

Evaluation of the olfactory pattern of black olives stuffed with flavored hydrocolloids

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ABSTRACT

A sensory panel and an electronic nose (*E-nose*) were used to discriminate olives stuffed with flavored hydrocolloids submitted to different thermal treatments. The aroma perceived by the tasting panel before the sterilization was considered to be highly intense. However, the application of a single sterilization caused a 35–42% decrease in aroma intensity perceived by tasters. The aroma intensity also decreased when the number of sterilizations increased, but the tasting panel did not detect differences between them. The sterilization led to an increase in the ‘cooking effect’ that was less detected by panelists when the olives were flavored. The *E-nose* showed that the olives subjected to sterilization presented a different aromatic profile. Thus, the *E-nose* was able to discriminate the three treatments applied with greater precision than the tasting panel. *E-nose* technology offers a fast, inexpensive and non-destructive method for discriminating between olives stuffed with flavored hydrocolloids submitted to sterilization.

1. Introduction

According to the International Olive Council (IOC), the average consumption of table olives over a five-season period (2015–2020) amounted to 2,814,100 tons. Consumption was distributed in countries such as Egypt, Turkey, Algeria, the United States and Spain, with the latter consuming 187,500 tons. In addition, as per the Food Consumption Panel of the Ministry of Agriculture, Food and Environment of Spain (MAGRAMA), the consumption of table olives in Spain increased by 10.3% in 2020.

Currently, the olives most commonly found in Spain are stuffed green olives. Black olives are generally sold whole, pitted or chopped, and there are no stuffed oxidized black olives without covering liquid. Fillings of green table olives tend to be peppers, onions, almonds, celery, anchovies, capers or their paste, spices and aromatic herbs or their natural extracts and authorized additives, including flavorings. The use of hydrocolloids (polysaccharides, proteins or lipids) to fill olives with different natural or artificial aromas is widespread in the table olive industry.

These hydrocolloids can influence the food processing, sensory aspects and nutritional benefits of the final product (Lu, Nishinari, Matsukawa, & Fang, 2020). The use of flavored hydrocolloids to fill olives is therefore of great interest to the industry, as it leads to lower costs compared to using fillings with natural food paste.

Black table olives, also called ‘Californian style’, are subjected to an alkaline (NaOH) and air treatment until the fruit is blackened by oxidation and polymerization of phenolic compounds. They are then generally packaged with a saline solution. For the product to be microbiologically stable, it requires a sterilization phase (121–126 °C for at least 15–30 min), unlike green olives which are pasteurized (Martín-Vertedor, Fernández, et al., 2020; Fernández et al., 2020). The sterilization in table olives is calculated as the ‘accumulated sterility value’ which is the sum of the partial lethality values reached during the sterilization process and is expressed in terms of exposure times at a reference temperature (IOC, 2004).

The thermal sterilization treatment can change the aromas of the olives. In addition, prolonged sterilization may bring about the ‘cooking effect’ (Martín-Vertedor, Rodrigues, et al., 2020). Changes in the odor

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profile of table olives after sterilization treatments could be why black olives filled with added food flavorings are not currently marketed. For this reason, it is necessary to study the combination of black olives with food fillings and flavors that are both stable at the sterilization temperature and pleasant for the consumer.

Since aroma is such a necessary attribute for food acceptability, it is important to obtain sensory evaluations from a tasting panel. This method is used for the sensory analysis of different types of olives (IOC, 2011) and is the only method to determine how the consumer will perceive the aromas and rate them sensually. However, sensory analysis by a tasting panel is often expensive and time-consuming (Panagou, Sahgal, Magan, & Nychas, 2008). In addition, a good result is dependent on a reasonable number of trained panelists, the availability of which is not always possible. The use, therefore, of an analytical instrument that functions as that of human smell, such as the *E-nose*, would be very interesting.

The *E-nose* is an instrument that combines a series of gas sensors and pattern processing techniques to detect odors that have been proven by different researchers (Radi et al., 2021). The sensor array defines an odor made up of a large number of different volatile compounds in the headspace of a sample, providing its odor pattern. The *E-nose* can be used as a rapid and automated method and alternative technique to determine food additive concentrations (Qiu & Wang, 2017). The *E-nose* designed at the University of Extremadura is able to detect changes in the intensity or concentration of food odors through a series of metal oxide sensors (Arroyo et al., 2020; Sánchez et al., 2021; Sánchez, Martín-Tornero, et al., 2022). Thus, when the volatile compounds emanating from the sample react with the sensor surface, an oxygen exchange occurs with a decrease in electrical conductivity (Martínez Gila, Gámez García, Bellincontro, Mencarelli, & Gómez Ortega, 2020; Sánchez et al., 2021).

