and trienes is proved to be better estimation of oxidation state due to their stability in the frying oil.[10] In accordance with this finding, the instability of peroxide molecules may also explain the decrease in PV during advanced stages of rancidity. During lipids oxidation their breakdown into lower molecular compounds can be expected. The increase in K_{232} and K_{270} is proportional to the uptake of oxygen and formation of peroxides during the early stages of oxidation as well as with the degradation rate of linoleic acid.[10,11]

The above-mentioned methods for oils characterization have found widespread applications as routine tests to determine oxidative deterioration of lipids. However, they provide a single index, which does not give information on actual chemical composition of the formed products, and thus provide limited insight of the problem.

Different chemical transformations of oils during intensive heating and direct oxygen exposure initiate chain reactions in which first stage hydroperoxide are formed. Formed aldehydes, hydroxyaldehydes and hydrocarbons are unstable compounds. Their degradation produces several volatile molecules, such as alcohols, free fatty acids, glycerides, short chain fatty acids, trans fatty acids, conjugated fatty acids, cyclic fatty acids or other secondary oxidation products.[12,13] Therefore, the identification of the composition of different oils as well as the understanding of reactions occurring at elevated temperature is of particular interest.

Recently, FTIR spectroscopy has been increasingly applied to food analysis as it is a non-destructive, fast, minimal staff training and ecological friendly method. It enables organic component analysis based on the vibration of bonds between the atoms so that the functional groups of organic compounds can be identified. MID-infrared spectra have been applied for characterization of fats and oils as they can assort and give information about the composition and nature of the sample based on the peak intensity and frequency.[14-16] Navarra et al. studied the effects of the oxidation process induced by thermal treatment on some extra-virgin olive oil samples, investigated by FTIR techniques. They confirm that the oxidation process started with the formation of hydroperoxides. Their instability and degradation with formation of secondary oxidation products, such as alcohols, aldehydes and ketones, evidenced by the modification of the spectral component at 3530 cm^{-1} is reported. Other spectral changes are not described.[17] Vlachos et al. reported the results from application of specific FT-IR spectral regions: 3050–2800 cm^{-1} and 1745 cm^{-1}, to monitor the oxidation process at 245 ^{o}C in edible oil samples. Additionally, a different level of shifting of the absorption peak at 3009 cm^{-1} depending of the type of studied oil is observed.[18] The proposed by Vlachos' group methodology allows evaluation of the oxidative state of edible oils in a simple and fast way.[18] A recent study on repeated heating and frying mustard and corn oil shows gradually diminishing of the intrusive health-protective effects of the oils.[19] The formation of secondary oxidized products in mustard oil heated at boiling point is proved by the appearance of an additional peak at 3633.8 cm^{-1}. In corn oil at 35 °C and 145 °C formation of a saturated aldehyde functional group is supposed based on the overlapping of absorbance peak at 1728 cm^{-1}and the stretching vibrations peak at 1746 cm^{-1} of the ester carbonyl functional group of the triglycerides. The authors suggest FTIR spectroscopy for rapid analysis of oils with additional advantage to be cheaper and environmental friendly compared to the traditional chemical methods used in oil analysis.[19] FTIR is successfully used to monitor oil oxidation under moderate and accelerated conditions.[15] Main changes in FTIR bands are interpreted and related to oxidation mechanism.[20]

Several industries and consumers often have not paying attention to the duration of heating or even reused the treated oil. However, during common cooking process the oil occasionally may exceed the point of its fumigation, which in turn causes decomposition of oil components and formation of undesired secondary products. Such “bad practices” are sometimes used in domestic and commercial scale and consumers’ attention should be directed to appropriate use and storage of plant edible oils in order to obtain as much as possible health benefit of their natural composition. Therefore, it is necessary to carry out a prior monitoring of the physical and chemical parameters of the oil.

This paper presents the results from a study on the effect of thermal treatment of corn, olive and sunflower oils by FTIR spectroscopy and standards methods. The oxidation mechanism of plant edible oils under different thermal conditions is discussed. The FTIR spectroscopy is demonstrated to reveal correlated information on the molecular mechanisms involved in the early phases of the thermally induced oxidative process and to monitor the oil quality. Absorption ratios at specific wavenumbers are applied to predict degree of oxidation and unsaturation of edible oils during heating.

