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Evaluation of different storage conditions of extra virgin olive oils with an innovative recognition tool built by means of electronic nose and electronic tongue

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Abstract

In the present work, the oxidation of extra virgin olive oils was considered at different storage periods and conditions. The oxidation is usually evaluated by applying an accelerated thermoxidation, while in this case real storage conditions were used. In order to study the differences of the storage situations, multivariate statistical analysis was applied on classical chemical determinations, electronic nose and electronic tongue responses.

Results showed how the electronic nose was enough to define the extra virgin olive oil oxidation and appeared to be able to describe the different storage conditions, while classical chemical parameters and electronic tongue were not relevant. In fact, the classification model built by means of linear discriminant analysis (LDA) gave an equal classification performance by considering all the variables or just the electronic nose sensor responses. Compared to classical methods, this new approach could represent an alternative and innovative tool for faster and cheaper evaluation of extra virgin oil oxidation.

Keywords: Extra virgin olive oil; Oxidation; Storage; Electronic nose; Electronic tongue; LDA

1. Introduction

Extra virgin oil is properly processed from fresh and mature high quality olives (*Olea europea L.*) and presents a complex flavour which is greatly liked by native consumers and internationally appreciated by gourmets (Kiritsakis & Min, 1989). Flavour is usually divided into the subsets of aroma and taste, which are perceived in the nose and in the mouth, respectively. Many authors in fact have clearly demonstrated that the flavour is mainly produced by volatile and phenol compounds (Flath, Forrey, & Guadagni, 1973; Morales, Aparicio, & Rios, 1994), most of which have been identified and quantified in different extra virgin olive oils (Tsimidou, Papadopoulos, & Boskow, 1992; Vichi et al., 2003).

Lipolysis and oxidation are the processes leading to the most serious deterioration of olive oil. Lipolysis usually starts when the oil is still in the fruit, while the oxidation begins at the processing stage and proceeds during storage influenced by exposition to air, heat, light and metals. Though extra virgin olive oil is considered to be a stable oil due to the presence of natural antioxidants, it is also susceptible to oxidation (Rovellini & Cortesi, 2002a). Volatile compounds are the main responsible of the pleasant flavour and change in off-flavours during the storage (Angerosa, Basti, & Vito, 1999; Morales, Rios, & Aparicio, 1997).

At present the classical methods used to ascertain extra virgin olive oil quality are based on chemical analysis (Regulation EEC/2568/91) and sensory analysis (Regulation

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EEC/796/02). However, these methods are expensive and time consuming.

Recently HPLC/GC–MS was applied to detect changes in the chemical composition of olive oil during the storage. HPLC with different detection systems has been used for hydroperoxide analysis (Oshima, Hopia, German, & Frankel, 1996). GC/MS was used to detect hydroxy fatty acids and volatile compounds originated from hydroperoxide degradation (Morales et al., 1997) and to identify the products of triglyceride oxidation (Rovellini, Cortesi, & Fedeli, 1998).

Each of these analyses only gives partial information about the extent of oxidation and there is a large demand for rapid, cheap and effective techniques for quality control of extra virgin olive oils. In recent years, considerable efforts have been devoted to the development of innovative analytical instrumentation such as the electronic nose and electronic tongue, which can mimic the human sense of olfaction and of taste and provide low-cost and rapid sensory information for monitoring food quality and state of a process.

The electronic nose consists of an array of gas sensors with different selectivity, a signal collecting unit and a suitable pattern recognition software (Gardner & Bartlett, 1993). It is particularly useful for the quality control in food or beverage production for monitoring flavour changes (Bartlett, Elliot, & Gardner, 1997; Jonsson, Winquist, Schnuerer, Sundgren, & Lundstroem, 1997; Schweizer-Berberich, Vaihinger, & Gopel, 1994).

In the literature, there are several examples that demonstrate the possibility of using an electronic nose for the characterization of vegetable oils (Gan, Che Man, Tan, NorAini, & Nazimah, 2005; Martin, Pavon, Cardero, & Pinto, 1999) and for the quality control of olive oil aroma (Guadarrama, Mendz, Saia, Ros, & Olas, 2000), while information about the use of an electronic nose to predict shelf life of vegetable oils or to monitor oil oxidation under real life storage conditions are not frequent (Shen et al., 2001).

