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Storage time of nut spreads using flash gas chromatography E-nose combined with multivariate data analysis

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A R T I C L E I N F O

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A B S T R A C T

The quality assessment, in terms of lipid oxidative status, of food products stored in the long-term is of great importance, especially those with a high lipid content. Specifically, companies working in this sector need feasible, simple, and fast techniques that are suitable for quality or process control. Herein, a fingerprinting approach, based on headspace analysis carried out by flash gas chromatography electronic nose (FGC E-nose) and multivariate data analysis was applied to pistachio and gianduja spreads. These samples, differently packaged, were stored in climatic chambers at 40 °C for 180 days and their headspace fraction was analyzed periodically for a total of 15 sampling times. Principal component analysis showed a clear separation according to the packaging type for both pistachio and gianduja samples. Partial least squares regression models were developed to predict the storage time considering the aggregated data (R^2 up to 0.985, RMSEP = 6.16 days) or separately (R^2 up to 0.989, RMSEP = 5.71 days). Based on the obtained residual prediction deviation (RPD from 4.4 to 8.5 in prediction), the models can be considered suitable for use in quality control in an industrial environment.

1. Introduction

Nut spreads, having at least 40% nuts as an ingredient (Shakerardekani, Karim, Ghazali, & Ling Chin, 2013), are produced by mixing nuts, sweeteners, vegetable oils, and protein sources (Liedl & Rowe, 2007) until the desired cream texture is obtained (Gamlı & Hayoglu, 2012). The types of nuts used in these formulations can be different (e.g., pistachio, hazelnut, almond, peanut, cashew, macadamia nut, pecan, or walnut) and can be added in various forms, such as whole, pieces, paste, or slurry (USDA, 2006; Nielsen, 2010). Generally, nut spread is made by grinding roasted nuts into a paste that can be used like butter (Shakerardekani et al., 2013).

Because of their high lipid content with a large proportion of polyunsaturated fatty acids, in addition to thermal stress caused by possible use of roasted nuts, these products are particularly prone to lipid oxidation (Mureșan, et al., 2016). This leads to formation of hydroperoxides that further degrade into secondary oxidation products such as ketones, aldehydes, and other molecules (Frankel, 1980). The release in the head-space of these secondary oxidation compounds is associated with changes in the odor of the product, resulting in rancidity (Shakerardekani, Karim, Ghazali, & Ling Chin, 2015).

Deteriorative reactions may occur during storage, mainly in terms of lipid oxidation and browning (Maskan & Göğüş, 1997). For example, pistachio nut paste changes its color to brown in the presence of high-water activity as a consequence of Maillard reactions (Maskan & Göğüş, 1997). In addition, it has been reported that the whiteness of a greenish spreadable pistachio paste decreased after 8 months of storage at 20 °C due to degradation of chlorophyll into pheophytin b (grayish green) and browning reactions (Gamlı & Hayoglu, 2012). Furthermore, the effect of different packaging (sealed jar, vacuumed PP, and non-vacuumed PP) and storage conditions on the quality of pistachio nut paste has been evaluated (Gamli & Hayoglu 2007). It has been reported that peroxide values and free fatty acids are weakly affected by the packaging type. However, considering total acidity, moisture content, and browning indices, a sealed glass jar was found to be more suitable than polypropylene pouches. A similar conclusion was also reached by (Torun, 1999) for walnut paste. Measuring the oxidative stability of these products is therefore essential to determine their shelf life,

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consumer acceptability, and nutritional quality (Mureșan et al., 2016).

Analysis of volatile lipid oxidation products is a challenging task due to their physical properties, complexity of the food matrices from which they are released, and trace levels (Jeleń, Gracka, & Myśków, 2017). Different analytical techniques, such as headspace (HS) analysis coupled with a mass spectrometry (MS) detector, especially in nuts (Salcedo & Nazareno, 2015; Rogel-Castillo, Luo, Huang, & Mitchell, 2017), or flame ionization (FID) detector (Vichi, Pizzale, Conte, Buxaderas, & López-Tamames, 2003; Deiana et al., 2019; Khrisanapant, Kebede, Leong, & Oey, 2019; Pan, Ushio, & Ohshima, 2004) have been applied to study these compounds during storage under accelerated conditions (Franklin et al., 2018). However, most of the traditional analytical methods are time consuming and expensive.

