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Non-destructive fluorescence spectroscopy for quality evaluation of almond oils extracted from roasted kernel

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ABSTRACT

Almond oils extracted from roasted kernels at different roasting times at 150 °C were analyzed to quantify quality parameters such as acidity, peroxide value, K_{232}, K_{270}, antioxidant activity and the oxidative stability index. The roasting process induced oxidation of the chemical compounds in the oil, resulting in increased acidity, peroxide value, K_{232} and K_{270}. The antioxidant activity exhibited a decreasing trend over time, while the oxidative stability showed only slight changes. Excitation-emission matrices (EEMs) were directly scanned on almond oil samples. The combination of the EEMs with parallel factor analysis (PARAFAC) provided qualitative information about the main fluorophores and their evolution with the roasting time. Quantitative information was obtained using unfolded partial least squares (U-PLS), demonstrating the effectiveness of the fluorescence technique in combination with multivariate analysis to quantify analytical parameters in almond oils. Prediction models were developed, and subjected to external validation. The coefficients of determination in the external validation were higher than 0.94 for all parameters except k270.

1. Introduction

Almonds are the most extensively cultivated and consumed nut globally, with an annual production exceeding 4 million tonnes. The United States is the leading producer, followed by Spain. The production of almonds is increasing significantly due to their versatile applications in both food consumption, and in the pharmaceutical and cosmetic industries. Recently, there has been a growing interest in the extraction and consumption of almond oil, due to its numerous health benefits. Almonds are a rich source of essential nutrients including proteins, carbohydrates, fibre, minerals, vitamins, and triacylglycerols. Additionally, it is a rich source of other minor components such as tocopherols, sterols, and phenolic compounds, which endow them with antioxidant properties [1]. Almond oil consumption has been associated with a reduction in cardiovascular risks, as well as potential benefits in other diseases such as hypertension and diabetes [2]. Furthermore, edible oils such as almond oil, provide unique organoleptic properties to the food industry, influencing the aroma and flavor profiles of various food products. As a result, the production of almond oil has recently been the subject of research to improve the quality of this product [3].

Various methods are employed for almond oil extraction, with solvent extraction being the most widely used on an industrial scale. However, the use of solvents adversely affects the physical-chemical properties of the oil [4]. An alternative to traditional methods is supercritical fluid extraction [5], but the use of CO_2 tends to yield similar results to those obtained through traditional methods concerning almond oil properties. Pressure extraction is used to improve sensory attributes. Compared to solvent extraction, pressure extraction allows to obtain oils of higher quality, suitable for direct consumption after extraction. Moreover, this method proves to be more cost-effective and environmentally friendly than the previous one. Compared to supercritical fluid extraction, pressure extraction demonstrates better yields and lower costs [6].

There are two different forms for pressure extraction: hydraulic press and screw press. Between the two, the screw press has several advantages over the hydraulic press, including higher oil yield, cost effectiveness, and time efficiency [7]. Despite the advantages of the screw press, it is not advisable to use this method in conjunction with sample

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roasting, as the screw press has similar properties to the roasting process [8].

Oxidation of oils is one of the biggest problems in the industry. Almond oil, like other edible oils, is susceptible to oxidation due to various factors such as the presence of oxygen, exposure to light, high storage temperatures, among others. In addition, different storage conditions and types of packaging exacerbate the oxidation process [9]. However, the primary cause of rancidity and loss of oil quality is due to lipid oxidation, a process influenced by high temperatures and oxygen concentration [10]. These factors lead to increased levels of free fatty acids and other degradation compounds that cause the product to deteriorate, making it unfit for human consumption. [11]. Therefore, it would be advantageous to have tools to monitor the oxidation state of the final product. In this context, fluorescence spectroscopy has been proposed as a viable method for analysing and monitoring the oxidation of almond oil. Fluorescence spectroscopy offers numerous advantages over other determination techniques, such as its high sensitivity, selectivity, the absence of reagents and solvents, and low sample preparation requirements, among others.

Previous work using fluorescence spectroscopy has shown its potential as a promising tool for the analysis and monitoring of olive oil quality [12]. Cao et al. studied some edible oils during accelerated oxidation in an oven using fluorescence spectroscopy, showing that fluorescence spectroscopy is a rapid, non-destructive, and environmentally friendly method for monitoring the oxidation of oils [13]. Mishra et al. successfully monitored oxidation-induced changes in different commercial extra virgin olive oils (EVOOs) using a fluorescence spectroscopy-based prototype, suggesting this method as a rapid and cost-effective tool for the determination of oxidation in EVOOs [14]. Moreover, the discrimination between two olive oil varieties and two different irrigation treatments [15] or the monitoring of the oxidation of the olive oils packed in different containers [16] have been proposed using excitation-emission matrices combined with chemometrics. However, as far as we know this technique has not been applied for the monitoring of almond oil.

Therefore, the aim of this study is, on the one hand, to evaluate whether fluorescence spectroscopy combined with chemometric analysis provides sufficient information to monitor the evolution of almond oil with roasting time. On the other hand, it seeks to determine whether this technique could be a rapid and non-destructive alternative for evaluating the quality and physico-chemical parameters of almond oil.

2. Material and methods

2.1. Raw materials and oil extraction

'Comuna' variety almonds, obtained from local producers, were divided into 7 batches. These batches were subjected to different roasting times (15, 30, 45, 60, 90 and 120 minutes) in an oven at 150 °C (oven model 210, J.P. Selecta®, Barcelona, Spain). Roasting treatments were carried out in triplicate. One of the batches was used as the non-roasted control.

The oil extraction procedure was carried out as follows. The almonds were ground, and the resulting almond paste was pressed at room temperature using a hydraulic press (Mecamaq, model DEVF 80, Vila-Sana, Lleida, Spain) at a pressure of 200 bar for 10 minutes. The solid residues were then separated by centrifugation, and the extracted oil was stored in dark glass bottles at 4 °C.

2.2. Chemical reagents

Chemical reagents including acetic acid, chloroform, cyclohexane, diethyl ether, DPPH solution, distilled water, ethanol, Folin-Ciocalteau reagent, gallic acid, methanol, phenolphthalein, potassium hydroxide, potassium iodide, starch solution (1%), sodium carbonate, sodium thiosulfate, and 6-hydroxy-2,5,7,8-tetramethyl-chroman-2-carboxylic acid (Trolox), were supplied by Fisher Scientific (Fisher Scientific, Waltham, Massachusetts, MO, USA) and Panreac (Barcelona, Spain).