The principle of the electronic tongue is similar to that of the electronic nose, except for the array of sensors, which is designed for liquids. Many publications report the application of the array of electrochemical sensors for beverage analysis and wine discrimination (Gallardo, Alegret, & Del Valle, 2005; Legin et al., 2003). Olive oils contain some redox active compounds such as polyphenols, tocopherols, etc. that have an important relevance in their organoleptic characteristics and antioxidant properties and could be analysed by means of electrochemical sensors (Campanella, Favero, Pastorino, & Tommasetti, 1999; Mannino, Buratti, Cosio, & Pellegrini, 1999).

The aim of the present research is to show how non destructive techniques in combination with multivariate statistical analysis can represent an effective device for the evaluation of the oxidative status of an extra virgin olive oil. Furthermore, the study has been conducted with the use of real life storage conditions and not by applying an accelerated thermoxidation process. In comparison to classical techniques, this approach could represent a faster and cheaper recognition tool for monitoring oil oxidation.

2. Materials and methods

2.1. Sample preparation

Fresh and mature olive samples were collected during years 2001 and 2002, from different cultivars and different Italian areas. From these olives, 61 mono-varietal samples of extra-virgin olive oil were properly obtained using a micro-oil press equipped with a hammer crusher, a vertical mixer and a two phase decanter (Alfa Laval). Each 2002 oil sample was divided in two aliquots: the first aliquot was stored under normal light, the second one under dark for one year. Instead, each 2001 oil sample was stored for two years under dark. All the samples were left at room temperature in 200 ml amber and transparent glass bottles (dark and light condition).

2.2. Chemical analysis

The chemical analysis included the measurement of several parameters. The acidity (acidity), which is indicative of the free fatty acid content of the oil expressed as oleic acid (%); the peroxide value (PV), which is a measure of the amount (meqO_2/kg) of the hydroperoxides formed through oxidation during storage; finally, the absorbances UV at 232 and 270 nm (K_{232}, K_{270} and ΔK) provide a measurement of the state of oxidation of the oils. The chemical analyses were performed in triplicate on each oil sample before and after storage according to official methods of the European Commission (Regulation EEC/2568/91).

All the used chemicals and solvents were of analytical grade.

2.3. Electronic nose

2.3.1. Apparatus

Analyses were conducted with a commercial electronic nose (model 3320 Applied Sensor Lab Emission Analyser, Applied Sensor Co., Linkoping, Sweden), comprising three parts: an automatic sampling apparatus, a detector unit containing the array of sensors, and a pattern recognition software. The automatic sampling system supports a carousel of 12 sites for loading the samples and permits the control of internal temperature.

The sensor array was composed by 22 different sensors. Ten sensors were metal oxide semiconductor field effect transistors (MOSFET), 12 were Taguchi type sensors metal oxide semiconductors (MOS). The MOSFET sensors were divided into two arrays of five sensors each, one array operating at 140 °C and the other at 170 °C, while the MOS sensors were kept at 400–500 °C during all the process phases.

2.3.2. Operating procedure

Aliquots of 1 g of each sample were introduced in 40 ml Pirex® vials with a pierceable Silicon/Teflon disk in the cap.

The measurement sequence started with the sample incubation at 40 °C for 10 min, before injection. After the headspace generation, volatile compounds were sampled by an automatic syringe and were pumped over the sensor surfaces for 60 s. During this time the sensor signals were recorded. Then sensors were exposed to filtered air at a constant flow rate (60 ml/min) in order to keep the gas sensor signal back to the baseline.

In a previous work, sample volume, incubation temperature, time of sampling step, injection time and temperature optimisation procedures were studied in order to obtain reproducible responses (Buratti, Benedetti, & Cosio, 2005). Each sample was evaluated in triplicate and the average of the results was used for subsequent statistical analysis.

2.4. Electronic tongue

2.4.1. Reagents

Chloroform was obtained from BDH (Poole, England); acetic acid was purchased from Riedel-de Haen (D-30926, Germany); hydroxy-2,5,7,8-tetramethylcroman-2 carboxylic acid (Trolox) and tetrabutyl-ammoniumbromide were purchased from Sigma–Aldrich (St. Louis, Mo, USA).