Results and Discussion

The quality of sunflower, corn and olive oils after different periods of thermal treatment was estimated by standard parameters such as peroxide value, iodine value, K_{232} and K_{270}. Two brands of each plant edible oil were analyzed in triplicate and the mean values were presented in Table 1.

Peroxide value

Peroxide value was used as an indicator for the primary oxidation of edible oils. Primary products of lipid oxidation were known to be hydroperoxides - labile species which degraded to different secondary products. Determination of peroxides could be used as an oxidation index for the early stages of lipid oxidation.[7,24] However, the information provided by the content of primary oxidation products was limited due to the transitory nature of hydroperoxides. Yet their presence might indicate a potential for later formation of toxic compounds.

As the results presented in Table 1 showed, peroxide value for all types of oils increased with increasing the thermal treatment time. Peroxide value of sunflower oil increased more significantly especially the third thermal treatment cycle (24 hours of total heating). Peroxide value of other studied oils slightly increased. It should be noted that PV of olive oil after 16 hours of heating decreased. In general PV increased only when the rate of peroxides formation exceeded that of its degradation. Decreasing of PV after the initial increase of its value confirmed that peroxides, formed in the early stages of oxidation, were unstable and highly susceptible to further changes forming secondary oxidation products.[25] Probably, the hydroperoxides accumulated in the initial stage of heating were decomposed due to the higher temperature. Hence, a low peroxide value represented either early or advanced oxidation.

Table 1. Values obtained from the official reference analysis (n=6; P=95%).

	SFO				CO				OO			
hours	**K232**	**K270**	**PV**	**IV**	**K232**	**K270**	**PV**	**IV**	**K232**	**K270**	**PV**	**IV**
0	1.2±0.2	0.25±0.01	0.7±0.2	119±0.8	0.9±0.1	0.1±0.01	0.2±0.1	125±1.2	1.7±0.3	0.08±0.01	2.5±0.1	89±0.65
	1.6±0.1	0.36±0.01	1.1±0.1	124±1.1	1.2±0.2	0.3±0.01	0.4 ±0.1	130±1	2 ±0.2	0.12±0.01	2.1±0.1	95±0.88
8	1.3±0.2	0.25±0.01	0.5±0.1	112±1	1.1±0.2	0.15±0.01	0.6 ±0.1	124±1.5	2.2±0.3	0.09±0.01	3.3±0.1	84±0.8
	1.9±0.1	0.4 ±0.01	0.8 ±0.1	115±1.2	1.2±0.2	0.35±0.01	0.35±0.1	131±1	2.1±0.2	0.15±0.01	2.7±0.1	91±0.9
16	2.8±0.3	0.4 ±0.01	0.9±0.1	102±1	1.3±0.2	0.2±0.01	1.1 ±0.1	121±1	3.2±0.2	0.13±0.01	2.8±0.1	75±0.5
	2.6±0.1	0.35±0.01	1.2±0.1	98±1	1.4±0.2	0.3±0.01	0.5 ±0.1	124±1	2.5±0.2	0.15±0.01	2.5±0.1	86±0.8
24	2.1±0.2	0.4 ±0.01	2.8±0.1	96±0.9	1±0.1	0.22±0.01	0.9±0.1	120±1.2	2.8±0.1	0.17±0.01	3 ±0.1	69±0.8
	3.1±0.1	0.43±0.01	2.3±0.1	92±1.1	1.5±0.2	0.4 ±0.01	1.0±0.1	122±1.5	2.6±0.2	0.22±0.01	3.2±0.1	74±1.1

Iodine Value

Iodine value was used to measure unsaturation or the average number of double bonds in fats and oils. Decrease in iodine value showed decrease in the number of double bonds and indicated oxidation of the oil. The iodine values of oils before and after heating were compared in Table 1. It was noted that the iodine value of all studied oils decreased upon heating and the trend correspond with literature data. The decreasing trend in iodine value of the oil during deep-fat frying was discussed before.[26]. The observed decrease in iodine value during repeated thermal treating of sunflower, corn and olive oils was used as an indicator of lipid oxidation.[27] and was consistent with the decrease in oil double bonds during oxidation.[28] The obtained results showed the lowest decrease in IV of the corn oils samples before and after heating (Table 1). It could be supposed that the iodine value of the studied oils decreased during frying due to consumption of double bonds by oxidation and polymerization.[29]

