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Assessment of the Hazelnuts Roasting Process by Pressure Differential Scanning Calorimetry and MID-FT-IR Spectroscopy

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Abstract The effect of the roasting process on the quality of hazelnuts (*Corylus avellana* L.) lipidic fraction was investigated by pressure differential scanning calorimetry (PDSC) and middle Fourier transform infrared (MID-FT-IR) spectroscopy. The data obtained were referred to and related with fatty acid composition, free fatty acids content, peroxide value, anisidine value and tocopherols concentration measured by standard techniques. These methods were used to decipher between the roasted hazelnuts (shelled and in-shell) treated in different thermal conditions (100 °C, 130 °C and 160 °C) and time (10, 30 and 60 min). The results of free fatty acids (FFA), peroxide value (PV) and anisidine value remained low for all roasting conditions applied and were within quality requirement ranges. The shell left on hazelnuts during the roasting process limited hazelnuts oxidative deterioration, hence it showed protective function. Minor changes occurred in the fatty acid and tocopherol contents and compositions. PDSC, as an appropriate unbiased method for assessing the oxidative stability, revealed a slight elevation of oxidative stability as the temperature and time of the roasting process increased ($p<0.05$). Discriminant models constructed with the use of principal components (PC) procedure confirmed the ability of MID-FT-IR to monitor the roasting process within a certain range of temperature and time applied.

Keywords PDSC · Oxidation stability · MD-FT-IR · PV · AV · FAA · Tocopherols

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Introduction

Hazelnuts (*Corylus avellana* L.) which have a unique and unrivalled flavour are used as an additive in a variety of food products, such as, confectionary, chocolate, biscuits, both in a raw and roasted form (Donno et al. 2013; Demir and Cronin 2005). Due to the complete dehydration (Ciemniewska-Żytkiewicz et al. 2014a; Perren and Escher 1997) which induces their specific organoleptic properties, such as, taste and crunchiness, hazelnuts are generally preferred roasted (Demir and Cronin 2005). The roasted hazelnuts might differ in both chemical and physical properties, as the roasting conditions commonly used by processors are widely ranged in both temperatures, 100–160 °C and times, 10–60 min. Therefore, deciding upon a robust analytical system to allow for objective, control of roasted hazelnut quality is necessary. For the processing industry, it is crucial to predict the impact of roasting conditions, e.g. the time and temperature have a major impact on the hazelnut's quality attributes like moisture, colour and rancidity (Özdemir and Devres 2000). The oxidative stability determines the shelf life of roasted nuts as well as manufactured products containing roasted nuts (Perren and Escher 1997).

Nuts and oilseeds contain oil with a high amount of unsaturated fatty acids. Thus, the oil represents the most sensitive component in regard to oxidation, which in turn limits shelf life and sensory characteristics of the roasted products. The retention of the oxidative stability of roasted products, as a balance between the high unsaturated fatty acids content and changing antioxidant capacity, is an important issue in industrial nut manufacturing (Özdemir and Devres 1999; Perren and Escher 1997; Amaral et al. 2006).

Differential scanning calorimetry (DSC) measures the heat flow associated with transition of state of the sample (material) as a function of time and temperature. As a result, unique energy profile of sample is obtained (Tan et al. 2002). DSC

technique coupled with a pressure cell (PDSC—pressure differential scanning calorimetry) have the potential to be used as an accelerated thermal method to determine oil quality. It has previously been successfully used for hazelnut oil quality assessment (Ciemniewska-Żytkiewicz et al. 2014b).

The major advantages of Fourier transform infrared (FT-IR) spectroscopy over other techniques include fast and easy equipment operation along with the possibility to conduct non-destructive analyses on samples at any state (solid, liquid, paste, gas) with convenient and environmentally friendly sample preparation (Bevilacqua et al. 2013). Originally, FT-IR has been used for pure sample analysis exclusively; however, recently, it has been successfully used for mixture analysis as well. The FT-IR procedure includes both reference (Sherazi et al. 2009) and discriminant analysis (Yang et al. 2005). Once the statistical model for a given type of mixture is established, measuring the amount of a given substance or discriminating of samples requires registration of one spectrum only followed by entering spectral data into a dedicated software.