Rapid and innovative instrumental approaches have also been developed to satisfy the need for simpler and faster techniques that can also be used for quality assurance within food companies. Flash gas chromatography electronic nose (FGC E-nose) is a highly selective and sensitive gas chromatograph for analysis of the volatile fraction and is capable of performing very fast hydrocarbon measurements at low concentrations in laboratory or field conditions. Its novel features include versatility and higher analysis speed over conventional gas chromatographs (Marion, Herve, & Fatma, 2011).

This technique has recently been used to evaluate the quality and authenticity of olive oil (Melucci et al., 2016; Barbieri et al., 2020; Palagano, Valli, Cevoli, Bendini, Gallina Toschi, 2020) to measure the flavor changes of rapeseed oils used for frying (Xu et al., 2019), in age identification and brand classification of brandy (Yang, Zhao, Zhang, Ni, & Zhan, 2012), and to predict storage time and quality changes of hen eggs (Yimenu et al., 2017). Additionally, it has been used to help identify the causes of rancidity and in monitoring of global sensory quality in nut mixes (Marion et al., 2011). In all these studies, multivariate chemometric methods [principal component analysis (PCA), partial least squares regression (PLS), PLS discriminant analysis, and cluster analysis (CA) have been used to elaborate chromatographic data, adopting targeted and untargeted approaches.

From an industrial point of view (quality control), it is important to implement rapid screening approaches. Since to the authors' knowledge all studies reported in the literature have investigated the oxidative stability of nut spreads by traditional analytical techniques, the aim of this work was to evaluate the storage time of two nut spreads (pistachio and gianduja) using a rapid screening method, i.e. FGC E-nose. Chromatograms were elaborated by applying an untargeted multivariate approach based on PCA (group the sample according to packaging type) and PLS models (predict storage time).

2. Materials and methods

2.1. Samples

Pistachio and gianduja spreads, usually used as ingredients in the pastry and ice cream sector, were supplied by a food company immediately after production. The ingredients of the two spreads are reported in Table 1, and the shelf life of the products given by the manufacturer was 18 months.

Both the spreads were packaged, directly by the company, in PP5 cylindrical containers characterized by two flush edge capacity, L and S, respectively, in the 3 and 0.35 L formats in which they are generally marketed. Furthermore, the product inside the L container was hermetically covered by a plastic film (nylon Bx + PP).

Storage conditions at 40 °C for 180 days were chosen to accelerate storage tests and simulate approximately 18 months at room temperature (25 ± 2 °C), according to Ling, Hou, Li, and Wang (2014) and Dordoni, Cantaboni, and Spigno (2019) that reported Q10 values (oil oxidation) ranging from 2.68 to 3.4. All samples were stored in climatic chambers (Constant Climate Chamber with Peltier technology, model HPP 108/749- Memmert, Germany) and analyzed at 0, 3, 7, 11, 14, 18, 21, 25, 28, 32, 42, 60, 74, 83, 130, and 180 days for a total of 15 sampling times (50 ± 5% of relative humidity). The sampling times were chosen considering that the main chemical and physical modifications of pistachio spread stored at room temperature take place during the first 4–6 months (40–60 days at 40 °C) (Gamlı & Hayoglu, 2012). Within the same product (pistachio and gianduja) and type of packaging (L and S), three samples were analyzed for each storage time (15), for a total of 180 samples.

Table 1
Ingredients of gianduja and pistachio spreads.

Gianduja spread	Pistachio spread
Sunflower oil	Sunflower oil
Sugar	Sugar
Roasted hazelnuts	Maltodextrin
Dextrose	Roasted Pistachio
Low-fat cocoa powder	Dextrose
Skimmed milk powder	Vegetable fibre
Soy lecithin	Cocoa butter
Bourbon vanilla pods	Soy lecithin
Tocopherols	Salt
	Tocopherols
	Brilliant Blue FCF
	Carotenes

2.2. Flash gas chromatography

The analysis of volatile compounds was carried out using the FGC Electronic Nose Heracles II (Alpha MOS, Toulouse, France) based on ultra-fast gas-chromatography technology. The instrument was equipped with two metal capillary columns working in parallel mode and characterized by different polarity and stationary phase: a non-polar column (MXT5: 5% diphenyl, 95% methylpolysiloxane, 10 m length and 180 μm diameter) and a polar column (MXT-1701: 14% cyanopropylphenyl, 86% dimethyl polysiloxane, 10 m length, 180 μm diameter). At the end of each column, a FID detector was placed and the acquired signal was digitalized every 0.01 s.