K_{232} and K_{270} indices

K_{232} and K_{270} indices were determined by measuring the absorption at typical wavelengths of conjugated dienes and trienes. Compounds with isolated double bonds and non-conjugated double bond did not show the characteristic bands in the spectral region between 210 nm and 300 nm, whereas the conjugated dienes showed maximum absorbance at 232 nm. The wavelength of maximum absorbance of conjugated trienes was known to be 270 nm. As the results showed the oxidative process in the studied oils caused an increase in absorbance at 232 nm and 270 nm. The lowest K_{232} value was found in the corn oil, afterward this index quickly increased after 16 hours of heating. Longer heating resulted in decrease of K_{232} indiex. Similar trend was observed in the case of sunflower oil and olive oil in Table 1. This could be due to the subsequent oxidative reaction to which the primary oxidation products were subjected. On the contrary, the K_{270} increased constantly with time and temperature. Both K_{232} and K_{270} indices confirmed the observations reported by others.[30] The authors noted an initial increase and a subsequent decrease in K_{232} and constant increase in K_{270} during heating 24 hours of edible oils.

Evaluation of FTIR spectra

The oil samples were analyzed after each cycle of heating by FTIR spectroscopy. The thermally induced structural changes due to the oxidation process were followed by assessing both intensity and frequency of the bands. The band assignments and their respective mode of vibrations are shown in Table 2. The characteristic bands of the hydroperoxides and triglycerides were observed: 3600 – 3000 cm^{-1} due to O-H bond of hydroperoxide, 3008 cm^{-1} for SFO and CO and 3005 for OO due to =C-H stretching of *cis*-double bonds and 1745 cm^{-1} due to C=O stretching of ester groups from triglycerides. The intensity and position of the bands depended on the heating time. In the spectra of SFO and OO, minor changes of the band near 3472 cm^{-1} could be seen. The changes corresponded to the formation of unstable products of oxidation of hydroperoxide. Disappearance of *cis*-double bonds =C-H in thermally treated oils was supposed based on the significant shifts and intensity changes of the band around 3008 cm^{-1}. Additionally, the results showed that the C=O band around 1745 cm^{-1} shifted towards higher frequency with heating time. The observed changes of FTIR spectra of the thermally treated oils proved the oxidative degradation of lipids.[31-33] Specific details for studied oils at the conditions of repeated thermal treating at the boiling point are discussed below.

Table 2. FTIR absorbance bands and their characteristic functional groups.

Wavenumbers cm^{-1}	**Characteristic group and mode of vibration**
3008	=C-H Stretching (cis)
2925	−CH(CH_2) Asymmetric stretching
2854	−CH(CH_2) Symmetric stretching
1745	−C=O (ester) Stretching
1653	−C=O (ester) Stretching
1463	−C−H (CH_2 and CH_3) Bending
1377	−C−H (CH_3) Symmetric bending
1237	Stretching vibration of the C−O ester groups
1163	Stretching vibration of the −C−O ester groups
1099	−C−O Stretching