Few studies about the fatty acid composition and tocopherol level changes during the roasting process of hazelnuts have already been reported (Amaral et al. 2006; Alasalvar et al. 2010), however, the roasting of hazelnut varieties grown in Poland has not been studied at all, to our knowledge. The objectives of this study was to assess the oxidative stability of roasted hazelnuts using PDSC methodology combined with more common fatty acids and tocopherol determinations and middle FT-IR (MID-FT-IR) spectroscopy analysis referred to classic quality oil assessments.

Material and Methods

Reagents and Standards

All the solvents and reagents were purchased from P.O.Ch Co. (Gliwice, Poland); standard compounds were supplied by Sigma-Aldrich (Saint Louis, MO, USA). All solvents and reagents used in the analyses were of chromatographic or analytical grade.

Samples

The samples analysed were of the *Kataloński* hazelnut (*Corylus avellana* L.) variety, collected from the orchard located in the south of Poland (Jankowice, Pszczyna 50° 0′ 5″ N 18° 59′ 18″ E) in 2012. Hazelnuts in shell, classified in "Extra" class according to Commission Regulation (EC) No 1284/2002, with a diameter equal to or above 16 mm, were exclusively included in this study. In-shell fruits were collected at technological maturity, sun-dried for 3 days (20-25 °C) and then stored in shell at 4 °C until they were analysed.

Hazelnuts Roasting

Hazelnuts were roasted (shelled and in-shell forms) at nine specific temperature/time conditions: 100 °C/10 min, 100 °C/30 min, 100 °C/60 min, 130 °C/10 min, 130 °C/30 min, 130 °C/60 min, 160 °C/10 min, 160 °C/30 min, 160 °C/60 min, at a constant air flow rate (0.8–1.0 $m \times s^{-1}$). These conditions were set according to the range commonly used in the hazelnut industry. The average air flow was determined using Kestrel 4000 (Nielsen-Kellerman) anemometer. Roasting was conducted in a laboratory convective dryer, Memmert UFP400. Every roasting process was duplicated. After roasting, nuts were cooled immediately and stored at −18 °C until they were analysed.

Oil Extraction

Cold pressing was performed using an oil expeller (Piteba, Nederlands), and then the oil was centrifuged at 4000 rpm/20 min at 4 °C. The obtained oils were stored in −18 °C with no light access until they were analysed.

Basic Quality Analyses of Hazelnut Oils

Hazelnut oil samples were initially characterized by basic quality parameters according to the ISO standard methods. The peroxide value (PV) of oils were determined by iodometric technique, the free fatty acids (%FFA) by titration with 0.1 M ethanolic potassium hydroxide and the anisidine value (AV) spectrophometrically, in accordance with standards ISO 3960:2007, ISO 660:2009 and ISO 6885:2012, respectively.

Fatty Acids Determination

The fatty acid composition of hazelnut oil was determined as fatty acid methyl esters (FAMEs) by alkaline treatment and capillary gas chromatography analysis, as described by Christie (1982). The chromatographic conditions were the same as reported by Bryś et al. (2013). The results were expressed as relative percentages of each fatty acid, calculated by external normalization of the chromatographic peak area. Fatty acids were identified by comparing the relative retention times of FAME peaks with FAME chemical standard.

PDSC Determination

The oxidative stability of the tested oils were determined using differential scanning calorimeter (DSC Q20, TA Instruments) coupled with a high-pressure cell (Q20P) as reported previously by Ciemniewska-Żytkiewicz et al. (2014b). The isothermal temperature for each sample was programmed at temperature 140 °C.

Tocopherols Determination

Due to tocopherols determination, approximately 300 mg of hazelnut oil was dissolved in 1 mL of n-hexane, respectively, and then extracts were filtered through a 0.45-μm nylon filter. The tocopherols were determined by HPLC (Agilent 1200 series, Palo Alto, CA, USA) equipped with a fluorimeter detector (Agilent, Palo Alto, CA, USA). The excitation wavelength was 290 nm, and the emission one was 325 nm. The column used was a Luna Hilic Phenomenex column (250× 4.6 mm i.d., 5 μm particle size) in isocratic conditions as reported by Gómez-Caravaca et al. (2010). The calibration curve was constructed with α-tocopherol standard solution, and it was used for quantification.

