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Analysis of Virgin Olive Oil Volatiles by a Novel Electronic Nose Based on a Miniaturized SAW Sensor Array Coupled with SPME Enhanced Headspace Enrichment

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A novel electronic nose based on solid-phase microextraction (SPME) coupled with a surface acoustic wave (SAW) sensor array has been used to analyze different quality virgin olive oils. A mathematical model was designed with 37 samples to distinguish lampante from the other virgin olive oils categories (extra-virgin and virgin), because lampante-virgin olive oils cannot be consumed without a previous refining process. The model, successfully validated with a test set of 16 samples, was able to classify 90% of the samples correctly. Misclassifications were explained by SPME-HRGC analyses and a second sensory evaluation.

KEYWORDS: **Surface acoustic wave sensors; electronic nose; solid-phase microextraction; virgin olive oil**

INTRODUCTION

According to the current European Union (EU) regulation (*1*), virgin olive oils (VOOs) are classified into three categories of sensory quality: extra-virgin, virgin, and lampante. It is important to distinguish lampante-virgin olive oils from these categories because they cannot be consumed without a previous refining process. Furthermore, these designations also affect the market prices of the oils. The classification of oils into the three categories is performed by sensory and chemical analyses, mainly carried out by panel test (sensory assessment) or chromatographic techniques (HRGC) (*1*, *2*). However, these methods are lengthy and expensive, and they cannot be applied on-line. Other inconveniences are the subjectivity of assessors or analysts' errors, which increase the risk of wrong classifications.

The alternative to these methods is the use of sensors for detecting volatile compounds present in the headspace of foodstuffs. Sensors usually have the advantages of low cost, simple handling, portability, and small size. Furthermore, they do not need reagents, and they are rapid supplying results to the analyst (*3*). Yet sensors obviously have disadvantages mainly focused on their signal drift, recovery, and humidity and temperature dependence (*3*, *4*). Recently, metal oxide sensors have been used in distinguishing different quality virgin olive oils (*5*, *6*). On the other hand, surface acoustic wave (SAW) sensors have already been proven to be suitable in electronic nose applications. These sensors have very fast response times, and they are used at room temperature. The sensing mechanism of this kind of sensors is based on the change in mass, which results from the interaction between an analyte and an interactive coating (*7*).

Although sensor systems are useful for on-line screening, many studies are being carried out to enhance their performance (*3*). Concerning SAW sensors, the improvements are mainly focused on developing new coatings and sampling systems (*8*, *9*) to detect volatiles in the ppm−ppb range with good reproducibility. A further increase of sensitivity is typically achieved by preconcentrating the volatiles from the sample matrix prior to the analyses. The enrichment and preconcentration techniques for volatile compounds are commonly based on a preconcentration unit, containing a sorbent material which adsorbs the analyte from the sample headspace. The thermally desorbed volatiles are then swept by the carrier gas to the sensor system. In this way, many analytes can be preconcentrated by several orders of magnitude (*9*). Recently, solid-phase microextraction (SPME), a preconcentration technique previously used in gas chromatography, has been proposed as a general enrichment method for volatile compound analyses (*10*). Thus, the SPME technique has been applied in many fields, including food flavor analysis, because it is rapid, sensitive, and solvent-free (*11*). In fact, SPME fibers have been used for extracting volatile compounds from the headspace of virgin olive oil to be injected into a GC system (*12*).

The aim of the current paper was to optimize and develop a method based on a SAW-based micro-nose coupled with a SPME technique to distinguish lampante from nonlampante virgin olive oils. A mathematical model was designed with a

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training set and was validated with an external set of samples to check the performance of the method for this application.

MATERIALS AND METHODS

Sensor Coatings. The polymer coatings were as follows: poly(methacrylic acid) butyl ester (PBMA), polyisobutylene (PIB) and polyepichlorohydrine (PECH) (all Fluka, Buchs, Switzerland); ethylene glycol adipate (Riedel-de Haën, Seelze, Germany); glycidoxypropylmethyl dimethylsiloxane (ABCR, Karlsruhe, Germany); L grease (Apiezon, London, UK); poly(chlorotrifluoroethylene-*co*-vinylidene fluoride) (Aldrich, Milwaukee, WI); polyurethane alkyd resin with trace isocyanates (RS Components, Corby, UK); and silar-10C (Alltech, Deerfield, IL).

Samples. A lampante VOO (*var*. Hojiblanca) was used to optimize the procedure, while an extra-virgin olive oil of the same variety was the reference standard used in the repeatability studies. Thirty-seven samples of virgin olive oil (*var*. Hojiblanca) were used for training the sensors (training set). The samples were supplied by an association of cooperatives (Hojiblanca SCA, Málaga, Spain) that represents 4% of the total Spanish olive oil production. The assessors of the cited association qualified 18 of these samples as lampante VOO. On the other hand, the mathematical model (canonical equation) was checked with a test set of 16 samples (*var*. Arbequina, Cornicabra, and Picual), collected in different geographical regions, supplied by ACESUR (Seville, Spain), five samples being classified as lampante by the trained assessors of the enterprise. All of these samples were sensory evaluated by assessors of Instituto de la Grasa.

