

Article

Investigation of Oil Extracted from Roasted and Unroasted Oats with Use of Chemometrics

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Abstract: One of the beneficial components of oats is oil that is rich in fatty acids and has excellent health and technological potential. During thermal processing, the oil is prone to chemical changes, both beneficial and adverse. One such processing method is roasting, which involves heating the product uniformly at a temperature below its melting point. The primary objective is to evaluate and report with statistical models how the chemical changes that occur during the roasting of whole oat grains affect the properties and quality of the oil found in the oat grains. To achieve this goal, a pressure differential scanning calorimeter, infrared spectroscopy calorimetric bomb, and gas chromatography were used. Using chemometric methods, the spectral data were combined with calorimetric data, automatic titration data, and chromatographic data. The discriminant and reference models of high statistical significance were calibrated and validated to rapidly and robustly evaluate the properties of oat oil and the changes that occurred due to the roasting process. It has been shown that roasting oat grains increases the oxidative stability of the oil contained in grains. The acid and peroxide values of oil extracted from roasted oat grains are lower than those determined for oil from fresh oat grains. The composition of fatty acids was not statistically significantly affected by the roasting process of oat grains.

Keywords: chemometrics; oats roasting; fatty acid composition; oxidative stability



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1. Introduction

Oats (*Avena sativa* L.) are one of the crops that have been grown and consumed worldwide since ancient times; they are considered highly valuable due to their nutritional properties, e.g., fibre content [1] and high amount of healthy fats [2]. Oat grains are an essential source of protein, minerals, and oil [3].

Avena sativa L. is a grass that grows up to 1.5 m tall, with tufts or solitary culms, an erect or bent base, and a smooth texture. The leaves are unarticulated, green, and have spherical sheaths on the back. Seed size is commonly around 30,000 seeds per kilogramme of crop, although it can vary depending on the cultivar [3]. Wild oats (*Avena fatua*) and common oats (*Avena sativa*) look similar, but wild oats are not being used for grain production. Oats have been grown for over 2000 years in various parts of the world. They are typically grown in temperate regions and require less summer heat than other cereals like wheat, rye, or barley. Oats are also more rain-resistant, making them particularly significant in areas with cool, wet summers. Oats are a perennial plant that can be cultivated either in autumn (harvested in late summer) or in spring (harvested in early autumn) [4]. The common *Avena sativa* L. is the most important cultivated oat, and it is also the most unusual compared with other cereal grains due to the storage of high amounts of oil in the endosperm, which can be up to 90% of the total grain oil [5]. The lipid fraction of the oat grain determines its energy content in considerable measure and significantly impacts nutritional quality via the fatty acid composition [6].

Roasting is a typical food processing operation involving dry heating where hot air covers the food, cooking it evenly on all sides [7]. The temperature applied should be at least 140 °C. The oven uses a combination of convection, conduction, and radiation to heat the food product. However, the impact of each heat transfer mechanism may vary at different stages of the process. Roasting is a crucial method for food processing that significantly enhances the taste, aroma, tenderness, colour, and crispiness of various foods, such as seeds, nuts, grains, and plant leaves. This thermal process involves heating the product to a temperature lower than its melting point.

Roasting and other heating methods can enhance food's digestibility, palatability, and bioavailability by modifying the food matrix through physicochemical and structural changes. Roasting is a cooking method for all sorts of foods that convert macro-nutrients into a more digestible form (the bigger molecules, e.g., polymers, are converted into smaller ones, e.g., simple sugars). The process reduces water activity, improves shelf-life, and changes antioxidant and functional properties, leading to better consumer acceptance [8]. The roasting process is commonly defined as "The process of cooking foodstuffs on an open fire or in an oven". This does not differ much from the scientific definition. However, the roasting conditions must be mentioned, e.g., temperature or gaseous flow inside the oven.

This process can also modify the profile of phenolic compounds, sometimes enhancing their antioxidant capacity and improving their health benefits [9]. Roasting has a positive effect on the oil properties. Roasting enhances the extraction yield of oil in oilseeds [10]. Dry roasting exhibits a significant impact on the physicochemical characteristics of peanut oil [11]. In this paper, we have discussed how roasting affects the oil properties. For this reason, roasting on hemp seed and its effect on its oil was discussed in the Results Section [12], and how roasting affects oils' acid and peroxide values was discussed in the Results Section and cited in [13–16].

The oxidative stability determines the shelf life of roasted seeds and nuts as well as manufactured products containing roasted seeds and nuts [17]. In research conducted by scientists, it was found that oxidative stability was slightly elevated with the increased temperature and longer duration of the roasting process [18]. The crucial Maillard reaction could partially explain this increase, the interaction of proteins with reducing sugars during high-temperature roasting treatment, leading to Maillard reaction products' formation [19]. As reported by [20], melanoidins, products of non-enzymatic browning, reportedly show strong antioxidant activity, which can positively affect the oxidative stability of roasted seeds and nuts. Pressure differential scanning calorimetry (PDSC) is an appropriate unbiased method for assessing oxidative stability [18].

The acid value (AV) and peroxide value (PV) are two critical measures of the quality of vegetable oils. The AV indicates the level of oil hydrolysis and is expressed as the amount of KOH (in milligrams) required to neutralise the free fatty acids present in 1 g of oil [21]. Determining the PV of edible oils is imperative, as PV is one of the most typically utilised quality parameters for monitoring lipid oxidation and controlling oil quality. Various methodologies have been devised to determine the PV of oils, but iodometric titration is the generally preferred and widely used method for PV determination [22]. The PV of edible oils is measured in milliequivalents (meq) of active oxygen per kilogramme of oil. If the PV exceeds the critical value, the oil can taste rancid and cause food poisoning [23].

The spectral data model, a tool that has gained significant traction in various research fields over the past decade, is known for its reliability in calibrating parameters like the peroxide value. Its consistent delivery of accurate and dependable results has made it a trusted ally for researchers, who have used it to enhance the reliability of their studies in diverse research areas.

IR spectroscopy is thoroughly used for spectral analysis of edible oils, as presented in the literature [19,24]. The methodology utilises the PCA and MCR [24]. It also uses SVM-DA, SIMCA, and PLS-DA techniques [19].

The spectral models established for oils can accurately determine the level of saturation or unsaturation in edible oils and provide precise quantitative measures for the amount of

oleic and linoleic acids present [11]. They can also be used to study the oxidation of edible oils and the determination of peroxide value in olive, sunflower, and rapeseed oils [24]. They can also serve to classify edible oils, e.g., to differentiate canola, sunflower, corn, and soybean oils [19].

The purpose of the current investigation was to use the chemometrics approach to construct a series of statistical reference and discriminant models based on spectral and classical reference data to show the ability of IR spectroscopy to evaluate the sample of unknown oil versatily. It aimed to model/determine the oxidative induction time, acid value, and peroxide value of oil extracted from thermally treated oats (160 °C). Next, the reconstruction of technological process details, i.e., the time of roasting oats and the oil extracted from them, was planned. Finally, rapid discrimination of oil extracted from unroasted and roasted oats was intended. Additionally, with the use of instrumental methods and the application of a constructed model, the effect of the roasting process on the quality of oil contained in oats was designed. In general, chemometrics is the activity that combines and correlates data from different analytical methods. As a result, the most appropriate method for a given purpose can be used instead of other, more laborious, or more expensive methods.