This work presents a double novelty; on the one hand, a new table olive product has been elaborated to be marketed and, on the other hand, the *E-nose* technique has been applied to discriminate table olives according to the different aromas studied. The new product consists of Californian-style black olives filled with a consistent and economical hydrocolloid with various natural aromas added. The aromas are used to make the product more attractive to the consumer and, at the same time, mask the possible cooking effect that can be produced during sterilization. The absence of brine solution means the product can be packaged as a snack, easily consumed on the go. Moreover, the application of the *E-nose* technique is novel since it could be used in the industry for table olive discrimination.

For that reason, the main objective of this work was to study the olfactory sensory evolution of black olives stuffed with different flavored hydrocolloids and submitted to different sterilization treatments using a tasting panel and an *E-nose*.

The underlying hypothesis is that an *E-nose* discriminates samples according to the sterilization treatment received, regardless of the aroma added to the filling. At the same time, it is expected that all the aromas used can mask the cooking effect that arises after a certain sterilization time.

2. Materials and methods

2.1. Experimental design and sample preparation

Olives (*Olea europaea*) of the 'Hojiblanca' variety were elaborated as Californian-style black olives by a company located in the northwest of Spain (Martín-Vertedor, Fernández, et al., 2020). The following substances were used for the Californian-style black olive elaboration: a solution of acetic acid (Panreac Applichem, Darmstadt, Germany), calcium chloride (Tetra Chemicals, Helsingborg, Sweden), ferrous gluconate and sodium chloride (Sigma-Aldrich, St. Louis, MO, USA). After the elaboration process, table olives were pitted and placed into jars (250 mL) with a solution containing 2% NaCl and 0.015% (10–40 ppm)

ferrous gluconate. Next, the solution was removed, and the olives were stuffed with flavored hydrocolloids with edible aromas of 'eggplant', 'mojo picón', 'thyme', 'oregano' or 'sangaree', or 'without aroma'.

The hydrocolloids were prepared using the following food-grade ingredients: two parts of sodium alginate (Saporepuro, Torino, Italy), one part of guar gum (Saporepuro, Torino, Italy) and one part of the corresponding natural aroma (Neroliane, Grasse, France) were mixed with distilled water to obtain a volume of 100 mL. The additives were mixed using a commercial mixer for 1 min. The final mixture resembled snail mucus. One batch of table olives was filled with an unflavored hydrocolloid. Olives were manually filled using a syringe. The stuffed olives were placed into a 7.5% calcium chloride solution for 30 s and, later, into another 0.25% calcium chloride solution for 24 h. This liquid was then removed, and the jars were prepared to be sterilized. Five replicates per sample were prepared for the *E-nose* analysis and eight replicates were prepared for the tasting panel. Jars containing the control stuffed olives were kept in the refrigerator until the analysis was done. The other jars were subjected to different sterilization cycles as indicated in the following section.

2.2. Thermal sterilization treatments

Olive jars were submitted to three different sterilization treatments which corresponded to the following F_0 values (accumulated lethality): $F_0 = 9$ min (T1), $F_0 = 12$ min (T2) and $F_0 = 15$ min (T3) following the method proposed by Martín-Vertedor, Fernández, et al. (2020). All experiments were performed in quintuplicate. Sterilization was carried out in a laboratory autoclave (JP Selecta model Presoclave III 80, Barcelona, Spain). Two Pt100 temperature sensors (TC, United Kingdom) were placed in the middle of the jar connected to a computer in order to monitor the F_0 value calculated according to Martín-Vertedor, Fernández, et al. (2020). Jars were stored at room temperature until analysis.

2.3. Analyses

The following analyses were carried out on the stuffed black olives subjected to sterilization treatments. Specifically, sensory analysis and *E-nose* measurements were performed.

2.3.1. Sensory analysis

The sensory analysis was carried out by a group of table olive panelists located in the Technological Institute of Food and Agriculture (CICYTEX-INTAEX) facilities, following the recommendations for tasting room conditions (ISO, 2007) and the indications established by the IOC (2011). A scoreboard was designed for the purpose of this experiment to evaluate the intensity of the aroma and the defects according to a 10 cm structured scale. Sensory evaluation outcomes were expressed as average values. Values were considered reliable when $CV < 20\%$ (IOC, 2011).

A one-way ANOVA was used followed by Tukey's multiple range test to establish statistically significant differences between different thermal treatments within each of the table olive varieties. Significance was set at $p < 0.05$. SPSS 18.0 software was used for statistical analysis (SPSS Inc., Chicago, IL, USA). Data were expressed as means and standard deviations (SD).