Changes in the spectral region 3100 - 3600 cm^{-1}

In the case of olive oil, a new band at 3473 cm^{-1} appeared and gradually increased at the third cycle of heating (16-24 hours of heating). This band was attributed to the newly formed hydroxyl groups of hydroperoxides as a result of oxidative degradation of polyunsaturated lipids. The result was in agreement with the data reported for heating of salmon oil[33] and docosahexaenoic acid[31,34] first reported on the correlative changes between FTIR bands and applied absorbance ratios to follow the oxidation fate of functional groups in oil. In our study the ratio 3530/3472 was used to monitor the thermal induced changes in plant edible oils. Hydroperoxides continuously formed in the oxidation process, were represented by the peak at 3472 cm^{-1}. Simultaneously a second process of hydroperoxydes decomposition took place. The formed secondary oxidation products were manifested by the band at 3530 cm^{-1}. By using ratio of the intensity of two bands the trend of oxidation could be revealed. The absorbance intensity ratio at 3530/3472 as a function of heating time is presented on Figure 1. As can be seen from the Figure the ratio values increased for all three oil samples, but at different heating cycles. It should be noted that the olive oil before heating contained increased level of oxidized products probably due to autoxidation during transport or storage. Corn oil was shown to be more resistant to heating, its ratio rapidly increases after 8 hours of heating indicating fast oxidation. In the case of sunflower oil, the ratio values increased at the very early periods of heating. After the third heating cycle (16 hours of total heating) the sunflower and olive oil samples showed decreased ratio. The results demonstrated that the corn oil sample were more stable to oxidation compared to sunflower and olive oil samples. Their reactants susceptible to oxidation were probably already consumed at the second cycle of heating and more advanced oxidation state could be supposed. To summarize, the corn oil exhibited a stronger stability compared to the olive and sunflower oil. The presented results corresponded well to the UV indices (K_{232} and K_{270}) presented in Table 1.

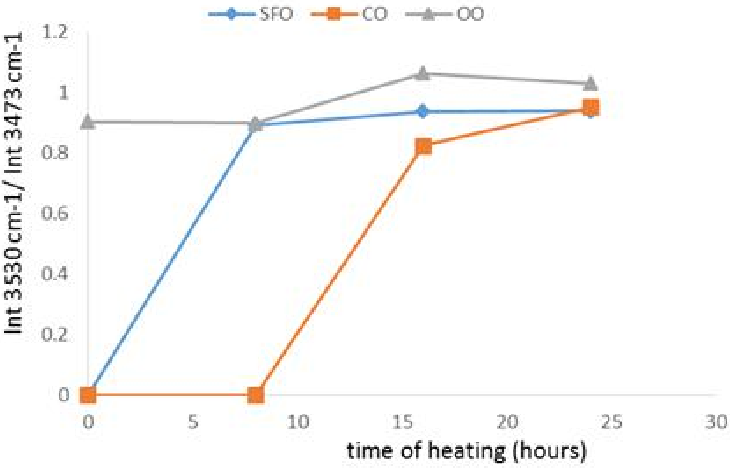

Figure 1. Intensity ratio at 3530 cm^{-1} and 3473 cm^{-1} as function of heating time: (1) sunflower oil; (2) corn oil and (3) olive oil.

Changes in the spectral region 3000 - 3010 cm^{-1}

FTIR spectra of studied oil samples showed notable differences in the band around 3006 cm^{-1} assigned to the C-H stretching vibration of the *cis*-double bond (=CH). The oil composition affected the exact position of the band and yielded shifts when the proportion of the fatty acid changes. The results showed that the wavenumber of this band in non-oxidized oil samples varied significantly from 3009 to 3005 cm^{-1} in Figure 2. Sunflower oil and corn oil showed a maximum absorbance at ~3009 cm^{-1}, olive oil - at ~3005 cm^{-1}. During heating gradually shift to lower wavenumbers of the band position was observed: from 3008.95 to 3005 cm^{-1}for SFO and from 3008.95 to 3007 cm^{-1} for CO. The difference in band shift of the three types of edible oils was supposed to be due to their composition; SFO and CO contained higher proportion of linolenic or linoleic acyl groups whereas olive oil contained higher proportion of oleic acyl groups. The obtained results were in agreement with the observations.[35]

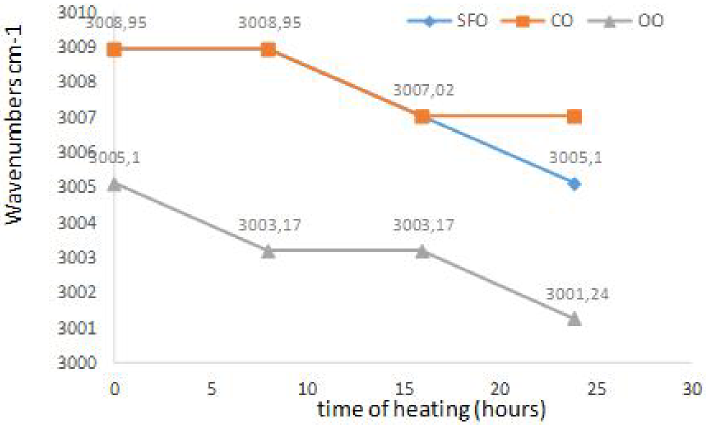

Figure 2. Shift of absorbance band assigned to the C-H stretching vibration of the *cis*-double bond in sunflower, corn and olive oil samples as a function of heating time.