From the literature survey, only a few scientific positions dealing with applying IR spectroscopy to investigate chemical changes in roasted oat grain oils have been found. Hence, the current topic covers a particular scientific gap.

2. Materials and Methods

2.1. Research Material, Roasting Conditions, and Extraction of Oil from Oats

Bingo-variety oats came from a Polish breeding and seed company, Hodowla Roślin Strzelce Sp. z o.o. Grupa IHAR (Strzelce, Poland). Whole grains were roasted in a laboratory oven (manufacturer: POL-EKO, Model: Drying oven SLN STD 115). Roasting was carried out at 160 °C for 10, 20, 30, 40, 50, and 60 min. Before the fat extraction, the oat was grounded. The fat was extracted according to the procedure depicted by Boselli et al. [25] and Dolatowska-Zebrowska et al. [26]. The applied Soxhlet method relies on cyclical extraction—an extraction technique involving a steady transfer of non-volatile samples through the continuous reflux of organic solvents. The apparatus is slowly filled with solvent to the upper level of the syphon. When this level is reached, it is automatically emptied and refilled with another portion of fresh solvent. Thus, multiple extraction takes place [25]. The reagents used for extraction were 99.9% pure hexane and 100% pure nitrogen. For calorific value determination, 100% pure oxygen was utilised. Each experiment was made in triples.

2.2. GC Analysis

According to the ISO method, fatty acid methyl esters were used to determine the fatty acid composition of the fat extracted from the oat. The YL6100 (Young Lin Bldg., Anyang, Hogyedong, Republic of Korea) gas chromatograph equipped with a flame ionisation detector and a BPX-70 capillary column (SGE Analytical Science, Milton Keynes, UK) was used. According to Bryś et al. [27] procedure, the determination was carried out. The oven temperature was programmed as follows: 60 °C for 5 min and then it was increased by 10 °C min⁻¹ to 180 °C; from 180 to 230 °C, it was increased by 3 °C min⁻¹ and then kept at 230 °C for 15 min. The temperature of the injector was 225 °C, with a split ratio of 1:100, and the detector temperature was 250 °C. Nitrogen flowing at a rate of 1 mL min⁻¹ was used as the carrier gas.

2.3. Oxidative Stability by Pressure Differential Scanning Calorimetry (PDSC) Method

The oils' oxidative stability was determined using a PDSC instrument (DSC Q20 TA Instruments, Newcastle, WA, USA). The experiment was conducted at a constant temperature of 120 °C under 1400 kPa of oxygen. The determination of the PDSC induction time was carried out according to Symoniuk et al.'s [28] procedure.

2.4. Calorimetric Bomb Method

The calorific value of whole grains was determined by using the calorimetric bomb in correspondence with ISO standards 1928:2009 [29]. A calorimetric bomb allows the combustion of the sample in controlled conditions with a bomb filled with oxygen. The temperature of the surrounding water is registered and used to calculate the amount of heat evolved.

2.5. Acid Value Determination

AV was determined by titration with 0.1 methanolic potassium hydroxide in correspondence with ISO standards 660:2009 [30]. Dedicated titrators were used to titrate fat samples with a standardised NaOH solution. This way, the content of free fatty acids is determined.

2.6. Peroxide Value Determination

The iodometric technique determined the PV of oils in correspondence with ISO standards 3960:2007 [31]. After titration is conducted in a dedicated titrator, the number of oxides; hence, the quality of fat, can be evaluated.

2.7. IR Spectra Registration

The first step involves registering the background spectrum to ensure the accuracy of IR spectra. This step aims to eliminate any potential influence of carbon dioxide and water vapour on the working sample spectrum. To carry out the measurement process, a drop of oil is carefully placed between KRS plates to form a thin film. These plates are stored in a dedicated folder and then inserted into the measuring chamber of the System 2000 Perkin Elmer spectrometer. The final spectrum is obtained by taking an average of ten scans in the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} using the transmission mode.

2.8. Chemometrics

The general definition of chemometrics was given above at the end of the introduction section. The spectral data and data collected from other methods were entered into the TQ Analyst 9.4 software. A discriminant model was then applied to differentiate samples based on the IR spectra of oil originating from roasted and fresh oat samples. Reference models were constructed to relate data registered by the spectral method with data collected using titration, calorimetric, and chromatographic methods. The PLS technique was then applied to reduce the number of spectral data and calculate principal components that depict a given sample over a set of other samples. Correlation coefficients were calculated for every calibrated reference model, followed by root mean square error of calibration (RMSEC) and root mean square error of prediction (REMSEP).

2.9. Statistical Procedures

The roasting conditions were kept constant for all the experiments (oven NAME has been used) to keep the results fair. Besides the described above chemometrics that include statistical performance, some simple approaches, e.g., showing the dependence between roasting time and oxidation induction time, peroxide value, or acidic value, were performed.

3. Results and Discussion

In the following Sections 3.1–3.4, data from various methods, including calorimetry, chromatography, automatic titration, and spectroscopy, will be presented and discussed. The focus will mainly be on changes that occur during the roasting process over increasing time intervals, precisely 10, 20, 30, 40, 50, and 60 min, while keeping all other roasting conditions constant. This allows for evaluating the effect of time and temperature treatment alone. In Section 3.5, statistical correlations such as discriminant and reference models

combining the data from Section 3.4 with the data from Sections 3.1–3.3 will be presented and discussed.

3.1. Calorimetry

Although several methods have been attempted to analyse and monitor the lipid oxidation process, single methods are the only ones capable of accurately monitoring the results of these complex oxidation reactions [32]. The pressure differential scanning calorimetry (PDSC) method was used to measure the oxidative stability of the oil, as determined by the oxidation induction time (OIT). Generally, the stability of oil increases as the OIT period increases. In a recent study [12], researchers used PDSC and FTIR techniques to analyse the oil extracted from roasted hemp seeds. They determined the oxidative induction time from the PDSC curves. After roasting at higher temperatures, samples of oil extracted from hemp seeds were characterised by lower induction time than oil from hemp seeds roasted at lower temperatures. The data in Figure 1 confirm that even a short roasting time affects the OIT of the oil. Surprisingly, the oil extracted from oats roasted for 10 min showed a higher OIT than the unroasted oil. The statistical difference between the results ruled out the possibility of experimental error. Longer roasting times have resulted in lower OIT, as seen in Figure 1 and confirmed by visual inspection. The data obtained with PDSC were statistically correlated with spectral data, as presented in Section MODEL 3: Induction Time and Spectral Data.