All solutions were prepared with double-distilled water.

2.4.2. Apparatus

A measurement system based on flow injection analysis (FIA) with two amperometric detectors was set up.

The FIA apparatus consisted of a Jasco (Tokyo, Japan) model 880 PU pump and two EG&G Princeton Applied Research (Princeton, NJ, USA) Model 400 thin-layer electrochemical detectors connected in series. Each detector was equipped with a working electrode (a dual and a single glassy carbon electrode, respectively), a reference (Ag/AgCl saturated) electrode and a platinum counter electrode. The connecting tubes were of peek (1.5 mm o.d. × 0.5 mm i.d.). Data were recorded using a Philips (Eindhoven, Netherlands) PM 8252 recorder.

In the flow system, a carrier solution was continuously pumped through the amperometric detectors and the samples were injected into the flow stream.

2.4.3. Operating procedure

Flow injection experiments were performed at room temperature using chloroform containing 2% acetic acid and 3.2% tetrabutyl-ammoniumbromide as carrier solution. The composition of the carrier solution was chosen on the basis of a previous work (Mannino et al., 1999).

Flow rate of 1 ml/min and injection volume of 20 μL were used. No sample preparation was needed except 1:100 dilution with the carrier solution before injection. Each sample was evaluated in triplicate and the average of the results was used for subsequent statistical analysis.

Amperometry is based on the oxidation or reduction of electroactive compounds at the working electrode, when a constant potential is applied; the measured current (μA) is a direct measurement of the electrochemical reaction rate. In the present work, a dual and single glassy carbon electrode in parallel configuration was used. The parallel configuration monitored in oxidative state at potential of +0.5, +0.6 and +0.8 V (vs. Ag/AgCl).

Furthermore, the FIA technique allows the control of the sensor drift by using a calibration sample that can be injected within a measurement series. In our work, the injection of a trolox standard solution before each oil sample and the recording of the ratio between the trolox and the sample signals solved the problem of sensor drift.

2.5. Data analysis

A data matrix with 61 rows (oil samples) and 30 columns (variables) was built. The variable description is provided in Table 1. Initially, this matrix was analysed by means of principal component analysis (PCA), in order to display the structure of the multivariate data. PCA is a well-known pattern-recognition technique, which projects the data in a reduced hyperspace, defined by the principal components. These are linear combinations of the original variables, with the first principal component having the largest variance, the second principal component having the second-largest variance, and so on. Since the variables have been measured in different units, the original variables were autoscaled.

Afterwards, samples were divided in three classes (see Table 2) and linear discriminant analysis (LDA) was applied in order to find a predictive classification model. LDA is one of the most used classification techniques (Lachlan, 1992): the method is a probabilistic parametric classification technique and maximizes the variance between categories and minimizes the variance within cat-

Table 1
List of the variables considered in the experimentation

	No. Variables	Variables	Code
Chemical	5	Acidity (%)	Acidity
		Peroxide value (meq O_2/kg)	PV
		Absorbance UV at 232 nm, 270 nm and ΔK	K_{232}, K_{270}, ΔK
E-nose	22	10 MOSFET sensors	FE
		12 MOS sensors	MO
E-tongue	3	3 Carbon electrode (+0.5, +0.6, +0.8 V) (vs. Ag/AgCl)	P500, P600, P800

The number of variables for each typology (chemical, electronic nose and electronic tongue) and the variable code are reported.

Table 2
Class definition

Class code	Storage condition	Storage period	No. samples
Class 1	Dark	1 year	16
Class 2	Light	1 year	16
Class 3	Dark	2 years	29

The storage condition, the storage period and the number of samples of each class are reported.

egories, by means of a data projection from a high dimensional space to a low dimensional space. In this way, a number of orthogonal linear discriminant functions equal to the number of categories minus one is obtained. The classification model was validated using a leave-one-out procedure. Each sample is removed from the data set, one at a time. The classification model is rebuilt and the removed sample is classified in this new model. All the samples of the data set are sequentially removed and reclassified. Finally a percentage of correct classification is calculated. The quality of the LDA classification model was considered on the basis of the validation results.