Each sample was analyzed in triplicate, weighing 2 ± 0.1 g of paste in a 20 mL vial sealed with a magnetic cap. Before removing the sample, the spreads were mixed to avoid ingredient separation. The analytical conditions applied have been described in detail by Palagano et al. (2020).

2.3. Data processing

Considering an untargeted approach similar to those proposed by Barbieri et al. (2020), Palagano, et al. (2020), Xu et al. (2019), Yang et al. (2012) and Yimenu et al. (2017), the full chromatograms were used to estimate the storage time of the products according to packaging type. The raw data of each chromatogram was composed of the intensity values for each point acquired every 0.01 s.

The mean chromatograms calculated on three replicates were aligned with the COW (Correlation Optimized Warping) algorithm (Tomasi et al, 2014), centered (mean-centering), and pretreated using two approaches: (i) Pareto-scaling; (ii) normalization by Standard Normal Variate (SNV).

Pareto-scaling gives equal importance to all variables, but to a lesser extent than standard autoscaling which may cause loss of important information in chromatographic fingerprints, since it significantly increases the weights of minor noisy variables (Aliakbarzadeh, Parastar, & Seresthi, 2016). Furthermore, the data structure remains partially intact (Van den Berg, Hoefsloot, Westerhuis, Smilde, & Van der Werf, 2006). SNV is a pretreatment usually used with spectroscopic data to correct for both baseline shift and global intensity variations. In addition, in this case, the shape of the chromatogram is not altered.

The data were subjected to PCA and PLS regression to discriminate samples as a function of different storage times or packaging type, and to extrapolate the storage times. Considering PLS regressions, for each product type (pistachio or gianduja), three different models were developed, two considering the samples separately according to the packaging type and one considering all samples together. The predictive power of the models was tested by performing venetian blinds cross validation (10 segments) and external test set. The dataset was split into two sub-sets, one to calibrate the model (80% of the entire data-set) and the other (20%) to externally validate it (test-set) using the Kennard-Stone method (selects samples that best span the same range as the original data, but with an even distribution of samples across the same range) (Kennard & Stone, 1969).

Results were analyzed in terms of determination coefficient (R^2), root mean square error (RMSE), and residual prediction deviation (RPD):

$$R^2 = \frac{\sum_{i=1}^{N}(\widehat{y_i} - \overline{y})^2}{\sum_{i=1}^{N}(y_i - \overline{y})^2} \quad (1)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(\widehat{y_i} - \overline{y})^2}{N-k}} \quad (2)$$

$$RPD = \frac{SD}{RMSE} \quad (3)$$

where y_i is the actual storage time (days), $\widehat{y_i}$ is the predicted storage time (days), $\overline{y}$ is the mean of the actual values, N is the number of samples, k is the number of latent variables retained in the model, and SD is the standard deviation of reference values.

To avoid over-fitting the model, the optimal number of latent variables was chosen by plotting the RMSE in cross validation (RMSECV) as a function of the number of components and by identifying where the curve reaches a minimum. The results obtained for the external validation set were used to evaluate the model's robustness in terms of degree of model generalization (Putri & Fukusaki, 2015). All data analyses were carried out using PLS Toolbox for Matlab 2018a®.

3. Results

The chromatograms of gianduja and pistachio spreads are reported in Fig. 1a and b, respectively. The chromatograms of the two spreads are quite different, and most peaks were observed in the initial part of the chromatogram (from 2000 to 14,000). Differences, in terms of variable intensities between the L and S samples, are highlighted with different colors, confirming the discriminating power of the volatile profile related to the packaging. A fingerprinting approach involving chemometric elaboration of the entire profiles (X-variables from 2000 to 14,000) of volatile compounds without identification and quantification was applied to estimate the storage time or packaging type.

PCA (Fig. 2) of whole chromatograms was used as explorative technique to visualize samples according to the storage time and packaging type. From evaluation of the score plot obtained for gianduja samples (Fig. 2a), a clear separation between L and S samples was observed along PC2 (37.18%), while all samples (L and S) were arranged on PC1 (51.41%) according to storage time identified by the numbers placed near the points. The storage time increased from right to left.