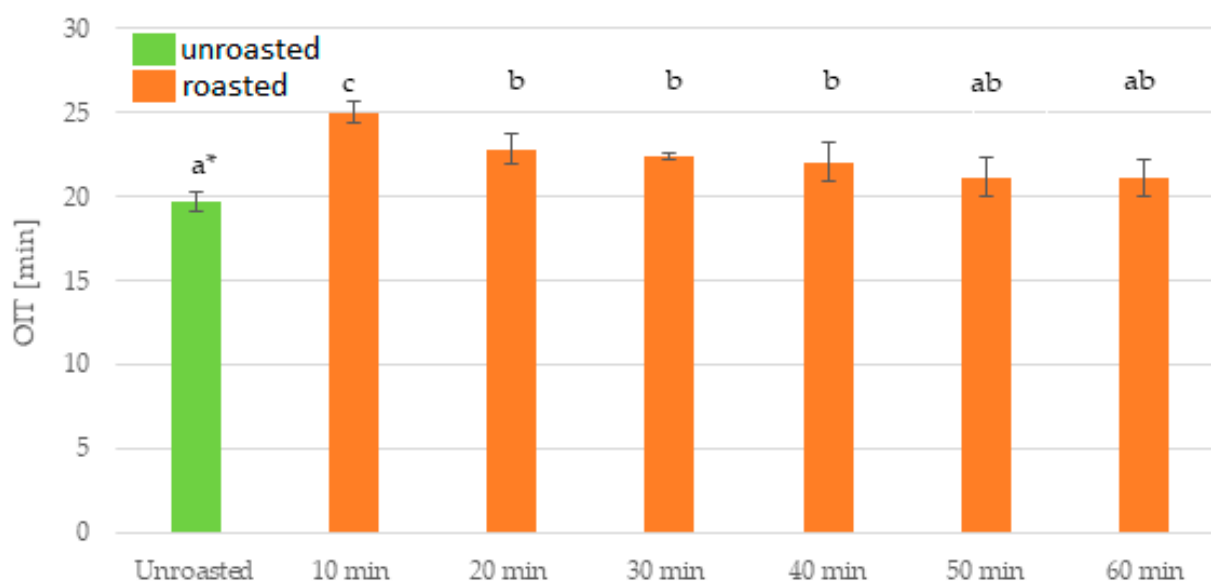
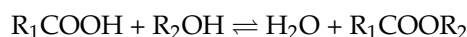


Figure 1. Oxidation induction time (OIT) of roasted and unroasted grains' oil. * Different letters indicate that the samples differ significantly at $p < 0.05$.

The roasting time influences the levels of thermally unstable compounds found in oils, such as phosphatides, mono- and diglycerides, fatty alcohols, sterols, and fat-soluble vitamins (like vitamin A and vitamin E). As the roasting process progresses, the content of these compounds decreases because they decompose when exposed to heat. Consequently, the oxidation induction time (OIT) and oxidation stability (OS) increase as compared to unroasted grains (green bar in Figure 1). This is because these compounds can act as catalysts in the oxidation process; therefore, when their levels are lower, the oxidation process slows down, resulting in higher OIT and OS values. Additionally, the acid value decreases, likely because free fatty acids react with free mono- and diglycerides to form esters. The esterification and hydrolysis reactions are reversible and governed by equilibrium. When heated, some water is removed, causing a shift in the equilibrium toward the formation of esters, according to Le Chatelier's principle. As a result, there is a lower concentration of free fatty acids after roasting.

The reaction can be represented as follows:



This Equation illustrates that a carboxylic acid and an alcohol are at equilibrium with an ester and water.

For hempseed oil, authors [12] studied the effect of different roasting temperatures (lower and higher) on hemp seeds on the OIT but not the impact of roasting in different time intervals at the same temperature.

Classical calorimetry, also known as calorimetric bomb, was used to determine the calorific value of oat grains and the impact of the roasting process on their change. This study examined the effect of temperature treatment on the calorific value of whole oat grains. It concluded that the calorific value of samples roasted at 160 °C for different durations increased systematically, with the samples roasted for 60 min having the highest calorific value. The data are presented in Figure 2, where calorific values, given in $\text{kJ} \times \text{kg}^{-1}$, are plotted against 0, 10, 20, 30, 40, 50, and 60 min of roasting. The calorific values at different times are significantly different from each other. It has been concluded that the calorific value of samples roasted at 160 °C is statistically higher with the heat treatment than the unroasted samples. Heat treatment increased calorific values of oat grains and increased dry matter. Both effects were undoubtedly related to the loss of water contained in whole grains. During roasting, water evaporated, making grains denser and more calorific per 1 g of mass. These two effects were somewhat expected; however, roasting caused another consequence of a cause-effect nature. They are described in the following sections. In the studies [33], microwave torrefaction of oat hull was conducted to change its physicochemical properties. The results showed that the heat treatment performed at high temperatures increases the calorific value, decreasing the mass yield.



Figure 2. The calorific value of roasted and unroasted whole oat grains. * Different letters indicate that the samples differ significantly at $p < 0.05$.

3.2. Chromatography

Data considering the composition of fatty acids in the investigated samples are presented in Table 1, Figure 3. It is observed that the content of unsaturated fatty acids significantly dominates the saturated fatty acid content of oat oil, with a ratio of 80:20%, respectively. The ratio does not change statistically considerably after 60 min of the roasting process. Among unsaturated fatty acids, monounsaturated acids account for 39–42%, with oleic acid being the most abundant (range of 38–41% of this fraction). Of the polyunsatu-

rated fatty acids (38–40% in total fatty acids), linoleic acid is the most abundant (range of 37–39% of this fraction) (see Figure 3). The roasting process did not significantly impact the composition of the unsaturated fatty acids group. The studies [34] discussed the effects of seed roasting on mustard seed oil. The results showed that roasting the seeds did not impact the fatty acid composition of the mustard seed oil extracted after the roasting process.

Table 1. Fatty acid composition is present in unroasted and roasted oat oil.

Fatty Acid	Unroasted	160 °C 10 Min	160 °C 20 Min	160 °C 30 Min	160 °C 40 Min	160 °C 50 Min	160 °C 60 Min
C14:0	0.39 ± 0.06	0.28 ± 0.01	0.21 ± 0.06	0.19 ± 0.02	0.36 ± 0.04	0.22 ± 0.02	0.28 ± 0.02
C16:0	19.59 ± 1.46	18.30 ± 0.99	15.42 ± 1.50	14.80 ± 0.20	19.64 ± 1.32	15.59 ± 0.27	17.22 ± 1.27
C16:1	0.25 ± 0.04	0.18 ± 0.01	0.18 ± 0.01	0.14 ± 0.01	0.18 ± 0.02	0.14 ± 0.01	0.16 ± 0.02
C18:0	2.28 ± 0.02	2.19 ± 0.15	2.48 ± 0.15	2.35 ± 0.01	1.66 ± 0.28	2.37 ± 0.11	2.24 ± 0.12
C18:1 n-9	37.83 ± 0.73	40.11 ± 1.75	40.28 ± 0.54	40.84 ± 0.07	39.02 ± 1.35	40.64 ± 0.01	40.07 ± 0.70
C18:2 n-6	37.65 ± 0.66	36.93 ± 1.40	39.01 ± 0.40	39.18 ± 0.38	37.54 ± 0.30	38.59 ± 0.22	37.84 ± 0.04
C18:3 n-3	1.37 ± 0.03	1.32 ± 0.26	1.44 ± 0.06	1.23 ± 0.021	0.90 ± 0.07	1.31 ± 0.01	1.14 ± 0.21
C20:0	0.08 ± 0.01	0.09 ± 0.01	0.12 ± 0.01	0.18 ± 0.04	0.11 ± 0.01	0.12 ± 0.02	0.13 ± 0.03
C20:1	0.61 ± 0.11	0.62 ± 0.23	0.88 ± 0.40	1.11 ± 0.27	0.62 ± 0.06	1.04 ± 0.06	0.93 ± 0.36