Principal component analysis was performed by using the statistical package SCAN (Minitab Inc., PA, 1995), and linear discriminant analysis by using SPSS (Inc., Chicago, 2004). The package STATISTICA (Statsoft. Inc., Tulsa, OK, 1998) was used for graphics.

3. Results and discussion

The quality of extra-virgin olive oils was ascertained with the following analytical parameters: acidity, PV, K_{232}, K_{270} and ΔK. As suggested by Regulation EEC/2568/91, these parameters are valuable olive oil freshness indices and the following limits for extra-virgin olive oils are established: acidity $\leqslant 0.8$, PV $\leqslant 20$, $K_{232} \leqslant 2.4$, $K_{270} \leqslant 0.22$ and $\Delta K \leqslant 0.01$ (Regulation EEC/1989/03).

The 61 oil samples, analysed before the storage, widely respected the limits of the afore-mentioned Regulation, confirming a good overall quality: these oils could be labelled as ''extra-virgin'' according to the European legislation.

Then the samples were analysed after 1 year of storage under dark (class 1), under normal light (class 2), and after 2 years under dark (class 3). All samples of the three classes presented an acidity value lower than 0.4, PV from 16 to 20 (class 1), from 17 to 61 (class 2) and from 17 to 39 (class 3). Except for class 1, most of the samples of class 2 and class 3 had UV values higher then the law limits.

At the end of their storage period, all the oil samples were also analysed with alternative and innovative techniques (electronic nose and electronic tongue). The responses obtained with the electronic nose (22 sensors) and the electronic tongue (three sensors) together with the classical chemical determinations (five parameters) calculated at the end of the sample storage period were considered all together and used for statistical analysis.

Initially, the data matrix with 61 rows (oil samples) and 30 columns (variables) was analysed by means of PCA, in order to study how the different storage conditions characterized the oil samples. The first principal component and the second principal component were enough to display the data structure, since they explained 61% of the total variance. Examining the score plot (see Fig. 1) in the area defined by the first two principal components, a separation of the samples into three groups was found according to the different storage conditions and storage periods. Only few samples belonging to class 3 were projected in the middle of class 1, but this does not affect the effectiveness of the plot.

Furthermore, on the basis of the position of each group in the plot, it was possible to assign a particular meaning to each component. The first component was able to separate the oil samples belonging to class 3 (characterized by negative values) from all other samples, i.e., the first component was able to characterize the samples on the basis of the storage period.

In fact, samples belonging to class 3 were characterized by a storage period of two years, while all the other samples by a storage period of only one year. On the second principal component, oil samples of class 2 had negative values, while all other samples had positive values, i.e., the second principal component was able to describe the samples on the basis of the storage conditions. In fact, class 2 samples were stored under light, while all other samples under dark.

Finally, a sample belonging to class 1 appeared far from its class space in the score plot. The highest scores on the first and the second component characterized this sample, labelled in the score plot as sample no. 10. As described before, the meaning of each component is related to the quality of the storage period and conditions. The highest positive scores on the two components were associated to the best storage situation, i.e., conservation under dark for one year. The behaviour of sample no. 10 confirmed this hypothesis: in fact, all the values of classical chemical

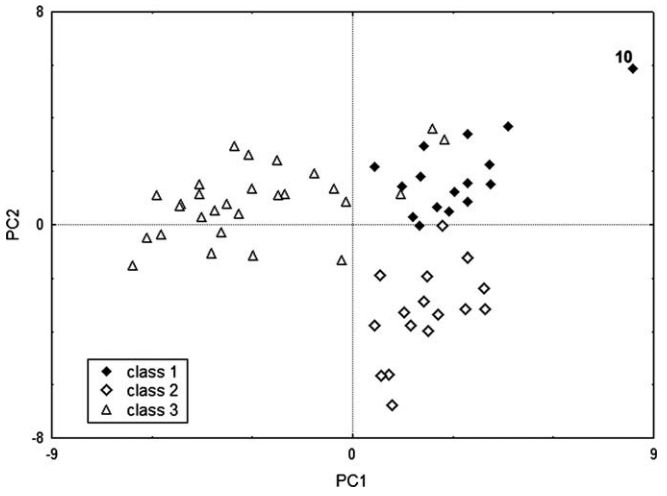

Fig. 1. PCA on autoscaled data: score plot. Classes are shown with different symbols (see Table 2 for class description).

parameters for this sample respected widely the law limits and allowed it to be considered as a extra-virgin olive oil. All other samples of class 1 could be considered as extra-virgin olive oils but presented PV and UV values near the law limits.