MID-FT-IR Spectroscopy Analysis

Infrared spectra were registered for every sample in the classic range of 4000–400 cm^{-1} with 1 cm^{-1} resolution, using System 2000 Perkin Elmer spectrophotometer. The Grams AI 8.0 and TQ Analyst 8 software were used for spectral data processing, statistical modelling and evaluation. Samples of hazelnut oils extracted from roasting samples were registered as a film between two KRS plates. Samples were placed on a plate as a single drop of volume 0.05 mL. Registration of 10 spectra for each sample with 20 scans for every spectrum was followed by spectra averaging and processing of the averaged spectrum.

Statistical Analysis

Relative standard deviation was obtained, where appropriate, for all data collected. All chemical analyses were carried out in triplicate (n=3) for each sample. In the case of oxidation stability determination, for each oil at each time and temperature conditions, three experiments were performed and the average τ_{max} (PDSC maximum induction time) values were calculated. The data were statistically processed using the analysis of variance with use of Tukey's test, considering a level of significance of less than 5 % (p<0.05) with the use of Statgraphics Plus for Windows software, version 4.1 (Statistical Graphics Corporation, Warrenton, VA, USA). Discriminant models were calculated based on principal components analysis (PCA) with the use of the mean centering technique. Eight to ten principal components representing at least 95 % of total variability of the samples spectral data, both frequencies and intensities, were used to construct multi-linear models to allow distinguishing between samples of different chemical composition. Regions representing the highest variations were applied instead of whole spectral region. Mahalanobis distances were used to evaluate membership of a sample to a given group. Performance index (PI) was calculated to every trial with focus on finding the highest value.

Results and Discussion

Oxidative Stability of Roasted Hazelnuts

Hazelnuts roasting leads to a number of flavour, sensory and physical alternations, oxidation metabolites formation, as well as, biochemical changes, such as lipid structure modifications (Amaral et al. 2006). The free fatty acid concentration (%FFA), peroxide value (PV), anisidine value (AV) and calculated total oxidation value (TOTOX) of the oils extracted from roasted hazelnuts are gathered in Table 1.

The amount of FFA is a widely accepted indicator of oils and fats quality and represents progress of triglycerides hydrolysis. Accordingly to preliminary considerations, the highest level of %FFA were observed for oils extracted from hazelnuts in 160 °C for 60 min (p<0.05); however, the %FFA occurred to be very low for all oils tested. Hence, the %FFA levels in oils extracted from roasted hazelnuts are only slightly affected by the high-temperature treatment. PV is the well recognised indicator for primary oxidation (Gharby et al. 2011) which shows the amount of hydroperoxides present. The PV values for cold-pressed oils, including hazelnut oils, should not exceed 15 meqO_2/kg of oil (Codex Alimentarius 2013). The results of PV obtained, herein, remained low (<2.5 meqO_2/kg of oil) for all roasting conditions applied, which is within quality requirements range. Under the influence of unfavourable conditions, such as long-term heating, applying a too high temperature or extreme exposure to light, the hydroperoxides break down to carbonyl compounds (alpha-beta unsaturated aldehydes) of low molecular mass. The content of these secondary oxidation products can be measured using the anisidine value. The significant increase in AV values with an increase in roasting time was observed for 130 and 160 °C, for both shelled and in-shell hazelnuts (p<0.05). The AV values of samples roasted in 160 °C for 60 min were about 20 and 12.5 times higher for shelled and in-shell hazelnuts, respectively, as compared to unroasted nuts. It suggests that shell left during the roasting process had a protective function and limited hazelnuts oxidative deterioration. Additionally, there was noticeable regularity between PV and AV values presented in Table 1, samples with higher PV had lower AV and vice versa.

Since PV and AV present only part of oil oxidation status, total oxidation (TOTOX) value, marker of oil oxidative history and current oxidation status was calculated as well. The high quality oils should have TOTOX value <10 (Rossell and Pritchard 1991; Škevin et al. 2012). The highest TOTOX index was observed for hazelnuts roasted without shell in the most radical conditions tested (160 °C, 60 min.) and even if the TOTOX value changed significantly (p<0.05), it did not exceed quality limits in any case.