2.3. Physicochemical parameters

The acidity of almond oil was determined by the titration of a 10 g oil solution in 50 mL of diethyl ether/ethanol (1:1) using 0.1 M potassium hydroxide as titrant. The potassium hydroxide was previously contrasted using phenolphthalein as indicator, following the guidelines outlied in CEE (1991). The acidity is expressed as percentage of oleic acid since this is the predominant compound.

The peroxide value was determined following the method described by Roncero et al. [3]. Briefly, 2 g of almond oil, 10 mL of chloroform, 15 mL of acetic acid and 1 mL of saturated KI solution were mixed and allowed to react. After darkening, 75 mL of distilled water and a few drops of 1% starch solution were added. The solution obtained was titrated with 0.1 M sodium thiosulfate. The peroxide value is expressed as milliequivalents of active oxygen per kilogram of oil ($meqO_2\ Kg^{-1}$ oil).

The determination of absorption coefficients, K_{232} and K_{270}, was carried out by preparing a 0.2 % and a 2% (m/v) almond oil solution in cyclohexane. Absorbance at 232 nm and 270 nm was measured using an Agilent Cary 60UV–Vis Spectophotometer (G6860A).

2.4. Total phenol, antioxidant activity and oxidative stability index

2.4.1. Total polyphenol contents (TPC)

Sample preparation was carried out following the method described by [17]. The determination of TPC in the almond oils was performed according to the Folin-Ciocalteau colorimetric method [18], using gallic acid as standard. The results of TPC in the almond oil samples are expressed as gallic acid equivalents (mg gallic acid/g oil).

2.4.2. Antioxidant activity

The antioxidant activity of the almond oil was determined as described in a previous work [9]. In summary, a 300 μL sample of almond oil extracted and dissolved in 1.5 mL of methanol/water (1:1, v/v) was added to 2.7 mL of DPPH solution. After stirring, the solution was left in darkness for 1 hour, and the absorbance was measured at 517 nm. The results were expressed as Trolox equivalent values (mg Trolox•100 mL).

2.4.3. Oxidative stability

The oxidative stability of the almond oils was measured using a 743 Rancimat (Metrohm, Herisau, Switzerland), an eight-channel oxidative stability instrument. A 2.5 g sample was introduced in the 743 Rancimant, and the system was heated to 120 °C with a 10 L/h air flow [17]. The results were expressed as induction period per hour.

2.5. Fluorescence measurements

In order to obtain the fluorescence excitation-emission matrices (EEMs) an Agilent Cary Eclipse Fluorescence Spectrophotometer equipped with two Czerny-Turner monochromators, a xenon light source and a photomultiplier tube as detector was used. For data collection Cary Eclipse software 1.2 was used. A 1.0 cm quartz cell was used, and a slit width of 5 nm was set in both the excitation and emission monochromators.

The EMMs were recorded in normal mode, over a range of excitation wavelengths between 260 and 600 nm, at 5 nm intervals. Emission spectra were registered in the range of 300 to 750 nm, at 2 nm intervals, for each excitation wavelength. The photomultiplier tube sensitivity was set at 700 V. All results were exported in ASCII format for further chemometric analysis.

2.6. Multivariate analysis

EEM data were exported to ASCII code and processed using Matlab software (Matlab R2016b). The Rayleigh dispersion correction was made employing the EEM_corr routine [19], freely downloaded from https://fbcb.web1.unl.edu.ar/laboratorios/ladaq/download/. The graphical interface MVC2 (http://www.iquirconicet.gov.ar/descargas/mvc2.rar) was used for PARAFAC [20] and U-PLS [21] calculations. PARAFAC was used to perform an exploratory analysis of the EEMs, while U-PLS was used to build quantitative models to predict quality parameters from the fluorescence data.

The performance of the U-PLS model was estimated using the following statistic parameters: the coefficient of determination for the cross-validation (R^2_{CV}), and prediction (R^2_P) (Eq. (1)); the root mean square error for cross-validation (RMSECV), and prediction (RMSEP) (Eq. (2)); and the relative error of prediction (REP (%)) (Eq. (3)).

$$R_2 = 1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - y_{media})^2} \quad (1)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{N}} \quad (2)$$

$$REP\ (\%) = \frac{RMSE}{y_{mean}} x\ 100 \quad (3)$$

where y_i represents the experimental measurement for the sample i, $\hat{y}i$ represents the corresponding value obtained for cross validation (RMSECV) and prediction (RMSEP), y_{mean} represents the mean value of the experimental measurements, and N is the number of samples.

3. Results and discussion

3.1. Influence of roasted kernels on the physico-chemical parameters of almond oils

Table 1 summarizes the physico-chemical parameters. An overall increase in the acidity is observed as the roasting time increases, although not following a strictly linear progression. The natural (unroasted) almond oil exhibits the lowest oleic acid percentage (0.64 %). From the natural sample to the one subjected to 60 minutes of roasting, the increase in acidity shows a linear trend. This is expected, since the elevated temperatures reached during roasting lead to the oxidation of various oil compounds to oleic acid. However, for roasting times of 90 and 120 minutes, the rise in the percentage of oleic acid is less pronounced. This can be attributed to the extended exposure to high temperatures, resulting in fewer remaining compounds yet to be fully oxidized. Despite the acidity increase during roasting, all samples are within the recommended limit by Codex Alimentarius, which stipulates that acidity in unrefined oils should be less than 5 % (ranging from 0.64 % to 1.34 % in this study).

With respect to the peroxide value, a noticeable increase is observed as the roasting time increases, with the last sample (120 min roasted, 4.25 meqO_2/Kg) even doubling the value of the natural sample (unroasted, 2.25 meqO_2/Kg). The increase in this parameter follows a linear trend from the natural sample to the one roasted for 60 minutes. Subsequently, there is a gradual increase in the peroxide value up to the sample roasted for 120 minutes. This is in agreement with other studies [2] where an increase in temperature was associated with an elevation in the peroxide value. Similarly, prolonged exposure to high temperatures may contribute to the growth of this parameter over time.