The absorbance ratio at 3012 cm^{-1} and 2854 cm^{-1} was suggested as a marker of oxidation of docosahexaenoic acid and applied for estimation of degree of unsaturation.[31] In the present study this absorbance ratio was applied to monitor oxidation of more complex matrix like plant edible oils. The matrix could influence the specific bands due to interference, signal overlapping or different oxidation rate. The effects were expected to be more pronounced in the case of edible oils. Moreover, stretching vibration of *cis*-double bonds =C-H and symmetric stretching vibration of saturated CH_2 groups were in correlation and accordingly their FTIR spectra. The time until the band at 3008 cm^{-1} began to shift and decrease in intensity, as well as the bands around 2850 cm^{-1} intensified could be applied as an indicator of oxidation.[36] These spectral changes were observed in the studied oil samples before and after heating at boiling point for 8, 16 and 24 hours. The ratio between the absorbance at 2853 cm^{-1} and 3008 cm^{-1} as a function of heating time was applied to follow the oxidation progress in the studied oils in Figure 3. The increase of the absorbance ratio 2853/3008 was attributed to disappearance of *cis*-double bonds of lipids and formation of saturated bonds during oxidation. The corn oil samples showed low oxidation rate and consequently were more resistant to degradation. In contrast, sunflower and olive oils showed increased oxidation rate and easy degradation upon repeated heating conditions.

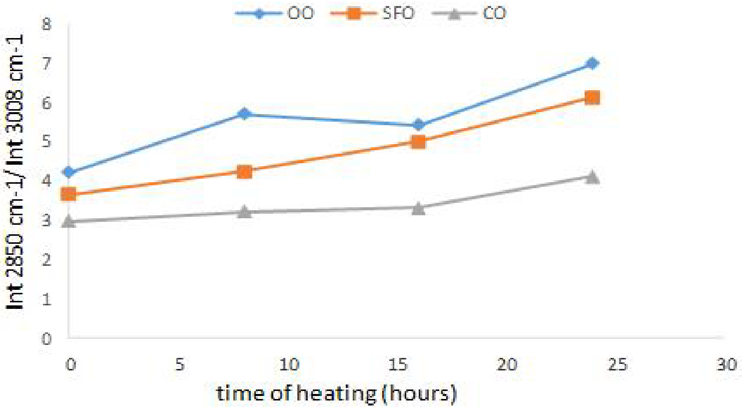

Figure 3. Intensity ratio at 2850 cm^{-1} and 3008 cm^{-1} as function of heating time: (1) olive oil; (2) sunflower oil and (3) corn oil.

Changes in the spectral region 1000 - 1800 cm^{-1}

Changes in the spectral region 1000 – 1800 cm^{-1} allowed to follow the formation of secondary oxidation products, especially aldehydes responsible for rancidity. As it was reported in the literature, the shift of the band of ester carbonyl bond towards higher frequency illustrated lipid oxidation and formation of aldehydes.[37,38] A characteristic band at 1745 cm^{-1}, corresponding to ester carbonyl bond stretching, was observed in the spectra of studied oil samples. The position of this band as a function of heating time is presented on Figure 4. During heating of oil samples, the C=O stretching band shifted and the changes in band position depended on the type of oil. The band position of corn oil didn't change during studied period of heating. Whereas, in the case of olive oil the band position was stable during 16 hours of heating and shifted towards 1743 cm^{-1} after 24 hours of heating. The band position of sunflower oil before heating was 1747 cm^{-1}, after 8 hours of heating shifted to lower wavenumbers and stabilize at 1745 cm^{-1} during heating up to 24 h.