Determining oxidative stability is a tedious and time-consuming method when analysed at room temperature (Mateos et al. 2006), but even if accelerated methods like

Table 1 Free fatty acids, peroxide and anisidine values and TOTOX value of oils obtained from roasted hazelnuts

Roasting conditions		Free fatty acids		Peroxide value		Anisidine value		TOTOX	
Temperature [°C]	Time [min]	% of oleic acid		$meqO_2/kg$					
		Shelled	In-shell	Shelled	In-shell	Shelled	In-shell	Shelled	In-shell
Unroasted		0.09±0.00d	0.09±0.00 de	0.79±0.00e	0.79±0.00b	0.23±0.03e	0.23±0.03ef	1.81±0.03e	1.81±0.03d
100	10	0.08±0.00d	0.08±0.00e	0.99±0.00cde	0.79±0.05b	1.53±0.01e	0.09±0.01f	2.20±0.01e	1.66±0.08d
100	30	0.15±0.01c	0.14±0.00b	2.27±0.12a	1.76±0.01a	0.22±0.06d	0.27±0.03ef	5.48±0.18b	3.78±0.04a
100	60	0.14±0.01cd	0.14±0.01b	1.39±0.01b	0.88±0.14b	0.95±0.11c	0.82±0.08d	4.30±0.13c	2.58±0.37bc
130	10	0.11±0.00cd	0.14±0.00b	0.88±0.14de	0.48±0.01c	0.36±0.05e	0.11±0.01f	2.12±0.23e	1.06±0.01e
130	30	0.11±0.01cd	0.14±0.01bc	1.16±0.13bcd	0.96±0.04b	0.73±0.16d	0.91±0.02cd	3.05±0.41d	2.83±0.11b
130	60	0.33±0.02b	0.13±0.01bc	nd	0.10±0.00d	2.00±0.02b	1.67±0.07b	2.00±0.02e	1.87±0.07d
160	10	0.14±0.01cd	0.11±0.00cd	0.98±0.04cde	0.79±0.06b	0.07±0.01e	0.46±0.01e	2.03±0.10e	2.04±0.10cd
160	30	0.10±0.00cd	0.12±0.01bcd	1.27±0.09bc	0.98±0.00b	1.28±0.03c	1.08±0.14c	3.81±0.16c	3.04±0.14b
160	60	0.52±0.04a	0.34±0.01a	1.16±0.00bcd	0.43±0.04c	4.56±0.13a	2.89±0.04a	6.88±0.13a	3.75±0.05a

Data expressed as means±standard deviation (n=3). The different lower case letters (a–f) in the same column indicate significantly different values (p<0.05)

Rancimat are applied, the time of one analysis can last long. In the present study, to get a complete picture of the oxidative stability of oil cold pressed from roasted hazelnuts, PDSC measurements were conducted. Results obtained at 140 °C are presented in Table 2. As reported previously (Ciemniewska-Żytkiewicz et al. 2014b), statistically significant linear correlations between PDSC maximum induction time (τ_{max}) and the Rancimat values imply that PDSC can be recommended as an appropriate unbiased method for assessing the oxidative stability of hazelnut oils. According to Ciemniewska-Żytkiewicz et al. 2014b, the Pearson correlation (R>0.99) (Eq. 1) enabled the authors to express, herein, the obtained results of oxidative stability through Rancimat induction time, as well (Table 2.).

$$\tau_{\mathrm{Racimat}[h]} = 0.0446\tau_{\mathrm{PDSC}[\mathrm{min}]} + 0.1815 \quad (1)$$

The results of τ_{max} were in the range of 31.52–39.49 and 31.65–38.33 min for shelled and in-shell hazelnuts, respectively. As a resultant of all changes that occurred, the oxidative stability was slightly elevated with the increased temperature and time of roasting process. The highest oxidative stability levels for both shelled and in-shell hazelnuts were noticed after 130 °C/60 min of roasting process (p<0.05); however, all the results obtained confirmed high overall oil oxidative quality.