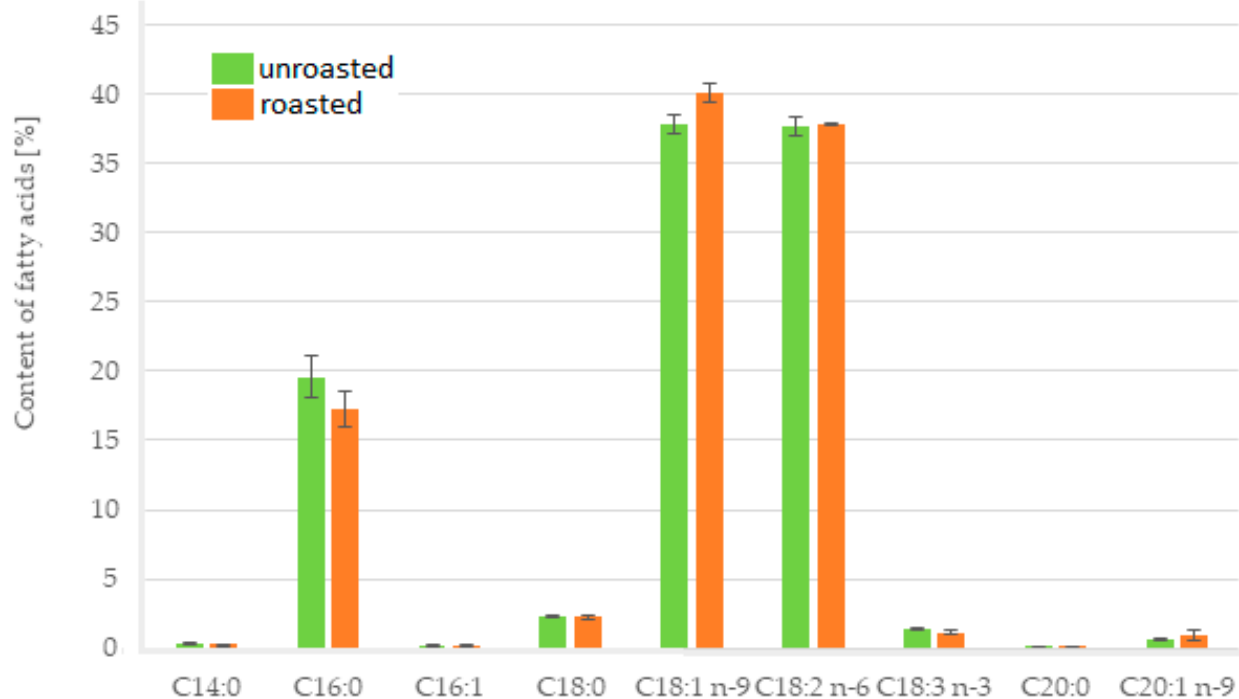


Figure 3. Fatty acid composition of oil from unroasted and roasted at 160 °C for 60 min oat grains.

High levels of oleic acid in oat grains are a distinctive feature of the fatty acid profile that is of interest from a nutritional perspective. Of particular importance is the fact that this profile remains unchanged even after exposure to a 60 min roasting process.

3.3. Titration Methods

The AV is a widely accepted indicator of the quality of oils and fats and represents the progress of triacylglycerol hydrolysis. The PV is a well-recognised indicator for primary oxidation, showing the amount of hydroperoxides present [18].

After heat treatment, oat oil's acid value (Figure 4) increases at the 10 min mark, but roasting for longer durations decreases it. However, it was observed that in all roasted samples, the peroxide value (Figure 5) decreased after roasting. Generally, the longer the

time, the lower the peroxide value. Other studies have also reported a rise in the AV of oil in the walnut-roasting process [13]. The studies [14] discussed the effects of boiling and roasting on different sesame varieties. The results showed that roasted sesame seeds' AV was higher than unroasted sesame seeds. Results from the argon oil study [15] showed that acid value increased with temperature and roasting time.

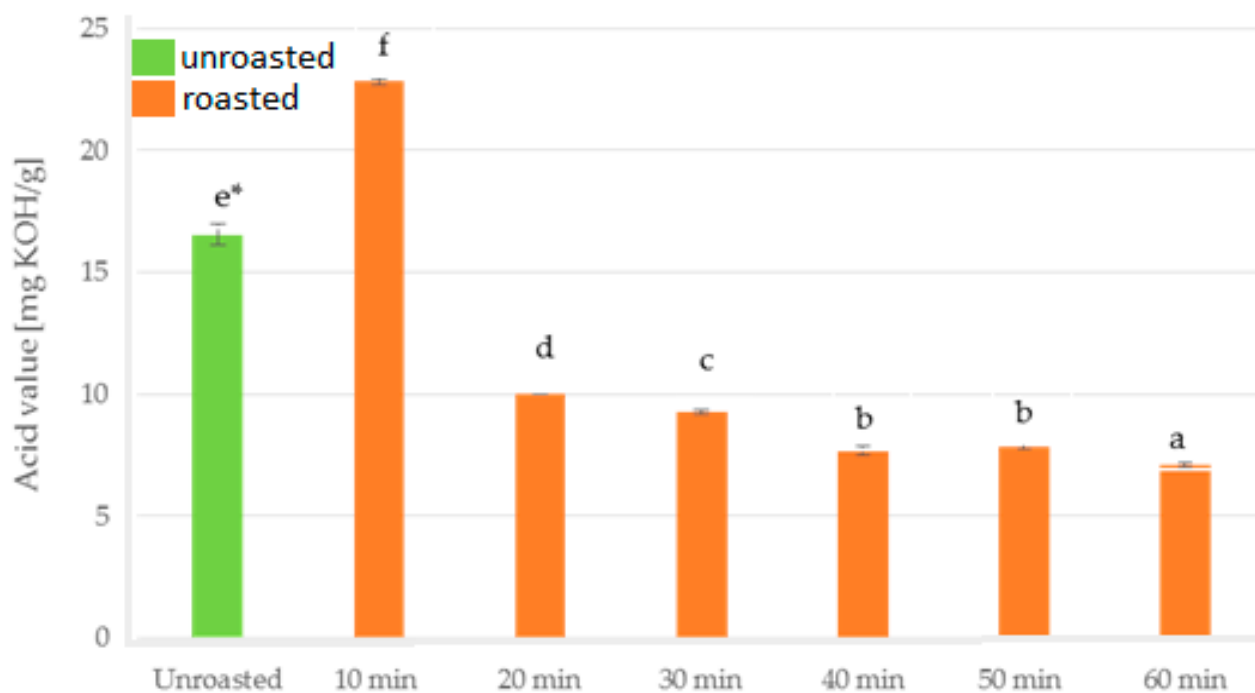


Figure 4. Acid values of samples. * Different letters indicate that the samples differ significantly at $p < 0.05$.