Since samples were well described in the score plot, the loading plot was analysed in order to show which variables influenced the group separation. As can be seen in the loading plot of the first two principal components (see Fig. 2), the majority of electronic nose sensors characterized the first principal component, while electronic tongue sensors, two sensors of electronic nose (FE101A and FE101B), and the PV were relevant on the second component. First of all, it is clear how the electronic tongue sensors were correlated giving the same information, as expected. The two types of electronic nose sensors (MOSFET and MOS) appeared different, since they grouped in different areas on the second component.

Furthermore, MOSFET sensors appeared more informative, since they showed high loading values on both components. It is important to notice that classical chemical variables did not appear relevant for the description of the samples under study. Acidity was placed in the middle of the loading plot: this variable did not have an impact on the group separation, i.e., in the description of the storage period and the storage conditions. Among classical chemical variables, the PV is the only with a high loading value, but, as can be seen in the loading plot, two electronic nose sensors (FE101A and FE101B) were placed close to it. This means that all these three variables had the same information, i.e., the PV could be removed without a decrease of discrimination capability. In conclusion, electronic nose sensors and electronic tongue sensors gave sufficient information to describe the different storage conditions and storage periods and appeared to be enough for the characterization of the three classes of oil samples.

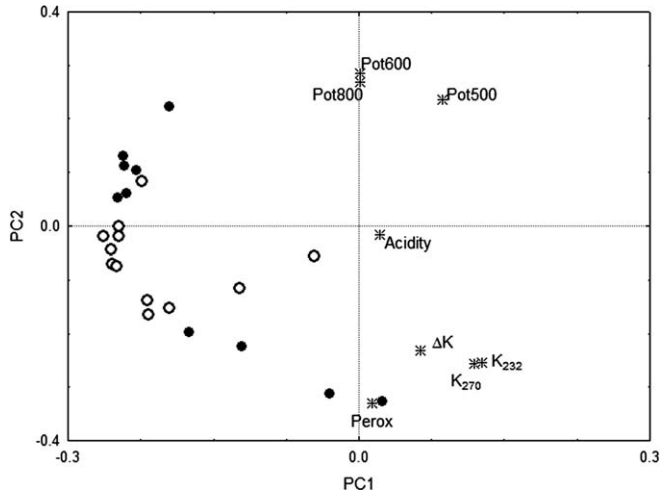

Fig. 2. PCA on autoscaled data: loading plot. Variables are shown with different symbols: electronic nose MOSFET sensors (dark circle), electronic nose MOS sensors (white circle), electronic tongue sensors and classical chemical variables (white square).

Since the data structure analysis gave a good sample characterization, a classification model was built. LDA analysis was applied in order to find a predictive classification model, able to separate the three described classes (see Table 2). In Table 3, the results of LDA and leave one out cross validation are reported. As can be seen, LDA applied to the complete data set gave a recognition percentage of 100%, while only one oil sample was not correctly classified in the validation procedure. Even if this model performed a good classification result, the classification after selection of a minimum number of variables was also considered. In fact, the PCA loading plot highlighted how the classical chemical variables did not appear relevant for the class discrimination or appeared correlated to electronic sensors and nose sensors. For this reason and in order to simplify the classification model by reducing the number of the considered variables, LDA was repeated by considering only the electronic nose and electronic tongue features. The classification model gave again 100% correct classification for three classes and only one wrong assignment in the validation procedure. The discriminant scores for the classification model with only the electronic nose and electronic tongue features (see Fig. 3) showed a clear class separation. More conclusions can be obtained by observing the plot of the standardized canonical discriminant function coefficients (see Fig. 4). In this plot the behaviour and the rule of each variable in the classification model can be analysed. It is clear that few sensors had high canonical discriminant function coefficients and that the electronic tongue sensors did not show a relevant role in the classification model, since they were placed in the middle of the plot, close to the axis origin. This result suggested the possibility of removing the electronic tongue sensors from the model, without a decreasing of its classification capability. Therefore, in order to simplify once more the classification model, LDA was repeated by considering only the electronic nose features.