2.3.2. *E-nose* system

The *E-nose* device was designed by the Research Group on Perception and Intelligent Systems of the University of Extremadura. It contains a novel chip with 11 types of metal oxide semiconductor (MOX) commercial gas sensors purchased from different manufacturers which exhibit global selectivity: i) BME680 (Bosch Sensortech GmbH, Reutlingen, Germany): temperature (°C), pressure (hPa), humidity (%RH) and gas measurement (Ω); ii) SGP30 (Sensirion AG, Stäfa, Switzerland): eCO_2 (ppm), TVOC (ppb), H_2 (2) and ethanol; iii) CCS811 (ScioSense B. V., Eindhoven, The Netherlands): eCO_2 (ppm), TVOC (ppb) and sensor

resistance (Ω); and iv) iAQ-Core (ScioSense B.V., Eindhoven, The Netherlands): eCO₂ (ppm), TVOC (ppb) and sensor resistance (Ω). Odor evaluation using an *E-nose* provides an odor pattern for each sample. This device has low power consumption and is the size of a hockey puck, thereby making it easily portable and convenient (Arroyo et al., 2020). This type of *E-nose* sensor has been studied on previous occasions and can be found in bibliographic references such as Lozano, Santos, and Horrillo (2016); Arroyo, Lozano, and Suárez (2018); Portalo-Calero, Arroyo, Suárez, and Lozano (2019); Arroyo et al. (2020).

Olive measurements were carried out according to the recommendations established by the International Olive Council for sensory analysis (IOC, 2011). Standard glasses containing three olives were placed on a heating block at 25 °C and covered with a watch glass. Another glass without olives was left on the block to measure the air inside and to serve as a reference. The *E-nose* was located on the sample glass for 60 s and the sensor signals were recorded. Next, the *E-nose* was moved to the glass without samples to perform desorption with free air for 30 s to return the gas sensor signal to the baseline. The system took a reading of the resistive value provided by each sensor at 1 s intervals. Five measurements were taken for each sample.

Each sensor response curve was composed of N points corresponding to the measurements of the sensor with the time. The features used to characterize the sensor response curves were maximum signal value less minimum one, plus 100, less one in our case. As a result, a vector of data with 11 rows (sensors) for each sample was obtained.

2.4. Multivariate data analysis

Data provided by the *E-nose* were analyzed using multivariate algorithms. First, a principal component analysis (PCA) was applied (Wold, Esbensen, & Geladi, 1987) to explore the main variation among the four groups of samples. This is an unsupervised method and was used to determine whether there were clusters between the samples without using membership information. The data for each of the fillings were analyzed independently.

Next, a partial least square discrimination analysis (PLS-DA) (Barker & Rayens, 2003) was used as a classification algorithm in order to evaluate the possibility of sample discrimination according to the thermal treatment applied. Full cross-validation was performed to evaluate the performance of the model. Data were autoscaled before multivariate analysis in order to avoid the effect of the different dimensions.

Data analysis was carried out in MATLAB version R2016b (The MathWorks Inc., Natick, MA, USA) and PLS Toolbox version 8.2.1 (Eigenvector Research Inc., Wenatchee, WA, USA).

Table 1

Sensory evaluation of stuffed olives with flavour hydrocolloids. Results are expressed as mean \pm SD of samples. Different lowercase letters mean a statistical significant difference between sterilization treatment (one-way ANOVA followed by Tukey's test, $P < 0.05$). For the same sterilization treatment, different uppercase letters mean a statistical significant difference between aromas (one-way ANOVA followed by Tukey's test, $P < 0.05$).

Hydrocolloids	Flavoring															
	C			T1			T2			T3						
'Without aroma'	–			–			–			–						
'Mojo picón'	5.1	\pm	0.78	c A	3.1	\pm	0.46	b NS	1.7	\pm	0.59	a A	1.4	\pm	0.70	a A
'Thyme'	6.1	\pm	0.93	c B	3.8	\pm	0.62	b NS	2.6	\pm	0.22	a B	2.7	\pm	0.55	a B
'Aubergine'	6.4	\pm	0.30	c B	4.1	\pm	0.24	b NS	2.7	\pm	0.32	a B	2.0	\pm	0.64	a B
'Sangaree'	7.1	\pm	0.36	c C	4.7	\pm	0.37	b NS	2.3	\pm	0.31	a C	2.9	\pm	0.61	a B
'Oregano'	7.7	\pm	0.34	c D	4.4	\pm	0.34	b NS	2.5	\pm	0.20	a C	2.7	\pm	0.34	a B
Hydrocolloids	Cooked effect															
	C			T1			T2			T3						
'Without aroma'	0.0	\pm	0.30	a NS	3.5	\pm	0.45	b B	4.7	\pm	0.35	c C	6.5	\pm	0.57	d D
'Mojo picón'	0.1	\pm	0.29	a NS	2.0	\pm	0.24	b A	3.3	\pm	1.11	c B	3.5	\pm	0.79	c C
'Thyme'	0.0	\pm	0.46	a NS	2.0	\pm	0.10	b A	3.5	\pm	0.51	c B	3.5	\pm	0.58	c C
'Aubergine'	0.0	\pm	0.54	a NS	2.0	\pm	0.60	b A	2.8	\pm	0.55	c A	3.2	\pm	0.39	c B
'Sangaree'	0.0	\pm	0.21	a NS	1.7	\pm	0.36	b A	2.5	\pm	0.40	c A	2.6	\pm	0.38	c A
'Oregano'	0.1	\pm	0.11	a NS	1.9	\pm	0.36	b A	2.3	\pm	0.23	c A	2.5	\pm	0.31	c A

3. Results and discussion

The results were analyzed by a tasting panel to classify the different aromas in the stuffed black olives. Next, outcomes were checked by applying *E-nose* technology to distinguish between the olives stuffed with different flavored hydrocolloids and to discriminate between different sterilization treatments.