In addition, the band around (~1745 cm^{-1}) due to carbonyl groups widened in shape and increased in intensity in the thermally treated olive and sunflower oil samples. In contrast, no significant increase in intensity of this peak was observed in corn oil samples. It could be supposed that the observed effect was due to the production of saturated aldehyde functional groups or other secondary oxidation products absorbing at 1728 cm^{-1}. The new peak overlapped with the stretching vibration at 1746 cm^{-1} of the ester carbonyl functional group of the triglycerides. When new carbonyls compounds were formed (aldehyde and ketone) the maximum absorbance was in the region between 1700 and 1726 cm^{-1}. However, the major peak of carbonyl groups of the main components of oils – triglycerides, was found in the same absorbance region (1743 cm^{-1}). In the literature a band at 1654 cm^{-1} was reported to appear.[34] This band was assigned to α,β-unsaturated aldehydes and ketones formed as secondary oxidation products of oils. In contrast of these data, no significant change in FTIR spectra at this frequency was observed during heating of studied oils at boiling point. During the oxidation of oil at different temperatures other deformations and bending at 1460–1462 cm^{-1} of −C−H bending vibrations of the CH_2 and CH_3 aliphatic groups and at 1373.2–1377 cm^{-1} of −C−H bending vibrations were changed. The major peaks in these spectra due to the stretching vibration of C−O were at 1163.0–1236.3 cm^{-1}. The changes in FTIR spectra in this region showed changes in oil composition during the thermal induced oxidation process.

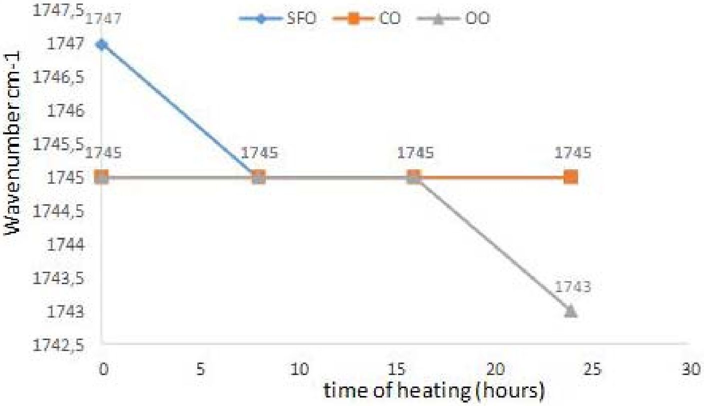

Figure 4. Shift of absorbance band assigned to the ester carbonyl bond stretching in sunflower, corn and olive oil samples as a function of heating time.

Correlations

The results from the study of FTIR spectra discussed above are in good agreement with the results from standard methods for oil estimation. As it was previously noted increasing of the values of UV indices K_{232} and K_{270} was proportional to the uptake of oxygen and formation of first and secondary oxidized compounds during the early stages of oxidation, as well as to the degradation rate of linoleic acid.[10,11] In the case of repeated heating at boiling point of plant edible oils, the obtained results in Table 1 showed that both processes caused positional rearrangement of the double bonds in all oil samples and, consequently, a part of the non-conjugated system was converted into conjugated diene and triene double bonds. However, UV indices did not show clear the type of chemical transformation in heated oil as they did not offer detailed information about the type of compounds. Measurements of peroxide value gave additional information for primary oxidized compounds and increasing of its value showed increasing of their level in oil. The decreased iodine values confirmed decrease of total unsaturated compounds and their conversion into saturated ones. The presented results showed that the extent of lipid oxidation was greater in the heated sunflower samples than in corn and olive oil samples. The iodine value of three types of edible oils increased with increasing heating period. However, the olive and sunflower oils showed higher rate of their iodine value increase compared with the corn oil. The ratio of absorbance intensity at 3530/3470 cm^{-1} corresponded well with the trend in the peroxide and conjugated dienes values (K_{232}). The intensity ratio at 2850/3008 cm^{-1} could provide information about the degree of saturation or unsaturation and the trend are in good agreement with the changes in the iodine value and conjugated trienes value (K_{270}). The observed shifting of the absorbance band at 3008 cm^{-1} confirmed the changes in the unsaturation degree, the changes of the band at 1747 cm^{-1} confirmed the changes in the oxidation level or formation of other oxidisable compounds. The high correlation indicated the potential of using FTIR spectroscopy to monitoring the quality of frying oils. Compared to the standard methods, FTIR spectroscopy offered the additional advantage to allow direct measurements without sample preparation, does not involve harmful chemicals, fast result within a few minutes, easy operation and reproducible spectral data. The information provided by FTIR spectra may also be extended to derive the correlation with other oil parameters such as fatty acid content, iodine value and color index, and thus developed into a single platform for quality analysis. It should be noted that further study is needed in order to obtain more reliable results for stability of pure components of edible oils such as oleic acid, linoleic acid or other constituents applying FTIR spectroscopy to identify decomposition products. In this way will be possible a deeper understanding of the mechanism of conversion of edible oils during thermal treatment and the study is in progress in our laboratory.