In order to investigate the degradation of almond oil samples over time, absorption coefficients K_{232} and K_{270} were determined. K_{232} evaluates the primary oxidation of oil compounds. Data show a linear behavior for all the samples, with K_{232} values ranging between 1.02 and 1.94. These values fall within the established limit ($\leq$ 2.60) reference. On the other hand, K_{270} is related to the secondary oxidation of the oil. K_{270} value shows a linear increase from the natural sample to the one roasted for 60 minutes. However, for the subsequent samples at 90 and 120 minutes of roasting, the increase in K_{270} is less pronounced. K_{270} values range between 0.03 and 0.22 for the natural sample and the sample roasted for 120 minutes, respectively.

3.2. Influence of roasted kernels on the antioxidant parameters of almond oils

The antioxidant parameters of the almond oils subjected to different roasting times are also shown in Table 1. The total polyphenol content (TPC) of almond oil, expressed as gallic acid equivalent in mg/g oil, ranges from 80.3 to 195.3 mg/g oil. The unroasted sample exhibits the lowest TPC and the highest is observed in the almond oil roasted for 120 minutes. However, the TPC reaches almost its maximum at 60 minutes of roasting time (193.7 mg/g oil), indicating a plateau in TPC beyond this roasting time. It has been documented that heat treatments can influence the release of bound phenolic acids, leading to an increase in the content of free phenolic compounds in foods [22], which can be transferred to the oil during extraction process [6].

In this study, a negative correlation between antioxidant activity and roasting time is observed. Similar behavior was observed by Alnsour et al. [23] between the antioxidant content and the degree of roasting in coffee, where no clear correlation was established between these parameters. Although this behavior contradicts the expectation that the antioxidant capacity of phenolic compounds should enhance antioxidant activity, these results are in agreement with previous studies [24]

Table 1
Physico-chemical and antioxidant parameters of almond oils subjected to different roasting times. Results are expressed as mean and standard deviations. Different letters in the same column indicate significant statistical differences (Tukey's test, $p < 0.05$) among roasting times.

Roasting times (min)	Acidity (% oleic acid)	Peroxide index (meq O_2 · Kg oil $^{-1}$)	K_{270}	k_{232}	Total polyphenol (mg galic acid · g oil^{-1})	Antioxidant activity (mg Trolox · g oil^{-1})	Oxidative stability (hours)
0	0.64±0.00a	2.25±0.08a	0.03 ±0.01a	1.02 ±0.01a	80.3±1.5a	1.54±0.10 g	23.5±0.6a
15	0.89±0.02b	2.54±0.09b	0.08 ±0.01b	1.24 ±0.01b	84.8±1.3b	1.27±0.08f	22.8±0.3a
30	0.95±0.01c	2.94±0.04c	0.10 ±0.01b	1.30 ±0.01c	103.6±2.0c	1.16±0.07e	26.7±0.4b
45	1.07±0.00c	3.29±0.03d	0.13 ±0.01c	1.37 ±0.01d	172.1±3.5d	0.90±0.05d	32.1±0.4c
60	1.17±0.06d	3.92±0.03e	0.19 ±0.02d	1.44 ±0.01e	193.7±2.5e	0.69±0.06c	34.9±0.7d
90	1.24±0.02e	4.08±0.05e	0.21 ±0.01d	1.48 ±0.01f	193.7±1.5e	0.53±0.05b	36.2±0.3d
120	1.34±0.01f	4.25±0.22f	0.22 ±0.01d	1.94 ±0.02 g	195.3±6.7e	0.27±0.04a	37.8±0.9d

that found a reduction in the antioxidant activity of almond nuts after roasting. Also, it was found that the decrease in antioxidants could be attributed to the high temperatures applied over time [25]. Moreover, it was suggested that gallic acid, despite being the predominant phenolic compound in almonds, may not be the primary contributor to antioxidant activity. This is supported by a previous work, where a significant reduction in every phenolic compound in almond after roasting, except for gallic acid is observed [26].

The oxidative stability values obtained in this study range from 23.5 to 37.8 h, for the unroasted and 120 min roasted samples, respectively. These results are higher than oxidative stability values found in other studies [27,28]. However, these discrepancies may be due to the different conditions affecting the oxidative stability of oils, such as storage, temperature, oxygen availability, light exposure and glyceridic composition [22,29]. Similar to other edible oils, the increase in oxidative stability with roasting time may be attributed to antioxidant compounds being easily extracted when certain bonds are broken under high temperature. Interestingly, this phenomenon appears unrelated to the TPC as suggested by Moayedi et al. [30].

3.3. Fluorescence monitoring

3.3.1. Application of PARAFAC on EEMs from almond oils obtained after different roasting times

To examine the fluorophores profile in almond oils obtained from kernels with different roasting times at 150 °C, EEMs of all samples were recorded. The Rayleigh scattering was removed by using the EEM_corr routine [31] because it interferes slightly in the area of interest. Additionally, the interpolation option was applied to minimize alterations in the matrix. A width of 10 nm was removed in both, the first (Ry1) and second (Ry2) level Rayleigh scattering correction.

In Fig. 1, the excitation-emission contour plots (with the Rayleigh scattering removed) are shown for almond oil obtained at different roasting times. For oils obtained from natural kernels and those roasted