3.1. Sensory analysis of flavored stuffed olives with hydrocolloid

Sensory analysis was carried out by a trained panel to determine the aroma intensity and cooking effect in Californian-style black olives ('Hojiblanca' variety) submitted to different sterilization treatments (T1, T2 and T3). The results from the one-way ANOVA showed that the intensity of the thermal treatment significantly affected the aroma intensity and perception of the cooking effect in table olives (P -value < 0.05) (Table 1).

The tasting panel evaluated their perception of the different aromas applied to the olives filled with flavored hydrocolloids as being highly intense. In fact, before being thermally processed, the olives presented an aromatic intensity greater than 5 for all the aromas used. This is a good result since applying this amount of aroma to the hydrocolloids is enough to achieve a highly intense aroma in the whole olives. The stuffed table olives with the lowest intensity were those with 'mojo picón' aroma, while the olives with the greatest intensity were those with 'sangaree' and 'oregano' aromas. These black table olives must be sterilized in order to ensure microbiological stability. The range of thermal applications in different industries is variable, thus the effect of different thermal treatments on the intensity of the perceived aroma was proved (T1, T2 and T3). The results showed that the application of a single thermal sterilization treatment (T1) caused a 35–42% decrease in aroma intensity perceived by the tasters. The application of thermal treatments causes a modification of the volatile compounds present in olives and olive oils (Messina, Sancho, & Walsøe de Reça, 2015), causing a significant loss of aromas. This may be one of the reasons why this type of olive product does not exist on the market. However, with the application of a low-intensity thermal treatment, we were able to obtain flavored hydrocolloid-stuffed olives with a good aroma intensity.

In addition, the tasting panel detected a more pronounced decrease in aroma intensity when the number of thermal treatments was increased (T2 and T3). However, the tasting panel did not detect significant differences in aroma intensity between T2 and T3 thermal treatments; the aroma intensity was approximately 57%–73% less than that for the control olives. The values for aroma intensity were less than

3 points. Most of the aromas studied showed a similar decrease with the application of the thermal treatments. The ‘mojo picón’ aroma had the most pronounced losses since the rest of the aromas presented similar values for sterilized olives. The table olives stuffed with the unscented hydrocolloid did not present any aroma after thermal treatments were applied. Therefore, it should be noted that it is not advisable to apply very severe thermal treatments since they contribute to a significant loss of aromas that affects the sensory perception of olives by consumers.

The thermal treatment applied to the Californian-style olives after the production process led to an increase in the cooking effect in the olives (Table 1), except for the control olives which did not show this defect. Thus, according to IOC regulations, the olives could be classified into different sensory categories following consideration of the defect predominantly perceived (DPP) by the tasting panel (IOC, 2011). However, even though the olives were flavored, the application of a thermal treatment (T1) caused an increase in the intensity of the ‘cooked’ defect in the flavored stuffed olives. Thus, these olives could be classified into the best commercial category denominated as ‘extra category’ or ‘fancy’ (DPP ≤2). The defect was perceived less in this type of olives than in those ‘without aroma’ which were classified as ‘first category’ or ‘select’ (2 < DPP ≤3.5). Therefore, it can be stated that the aroma of the filling caused a decrease in the perception of the cooked defect, with the intensity of this defect being similar in olives stuffed with the different flavored hydrocolloids.

When the intensity of the thermal treatment was more severe (T2 and T3), an increase in the intensity of the defect was observed. However, no significant differences in the cooked defect in the stuffed flavored olives were shown between the two treatments. The intensity of the defect was less than 3.5 points for all the aromas; therefore, these table olives could be classified into a category denominated as ‘first category’ or ‘select’.

It should be taken into account that olives ‘without aroma’ presented a significantly more intense cooked defect, which corresponds to a worse category than olives stuffed with flavored hydrocolloids. In addition, olives subjected to the most aggressive thermal treatment presented the highest defect intensity, thereby classifying them as unsellable (DPP >6.0).

Researchers have studied the application of different sterilization treatments to Californian-style olives, observing that longer and more aggressive sterilization treatments lead to a deeper and more unpleasant taste (Casado & Montano, 2008; Charoenprasert & Mitchell, 2014; Tang et al., 2016; Pérez-Navado, Cabrera-Bañegil, Repilado, Martillanes, & Martín-Vertedor, 2018; Martín-Vertedor, Fernández, et al., 2020). The olive sterilization process decreases the product quality in addition to causing changes in olfactory qualities such as color and texture. (Abriouel, Benomar, Gálvez & Pérez, 2014; Pérez-Navado et al., 2018). Thus, industries need to optimize thermal sterilization treatments, keeping F₀ as low as possible in order to obtain the highest quality sterilized olives.

