DEGRADATION OF OLIVE OIL BY LIGHT OR HEATING. ELECTRONIC NOSE AND SENSORY DATA ANALYSIS

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Abstract

A comparison is made between results of edible oils gathered by sensory analysis and data obtained from an electronic nose. Both techniques were applied to the following cases: separation of soybean oil, sunflower oil, olive oil (ordinary olive oil) and virgin olive oil. Evaluation of degradation effects of olive oil and virgin olive oil due to oxidation processes produced by their exposition to daylight and heat, were also analyzed.

The importance of sensory analysis has grown (particularly, in case of olive oils) because of legislation in several countries (among them, U.S.A and the European Community) that require the application of sensory analysis to food and beverages before commercialization. However, as sensory analysis exhibits limitations due to its dependence of many physical and psychological factors affecting the subjectivity of human judgement, it is interesting to compare sensory panel results with electronic nose data, that is to say, with results from an olfactory system exhibiting higher objectivity and invariable response with time (contributing to the success of a routine analysis).

Resumen

En este trabajo se efectua una comparación entre los resultados del análisis sensorial de aceites de oliva comestibles y los datos de una nariz electrónica. Ambas técnicas fueron aplicadas a los siguientes casos: separación de aceite de soja, aceite de girasol, aceite de oliva (aceite de oliva puro) y aceite de oliva virgen.

La evaluación de los efectos de la degradación del aceite de oliva y del aceite de oliva virgen, debidos a los procesos de oxidación producidos por su exposición a la luz del día y al calor, es también discutida.

La importancia del análisis sensorial ha crecido (particularmente, en el caso de los aceites de oliva) porque la legislación en varios países (entre ellos EE.UU y la Comunidad Europea) requiere el análisis sensorial de alimentos y bebidas antes de su comercialización. Como el análisis sensorial presenta limitaciones debido a su dependencia de factores físicos y sicológicos que afectan la subjetividad del juicio humano, ha resultado interesante comparar las evaluaciones del panel sensorial con los datos de una nariz electrónica, es decir, con los resultados de un sistema olfativo que presenta mayor objetividad y respuesta invariable con el tiempo (lo que contribuye al éxito de un análisis de rutina).

Introduction

Sensorial analysis (SA) is commonly used for quality control of food and beverages [1]. The importance of sensory results is growing since legislation in various countries requires sensory essays to be performed for commodities prior to their commercialization. In the case of olive oil, several descriptive norms have already been established [2,3]. In the European Community legislation there are standards by which the authenticity of virgin olive oil can be analized, taking into account not only its chemical composition but also its genuine sensory attributes [4].

However, sensorial analysis suffers from some major drawbacks arising from the subjectivity of human judgement, which strongly depends on many physical and psychological factors [5]. For these reasons, electronic noses (EN) have been developed and improved in the last decades to be used as comparative tools. The advantages of EN in comparison with the human olfactory system include: higher objectivity, invariable response with time that contribute to the success of routine analysis [6].

The aim of this work was to compare results of the SA and NE analysis of the odors of edible oils: soybean oil, sunflower oil, olive oil (ordinary olive oil) and virgin olive oil along with the characterization of the different oxidation processes of olive oil and virgin olive oil under daylight or heat.

A considerable increase of olive oil consumption due to its beneficial effect on health (prevention of coronary diseases, diabetes, obesity and thrombosis risks, among others) was observed in the last decade. The occidental diet includes a 60-70% of saturated fatty acids (SFA): lauric, miristic and palmitic acids which are responsible of the increase of cholesterol. An usual strategy is to reduce SFA in the diet by replacing them with poly-unsaturated (PUFA) or mono-unsaturated (MUFA) fatty acids to decrease the total cholesterol amount. PUFA like linoleic or linolenic acids as well as oleic acid (MUFA) are contained in olive oils [7].

Besides, there is another important problem to be considered: edible oils suffer degradation by exposition to air, heat, light being this oxidation also influenced by antioxidants and by the fatty acid composition of oils [8].