As expected, the classification model gave the same results as before, i.e., a recognition percentage of 100%, and only one wrong assignation in the validation procedure.

Since an equal classification performance was obtained by considering only the electronic nose sensors, it is evident that chemical analyses and electronic tongue sensors were not required in order to achieve a better sample discrimina-

Table 3
Confusion matrix of the LDA classification model with all the variables (fitting and validation results are both reported)

	Classes	1	2	3	Total
Fitting	1	16	0	0	16
	2	0	16	0	16
	3	0	0	29	29
Cross-validation	1	16	0	0	16
	2	0	16	0	16
	3	0	1	28	29

Rows represent the true class, columns represent the assigned class.

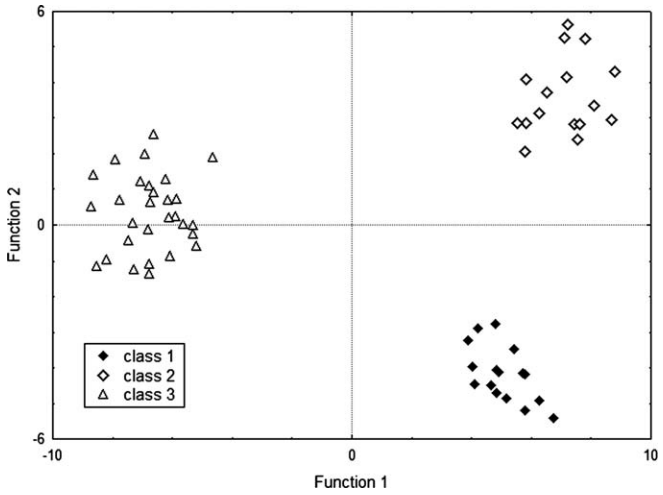

Fig. 3. LDA classification model with the electronic nose and electronic tongue sensors: discriminant scores. Classes are shown with different symbols (see Table 2 for class description).

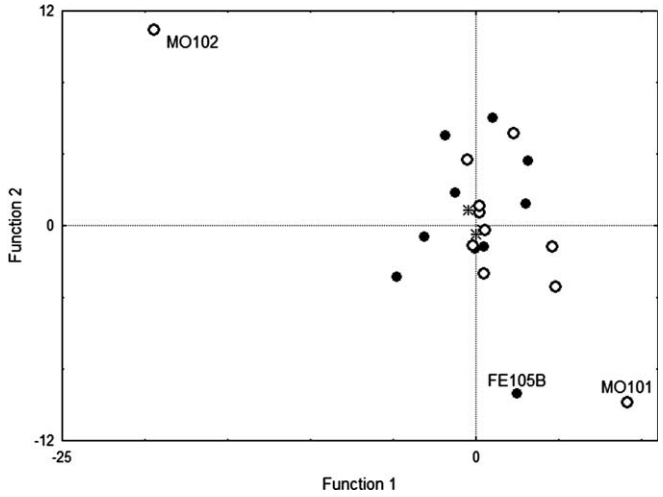

Fig. 4. LDA classification model with the electronic nose and electronic tongue sensors: standardized canonical discriminant function coefficients. Variables are shown with different symbols: electronic nose MOSFET sensors (dark circle), electronic nose MOS sensors (white circle), electronic tongue sensors (white square).

tion, i.e., chemical analyses and electronic tongue sensors did not improve the classification model.

4. Conclusion

This study evaluated the possibility of differentiate olive oil samples stored in different conditions and periods by using innovative analytical techniques, such as the electronic nose and electronic tongue, in combination with multivariate analysis.

Chemical parameters and electronic tongue did not appear as relevant in the LDA classification model. In fact, it has been showed that by removing chemical analysis and electronic tongue sensors, the classification performance is preserved and a more applicable model is obtained. The final classification model built by means of the electronic nose sensors was able to describe the samples storage conditions and could represent a simpler, faster, and cheaper recognition tool, since a minor number of variables must be determined.

In conclusion, this new approach could offer a valid alternative to the difficult and time-consuming traditional analytical methods and could be a useful tool for on line or routine determination of olive oil storage conditions.

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