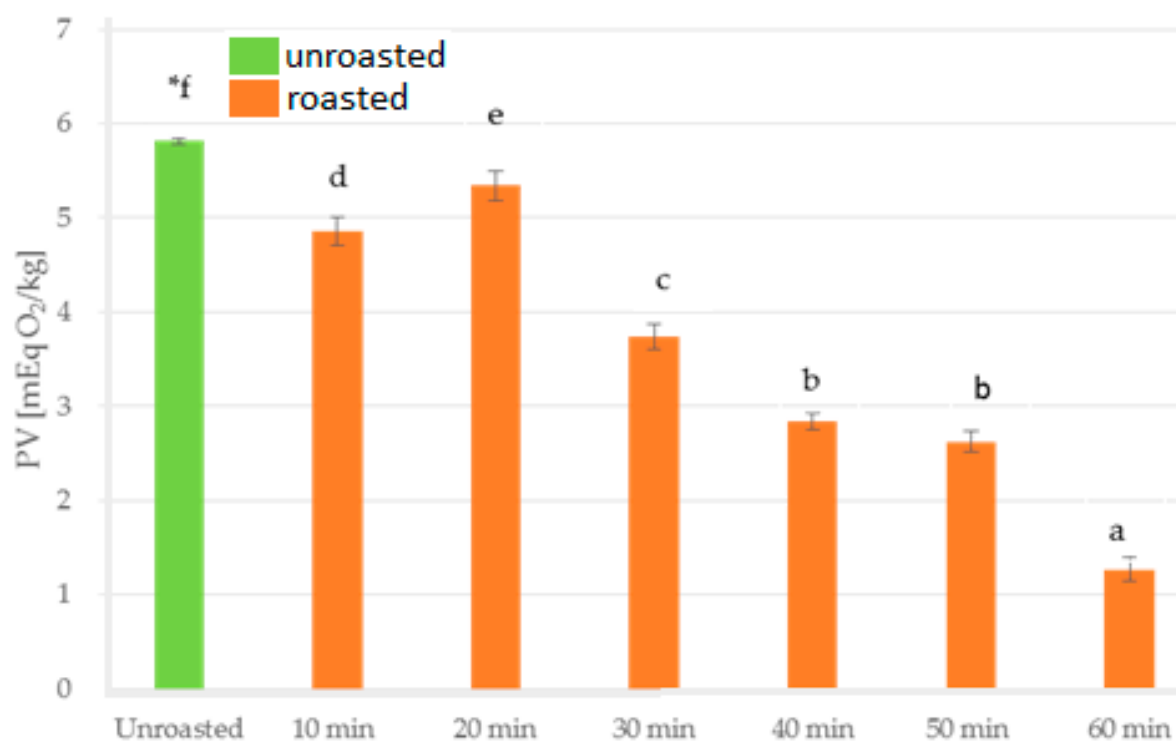


Figure 5. Peroxide value of roasted and unroasted oat oil. * Different letters indicate that the samples are significantly different at $p < 0.05$.

The study [16] discussed the effects of roasting on the chemical composition of safflower seeds. The results showed that the oils from safflower seeds roasted at 180 °C longer had much greater PV than oils from unroasted safflower seeds. Results from the argon oil study [33] showed that the peroxide value increased with temperature and roasting time. This suggests that the content of primary oxidation products may depend, among other things, on the type of oil and the roasting conditions.

3.4. IR Spectral Data

For example, infrared spectra of oils extracted from roasted (60 min, 160 °C) and unroasted oat grains are presented in Figure 6. The visual inspection of spectra and comparison of characteristic spectral regions, e.g., region of C=O double bond presence, did not result in significant differentiation of spectra in terms of wavenumbers and intensities of bands. Water evaporated during roasting was expected to dramatically change the spectrum course at various regions as the water interacts with all or almost all chemicals present in the grain. Although there are slight differences in the specific ranges, it is unclear which spectrum is registered for oil originating from roasted and which for oil from unroasted oat grains. The region of 3000 cm⁻¹ indicates C-H stretching. In further spectra, bands generated by double C=O bonds stretching are visible at around 1700 cm⁻¹. Upon visual inspection, no clear conclusions can be drawn as the spectra are generally very similar. Therefore, a statistical approach was introduced, described in detail in the following sections.

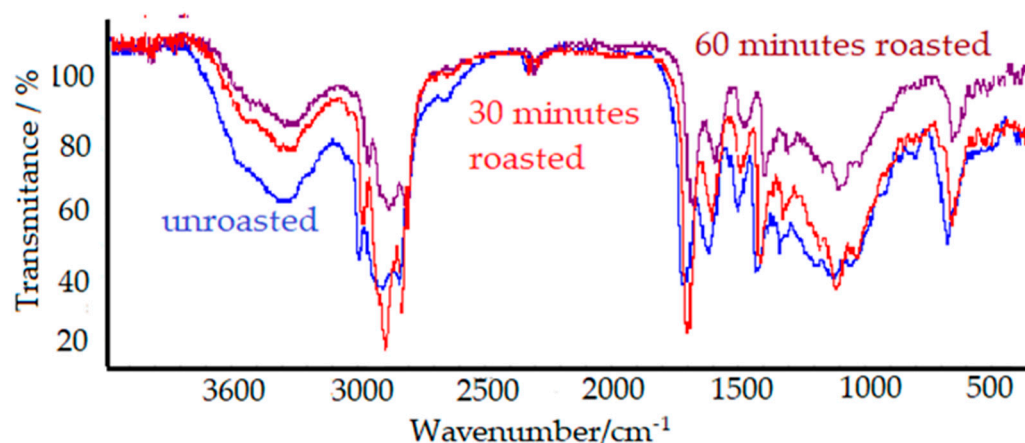


Figure 6. For example, infrared spectra of oils extracted from unroasted and different time-roasted oat grain samples.