Volatile compounds appear in different oils because of lipolysis and oxidation processes. Lipolysis (enzymatic and microbiological activity) usually starts when oil is still in the fruit, while oxidation begins after the oil is obtained from the fruit and proceeds mainly during storage [9]. Mainly carbonyl compounds, alcohols, esters and hydrocarbons, are found in the volatile fraction of virgin olive oil. The C6 and C5, especially C6 linear unsaturated and saturated aldehydes represent the most important fraction of volatile compounds, meanwhile C7-C11, monounsaturated adehydes or C6-C10 dienals, or C5 ramified aldehydes and alcohols reach high concentrations in the aroma of virgin oliva oil affected by organoleptic defects [10, 11].

Experimental Procedure

Sensory analysis

For both experiments, aliquots of 120 ml of oil samples were introduced in 250 ml polyethylene bottles and closed for a day before sensory analysis. Bottles were masked with paper strips to avoid visual cues of stimuli.

A forced-choice triangular test was employed, participants smelled the three coded bottles birhinally, knowing that two samples were identical and the third different. They had to select the different odorous sample. The customer six possible permutations were presented in balanced order to the panelists.

Experiment I: from a population with similar demographic background and age (20-22 years) three groups were asked to discriminate vegetable oils by their odor. Group A composed by 39 feminine (F) and 21 masculine (M) evaluated in two triads soybean oil versus extra-virgin olive oil and soybean oil versus olive oil, respectively. Group B (36F, 24M) compared in two triads sunflower oil versus extra-virgin olive oil and sunflower oil versus olive oil, respectively. Group C (50F, 10M) had to discriminate by odor only extra-virgin olive oil versus olive oil. The discrimination task of Group C was performed after tasks of A and B groups have already been done. Many panelists from groups A an B participated in group C, to avoid the possibility that insufficient understanding of the method might affect differences in olfactory discrimination of both olive oils.

Experiment II: another group with the same population (35F, 10M) evaluated, in the same way as in Experiment 1, two blocks (B1, B2) of two triangles each. Task B1 encompassed comparisons of recently opened samples of olive oil (extra-virgin or olive oil) versus those stored under daylight for a month. B2 group discriminated recently opened samples of olive oil (extra-virgin or olive oil) versus those heated at 180°C for an hour.

With regard to the statistical analysis, it was proved that panelist groups were able to appreciate differences among odors of the oils to be compared. For the case of 60 panelists, a significant discrimination of the whole panel ($p < 0.001$) was accepted if more than 33 panelists gave a correct judgment (55% of the group). For the case of 45 panelists, 26 correct decisions were minimally required (58% of the group) to obtain a significant discrimination of the whole panel ($p < 0.001$).

Frequency of gender and smoke status of panelists were subjected to χ^2 test to check whether those variables affected discriminatory olfactory ability.

Electronic nose analysis

MOSES II (MOdular SEnsor System) was the Electronic Nose (EN) used in the present work. It contains two modules of gas sensors: one of them with eight quartz microbalance sensors (QMB) with different polymer coatings and the other with eight SnO_2 semiconductor sensors (with pure or doped SnO_2). In the case of this work both sensor sets, tin oxide and QMB, were used in all the evaluations.

A DANI HSS 86.50 headspacer was used to incubate and thermostate the samples before placing them into the sensor chambers. Synthetic air was used as gas carrier, with a flow rate: 20 ml/min.

Experiment I:

The four oil types: sunflower oil (SFO), soybean oil (SO), olive oil (OO) and extra-virgin olive oil (EVOO) were analyzed with the MOSES II EN. Five specimenss of each oil, containing 3g each, were poured in 10 ml vials which were hermetically closed with Teflon septa and aluminium seals. Incubation for 5 min with intervals of 10 min between specimenss was performed at a temperature of 40°C.