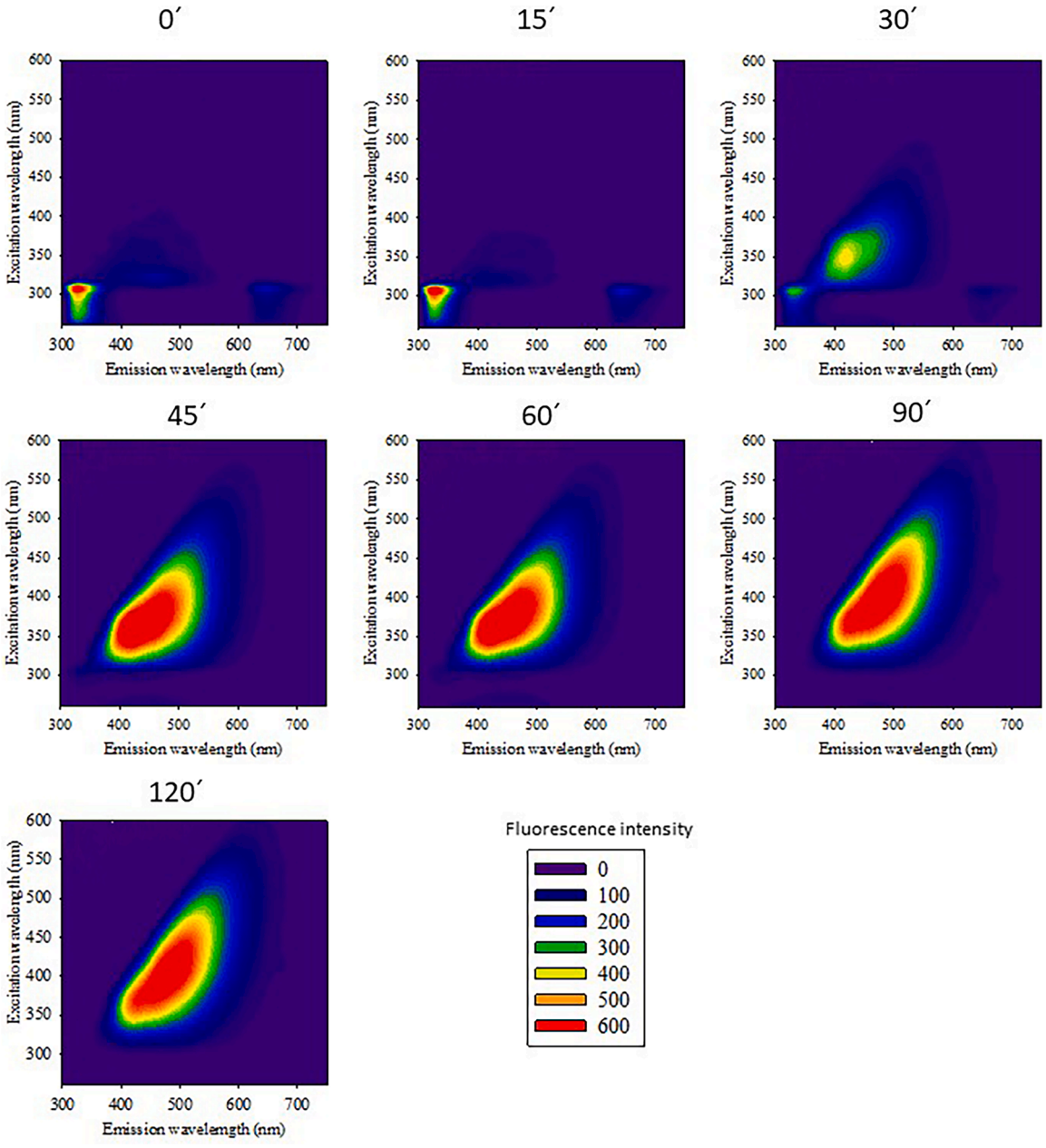

Fig. 1. Excitation-emission contour plots of almond oils obtained from almonds with different roasting time at 150 °C: 0, 15, 30, 45, 60, 90 and 120 min.

for 15 min, no changes are observed in the highest fluorescence region with λ_{exc} between 270–310 nm and λ_{em} between 310–340 nm. As the roasting time increases, the fluorescence in this region decreases, and a new fluorescence region appears between 400 and 500 nm due to the increase of the oxidation processes. The intensity and the fluorescence wavelength interval of this new region increases proportionally with roasting time.

PARAFAC analysis was applied to the three-dimensional array to extract the fluorophore profile in almond oil. Models with two to six components were generated applying non-negative constraints in all modes. The optimal number of factors was selected by using the core consistency test (CORCONDIA) [32] and the residual analysis [31]. When all samples were analysed, the model exhibited the optimal statistical values with five components. This number of components is in accordance with the five spectral regions described by Mani-Varnosfaderani et al. [33].

Fig. 2 displays the emission and excitation loading profiles for the five components obtained from the decomposition of the EEM. The first four components presents fluorescence bands between 400–600 nm, regions typically associated with primary and secondary oxidation products in other vegetable oils. The fifth component, in contrast, shows a fluorescence band between 300–400 nm.

The first component shows the maximum fluorescence intensity at excitation/emission wavelengths of 385/460 nm. The second and third components present maximum excitation/emission wavelengths at 430/500 nm and at 350/420 nm, respectively. In accordance with studies on other edible oils, these spectral regions are linked to primary and secondary oxidation products. This correlation is further supported by the evolution of the scores of these components, as depicted in Fig. 3.

The score values of the third component increase up to 45 minutes of roasting and then decrease for higher times. This pattern aligns with the accepted notion that primary oxidation compounds degrade into secondary oxidation compounds, explaining the decrease in score values with increased roasting time. Therefore, this component is tentatively assigned to primary oxidation products formed during moderate roasting times. On the other hand, initially the score values for the first and second components are very low and begin to increase after 30 min of roasting. This is in accordance with the fact that at room temperature or after soft roasting, the formation of secondary oxidation products takes place in a limited proportion since they originate primary oxidation products. Consequently, these components can be tentatively assigned to secondary oxidation products.