To understand how the X variables contribute to each of the PCs, the X-loadings were evaluated. High loading values (positive or negative) indicate that a variable has a strong effect on that principal component. In particular, positive loadings indicate a variable and a principal component a positive correlation: an increase in one results in an increase in the other. Negative loadings indicate a negative correlation. Accordingly, by analysis of the X-loadings (Fig. 3a), it was possible to observe the chromatographic zones characterized by the highest contribution to PC1 and PC2. Specifically, just before 6000 d a peak with strong positive loadings for the PC2 was observed, suggesting that this affects the separation between L (negative score) and S (positive score) shown in the score plot (Fig. 2a). The highest contribution to the PC1 (samples distribution according to storage time) was observed in the same zone of PC2, but with a negative correlation in the zones from 2000 to 4000.

For pistachio samples, the score plot (Fig. 2b), showed a clear separation according to the packaging type (S and L) along the PC1 only (73.32%). The X-loading evaluation (Fig. 3b) suggests that highest contribute is due, as for gianduja, to the peak at just before 6000. To observe the sample distribution as a function of storage time, two PCAs were developed considering S and L samples separately.

Gamlı and Hayoglu (2007) investigated the effect of different packaging types (sealed jar, vacuumed PP, and non-vacuumed PP) on the quality of pistachio nut spread, reporting that at 20 °C the shelf life calculated on the base of peroxide values and free fatty acid is weakly affected by the packaging type. However, considering total acidity, moisture content, and browning indices, a sealed glass jar was found to be more suitable than polypropylene pouches. Similarly, Torun (1999) reported that the moisture content of walnut paste decreased during storage at different temperatures with various packaging materials. Consequently, for the nut spreads investigated herein, PLS models to predict the storage time were developed considering samples L and S both together and separately.

The PLS results, in terms of determination coefficient (R^2) and RMSE, residual prediction deviation (RPD), and latent variable (LV) in

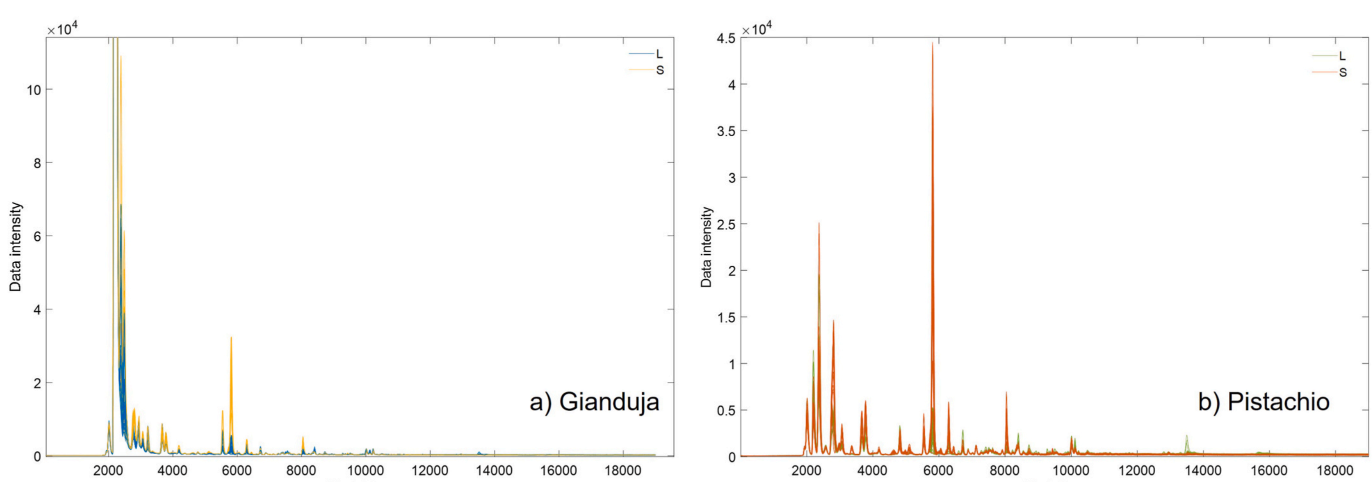

Fig. 1. Chromatograms of gianduja (a) and pistachio (b) spreads. L: large package, S: small package.