Experiment II:

Oxidation by light was produced exposing the specimens to daylight for four weeks. The specimenss consisted of 3 g of the five specimenss (extra-virgin olive oil and olive oil) poured in each 10 ml vial.

With regard to oils oxidation by heating: oils were fried at 180 ^{o}C for an hour. From fried extra-virgin olive oil and olive oils, five specimenss (3 g each) were taken. For comparison, five specimens (3 g each) of both oils (but taken from a recently open bottling) were used.

The incubation time was 5 min for both degradation processes at a temperature of 40 ^{o}C for each specimens, with 10 min intervals between them.

Results and Discussion

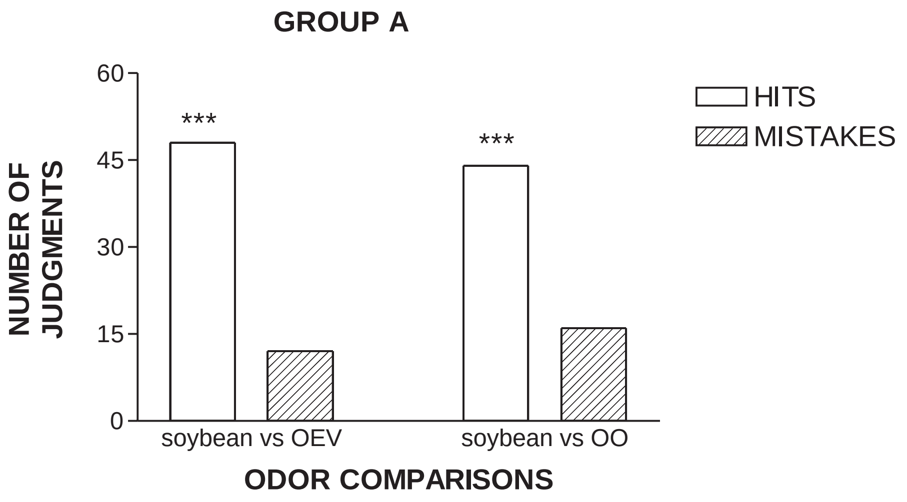
Sensorial Analysis

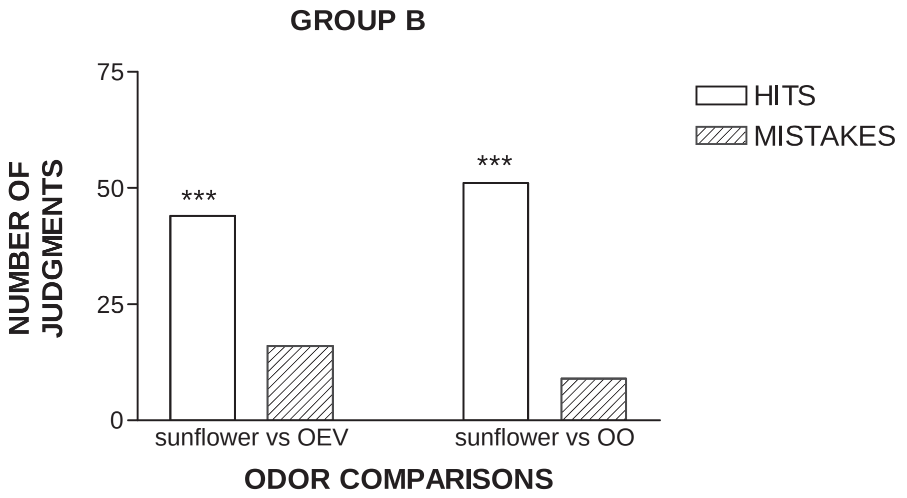
Figure 1 shows the discrimination results of groups A (top) and B (bottom). Both, extra-virgin olive oil and olive oil were significantly discriminated from soybean oil. Both types of olive oil were also discriminated from sunflower oil. Extra-virgin olive oil was discriminated by 73.3% of panelists of group B and olive oil was differentiated by 85% of panelists of group B. The achievement to distinguish among vegetable oils were qualified as trivial cases for the performance of commercial sensor devices [12] however they confirm the physiological ability of panel members.