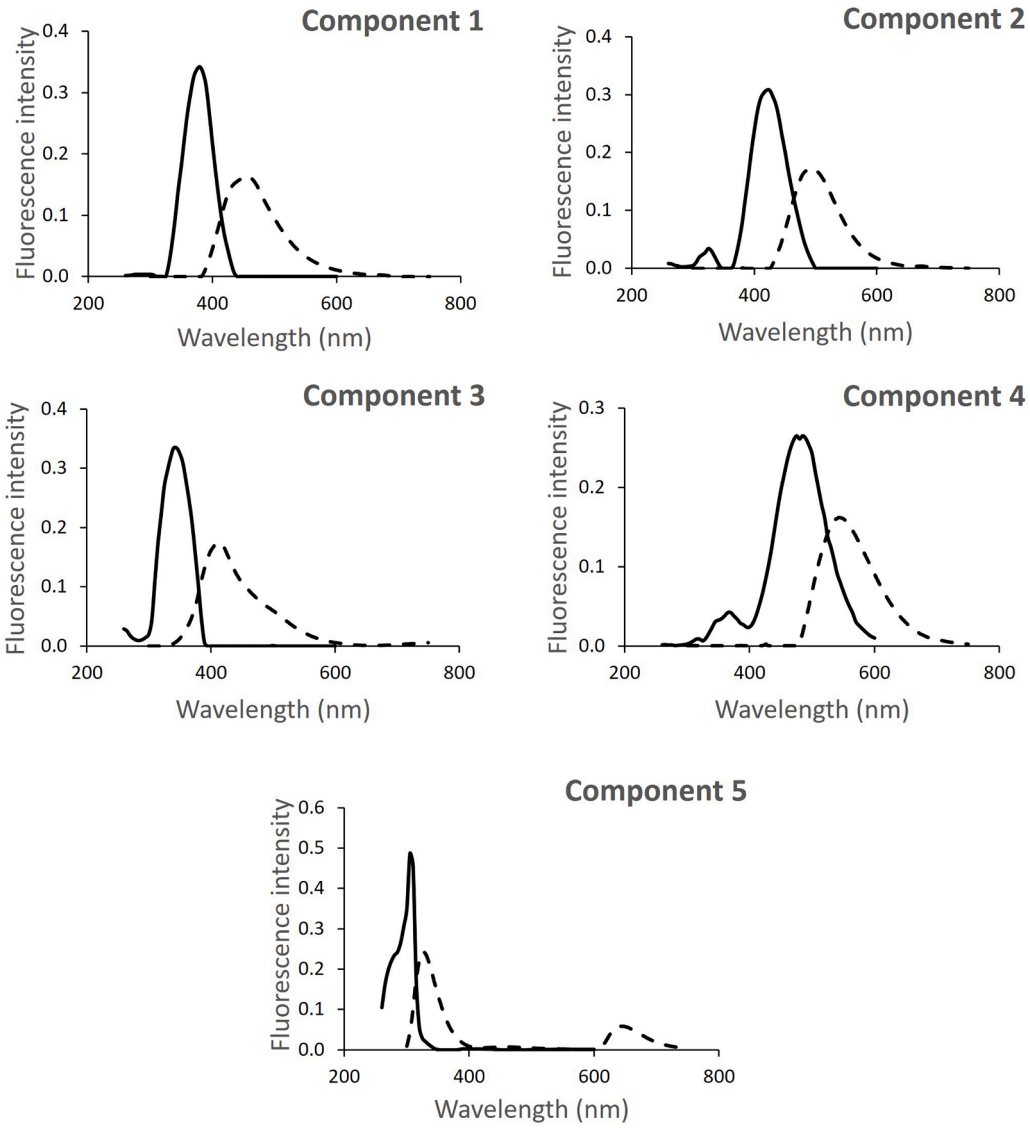

Fig. 2. Excitation and emission loading profiles obtained from the five components PARAFAC model. *Full line: excitation PARAFAC loading. Dotted line: emission PARAFAC loading.*

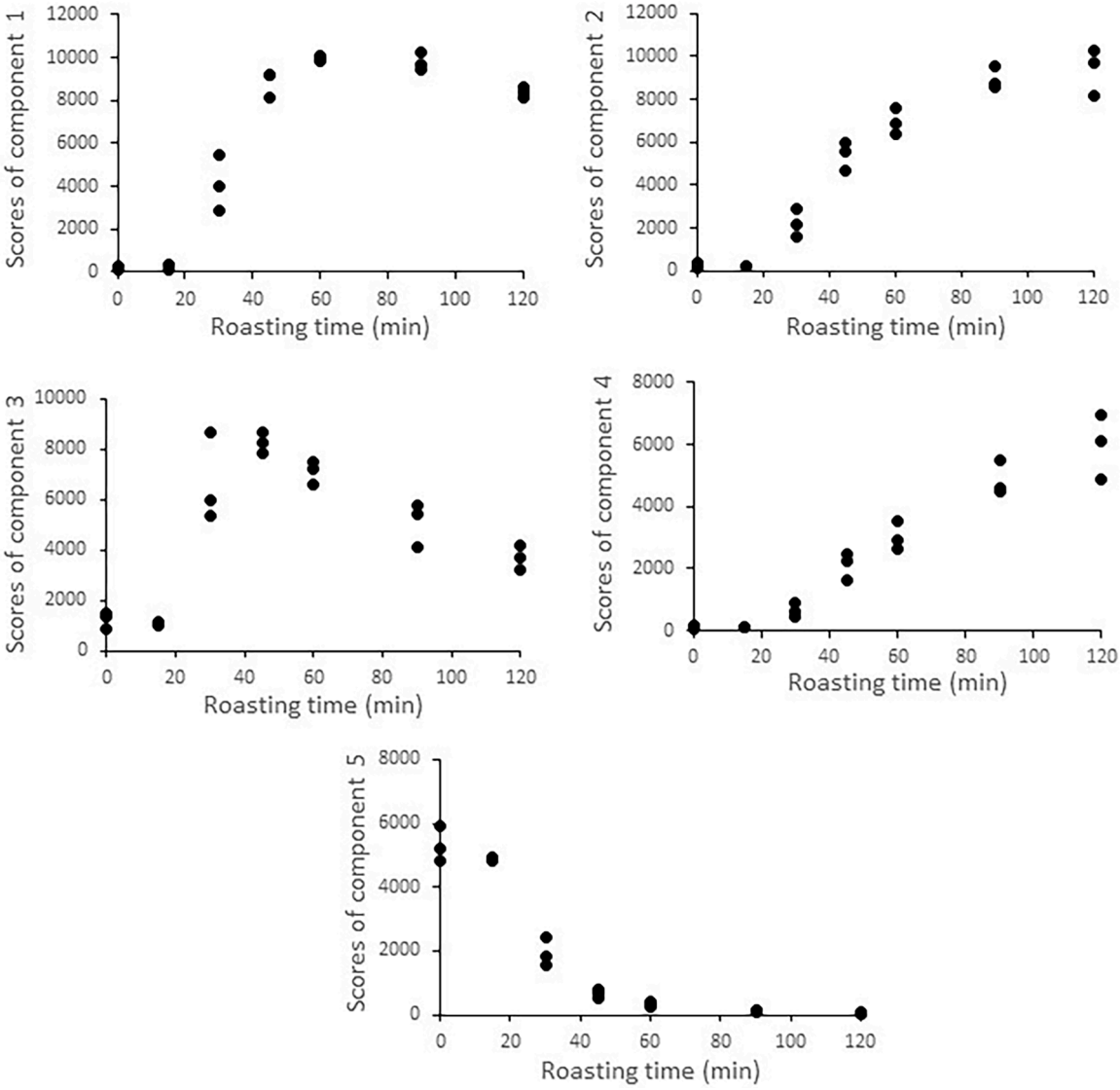

Fig. 3. Evolution of the PARAFAC scores with the roasting time.