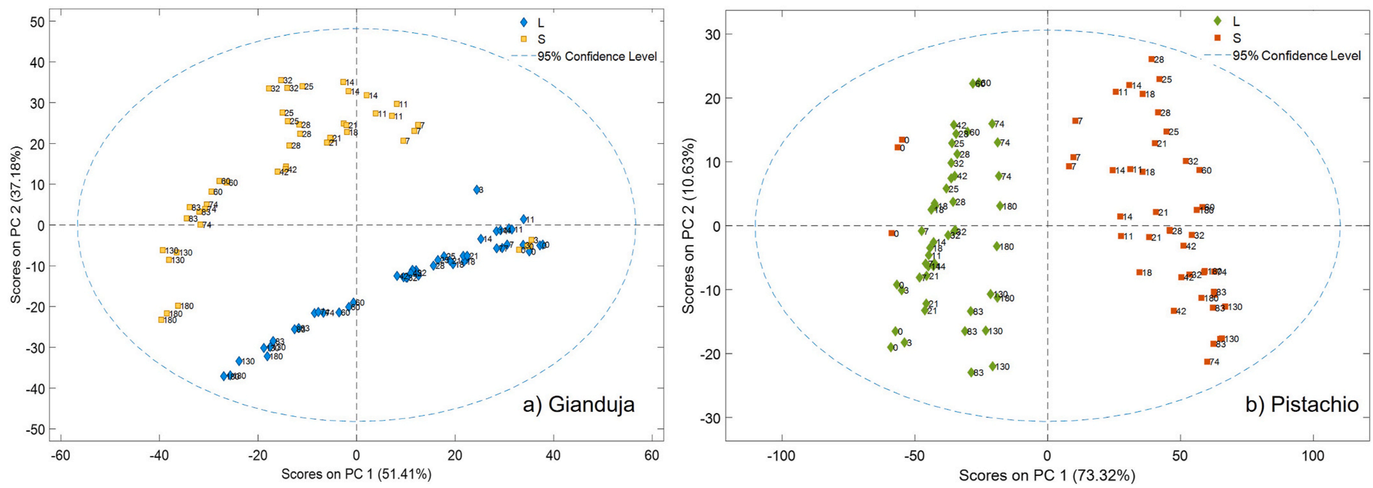

Fig. 2. Score plot obtained by the PCA for the gianduja (a) and pistachio (b) samples. L: large package, S: small package.

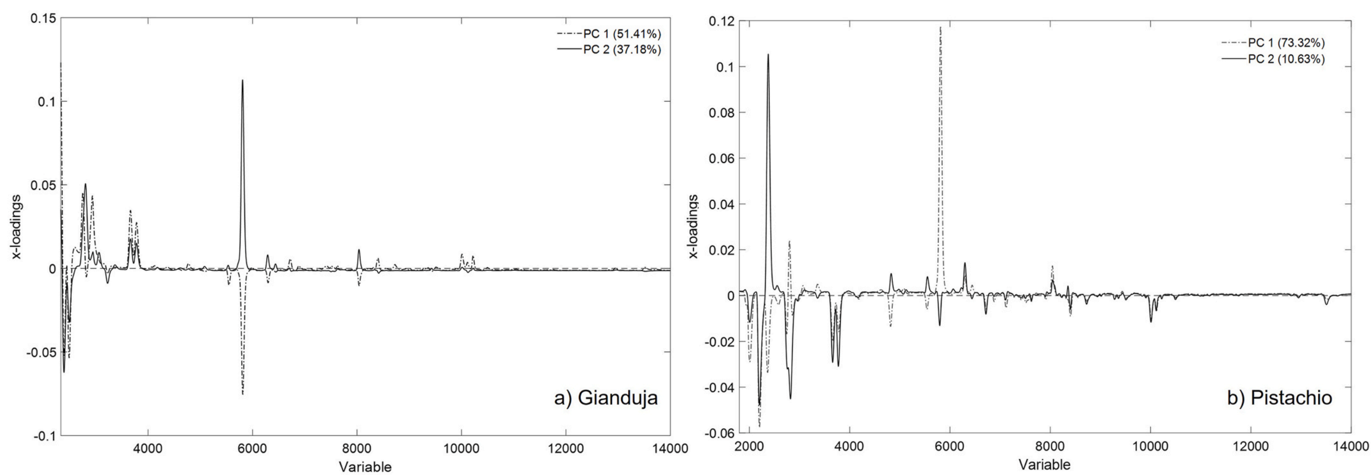

Fig. 3. X-loadings (PC1 and PC2) obtained by the PCA for the gianduja (a) and pistachio (b) samples.

calibration, cross validation, and prediction, are reported in Table 2. In general, for both spreads and packaging types, good results were achieved for calibration, cross-validation, and prediction data set.