Experimental

Samples and reagents

Plant edible oils (corn, olive and sunflower oils) purchased from local market in Mitrovica, R Kosovo were used. Two commercial brands of each type of oil were studied. All six oil samples were imported in local market. Sodium thiosulfate,potassium iodide, glacial acetic acid, chloroform, cyclohexane, iodine monochloride (p.a.grade; Merck, Germany) were used.

Procedures

Each sample was treated in following manner: 8 h heating to boiling point, 16h storage at room temperature. The treatment was repeated up to 24 h heating in three successive days. Aliquots for analysis were taken after each 8 h of heating. Each sample was analyzed to assess peroxide value, iodine value, K_{232} and K_{270} indices. FTIR spectra were studied by estimation of ratio of absorbance at characteristic wavenumbers as a function of heating time to estimate the heat induced changes in the studied edible oils.

Quality Parameters

Peroxide value and iodine value were determined titrimetrically according to the standard methods COI/T20/Doc No 35 and ASTM D 1959-97 method (1997).[21,22] Spectrophotometric indices K_{270} and K_{232} were determined according to the standard method COI/T20/Doc No 19.[23]

FTIR Measurements

An Irrafinity-1 Shimadzu FTIR spectrophotometer equipped with a deuterated triglycine sulphate (DTGS) detector was used to acquire FTIR spectra. The spectra were acquired at resolution of 4 cm^{-1}, data point spacing of approximately 1.9 cm^{-1}. The selected parameters allowed to avoid high noise level and to obtain spectra in reasonable time still providing frequency data with enough quality for all of the studied samples. Each spectrum was obtained in average from over 64 scans after Fourier transform and zero-filling. Oil aliquots were deposited between two CaF_2 crystals using a Pasteur pipette thus creating a thin film. All spectra were recorded from 4000 to 1000 cm^{-1} and processed using IR-Solution Software for Windows (Shimadzu). CaF_2 crystals was thoroughly cleaned up, washed with acetone and then dried between the experiments. FTIR spectral bands were assigned to specific vibrations based on literature data and software spectral library. Bands height and area were calculated by the FTIR software.

Conclusions

The effects of the oxidation process induced by thermal treatment on plant edible oils were studied by volumetric methods, UV-Vis and FTIR spectroscopy techniques. The IR spectra showed, in agreement with the literature, that the oxidation process started with the formation of hydroperoxides. In this work, FTIR was shown to be an excellent tool for following lipid oxidation, based on significant changes of characteristic bands. The shift of the position of the band related to =C-H bond stretching vibration of *cis*-double bonds at 3008 cm^{-1}, depended on the degree of unsaturation of the samples and was used as a marker for oil oxidation. The ratio between the absorbance at 3008 cm^{-1} and at 2853 cm^{-1} corresponding to the vibration of saturated C-H bonds was demonstrated to be a sensitive indicator for oil quality. To follow the products of the early oxidation stage the ratio of absorbance at 3472 cm^{-1}due to hydroperoxides and at 3530 cm^{-1} that corresponded to the vibration of secondary oxidized products was used. The changes in band position at 1745 cm^{-1}corresponding to C=O carbonyl groups from triglycerides proved the formation of other oxidized compounds. The study showed that FTIR spectroscopy could be applied by the food authorities as an innovative analytical method for the characterization of the oxidation degree of the edible oil samples in the very early phases of degradation.

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