The results show that stuffing olives with flavored hydrocolloids could be a strategy to mask the cooking effect caused by the application of thermal treatments, thereby making Californian-style black olives more palatable to the consumer.

3.2. E-nose discrimination between sterilized and non-sterilized stuffed olives

First, the use of the E-nose to discriminate between samples that had or had not been subjected to thermal treatments was studied. To determine whether there were differences between the two groups, PCA models were developed considering each type of stuffed olive individually. PCA analysis also allowed the detection of potential outliers and systematic artifacts in the samples. A total of six PCA models were developed: one for the stuffed olives ‘without aroma’ and five for the stuffed olives with aroma (five different aromas). Fig. 1 shows the score plots of the first two principal components of the PCA model for stuffed olives ‘without aroma’ and stuffed olives with ‘oregano’ aroma, as this is similar in behavior to the rest of the aromas used.

As can be seen, these two components suffice to verify that samples are clustered according to the thermal treatment. These two components explain 71.76% and 78.39% of the total variance in stuffed olives ‘without aroma’ and with ‘oregano’ aroma, respectively. Component 1 allows differentiation of the samples since higher scores were obtained for this component in the experiments with thermal treatments than for the control without sterilization.

It can also be observed in both types of samples that unsterilized stuffed olives presented scores closer together while those for olives submitted to thermal treatments were more dispersed and had a linear trend. This may be due to different sterilization treatments being applied, causing the values to be more dispersed.

The promising exploratory analysis suggests the use of a supervised classification method aiming to discriminate between unsterilized and sterilized samples. The supervised PLS-DA model was selected. Table 2 shows the correct prediction (for cross-validation using the leave-one-

Table 2

Confusion matrices obtained through PLS-DA for the discrimination between control samples and samples submitted to thermal treatments. Values are expressed in percentage.

	Predicted class			
	Without aroma		Oregano	
Real class	Control	Thermal treatment	Control	Thermal treatment
Control	25.8	0	24.5	0
Thermal treatment	0	74.2	0	75.5

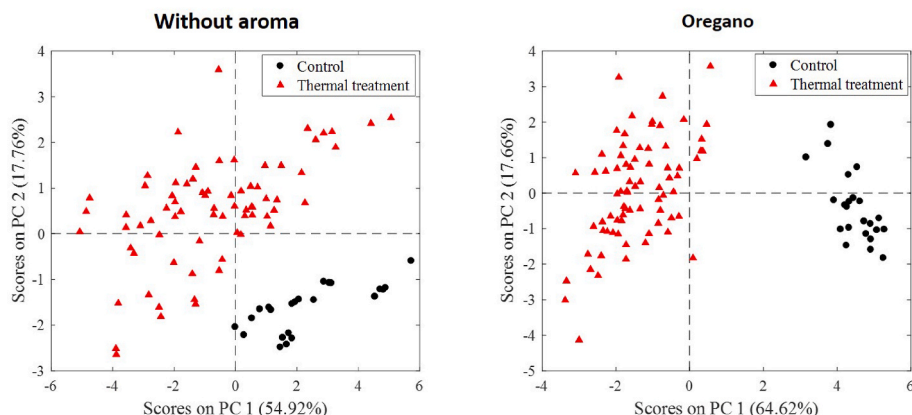


Fig. 1. PCA score plots of the two first principal components obtained from E-nose data for discriminating between control and sterilization treatments.

out approach) for both types of samples. The diagonal elements sum of the confusion matrices gives the percentages of correct predictions. In both cases, 100% of the predictions were correct, indicating that the model is suitable for use in stuffed olives.

Thus, the *E-nose* showed that the olives subjected to thermal treatments presented a different aromatic profile than those that had not undergone sterilization. As commented in the previous section, in stuffed olives ‘without aroma’, the tasting panel indicated that the aromatic sensation perceived was due to the cooking effect that was absent in the control samples. However, for stuffed olives with aroma, the differentiation was due to a simultaneous effect of the aroma and the cooking effect. Thus, in this case, the *E-nose* discriminated the whole aromatic profile detected in the sample. Sánchez et al. (2021), Sánchez, Martín-Tornero, et al. (2022) and Sánchez, Pérez-Navado, et al. (2022) discriminated anomalous fermentations in Spanish-style green table olives by using *E-nose*.

3.3. *E-nose* discrimination between sterilized stuffed olives submitted to different sterilization treatments

Once it had been verified that the *E-nose* was capable of accurately differentiating between samples that had or had not been subjected to sterilization treatments, the *E-nose* was used to differentiate between different thermal treatments. As above, data from each type of stuffed olive were first processed by PCA. The corresponding score plots of the first two principal components (PC1 and PC2) are shown in Fig. 2.