Considering Pareto-scaling pretreatment, R^2 (prediction set) ranging from 0.970 (RMSEP = 9.7 days) to 0.982 (RMSEP = 5.75 days) and from 0.972 (RMSEP = 8.22 days) to 0.979 (RMSEP = 7.31 days) were achieved for pistachio and gianduja spreads, respectively. Slightly lower R^2 values were obtained using the SNV pre-treatment, especially for pistachio samples (from 0.932, to 0.978).

The higher the RPD value, the greater the probability of the model to

Table 2
Results of the PLS models developed by using the whole chromatograms.

		Calibration			Cross-Validation			Prediction			LV
		R^2	RMSEC (day)	RPD	R^2	RMSECV (day)	RPD	R^2	RMSEP (day)	RPD	
Pareto scaling											
Pistachio	L + S	0.996	3.02	14.8	0.983	6.74	7.7	0.976	6.86	6.4	11
	L	0.990	5.21	10.1	0.967	9.73	5.5	0.970	9.7	5.8	11
	S	0.993	4.16	11.9	0.984	6.52	8.1	0.982	5.75	7.4	9
Gianduja	L + S	0.996	2.89	15.1	0.978	7.22	6.7	0.977	7.44	6.5	13
	L	0.998	2.05	22.3	0.979	7.81	6.9	0.979	7.31	6.9	6
	S	0.997	2.27	18.2	0.991	4.39	10.5	0.972	8.22	5.9	6
SNV											
Pistachio	L + S	0.992	4.97	9.7	0.961	10.7	4.6	0.932	11.1	4.4	15
	L	0.985	5.97	8.1	0.971	9.89	4.9	0.963	10.0	5.0	6
	S	0.985	5.63	8.7	0.967	9.91	4.9	0.978	8.72	5.6	9
Gianduja	L + S	0.981	6.45	7.5	0.968	9.21	5.9	0.985	6.16	7.8	9
	L	0.983	6.33	7.7	0.956	10.21	4.8	0.973	8.34	5.8	6
	S	0.991	4.63	10.5	0.978	8.1	6.0	0.989	5.71	8.5	8

Note: L: large; S: small; SNV: Standard Normal Variate; R^2: determination coefficient: RMSE: Root Mean Square Error; C: calibration; CV: ross validation; P: prediction; RPD: residual prediction deviation, LV: latent variables.

accurately predict the storage time of a new sample set. Williams and Norris (2001) and Natsuga and S. Kawamura (2006) reported the following RPD ranges: 0.0–2.3 as not recommended, 2.4–3.0 as very rough screening quality, 3.1–4.9 as screening quality, 5.0–6.4 as quality control, 6.5–8.0 as process control, and >8.1 suitable for any application. For all PLS models, the RPD value in prediction was greater than 5.0 (except for the model built considering all pistachio samples, 4.4), which make the models suitable to predict the storage time in quality or process control.

The robustness of the models, in terms of degree of model generalization, was expressed as the ratio between the apparent performance (R_C^2 and RMSEC) and external validation performance (R_P^2 and RMSEP). When the apparent and external validation predictive powers are similar, it is possible to affirm that the model is robust. PLS models developed for the gianduja spread, applying the SNV pre-treatment, were the most robust, with values of RMSEC/RMSEP from 0.76 to 1 and of R_C^2/R_P^2 from 0.99 to 1.

Appreciable differences between the results considering samples L and S both together and separately were not seen. This is probably since variation of some volatile compounds is independent of the packaging type. These results agree with data reported by Gamlı and Hayoglu (2007), suggesting the shelf life of pistachio pastes calculated on the basis of peroxide values is weakly affected by the packaging type.

Variable importance in projection (VIP) scores obtained by the PLS models were used to evaluate the importance of each variable in the projection used in a PLS model. In particular, the VIP score calculates the contribution of each variable according to variance explained by each PLS component. The 'greater than one' can be considered important in given model conventionally used as the criterion for variable selection. Accordingly, only the variables with VIP scores greater than one were selected. Figs. 4 and 5 show the VIP scores obtained by the PLS models developed considering all samples (L + S) for gianduja and pistachio spreads, respectively. For both products and pre-treatments, only a small portion of the chromatograms was characterized by scores greater than one, especially for the data normalized with the SNV method. The different pre-treatment techniques resulted in different effects. For instance, Pareto-scaling showed many large peaks characterized by a VIP score higher than one, while after SNV normalization only a few peaks, even if perfectly corresponding to those present in the raw chromatograms, were highlighted. This likely happens because Pareto-scaling gives equal importance to all variables, and it increases the weights of minor noisy variables. Consequently, the variable selection method based on VIP scores (>1) was used to reduce the original data set pre-treated by SNV and to remove redundant or unnecessary chromatogram regions (Indahl, Liland, & Næs, 2009). This method has been extensively used in different fields and adopted for a variety of data types (Farrés, Platikanov, Tsakovski, & Tauler, 2015).