Figure 2 depicted the fifth triangular output. The group C failed to discriminate by smelling between olive oil categories. Only one third of tasters reach the correct decisions.

The inability of the human panel may be the result of a cognitive deficit for this edible odor. Consumer status of olive oil was not considered, only the absence of olfactory dysfunctions was taken into account. On the other hand, subjective odor distances between different vegetable oils are larger than those exhibited by different categories of olive oil. Short-term memory capacity for odors was proved to be an important factor in discriminative performances [13]. In general, the largest number of panelists showed a memory span of three (three odors may be remembered in working memory) and the distribution of memory spans was almost normal. Thus, the task difficulty may be greater for only some subjects with low memory span for odors.

Gender and smoker status were not significant factors in olfactory discrimination for the three groups of panelists.





Figures 1: (a) *Sensory (triangle) indicating hits and mistakes for soybean oil discrimination from extra-virgin olive oil (OEV) and olive oil (OO), respectively and* ***(b)*** *Sensory analysis indicating hits and mistakes for sunflower oil discrimination from extra-virgin olive oil (OEV) and olive oil (OO), respectively.*

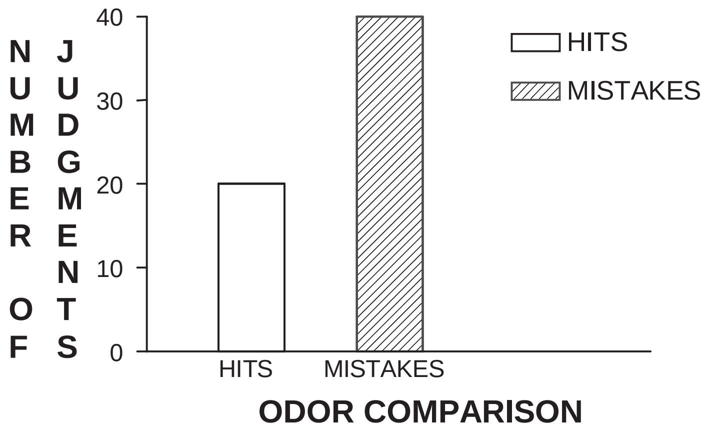


Figure 2: *Sensory analysis describing hits and mistakes for discrimination between extra-virgin olive oil and olive oil.*

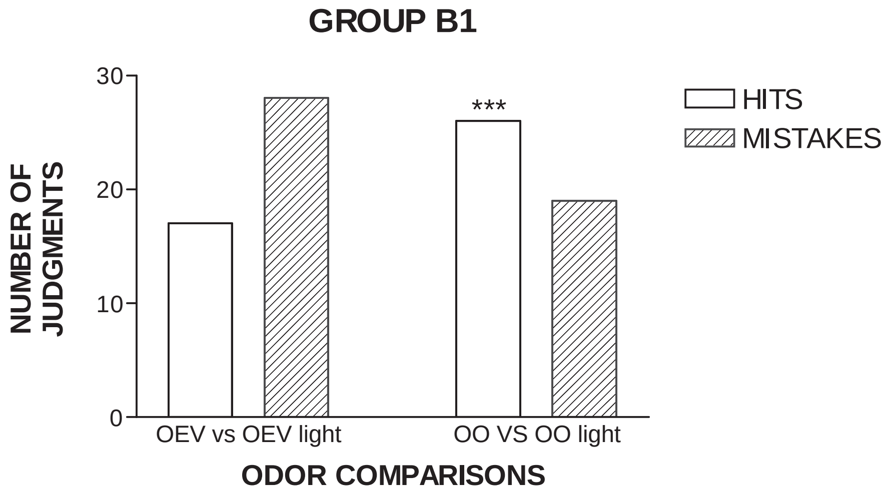


Figure 3: *Sensory analysis showing hits and miss-hits for discrimination of daylight-non-degraded olive oil (OO) and extra-virgin olive oil (OEV) from daylight-degraded olive oil (OO light) and extra-virgin olive oil (OEV light).*

Changes of olive oil odor after being exposed to daylight storage are shown in Figure 3. Significant changes were observed for olive oil. 58 % of the discriminated samples by the panel were stored for a month at room temperature, exposed to daylight, however the panel made a lot of mistakes ($p > 0.05$) by smelling recently opened bottles of extra-virgin olive oil samples compared with those stored under the same conditions.