3.5. Statistical Modeling

3.5.1. Discriminant Model. MODEL 1

Based on spectral data alone, discriminant analysis (DA) was performed to find differences between oil originating from roasted by 60 min and unroasted oat samples; 80% randomly selected by the TQ Analyst software samples were used for model calibration (squares and triangles in Figure 7), and the remaining 20% were used for calibration validation (crosses in Figure 7). The model constructed, named MODEL 1, classifies samples into adequate homologous groups with 100% effectiveness, which means all samples were assigned to appropriate groups without a single misclassification. The spectral data from the scanned spectral region, which is 4000–400 cm⁻¹, were used to calibrate MODEL 1. Ten principal components were used, and the model describes 99.8% of the overall variability. Results obtained with spectral data alone (no reference data are included in MODEL 1) are graphically presented in Figure 7. Two distinct groups, depicted squares and triangles for roasted and unroasted samples, respectively, are identified and circled to show they form homogenous groups. During the validation process, 20% of raw spectral data assigned to the validation group were considered unknown samples and used for validation. Addi-

tionally, new samples not included in the calibration or validation set (unknown samples) were controlled with the constructed model. All were correctly assigned to appropriate groups (see, the square number in Figure 7 is greater than the number of triangles). Five additional samples of oil extracted from 60 min roasted oat grains are presented in Figure 7. MODEL 1 demonstrates that IR spectral data alone can determine whether the oil is derived from roasted or unroasted oat grains. Figure 7 provides a clear visual representation of the effectiveness and versatility of MODEL 1. Mahalanobis distances were calculated, analysed, and compared. Notably, the Mahalanobis distances within the roasted samples indicate significant differences among them, greater than adequate distances in unroasted samples. This is due to variations in the final chemical composition of oil in grains after the temperature treatment despite the consistent heating conditions of 60 min at 160 °C for all samples. It finally means that unroasted samples are more similar. At the same time, the roasted samples are less identical to each other. Figure 7 presents two homogenous groups of samples. One group contains samples of oil extracted from unroasted grains (triangles), while another contains oil extracted from roasted oat grains (squares).

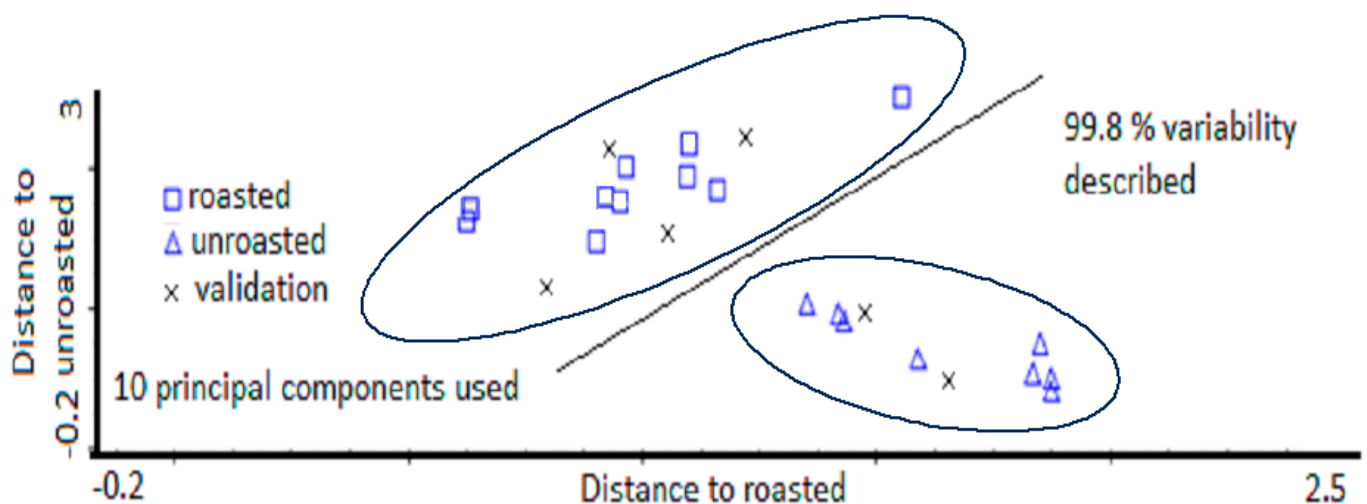


Figure 7. MODEL 1 application. Oil samples were extracted from unroasted oats (triangles) versus the oil samples extracted from oat grains that were roasted for 60 min at 160 °C (squares).

3.5.2. Reference Models

MODEL 2: Time of Roasting and Spectral Data

The discriminant model to assign samples to seven distinct homologous groups, i.e., 0, 10, 20, 30, 40, 50, and 60 min, was tried to be constructed, although unsuccessfully. Too many samples were assigned incorrectly. On the other hand, another model (MODEL 2) that correlates the roasting time with spectral data were successfully constructed. It is presented in Figure 8. MODEL 2 is a reference model in which time is the reference data. Both RMSEC and RMSEP are calculated to be 4.59 and 12.70, respectively. Resultant correlation coefficients are high, that is, 0.9771 and 0.8765 for calibration and prediction, respectively. The number of factors used to construct MODEL 2 was eight. Two spectral regions were used: 3636–3173 and 1790–1692 cm^{-1} . Actual versus calculated values are presented on the y (calculated) and x (actual) axis, respectively.

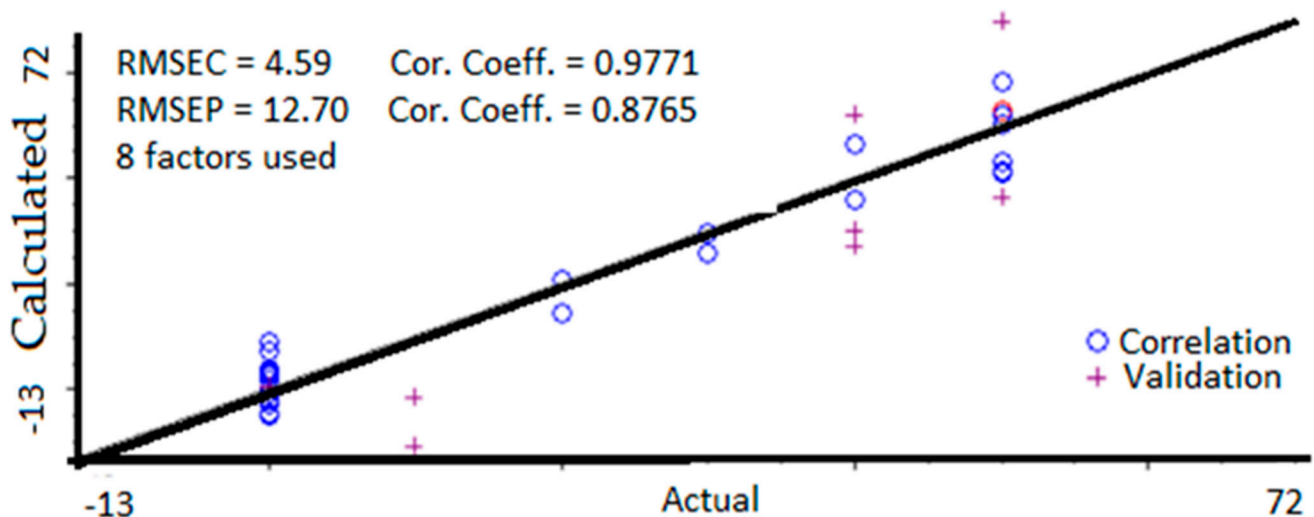


Figure 8. Time of roasting versus spectral data.