Results of PLS models developed using the variables selected by the VIP method are reported in Table 3. In general, the values of R^2 (0.948–0.989), RMSE (5.61–10.8 day), and RPD (4.5–8.6) in prediction are very similar to those obtained considering the entire chromatograms, suggesting that data reduction does not affect the goodness of the PLS models. Furthermore, the most robust results were obtained for gianduja spread (RMSEC/RMSEP from 0.74 to 0.84 and of R_C^2/R_P^2 from 0.99 to 1), as for entire chromatogram.

From an industrial point of view, especially considering the quality control sector, the proposed method allows to estimate, in a rapid way, the days of storage of nut spreads.

Future developments should focus on identification and quantification with standards, or through the use of appropriately selected reference materials, of volatile compounds with VIP >1 to better understand the phenomenon through a targeted approach.

4. Conclusions

Given the composition of pistachio and gianduja spreads, deteriorative reactions may occur during long-term storage. In fact, these products are particularly prone to lipid oxidation which leads to the formation of secondary oxidation products. In particular, the analysis of volatile compounds represents a key point in relation to shelf life, consumer acceptability, and nutritional quality of this type of product. For this reason, a FGC E-nose was used, thus providing a simple and fast technique that can also be implemented in industrial quality control. Herein, this analytical technique was combined with multivariate data analysis and used to estimate the storage time of pistachio and gianduja spreads also considering two different types of packaging. PCA showed a clear separation according to the packaging type for both pistachio and gianduja samples, while PLS models were developed to predict the storage time considering the samples both together and separately according to packaging type. In general, for both spreads and packaging types, good results were achieved for calibration, cross-validation, and the prediction data set. Furthermore, all PLS models presented an RPD value in prediction greater than 5.0 (except for one), which make these latter suitable to predict the storage time in quality or process control. The fingerprint method has been shown to be promising for applications in industrial food quality control, although further investigations are warranted to identify and quantify volatile compounds.

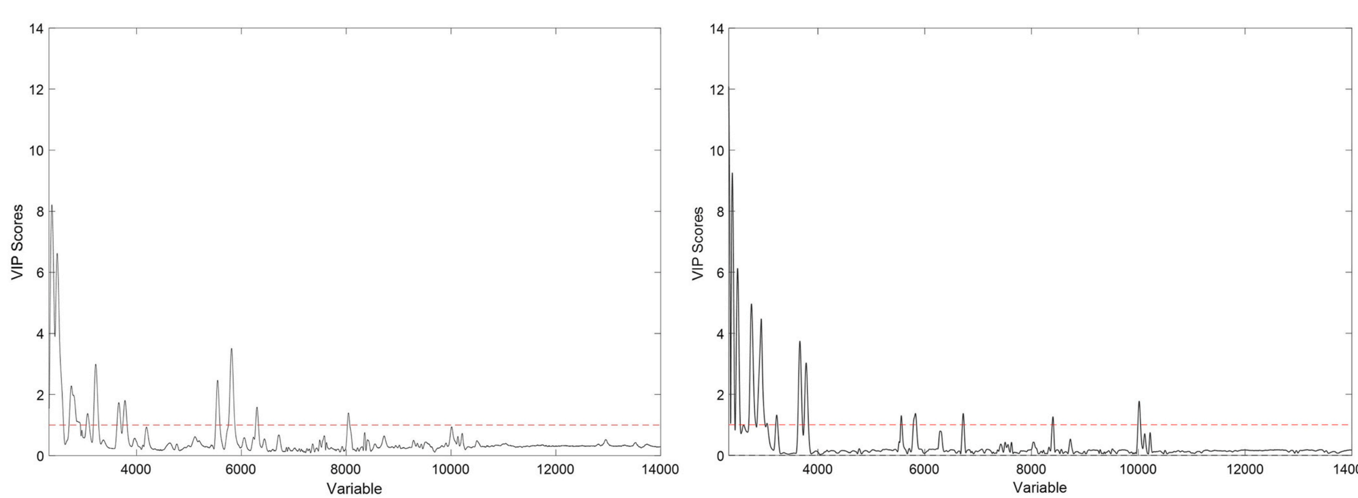

Fig. 4. VIP scores obtained by the PLS models developed considering all the gianduja samples and applying Pareto-scaling (a) and SNV (b) data pre-treatment.