It is interesting to point out that virgin olive oil exhibits a significant proportion of phenolic compounds caused by hydrolysis products of oleouropein, which are important because of their significant contribution to flavor, odor, bitterness, pungency, oxidation stability and nutritional value of this characteristic oil of the Mediterranean diet [14]. Perhaps, the antioxidant activity of the extra-virgin olive oil markedly reduces the sensory difference between control and treated samples.

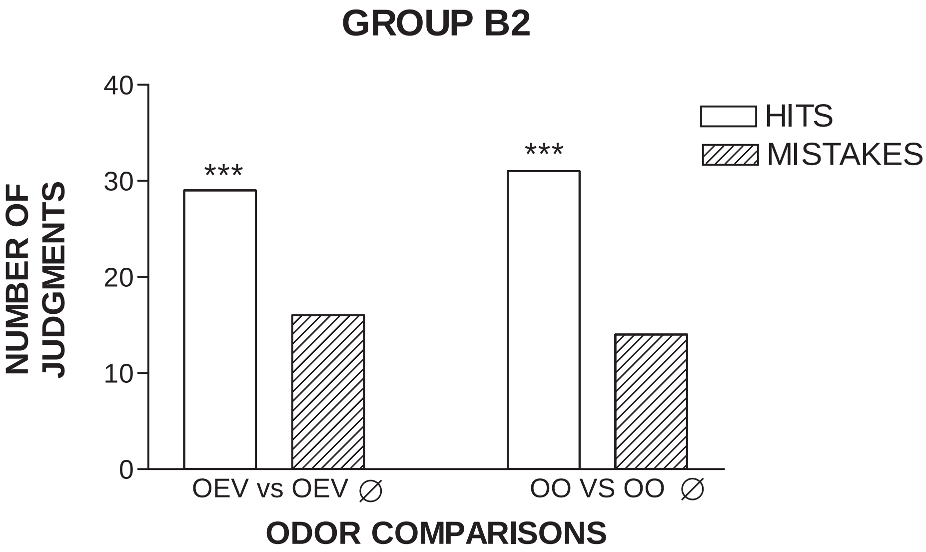


Figure 4: *Sensory analysis indicating hits and miss-hits for discrimination of olive oil non-degraded by heat (OO) and extra-virgin olive oil (OEV) from degraded olive oil by heat (OOϕ) and extra+virgin olive oil (OEVϕ).*

Results of fried oils (Figure 4) clearly showed differences in control and heated samples for both olive oils, extra-virgin with 64.4% of hits and olive oil with 68.9%. The relation between the odor perceived by a panelist and the chemical species present in the flask depends on many parameters, such as partition coefficients, volatility [15] and odor activity attributes [16]. Alternatively, the impairment of sensory quality may be detected by an increase of hexanal, which may be easily tracked by human nose. Once again, neither gender nor smoker status have affected the proportion of hits in these sensory difference tasks.

Electronic nose

Figure 5 is the PCA plot corresponding to the different types of studied edible oils, a good discrimination among their odors can be appreciated. It is also observed that the extra-virgin olive oil and the olive oil data are contained in nearer areas while the sunflower oil and the soybean oil data are situated in areas far from those of olive oils and nearer to data corresponding to an empty vial (EV) taken as reference. The whole information is 92.9%, corresponding a 7.1% to the PC3 contribution, which is not taken into account in the PCA plot.