MODEL 3: Induction Time and Spectral Data

The following model was designed to calibrate spectral data and oxidative induction time (OIT). MODEL 3 showed statistically significant values, with RMSEC and RMSEP values of 0.649 and 1.51, respectively. The correlation coefficient for calibration was 0.9635, while for prediction, it was 0.9022. MODEL 3 was constructed using seven factors. All data, the trend line, and the experimental point used for calibration and validation are presented in Figure 9. Circles stand for the calibration data set, while crosses stand for the validation set of data. Values calculated by the model are located on the y -axis, while actual, which means determined experimentally with the scientifically approved PDSC method, are on the x -axis.

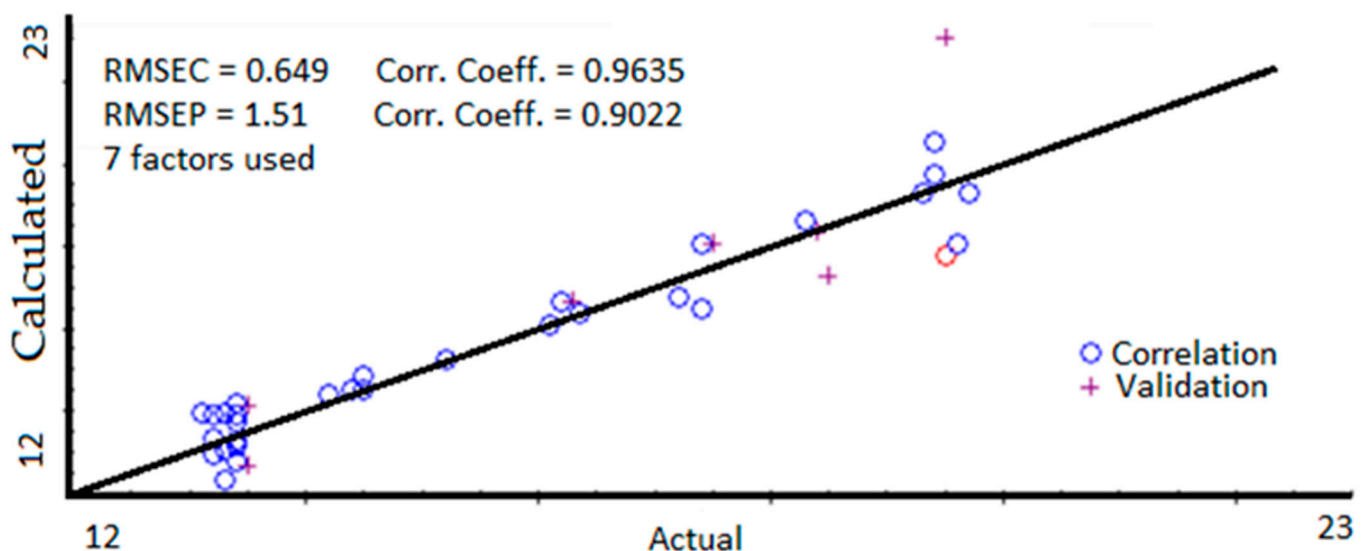


Figure 9. Calculated (model predicted) versus actual (determined with PDSC OIT) values.

Spectral data for MODEL 3 were in almost the entire spectral region, $3699\text{--}435\text{ cm}^{-1}$. Applying more narrow regions alone and in combination resulted in constructing models with worse statistical parameters, i.e., correlation coefficients and RMSEC and RMSEP.

MODEL 4: Acid Value and Spectral Data

Acid values determined experimentally are presented in Figure 4. Although determined with an automatic titrator, it took significant time to complete. With IR spectroscopy,

it takes up to 3 min to register the spectrum and enter it into the model. It does not require any chemical reactant except cleaning liquids and water used for cleaning after measurement. The time required to register the spectral data necessary for MODEL 4 construction (model presented in Figure 10) was about 10 min. Registering the spectrum of one unknown sample to be evaluated needs less than 1 min. With the model already constructed, it takes less than 0.5 min to introduce spectral data of unknown samples into the model and obtain the acid value. The regions of spectral data used for calibration and validation of MODEL 4 were 3636–3145 cm^{-1} and 1790–1692 cm^{-1} , respectively, with RMSEC = 1.69 and RMSEP = 2.64. The correlation coefficient for calibration is 0.9440, while for prediction, it is 0.9191. These values confirm the statistical strength of the model. If data from higher energy regions, i.e., 3636–3145 cm^{-1} , were rejected from the calibration and validation process, and data from only lower regions, i.e., 1789–1692 cm^{-1} , were used, then correlation coefficients were significantly lower, i.e., 0.8694 and 0.8897 for calibration and validation, respectively. Also, values of errors were higher, i.e., RMSEC = 2.51 and RMSEP = 2.71. It confirms that most chemical changes that decide on AV refer to bonds in these regions, where O-H and C=O bonds are present. Considering the maximum actual value of AV = 23 determined with automatic titration, the maximum percentage error of the prediction set is $(2.64/23.5) \times 100\% = 11.2\%$.

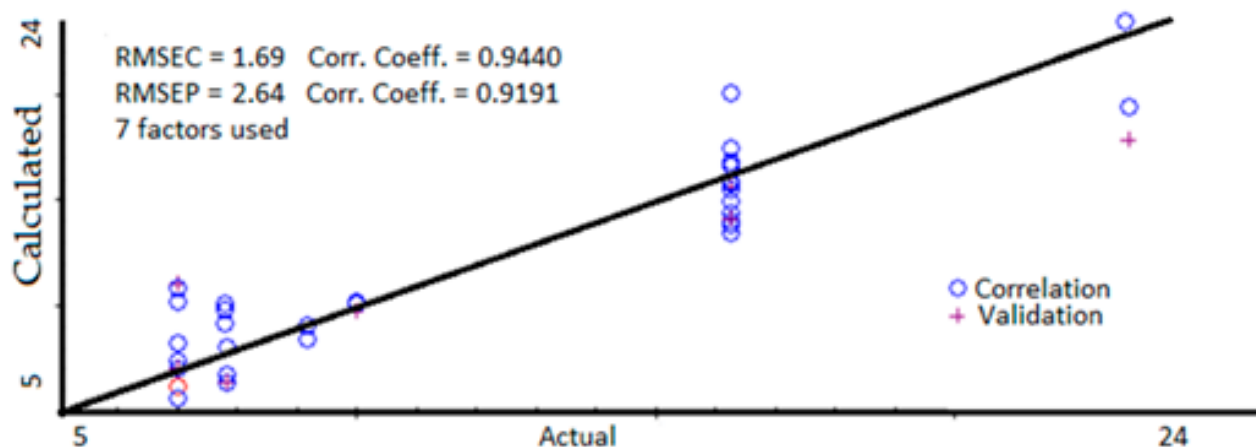


Figure 10. Calculated (model predicted) versus actual values of AV determined experimentally.