The fourth component presents the maximum excitation and emission wavelengths at 475/550 nm. The appearance of a broad emission band between 500–580 nm in almond oils has been previously reported [33]. The fluorescence signals in the 450/550 nm region have a complex origin; with potential contributors including vitamins E, A, K, and D, and NADH, NADPH, and Flavin [34]. However, in this sample, the evolution of the score values for this component with the roasting time (increasing as the roasting time increases) is incompatible with the presence of vitamins. Typically the fluorescence of vitamins decreases over time. Therefore, the observed trend suggests that other factors may be influencing the fluorescence signals in this region.

Finally, the fifth component, with an emission maximum at 335 nm and excitation maximum at 300 nm is assigned to tocopherols, in accordance with a previous work [33]. The higher initial score values for this component can be attributed to the high concentration of α-tocopherol in almonds, given that almonds are recognized as a rich source of α-tocopherol [35]. The impact of roasting on various nuts has been studied extensively [36,37], consistently showing a decrease in tocopherol concentration. This is in accordance with the observed trend in the score values of this component, which decrease with increasing roasting time.

Likewise, as can be seen in the figure, the score values remain relatively constant for roasting times of less than 30 minutes in all components.

3.3.2. *Determination of almond oil quality parameters by using the EEMs-UPLS*

We also studied the correlation between the quality parameters and the fluorescence of the almond oils using the U-PLS regression. This algorithm was selected since it is a pure calibration method while PARAFAC provides valuable qualitative information about the system.

Samples were divided into two sets to perform the quantification models. The 70% of the total number of samples was used as training set. This set was used to perform the calibration and the cross validation. The optimal number of factors, selected by leave-one-out cross-validation was optimized for each of the analyzed parameters, following the Haaland and Thomas criterion [38]. The optimal number of components was 6 for acidity, peroxide value, oxidative stability, TPC and k270, while the antioxidant activity required 5 components. Table 2 shows the statistical parameters obtained in the cross validation. In all cases, the coefficients of determination between predicted and nominal values, R^2, are higher than 0.99, except for K270 and K232, which presented R^2 values of 0.87 and 0.96, respectively. The RMSECV values ranged from 0.02 for acidity and k270 to 3.78 for TPC. The detection limits for all parameters were suitable for the study values.

On the other hand, the validation sets were constructed with the

Table 2
Figures of merit for the PLS models for the quantification of quality parameters in almond oils.

		Acidity (% oleic acid)	Peroxide index (meq O_2 · Kg oil $^{-1}$)	k270	k232	Total polyphenol (mg galic acid · g oil^{-1})	Antioxidant activity (mg Trolox · g oil^{-1})	Oxidative stability (hours)
	Components	6	6	6	6	6	5	6
Cross validation	R^2	0.99	0.99	0.87	0.96	0.99	0.99	0.99
	Slope	0.99	0.98	0.89	0.94	0.99	0.99	1.00
	Intercept	0.01	0.06	0.01	0.08	1.00	0.01	0.15
	RMSECV	0.02	0.08	0.02	0.06	3.78	0.05	0.34
	REP (%)	1.87	2.41	17.11	3.99	2.60	5.26	1.11
Validation	R^2	0.97	0.96	0.76	0.94	0.96	0.96	0.96
	Slope	0.89	0.75	0.70	0.90	0.82	0.89	0.81
	Intercept	0.01	0.73	0.06	0.12	21.48	0.11	5.47
	RMSEP	0.11	0.02	0.03	0.19	14.37	0.01	0.02
	REP (%)	10.11	0.67	19.79	13.72	9.87	0.68	0.67
	LOD	0.06	0.24	0.00022	0.17	11.16	0.0025	0.99
	LOQ	0.17	0.73	0.00066	0.50	33.47	0.0073	2.98

R^2: coefficient of determination; RMSECV: root mean squares error of the cross validation; RMSEP: root mean squares error of prediction; REP: relative error of prediction; LOD: limit of detection; LOQ: limit of quantification

remaining 30% of the samples and favourable predictions were achieved for most of the quality parameters (Table 2). The relative errors of prediction (%REP) were less than 10% in most cases and the R^2 values were very satisfactory, exceeding 0.96, except for peroxide k232 and K270 . The less favourable results for these two parameters can be attributed to the exclusion of the photometric signals measured at 232 and 270 nm in the selected range of excitation wavelengths.

4. Conclusions

The increase of the roasting duration of almonds before oil extraction induces substantial alterations in the oxidative chemical parameters of the resulting oil. PARAFAC was used to monitor these oils obtaining qualitative information of the evolution of fluorescence regions in almond oils and identifying five key fluorescent components. The score values of each of the five components correlate with primary and secondary oxidation products, as well as with the concentration of tocopherols. The score values of the first four components increased with roasting time, whereas the score values of the fifth component decreased with roasting time, coinciding with a reduction in its antioxidant capacity. Quantitative information was obtained using U-PLS and the results suggest that the model provides accurate predictions for most quality parameters.

This approach allows a rapid assessment of almond oil evolution with roasting time. The data obtained confirm that a roasting time of the almonds at 150 °C for less than 30 min does not adversely impact the quality parameters of the almond oil. This findings support the recommendation of employing a non-destructive technique, such as the fluorescence spectroscopy in combination with multivariate analysis, as complementary tool in routine analysis, offering the advantage of avoiding the use of solvents.