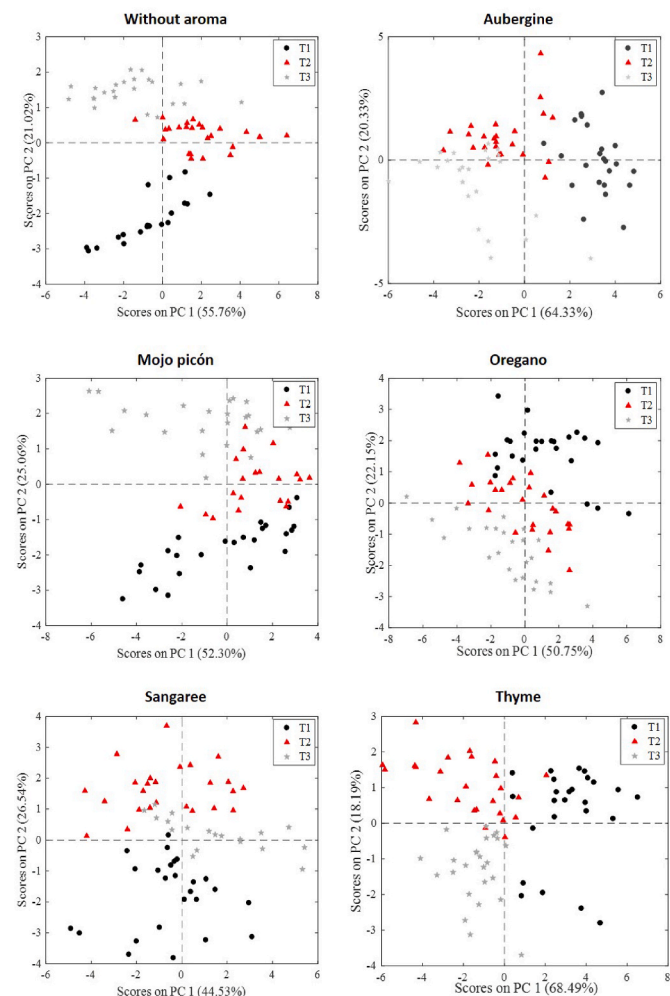


Fig. 2. PCA score plots of the two first principal components obtained from *E-nose* data for different sterilization treatments.

The first two principal components represented total variance values of around 80%, ranging from 71.1% for the filling with ‘sangaree’ aroma to 86.7% for the filling with ‘thyme’ aroma. Examining these plots, some grouping of samples according to thermal treatment was observed for each flavored stuffed olive. The scores are seen to progress with the intensity of the sterilization. For the olives stuffed ‘without aroma’ and with ‘mojo picón’ and ‘sangaree’ aromas, the score values for PC2 are higher as the sterilization time increases. However, for ‘eggplant’, ‘oregano’ and ‘thyme’, discrimination is along PC1, with the contribution of the first component being lower as the sterilization time increases. Therefore, the *E-nose* shows a different aromatic trace that classifies the sterilization treatments, which is influenced by the intensity of the perceived aroma and the aromas from the cooking defect. In the specific case of the filling ‘without aroma’, it can be stated that the *E-nose* classifies it, as does the tasting panel, depending on the cooking defect brought about by the different sterilization treatments.

Furthermore, a classificatory analysis was performed for each stuffing employing the PLS-DA; the results are shown as confusion matrices (Table 3). The models were cross-validated using the leave-one-out approach. The PLS-DA results confirmed the good classification of the different thermal treatments in all the samples studied: 100% of the predictions were correct in the ‘sangaree’ and ‘oregano’ stuffed models, and 98.6%, 94.6%, 93.3% and 92.7% of the predictions were correct for olives filled ‘without aroma’, and with ‘eggplant’, ‘thyme’ and ‘mojo picón’ aromas, respectively. In these samples, the results also demonstrated that no samples of T1 were assigned to T2 or T3 and vice versa. The few incorrect predictions were only within the T2 and T3 samples for these aromas.

As can be seen, the *E-nose* was able to discriminate between the three thermal treatments applied with greater precision than the tasting panel. In this sense, the panel sensorially interpreted T2 and T3 treatments as if they were of similar sterilization intensity, while the *E-nose* was able to differentiate them into different groups. This may be due to the aroma of the filling masking the perception of the tasters, causing them to find no differences between the sterilization treatments. In fact, the panelists indicated similar values between these sterilization treatments for both aroma intensity and cooking effect.

Therefore, the *E-nose* is an effective and more precise tool than a sensory panel since it allows the differentiation of olives subjected to different thermal sterilization treatments regardless of the aroma of the filling contained in the olives.

Table 3

Confusion matrix for the discrimination of thermal treatments applied to the olives based on PLS-DA and using leave one out cross-validation approach. Values are expressed in percentages.