If EN data taken from pairs of oils were compared, as it was already done with sensorial analysis, both oils were always clearly discriminated. All the PCA plots were similar, therefore was chosen only one pair of them (Figure 6) corresponding to extra-virgin olive oil and olive oil. Figure 6 was intentionally chosen because the EN clearly discriminated both oils by their odors while in the sensorial analysis only one third of panelists arrive at correct decisions.

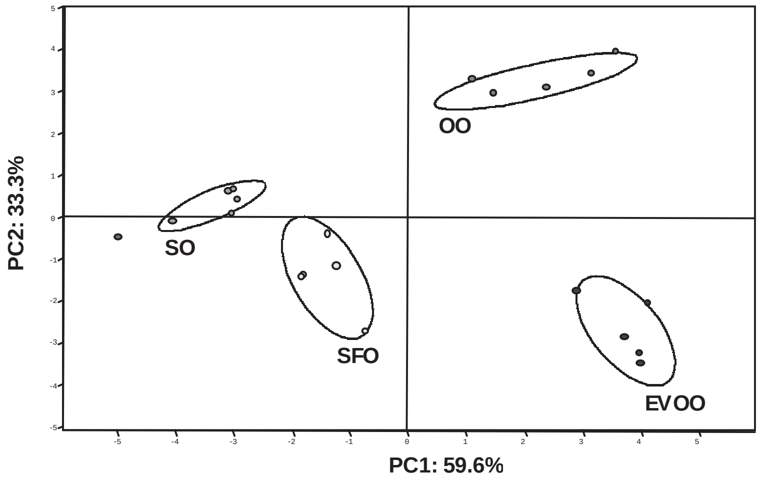


***Figure 5**: PCA plot discriminating the four types of studied edible vegetable oils: soybean (SO) sunflower (SFO), olive (OO) and extravirgin olive (EVOO).*

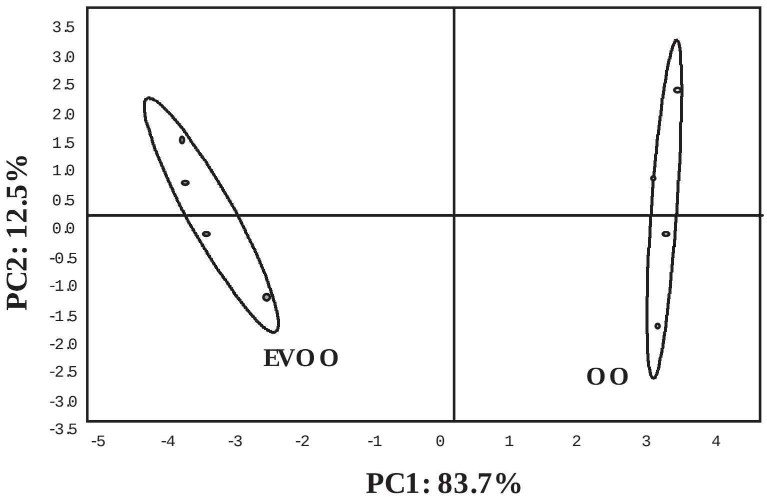


***Figure 6:** PCA plot discriminating between olive oil (OO) and extra virgin olive oil (EVOO).*

Figure 7 corresponds to the PCA plot of non-degraded by light and degraded by light extra-virgin olive oil and olive oil specimenss. Clusters corresponding to non-degraded and degraded specimens of the same type of olive oil, were well discriminated. The PCA plot showed that degradation seems to be stronger for olive oil since both clusters (degraded oil and non-degraded oil) are more separated. The information from (PC1 + PC2) resulted 99.4%.