CRediT authorship contribution statement

Elísabet Martín-Tornero: Writing – original draft, Methodology, Investigation, Formal analysis. **David Simón-García:** Writing – original draft, Investigation, Formal analysis. **Manuel Álvarez-Ortí:** Writing – review & editing, Conceptualization. **José Emilio Pardo:** Writing – review & editing, Conceptualization. **Isabel Durán-Merás:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Daniel Martín-Vertedor:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.talo.2024.100334.

References

[1] M. Ouzir, S. El Bernoussi, M. Tabyaoui, K. Taghzouti, Almond oil: a comprehensive review of chemical composition, extraction methods, preservation conditions, potential health benefits, and safety, Compr. Rev. Food Sci. Food Saf. 20 (2021) 3344–3387, https://doi.org/10.1111/1541-4337.12752.
[2] D. Barreca, S.M. Nabavi, A. Sureda, M. Rasekhian, R. Raciti, A.S. Silva, G. Annunziata, A. Arnone, G.C. Tenore, İ. Süntar, G. Mandalari, Almonds (Prunus dulcis Mill. D. A. webb): a source of nutrients and health-promoting compounds, Nutrients 12 (2020), https://doi.org/10.3390/nu12030672.
[3] J.M. Roncero, M. Álvarez-Ortí, A. Pardo-Giménez, A. Rabadán, J.E. Pardo, Influence of pressure extraction systems on the performance, quality and composition of virgin almond oil and defatted flours, Foods 10 (2021), https://doi.org/10.3390/foods10051049.
[4] M.M. Ozcan, F. Al Juhaimi, K. Ghafoor, E.E. Babiker, Characterization of physico-chemical and bioactive properties of oils of some important almond cultivars by cold press and soxhlet extraction, J. Food Sci. 57 (2020) 955–961, https://doi.org/10.1007/s13197-019-04128-3.
[5] F. Chemat, M.A. Vian, H.K. Ravi, B. Khadhraoui, S. Hilali, S. Perino, A.S.F. Tixier, Review of alternative solvents for green extraction of food and natural products: Panorama, principles, applications and prospects, Molecules 24 (2019), https://doi.org/10.3390/molecules24163007.
[6] A. Rabadán, M. Álvarez-Ortí, R. Gómez, A. Alvarruiz, J.E. Pardo, Optimization of pistachio oil extraction regarding processing parameters of screw and hydraulic presses, LWT 83 (2017) 79–85, https://doi.org/10.1016/j.lwt.2017.05.006.
[7] M.L. Martínez, M.G. Bordón, R.M. Bodoira, M.C. Penci, P.D. Ribotta, Walnut and almond oil screw-press extraction at industrial scale : effects of process parameters on oil yield and quality, Grasas y Aceites 68 (2017) e216, https://doi.org/10.3989/gya.
[8] E. Sena-Moreno, J.E. Pardo, L. Catalán, R. Gómez, A. Pardo-giménez, M. Alvarez-ortí, Drying temperature and extraction method in fluence physicochemical and sensory characteristics of pistachio oils, Eur. J. Lipid Sci. Technol. 117 (2015) 684–691, https://doi.org/10.1002/ejlt.201400366.