Isothermal pressure DSC conducted in 140 °C was previously used to determine oxidative stability of selected fresh

Table 2 Oxidation stability of oils obtained from roasted hazelnut

Roasting conditions		PDSC		Rancimat in 140 °C[a]	
Temperature [°C]	Time [min]	min		h	
		Shelled	In-shell	Shelled	In-shell
Unroasted		32.54±0.16g	32.54±0.16e	1.63±0.01	1.63±0.01
100	10	31.52±0.04h	34.81±0.06b	1.59±0.01	1.63±0.01
100	30	35.19±0.09d	32.92±0.09e	1.75±0.01	1.73±0.01
100	60	34.27±0.13e	31.84±0.18f	1.71±0.01	1.65±0.01
130	10	36.87±0.13c	33.99±0.01cd	1.83±0.01	1.70±0.01
130	30	38.68±0.04b	31.65±0.08f	1.91±0.01	1.59±0.01
130	60	39.49±0.11a	38.33±0.40a	1.94±0.01	1.89±0.02
160	10	32.67±0.08g	34.72±0.16b	1.64±0.01	1.73±0.01
160	30	33.65±0.03f	33.62±0.03d	1.68±0.01	1.68±0.01
160	60	36.65±0.23c	34.53±0.03bc	1.82±0.01	1.72±0.01

Data expressed as means± standard deviation (n=3). The different lower case letters (a–h) in the same column indicate significantly different values (p<0.05)

[a] Calculated based on Ciemniewska-Żytkiewicz et al. 2014b

vegetable oils (Kowalski et al. 2004; Ciemniewska-Żytkiewicz et al. 2014b). Thus, Kowalski et al. (2004) reported τ_{max} accounted for 22.0, 21.8 and 9.5 min for rapeseed, soybean and sunflower oils, while Ciemniewska-Żytkiewicz et al. (2014b) reported ranges 44.21–26.44, 39.20–27.47 and 22.85–17.66 min for hazelnut, olive and rapeseed oils, respectively. Therefore, the oxidative stability level of oil from roasted hazelnuts obtained herein seemed to be comparable or even higher than previously reported. It could be partially explained by the Maillard reaction products formation through the interaction of proteins with reducing sugars during high-temperature roasting treatment (Elizade et al. 1991). As reported by Michalska and Zieliński (2007), melanoidins, products of non-enzymatic browning, reportedly show strong antioxidant activity which can affect positively oxidative stability of tested hazelnuts.

In the present study, the highest results of Rancimat induction period (IP) values calculated accounted for almost 2 h for roasted hazelnuts (Table 2.). In the majority of papers on oxidative stability, Rancimat analyses are performed at 110 or 120 °C (Hassanien et al. 2014; Gharby et al. 2011); however, the Rancimat results are repetitive even at 140 °C (Mateos et al. 2006). IP values obtained in 140 °C for olive oils were in the range of 0.9 to 9.8 h (Mateos et al. 2006), and the results obtained herein for hazelnut oils were within the range presented for olive oil.

Fatty Acid Composition

As the fatty acids composition can be treated as an indicator of its susceptibility to oxidation, it could be used as a part of overall oxidation status description of hazelnut oil. In the raw *Kataloński* variety, 15 different fatty acids were detected, as previously reported (Ciemniewska-Żytkiewicz et al. 2015). In the present study, some minor changes in the fatty acid composition in roasted hazelnuts (both shelled and in-shell) were observed, and the data on selected fatty acids levels are gathered in Table 3. In general, there was a relationship observed between particular fatty acids percentage relative content and increasing roasting temperature and time of exposure. Slight but significant ($p<0.05$) increases in saturated fatty acid (palimitic and stearic) relative levels were observed for both shelled and in-shell roasted hazelnuts especially heated in the highest temperature tested—160 °C. In the case of oleic acid, the relative levels were found to be changed individually with no convergent pattern ($p<0.05$); however, even the biggest change was negligible (maximum 2.5 %).

In general, higher level of unsaturation favours oxidation process, for instance, by thermal processing, such as, dry roasting treatment. The autooxidation rates of oleic, linoleic, and linolenic fatty acids relate to degree of unsaturation and are 1:40:100, respectively (Frankel 1985; Arranz et al. 2008; Ciemniewska-Żytkiewicz et al. 2014b). Because of that, the C18:2 ω6 and C18:3 ω3 fatty acids should be more susceptible to the roasting process, especially in higher temperatures. Herein, for most roasting conditions studied, C18:2 ω6 relative level decreased ($p<0.05$) with some exceptions (Table 3); however, C18:3 ω3 and C16:1 levels were constant apart from increasing roasting temperatures, times of exposure and protective role of the shell. It could be explained by no relative changes occurring but also by the very low level of these FAs in tested samples and low results accuracy (first decimal place only). The results obtained are mostly consistent with other previously published papers on hazelnuts (Amaral et al. 2006), where authors noticed the modest increase in oleic and saturated fatty acids and a decrease of linoleic acid, as temperatures and roasting periods increased. On the other hand, the fatty acid profiles in several foodstuffs (walnuts, safflower seeds and chestnuts) previously subjected to the thermal treatment had not been changed significantly (Künsch et al. 2001; Lee et al. 2004; Vaidya and Eun 2013).