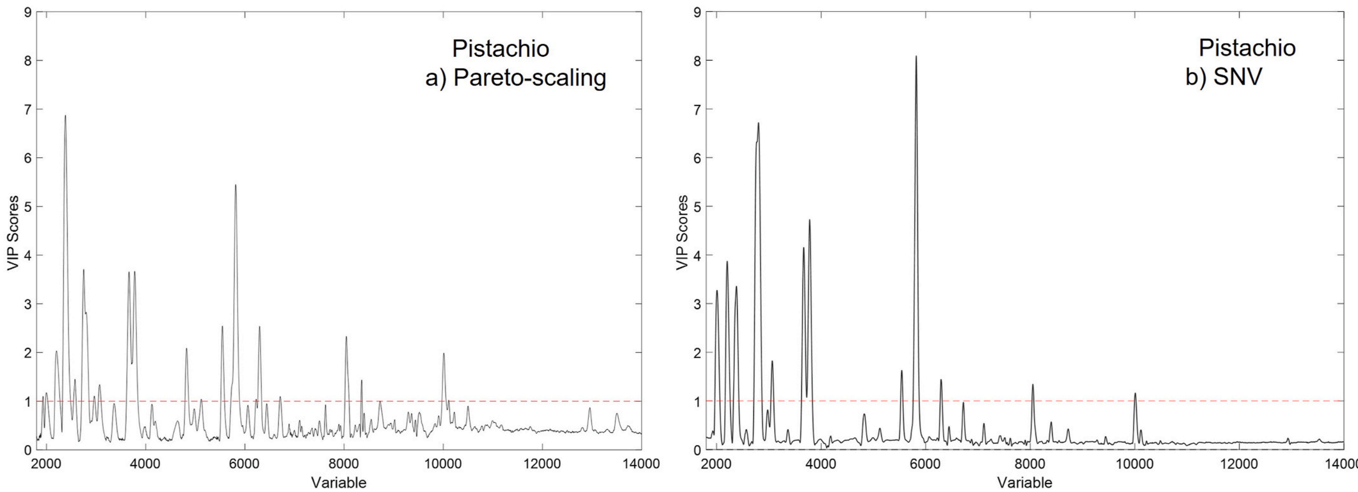

Fig. 5. VIP scores obtained by the PLS models developed considering all the pistachio samples and applying Pareto-scaling (a) and SNV (b) data pre-treatment.

Table 3
Results of the PLS models developed by using the variables selected by the VIP method.

		Calibration			Cross-Validation			Prediction			LV
		R^2	RMSEC (day)	RPD	R^2	RMSECV (day)	RPD	R^2	RMSEP (day)	RPD	
SNV											
Pistachio	L + S	0.993	4.61	10.4	0.956	10.1	4.8	0.948	10.8	4.5	16
	L	0.986	5.83	8.2	0.972	9.91	4.9	0.964	9.9	5.0	8
	S	0.987	5.61	8.8	0.971	9.89	4.8	0.981	8.05	6.1	10
Gianduja	L + S	0.986	5.45	8.9	0.971	8.11	5.9	0.985	6.51	7.4	13
	L	0.991	4.41	10.9	0.973	8.52	5.7	0.981	5.90	8.2	9
	S	0.993	4.12	11.7	0.982	5.92	8.1	0.989	5.61	8.6	10

Note: L: large; S: small; SNV: Standard Normal Variate; R^2: determination coefficient: RMSE: Root Mean Square Error; C: calibration; CV: cross validation; P: prediction; RPD: residual prediction deviation; LV: latent variables.

Competing interest

None.

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CRediT authorship contribution statement

Chiara Cevoli: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft. **Enrico Casadei:** Conceptualization, Data curation, Formal analysis, Investigation, Writing – review & editing. **Enrico Valli:** Conceptualization, Methodology, Resources, Visualization, Writing – review & editing. **Angelo Fabbri:** Conceptualization, Resources, Supervision, Writing – review & editing. **Tullia Gallina Toschi:** Conceptualization, Resources, Supervision, Writing – review & editing. **Alessandra Bendini:** Conceptualization, Methodology, Resources, Visualization, Supervision, Writing – review & editing.

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.

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