	Real class	Predicted class		
		T1	T2	T3
Without aroma	T1	28.6	0	0
	T2	0	35.7	0
	T3	0	1.4	34.3
Aubergine	T1	32.9	0	0
	T2	0	30.2	2.7
	T3	0	2.7	31.5
Mojo picón	T1	33.8	1.5	0
	T2	0	26.5	2.9
	T3	0	2.9	32.4
Oregano	T1	33.3	0	0
	T2	0	33.3	0
	T3	0	0	33.3
Sangaree	T1	36.2	0	0
	T2	0	36.2	0
	T3	0	0	27.6
Thyme	T1	33.3	0	0
	T2	0	26.7	6.7
	T3	0	0	33.3

4. Conclusions

The sensory analysis and the *E-nose* showed different olfactory profiles of stuffed black olives submitted to sterilization treatments. Therefore, the temperature and time of accumulated lethality need to be controlled by the industry. The tasting panel results showed that the flavored black olives stuffings were able to mask the intensity of the cooked defect caused by sterilization treatments. In fact, the sensory panel classified these olives into a higher category than they really would be. However, the *E-nose* discriminated flavored olives according to the intensity of the thermal sterilization applied, independently of the aroma used. Thus, the *E-nose* is a useful discrimination tool that can be applied in olives stuffed with flavored hydrocolloids submitted to different sterilization treatments. This device can be used to support the tasting panel and combined with chemometric analysis, can be used to perform fast, inexpensive, non-destructive and environmentally-friendly qualitative analysis.

Author Contributions

Conceptualization, R.S., E.-M.T., and D.-M.V.; Data curation, R.S., P. A., F.M., and J.L.; Formal analysis, R.S., E.-M.T., and D.-M.V.; Funding acquisition, D.-M.V.; Investigation, R.S., E.-M.T., and D.-M.V.; Methodology, P.A., F.M., and J.L.; Project administration, D.-M.V.; Resources, R.S., E.-M.T., and D.-M.V.; Supervision, J.L., and D.-M.V.; Validation, J. L., R.S., and D.-M.V.; Visualization, R.S. and D.-M.V.; Writing – original draft, R.S., E.-M.T., and D.-M.V.; Writing – review & editing, R.S., E.-M. T., J.L. and D.-M.V. All authors have read and agreed to the published version of the manuscript.

Compliance with ethics requirements

This research does not include any experiment using animal and/or human subjects.

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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References

- Abriouel, H., Benomar, N., Gálvez, A., & Pérez Pulido, R. (2014). Preservation of Manzanilla Aloreña cracked green table olives by high hydrostatic pressure treatments singly or in combination with natural antimicrobials. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology*, 56(2), 427–431. <https://doi.org/10.1016/j.lwt.2013.09.012>
- Arroyo, P., Lozano, J., & Suárez, J. I. (2018). Evolution of wireless sensor network for air quality measurements. *Electronics*, 7(12). <https://doi.org/10.3390/electronics7120342>
- Arroyo, P., Meléndez, F., Suárez, J. I., Herrero, J. L., Rodríguez, S., & Lozano, J. (2020). Electronic nose with digital gas sensors connected via bluetooth to a smartphone for air quality measurements. *Sensors*, 20(3). <https://doi.org/10.3390/s20030786>