[9] E. Martín-Tornero, R. Sánchez, J. Lozano, M. Martínez, P. Arroyo, D. Martín-Vertedor, Characterization of polyphenol and volatile fractions of californian-style black olives and innovative application of e-nose for acrylamide determination, Foods 10 (2021) 2973, https://doi.org/10.3390/foods10122973.
[10] S.F. Mexis, A.V. Badeka, M.G. Kontominas, Quality evaluation of raw ground almond kernels (Prunus dulcis): effect of active and modified atmosphere packaging, container oxygen barrier and storage conditions, Innov. Food Sci. Emerg. Technolog. 10 (2009) 580–589, https://doi.org/10.1016/j.ifset.2009.05.002.
[11] R. Morales, María T., Przybylski, olive oil oxidation, in: R. Aparicio, J. Harwood (Eds.), Handbook of Olive Oil, Second, 2000: pp. 479–522. https://doi.org/10.1007/978-1-4757-5371-4.
[12] E. Guzmán, V. Baeten, J.A.F. Pierna, J.A. García-Mesa, Evaluation of the overall quality of olive oil using fluorescence spectroscopy, Food Chem. 173 (2015) 927–934, https://doi.org/10.1016/j.foodchem.2014.10.041.
[13] J. Cao, C. Li, R. Liu, X.R. Liu, Y. Fan, Z.Y. Deng, Combined application of fluorescence spectroscopy and chemometrics analysis in oxidative deterioration of edible oils, Food Anal. Method. 10 (2017) 649–658, https://doi.org/10.1007/s12161-016-0587-2.
[14] P. Mishra, L. Lleó, T. Cuadrado, M. Ruiz-Altisent, N. Hernández-Sánchez, Monitoring oxidation changes in commercial extra virgin olive oils with fluorescence spectroscopy-based prototype, Eur. Food Res. Technol. 244 (2018) 565–575, https://doi.org/10.1007/s00217-017-2984-1.
[15] E. Martín-Tornero, A. Fernández, J.M. Pérez-Rodriguez, I. Durán-Merás, M. H. Prieto, D. Martín-Vertedor, Non-destructive fluorescence spectroscopy as a tool for discriminating between olive oils according to agronomic practices and for assessing quality parameters, Food Anal. Method. 15 (2022) 253–265, https://doi.org/10.1007/s12161-021-02112-2.
[16] E. Martín-Tornero, A. Fernández, I. Durán-Merás, D. Martín-Vertedor, Fluorescence monitoring oxidation of extra virgin olive oil packed in different containers, Molecules (2022) 27, https://doi.org/10.3390/molecules27217254.
[17] M.N. Franco, T. Galeano-Díaz, J. Sánchez, C. De Miguel, D. Martín-Vertedor, Antioxidant capacity of the phenolic fraction and its effect on the oxidative stability of olive oil varieties grown in the southwest of Spain, Grasas y Aceites 65 (2014) 1–10, https://doi.org/10.3989/gya.051513.
[18] S. Savini, M.R. Loizzo, R. Tundis, M. Mozzon, R. Foligni, E. Longo, K. Morozova, M. Scampicchio, D. Martin-Vertedor, E. Boselli, Fresh refrigerated Tuber melanosporum truffle: effect of the storage conditions on the antioxidant profile, antioxidant activity and volatile profile, Eur. Food Res. Technol. 243 (2017) 2255–2263, https://doi.org/10.1007/s00217-017-2927-x.
[19] FA Chiappini, MR Alcaraz, HC Goicoechea, A.C. Olivieri, A graphical user interface as a new tool for scattering correction in fluorescence data, Chemometri. Intell. Lab. Syst. 193 (2019) 103810, https://doi.org/10.1016/j.chemolab.2019.07.009.
[20] R. Bro, PARAFAC. Tutorial and applications, Chemometr. Intell. Lab. Syst. 38 (1997) 149–171, https://doi.org/10.1016/S0169-7439(97)00032-4.
[21] S. Wold, P. Geladi, K. Esbensen, J. Öhman, Multi-way principal components and pls-analysis, J. Chemom. 1 (1987) 41–56, https://doi.org/10.1002/cem.1180010107.
[22] E. Choe, D.B. Min, Mechanisms and factors for edible oil oxidation, Compreh. Food Sci. Rev. Food Saf. 5 (2006) 169–186, https://doi.org/10.1111/j.1541-4337.2006.00009.x.
[23] L. Alnsour, R. Issa, S. Awwad, D. Albals, I. Al-Momani, Quantification of total phenols and antioxidants in coffee samples of different origins and evaluation of the effect of degree of roasting on their levels, Molecules 27 (2022) 1591, https://doi.org/10.3390/molecules27051591.
[24] J.C.M. Barreira, I.C.F.R. Ferreira, M.B.P.P. Oliveira, J.A. Pereira, Antioxidant activity and bioactive compounds of ten Portuguese regional and commercial almond cultivars, Food Chem. Toxicol. 46 (2008) 2230–2235, https://doi.org/10.1016/j.fct.2008.02.024.
[25] M.L.L. Campidelli, J.D.S. Carneiro, E.C. Souza, M.L. Magalhães, E.E.C. Nunes, P. B. Faria, M. Franco, E.V.B.V. Boas, Effects of the drying process on the fatty acid content, phenolic profile, tocopherols and antioxidant activity of baru almonds (Dipteryx alata Vog, Grasas y Aceites 71 (2020) 1–11, https://doi.org/10.3989/gya.1170182.
[26] M.R.B. Lemos, E.M. de A. Siqueira, S.F. Arruda, R.C. Zambiazi, The effect of roasting on the phenolic compounds and antioxidant potential of baru nuts [Dipteryx alata Vog.], Food Res. Int. 48 (2012) 592–597, https://doi.org/10.1016/j.foodres.2012.05.027.
[27] J.M. Roncero, M. Älvarez-Ortí, A. Pardo-giménez, A. Rabadán, J.E. Pardo, Influence of pressure extraction systems on the performance, quality and composition of virgin almond oil and defatted flours, Foods 10 (2021) 1049.
[28] R. Melhaoui, S. Kodad, N. Houmy, K. Belhaj, F. Mansouri, M. Abid, M. Addi, A. Mihamou, M. Sindic, H. Serghini-Caid, A. Elamrani, Characterization of sweet almond oil content of Four European Cultivars (Ferragnes, Ferraduel, Fournat, and Marcona) recently introduced in Morocco, Scientifica (Cairo) 2021 (2021), https://doi.org/10.1155/2021/9141695.
[29] R. Mateos, M. Trujillo, M. Carmen Pérez-Camino, W. Moreda, A. Cert, Relationships between oxidative stability, triacylglycerol composition, and antioxidant content in olive oil matrices, J. Agric. Food Chem. 53 (2005) 5766–5771, https://doi.org/10.1021/jf0504263.
[30] A. Moayedi, K. Rezaei, S. Moini, B. Keshavarz, Chemical compositions of oils from several wild almond species, JAOCS, J. Am. Oil Chem. Soc. 88 (2011) 503–508, https://doi.org/10.1007/s11746-010-1701-z.
[31] F.A. Chiappini, M.R. Alcaraz, H.C. Goicoechea, A.C. Olivieri, A graphical user interface as a new tool for scattering correction in fluorescence data, Chemometr. Intell. Lab. Syst. 193 (2019) 103810, https://doi.org/10.1016/j.chemolab.2019.07.009.
[32] R. Bro, H.A.L. Kiers, A new efficient method for determining the number of components in PARAFAC models, J. Chemom. 17 (2003) 274–286, https://doi.org/10.1002/cem.801A.
[33] A. Mani-Varnosfaderani, M.J. Masroor, Y. Yamini, Designating the geographical origin of Iranian almond and red jujube oils using fluorescence spectroscopy and l1-penalized chemometric methods, Microchem. J. 157 (2020) 104984, https://doi.org/10.1016/j.microc.2020.104984.
[34] M. Zandomeneghi, L. Carbonaro, C. Caffarata, Fluorescence of vegetable oils: olive oils, J. Agric. Food Chem. 53 (2005) 759–766, https://doi.org/10.1021/jf048742p.
[35] N.P. Kalogiouri, P.D. Mitsikaris, D. Klaoudatos, A.N. Papadopoulos, V. F. Samanidou, A rapid hplc-uv protocol coupled to chemometric analysis for the determination of the major phenolic constituents and tocopherol content in almonds and the discrimination of the geographical origin, Molecules 26 (2021) 5433, https://doi.org/10.3390/molecules26185433.
[36] N. Hernández-Sánchez, L. Lleó, F. Ammari, T.R. Cuadrado, J.M. Roger, Fast fluorescence spectroscopy methodology to monitor the evolution of extra virgin olive oils under illumination, Food Bioproc. Tech. 10 (2017) 949–961, https://doi.org/10.1007/s11947-017-1866-7.
[37] M.H. Bruscatto, V.R. Pestana-Bauer, D.M. Otero, R.C. Zambiazi, Effects of heating temperature on the tocopherol contents of chemically and physically refined rice bran oil, Grasas y Aceites 70 (2019) 1–7, https://doi.org/10.3989/gya.0572181.
[38] D.M. Haaland, E.V Thomas, Partial Least-Squares methods for spectral analyses . 1 . Relation to other quantitative calibration methods and the extraction of qualitative information, Anal. Chem. 60 (1988) 1193–1202, https://doi.org/10.1021/ac00162a020.