Figure 8 is the PCA plot of non-degraded by heat and degraded by heat extra-virgin olive oil and olive oil specimenss. The information from (PC1 + PC2) resulted 98.9%. In case of heating, the degradation of both types of oils seems to be very similar

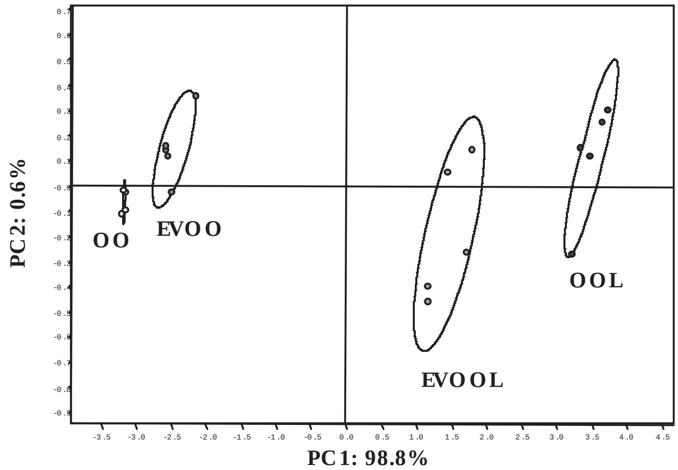


Figure 7: *PCA plot discriminating non-degraded by daylight olive oil (OO) and extra-virgin olive oil (EVOO) from degraded by daylight olive oil (OOL) and extra+virgin olive oil (EVOOL).*

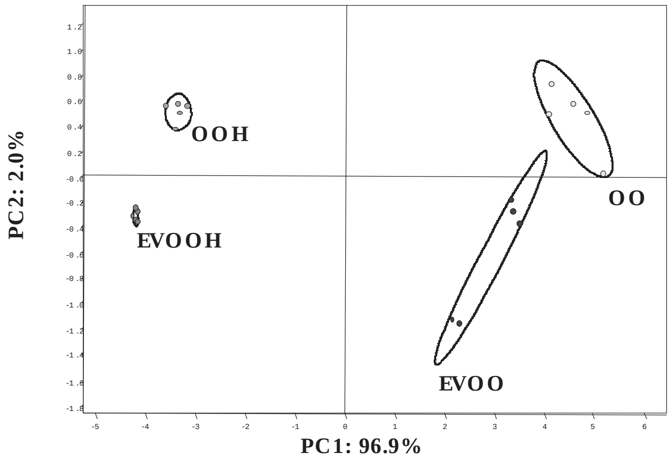


Figure 8: *PCA plot discriminating non-degraded by heat olive oil (OO) and extra-virgin olive oil (EVOO) from degraded by heat olive oil (OOH) and extra-virgin olive oil (EVOOH).*

since the separation of clusters of both, non-degraded and degraded specimens data, seemed to be the same.

Conclusions

- Sensorial panel discrimination by triangle analysis of soybean and sunflower oils comparatively with extra-virgin olive oil or olive oil was successful, panelists were not successful to discriminate the two types of olive oils between each other. On the other hand, the e-nose could clearly not only discriminate the four studied oils: soybean oil, sunflower oil, extra-virgin olive oil and olive oil but, also the two types of olive oils.

- Non-degraded and degraded by daylight specimens of both types of olive oils, as analyzed by sensorial panel, have shown opposite results, i.e. a higher number of miss-hits comparatively to hits for extra-virgin olive oil and a higher number of hits in comparison with miss-hits for olive oil. Discrimination with the e-nose has shown that olive oils degradation by light seemed to be stronger for olive oil than for the extra-virgin type. This fact enables to infer that odorous products from the most degraded by light olive oil could be more easily smelled by the panel.

- Non-degraded and degraded by heat specimens of both types of olive oils, as analyzed by the sensorial panel, have shown successful results in both cases since the number of hits is higher than that for miss-hits. Otherwise, the number of hits and miss-hits for both types of oils are very similar, indicating that the emission of odors from products of degradation was able to be smelled similarly by the panelists. E-nose data have shown a similar separation of non-degraded and degraded by heat specimens data pointing to a similar oxidation process by heat in both types of olive oils.

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