- Barker, M., & Rayens, W. (2003). Partial least squares for discrimination. *Journal of Chemometrics*, 17(3), 166–173. <https://doi.org/10.1002/cem.785>
- Casado, F. J., & Montaña, A. (2008). Influence of processing conditions on acrylamide content in black ripe olives. *Journal of Agricultural and Food Chemistry*, 56(6), 2021–2027. <https://doi.org/10.1021/jf072960b>
- Charoenprasert, S., & Mitchell, A. (2014). Influence of California-style black ripe olive processing on the formation of acrylamide. *Journal of Agricultural and Food Chemistry*, 62(34), 8716–8721. <https://doi.org/10.1021/jf5022829>
- Fernández, A., Talaverano, M. I., Pérez-Navado, F., Boselli, E., Cordeiro, A. M., Martillanes, S., & Martín-Vertedor, D. (2020). Evaluation of phenolics and acrylamide and their bioavailability in high hydrostatic pressure treated and fried table olives. *Journal of Food Processing and Preservation*, 44(4), Article e14384. <https://doi.org/10.1111/jfpp.14384>
- International Olive Council (IOC). (2004). *Commercial standard applicable to table olives*. Madrid, Spain: COI/OT/NC N° 1.
- International Olive Council (IOC). (2011). *Method for the sensory analysis of table olives* COI/OT/MO/Doc. N° 1/Rev.2. Madrid, Spain.
- ISO (International Organisation for Standardisation). (2007). *ISO 8589: 2007. Sensory analysis-General guidance for the design of test rooms*.
- Lozano, J., Santos, J. P., & Horrillo, M. C. (2016). Wine applications with electronic noses. In *Electronic noses and tongues in food science* (pp. 137–148).
- Lu, W., Nishinari, K., Matsukawa, S., & Fang, Y. (2020). The future trends of food hydrocolloids. *Food Hydrocolloids*, 103, 105713. <https://doi.org/10.1016/j.foodhyd.2020.105713>
- Martín-Vertedor, D., Fernández, A., Hernández, A., Arias-Calderón, R., Delgado-Adámez, J., & Pérez-Navado, F. (2020a). Acrylamide reduction after phenols addition to Californian-style black olives. *Food Control*, 108, 106888. <https://doi.org/10.1016/j.foodcont.2019.106888>
- Martín-Vertedor, D., Rodrigues, N., Marx, Í. M. G., Veloso, A. C. A., Peres, A. M., & Pereira, J. A. (2020b). Impact of thermal sterilization on the physicochemical-sensory characteristics of Californian-style black olives and its assessment using an electronic tongue. *Food Control*, 117, 107369. <https://doi.org/10.1016/j.foodcont.2020.107369>
- Martínez Gila, D. M., Gámez García, J., Bellincontro, A., Mencarelli, F., & Gómez Ortega, J. (2020). Fast tool based on electronic nose to predict olive fruit quality after harvest. *Postharvest Biology and Technology*, 160, 111058. <https://doi.org/10.1016/j.postharvbio.2019.111058>
- Messina, V., Sancho, A., & Walsøe de Reca, N. (2015). Monitoring odour of heated extra-virgin olive oils from Arbequina and Manzanilla cultivars using an electronic nose. *European Journal of Lipid Science and Technology*, 117(8), 1295–1300. <https://doi.org/10.1002/ejlt.201400651>
- Panagou, E. Z., Sahgal, N., Magan, N., & Nychas, G. J. E. (2008). Table olives volatile fingerprints: Potential of an electronic nose for quality discrimination. *Sensors and Actuators B: Chemical*, 134(2), 902–907. <https://doi.org/10.1016/j.snb.2008.06.038>
- Pérez-Navado, F., Cabrera-Bañegil, M., Repilado, E., Martillanes, S., & Martín-Vertedor, D. (2018). Effect of different baking treatments on the acrylamide formation and phenolic compounds in Californian-style black olives. *Food Control*, 94, 22–29. <https://doi.org/10.1016/j.foodcont.2018.06.021>
- Portalo-Calero, F., Arroyo, P., Suárez, J. I., & Lozano, J. (2019). Triangular test of amanita mushrooms by using electronic nose and sensory panel. *Food*, 8(9). <https://doi.org/10.3390/foods8090414>
- Qiu, S., & Wang, J. (2017). The prediction of food additives in the fruit juice based on electronic nose with chemometrics. *Food Chemistry*, 230, 208–214. <https://doi.org/10.1016/j.foodchem.2017.03.011>
- Radi, R., Barokah, B., Rohmah, D. N., Wahyudi, E., Adhityamurti, M. D., & Yuroto Putro, J. P. L. (2021). Implementation of an electronic nose for classification of synthetic flavors. *Bulletin of Electrical Engineering and Informatics*, 10(3), 1283–1290. <https://doi.org/10.11591/eei.v10i3.3018>
- Sánchez, R., Martín-Tornero, E., Lozano, J., Boselli, E., Arroyo, P., Meléndez, F., & Martín-Vertedor, D. (2021). E-nose discrimination of abnormal fermentations in Spanish-style green olives. *Molecules*, 26, 5353. <https://doi.org/10.3390/molecules26175353>
- Sánchez, R., Martín-Tornero, E., Lozano, J., Fernández, A., Arroyo, P., Meléndez, F., & Martín-Vertedor, D. (2022). Electronic nose application for the discrimination of sterilization treatments applied to Californian-style black olive varieties. *Journal of the Science of Food and Agriculture*, 102(6), 2232–2241. <https://doi.org/10.1002/jsfa.11561>
- Sánchez, R., Pérez-Navado, F., Montero-Fernández, I., Lozano, J., Meléndez, F., & Martín-Vertedor, D. (2022). Application of electronic nose to discriminate species of mold strains in synthetic brines. *Frontiers in Microbiology*, 1657. <https://doi.org/10.3389/fmicb.2022.897178>
- Tang, S., Avena-Bustillos, R. J., Lear, M., Sedej, I., Holstege, D. M., Friedman, M., et al. (2016). Evaluation of thermal processing variables for reducing acrylamide in canned black ripe olives. *Journal of Food Engineering*, 191, 124–130. <https://doi.org/10.1016/j.jfoodeng.2016.07.011>
- Wold, S., Esbensen, K., & Geladi, P. (1987). Principal component analysis. *Chemometrics and Intelligent Laboratory Systems*, 2(1–3), 37–52.