Tocopherol Content

Hazelnuts are an excellent source of tocopherols (Kornsteriner et al. 2006; Savage et al. 1997; Matth us and Özcan 2012; Ciemniewska-Żytkiewicz et al. 2015), strong antioxidants with significant biological effect, so these compounds are thought to be nutritionally valued in the human diet. The contents of the individual and total tocopherols in hazelnut oils obtained at various roasting temperatures and times of exposure are given in Table 4. Three compounds were detected and quantified (α-, β-, γ-tocopherols), whereas in all samples, α-tocopherol was the predominant component, followed by γ- and β- homologues, respectively.

Herein, with increasing roasting time and temperature, the three homologues presented different behaviours, with no apparent variability (Table 4). It could be ascribed by two opposed effects, such as, the tocopherol levels reduced and increased yield of extraction, both caused by thermal processing. Tocopherol levels can be reduced during roasting by the oxidation process and thermal degradation (Rossi et al. 2001; Alamprese et al. 2009); however, on the other hand, tocols are bound to the membrane and are linked to other compounds, such as phospholipids. They can be more easily released by heat treatment resulting in their higher concentration in oil (Amaral et al. 2006; Lee et al. 2004).

The α-tocopherol levels showed minor changes after the roasting treatment, however not statistically significant ($p<0.05$). The biggest losses were observed for γ-tocopherol, which accounted for over 20 % for 100 °C/30 min and 160 °C/

Table 3 Selected fatty acid composition in oils obtained from roasted hazelnuts

Roasting conditions		Fatty acid (mg/100 mg FAME)											
Temperature [°C]	Time [min]	C16:0		C16:1		C18:0		C18:1 ω9		C18:2 ω6		C18:3 ω3	
		Shelled	In-shell	Shelled	In-shell	Shelled	In-shell	Shelled	In-shell	Shelled	In-shell	Shelled	In-shell
unroasted		4.7ef	4.7bc	0.2a	0.2a	1.5bcd	1.5bc	80.4bc	80.4d	13.2bc	13.2a	0.1a	0.1a
100	10	5.2bc	4.6c	0.2a	0.2a	1.7a	1.4cd	80.3bc	82.3a	12.3f	12.0d	0.1a	0.1a
100	30	5.0cd	5.0a	0.2a	0.2a	1.7a	1.7a	80.1c	79.9ef	12.8e	12.8b	0.1a	0.1a
100	60	4.1g	4.3d	0.2a	0.2a	1.4cd	1.2d	81.8a	81.6b	12.4f	12.6b	0.1a	0.1a
130	10	4.5f	4.5c	0.2a	0.2a	1.3d	1.4cd	81.8a	81.8b	11.8g	11.8d	0.1a	0.1a
130	30	4.6ef	4.8b	0.2a	0.2a	1.5abc	1.6ab	80.5b	79.7f	12.8de	13.3a	0.1a	0.1a
130	60	4.8de	5.1a	0.2a	0.2a	1.5abc	1.6ab	81.5a	80.5cd	11.7g	12.2c	0.1a	0.1a
160	10	4.8def	4.8b	0.2a	0.2a	1.6ab	1.7a	79.5d	80.7c	13.5a	12.3c	0.1a	0.1a
160	30	5.5a	4.8b	0.2a	0.2a	1.7a	1.6ab	78.8e	80.1e	13.4ab	12.8b	0.1a	0.1a
160	60	5.3ab	4.8b	0.2a	0.2a	1.6ab	1.6ab	79.4d	79.8f	13.1cd	13.1a	0.1a	0.1a

Data expressed as means±standard deviation (n=3), The different lower case letters (a–f) in the same column indicate significantly different values (p<0.05)

30 min roasting without shell, when compared to the raw values. Herein, considering the results of all tocopherol homologues, α- homologue seemed to be most and β-, the least resistant to roasting conditions applied, which is in wide agreement with Amaral et al. (2006), but not necessarily with other literature available (Barrera-Arellano et al. 1999; Yoshida et al. 1993).