MODEL 5 Peroxide Value and Spectral Data

The model constructed for the relation of spectral data and peroxide value has good statistical characteristics; i.e., correlation coefficients are 0.9672 and 0.8186 for calibration and prediction, respectively. Adequate RMSEC and REMSEP are 0.338 and 0.998, respectively. These characteristics indicate a statistically significant correlation between spectral data and the PV. This relationship is a cause–effect correlation. Heating of oats results in chemical changes related to compounds having a C=O group in their structure. This is proven by the range of spectral regions used for model calibration. To calibrate MODEL 5 spectral data from one only, quite a narrow region, that is, 1852–1685 cm^{-1} , was used. Characteristics of the model are presented in Figure 11. The construction of the model with additional use of spectral data from other spectral regions, e.g., high region from MODEL 4 (3636–3145 cm^{-1}), resulted in models with much lower correlation coefficients and significantly higher errors for both calibration and validation of models (for calibration: correlation coefficient = 0.7527, RMSEC = 1.01 and for validation correlation coefficient = 0.0724, RMSEC = 1.64). The region that works for the calibrating and validating process (1852–1685 cm^{-1}) is characteristic of stretching vibrations of the C=O group occurring in many different compounds. This suggests that only changes in the bonds present in the region 1852–1685 cm^{-1} affect the PV.

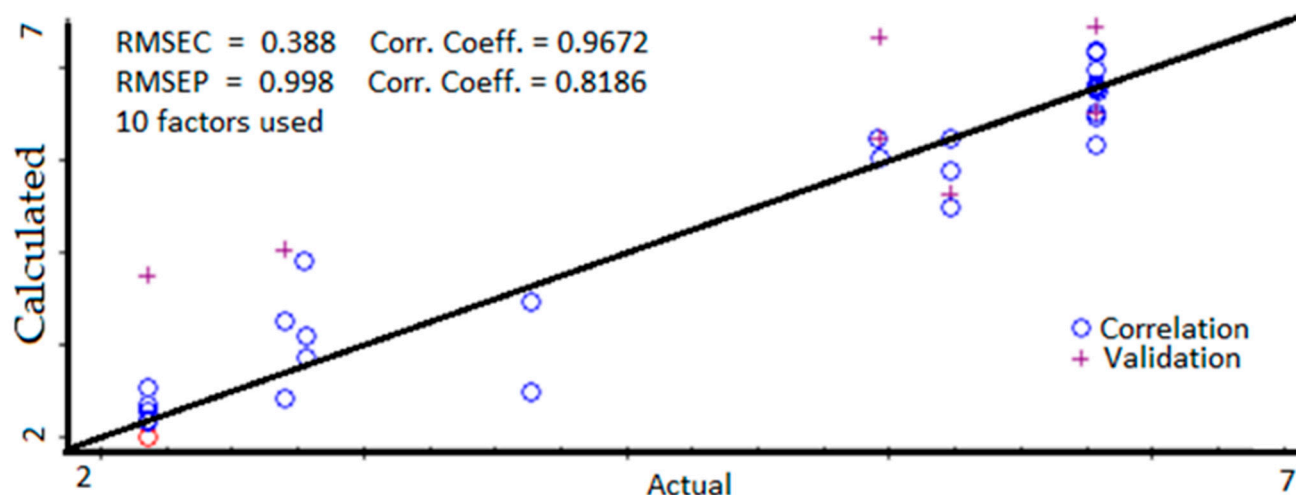


Figure 11. Calculated (model predicted) versus actual values of PV determined experimentally.

4. Conclusions

The conclusions drawn in the current investigation are based on a thorough research process involving determining oxidative induction time using a PDSC, acid values by titration, calorific value using a calorimetric bomb, and fatty acid compositions using gas chromatography. The oxidative stability of the oil increased after the roasting of oat grains. Oil from roasted oat grains is characterised by lower acid and peroxide values than oil from grains that have not been thermally treated. The longer the roasting time, the less acidic and peroxide value there is, thus providing better hydrolytic and oxidative quality of the oil. Roasting does not cause significant changes in the composition of fatty acids. Many factors can influence oxidative stability. The more unsaturated acids the oil contains, the faster it will oxidise. However, in addition to the composition of fatty acids, the content of free fatty acids and the content of substances with pro- and antioxidant activity may influence the oxidative stability and the content of primary oxidation products. During roasting, such substances may decompose or be formed. Therefore, the change in stability does not always correlate with the change in the composition of fatty acids.

Determination of every recorded value in the current investigation is laborious and requires the use of chemicals, except the spectral method. The chemical changes reported above were described using statistical models, and characteristic parameters are summarised in Table 2.

Table 2. Fatty acid composition is present in unroasted and roasted oat oil.

Name	Type	Spectral Regions Used for Construction	Correlation Coefficient		RMSE	
			Calibration	Prediction	Calibration	Prediction
MODEL 1	Discriminant	4000–400 cm^{-1}				
MODEL 2		3636–3173 cm^{-1}				
MODEL 3		and 1790–1692 cm^{-1}	0.9771	0.8765	4.590	12.70
MODEL 4		3699–435 cm^{-1}	0.9635	0.9022	0.649	1.510
MODEL 5		3636–3145 cm^{-1}	0.9440	0.9191	1.690	2.640
		and 1790–1692 cm^{-1}	0.9672	0.8186	0.388	0.998
		1852–1685 cm^{-1}				

The potential scientific applications of FT-IR spectroscopy for the rapid and comprehensive characterization of oils extracted from roasted oats are listed below. To determine every listed characteristic, it is necessary to construct a statistical model, which might be time-consuming. However, determination of a given characteristic is relatively straightforward.

ward once the model has been constructed. It has been concluded that IR spectroscopy can be applied for the following:

1. Discrimination of oil extracted from roasted and fresh oat grains;
2. Determination of acid value;
3. Determination of peroxide value;
4. Time of thermal processing;
5. Oxidation induction time.

Results obtained within the current investigation show that barely one method, FT-IR spectroscopy, can be used for versatile qualitative and quantitative evaluation of oat oil if statistical models are previously constructed, calibrated, and validated.

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Abbreviations

FTIR—Fourier-transform infrared spectroscopy, IR—Infra Red, PDSC—pressure differential scanning calorimeter, GC—gas chromatography, AV—acid value, PV—peroxide value, PCA—principal component analysis, MCR—multivariate curve resolution, SIMCA—the soft independent modelling of class analogy, SVM—support vector machine, PLS—partial least squares, WA, USA—Washington, United States of America, ISO—international organization for standardisation, RMSEC—root mean square error of calibration, REMSEP—root mean square error of prediction, OIT—oxidation induction time, OS—oxidation stability, PUFA—polyunsaturated fatty acid, MUFA—monounsaturated fatty acid, SFA—saturated fatty acid. KRS—“Kristalle aus dem Schmelz-fluss” means (crystals from the melt)-such plate made from thallium bromo-iodide.

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