In general, after all roasting treatments studied for shelled and in-shell hazelnuts, the amount of total tocopherols was still over 95 % of the original levels. Similar results were obtained previously for hazelnuts (Amaral et al. 2006), peanuts (Yoshida et al. 2003) and sunflower seeds (Yoshida et al. 2002), with at least 90, 85 and 90 % of tocols recovery after roasting process, respectively.

MID-FT-IR Analysis

Spectra registered for 27 roasted samples (160 °C, 30 and 60 min) and five raw samples were analysed due to differences between the three groups: roasted in shells—group 1 (11 samples), roasted shelled—group 2 (16 samples) and raw—group 3 (5 samples). Initially, visual inspection of the studied spectra was conducted. No significant differences were observed, although some slight discrepancies between the most

Table 4 Tocopherols content in oils obtained from roasted hazelnuts

Roasting conditions		α-Tocopherol		γ-Tocopherol		β-Tocopherol		Total	
Temperature [°C]	Time [min]	mg/kg oil							
		Shelled	In-shell	Shelled	In-shell	Shelled	In-shell	Shelled	In-shell
Unroasted		320.4±17.8a	320.4±17.8a	14.5±0.5 ab	14.5±0.5bc	7.6±0.2bcd	7.6±0.2b	342.6	
100	10	328.7±14.5a	315.3±10.4a	11.1±0.3e	12.4±0.2e	7.6±0.6bcd	7.3±0.3bc	347.4	335.0
100	30	306.0±3.2a	318.4±4.8a	13.0±0.5bcd	12.5±0.7e	6.6±0.5d	6.9±0.2cd	325.5	337.9
100	60	326.7±1.3a	320.4±1.1a	13.1±0.2bcd	12.9±0.1de	8.7±0.1ab	6.6±0.1d	348.4	340.0
130	10	319.5±2.2a	332.9±9.8a	15.7±0.5a	13.5±0.3cde	9.0±0.3a	7.5±0.1bc	344.2	353.9
130	30	332.6±8.1a	326.7±0.1a	15.9±0.8a	14.9±0.2b	7.9±0.1abc	7.6±0.0b	356.4	349.1
130	60	317.0±2.5a	311.5±4.1a	13.9±0.1bc	14.9±0.1b	7.0±0.1cd	7.9±0.1b	337.8	334.3
160	10	320.1±4.7a	320.3±1.6 a	12.5±0.0cde	14.2±0.4bcd	7.6±0.1bcd	7.5±0.1bc	340.2	342.1
160	30	308.3±7.1a	314.0±6.8a	11.6±0.3de	17.6±0.3a	7.2±0.4cd	7.7±0.1b	327.1	339.2
160	60	321.7±6.6a	320.4±0.7a	14.3±0.5ab	13.3±0.3cde	8.2±0.2abc	8.7±0.2a	344.2	342.4

Data expressed as means±standard deviation (n=3). The different lower case letters (a–d) in the same column indicate significantly different values (p<0.05)

distinctive spectra were observed in the regions: 1660 cm^{-1}, 878 cm^{-1}, 708 cm^{-1} and 689–672 cm^{-1}, respectively. This procedure did not however provide with the expected sufficient data to select distinctive groups of differently treated hazelnuts.

Visual inspection was followed by software digital analysis that considered mutual interaction of spectral changes (intensity and wave number) in different spectral regions. Three groups (raw, roasted in and out of shells) were successfully differentiated by discriminant analysis from the TQ analyst software with use of eight principal components, covering cumulatively 99.98 % of total variance. One hundred percent samples were correctly classified. Figure 1 shows discriminant analysis with three separate groups rounded with circles—dashed line circle for in-shell roasted group of hazelnuts, dotted for raw and regular line for shelled samples. Although only five samples have been used as a raw material representative against 16 and 11 samples representing roasted samples, respectively, statistically significant differentiation with PI equal to 88.71 was determined. All the groups are quite condensed, with members being relatively close to each other (the mean Machalanobis distance within group 1, 2 and 3 were 1.01±0.18; 0.89±0.23 and 0.86±0.25, respectively). Additionally, Fig. 1 shows that group 2 is significantly closer to group 3 then to group 1, with corresponding mean Machalanobis distances between groups 1/3 and 2/3 accounted for 1.59±0.30 and 2.01±0.34, respectively. This observation suggests that chemically, roasted hazelnuts in shells are more similar to raw material and shell left for roasting treatment protects nuts significantly against changes occurring during high-temperature processing. This protective effect delays fat oxidation mainly, which can reasonably be confirmed by values of total oxidation status (Table 1). The spectral regions selected to distinguish three groups, i.e. 3530–3430, 1820–1660 and 1480–1370 cm^{-1}, respectively, confirms this hypothesis, as similar spectral regions are quoted in the literature to be responsible for chemical alterations in fats during oxidation. As reported previously, the peroxides formation is responded by changes in the region of 3560–3360 cm^{-1} (Guillén and Cabo 2002). Changes within region 1820–1660 cm^{-1} that cover regions related to alterations in C=O vibrations of the aldehydes (1739 to 1724 cm^{-1}) and ketones (1724 to 1709 cm^{-1}) (Sadoudi et al. 2013). Region 1480–1370 cm^{-1} is related to bending vibrations of CH_2 groups, rocking vibrations of CH bonds of cis-disubstituted olefins and bending in plane vibrations of CH cis-olefinic groups (Vlachos et al. 2006). However, based on obtained IR data, it is not possible to state whether fat oxidation deletion for in-shell samples occurs due to shifting onset point of oxidation or any other mechanism.

Conclusions

The results of PDSC and reference methods obtained within this study both evaluated overall oxidative stability of roasting hazelnuts. They showed only slight effect of roasting conditions on quality and nutritional value of processed hazelnuts. Tocopherols are known to act as antioxidant and their content increases oxidative stability in general. Within this study, the level of tocopherols was reported to decrease during roasting. Interestingly, even though slight decrease of tocopherols occurred (up to 5 %), the oxidative stability did not drop down, but conversely increased slightly (by ~21 and ~18 % for shelled and in-shell hazelnuts, respectively) with statistical significance ($p<0.05$). The highest values of oxidative stability were obtained for roasting process performed at 130 °C for 60 min.

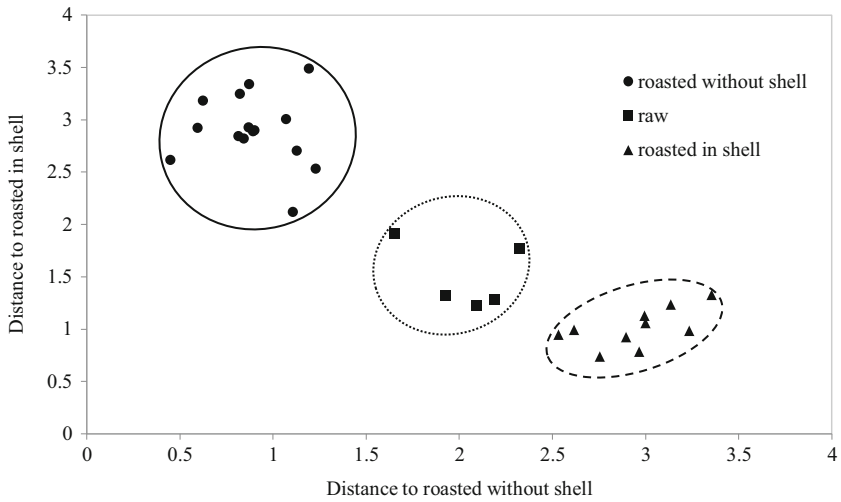

Fig. 1 Discriminant analysis forming three homologous groups of raw, shelled and in-shell roasted hazelnuts

Interpretation of statistically processed MID-FT-IR data proved that the protective role of the shell during roasting, as in-shell processed hazelnuts were more similar to raw material than to shelled ones, in terms of chemical composition. The spectral regions selected for distinguishing studied groups evidenced that the protective role is based on delaying the oxidation process. Studies conducted perceive IR as a valuable method for hazelnuts quality control and technological process monitoring.

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