SPME Sampling Equipment. Sampling was performed with a Multi-Purpose Sampler MPS2 (Gerstel, Mülheim an der Ruhr, Germany), equipped with headspace incubation chamber and SPME sampling unit. The SPME fiber holder and fibers fitting to the MPS2 were obtained from Gerstel (Mülheim an der Ruhr, Germany) and Supelco (Deisenhofen, Germany).

Fibers with several kinds of coating materials with different film thickness are commercially available. We tested the following (Supelco, Deisenhofen, Germany): poly(dimethylsiloxane) (PDMS) with a film thickness of 100 μm, 75 μm carboxen/poly(dimethylsiloxane) (CAR/PDMS), and 50/30 μm divinylbenzene/carboxen/poly(dimethylsiloxane) (DVB/CAR/PDMS).

Vials (22 mL) with magnetic screw cap and PTFE septum were purchased from Supelco. A septumless sampling head (Gerstel, Mülheim an der Ruhr, Germany) was used as the interface for the SAW system.

Sensor Devices and Micro Array. The sensor devices used in this work are based on a special surface transverse wave (STW) resonator design (*13*). The frequency of operation was 433 MHz. The sensors were coated with commercially available polymers to provide chemical selectivity. Eight noncontinuously working SAW oscillators were combined into a sensor array, each device being coated with a different coating material. The frequencies of the devices were gathered consecutively using a multiplexing technique (*14*), with a read-out period of 1 s. An additional uncoated SAW device, driven within a single continuously operating oscillator, was used as a common reference for frequency mixing with the single multiplexed sensor signal. Gas sampling was achieved via two milled parallel gas channels underneath four sensors in line.

The micro array was placed directly behind a permanent inlet port with an extra connector for the carrier gas. The sensors were permanently purged with nitrogen, providing a perfect baseline. Humid nitrogen, when it was used, was obtained by bubbling the nitrogen stream through a saturated salt solution of NaCl.

Method After Optimizing. First, 5 g of the sample was transferred to 22 mL glass vials with Teflon-coated septa and magnetic caps. The sample was preheated for 10 min of equilibration time, defined as the time necessary for the volatile substances of the solution to reach equilibrium with the headspace. Next, the SPME fiber (DVB/CAR/PDMS) was exposed for 40 min at 35 °C in the headspace; meanwhile the vial was agitated. After the exposure, the fiber was withdrawn from the sample and directly inserted into the septumless injector for thermal desorption at 230 °C and kept there until desorption finished (5 min). A stream of carrier gas (humid nitrogen) drained the desorbed volatile substances from the injector to the SAW detector at a flow rate of 0.75 mL/min. Blank runs were performed regularly prior to the sample analysis to ensure the removal of impurities. Each new fiber was conditioned before its use as recommended by the manufacturer.

Data Processing. The frequency shift was recorded by using in-house software. Although the sensor responses showed an exponential-like shape, only the maxima were selected because they showed the best differential properties.

The effects of fiber and sensor aging and the environmental conditions were checked by analyzing a standard sample after each series of analyses.

The detection of multivariate outliers was carried out by applying principal components analysis (PCA) (*15*). Mahalanobis distance, evaluated as χ^2, was used to discover outliers among cases (samples), while outliers among variables (sensor maxima) were detected by the squared multiple correlation.

Data were submitted to linear discriminant analysis (LDA) for the fiber selection. Stepwise linear discriminant analysis (SLDA) was applied under the strictest conditions for the selection of the variables to diminish over-optimistic models. Tolerance was fixed at 0.01, while the F-to-Enter value (6.0) was obtained from the F-distribution table at $F(F) = 0.975$ for the number of groups ($m = 2$) and the group with the minimum number of samples ($n = 18$) (*15*).

The Statistica software (Statsoft Inc., Tulsa, OK) release 5.5 (*16*) was used to perform the data processing and to implement multivariate data analyses.

SPME-HRGC Analysis. First, 0.5 g of virgin olive oil with 3.33 mg/kg of 4-methyl-2-pentanol added as internal standard were placed into a 20 mL glass vial. The vessel was tightly capped with a PTFE septum placed in a thermostatic block at 40 °C. The fiber (DVB/CAR/PDMS, 50/30 μm, Supelco, Deisenhofen, Germany) was exposed to the oil headspace for 40 min. After this extraction time, the fiber was inserted into the injector port of the GC at 260 °C.

GC analyses were performed on a Varian 3900 gas chromatograph (Varian Inc., Walnut Creek, CA) equipped with a flame ionization detector (FID) and coupled to an autosampler (Combipal CTC analytics AG, Zwingen Switzerland). The carrier gas was hydrogen at a flow rate of 1.5 mL/min. Separation of compounds was carried out on a capillary column TR-WAX of 60 m × 0.25 mm i.d. × 0.25 μm thickness (Teknokroma, Madrid, Spain). The column temperature was held at 40 °C for 10 min, and then increased to 200 °C at a rate of 3 °C/min. The detector temperature was 260 °C. The desorption time of the fiber into the injection port was 5 min. The signal was recorded and processed with WorkStation version 5.5.2 software (Varian Inc., Walnut Creek, CA).

Organoleptic Assessment. The sensory evaluation of olive oil is regulated inside the European Communities (*1*). The method describes a set of positive (fruity, bitter, pungent) and negative (fusty, musty, winey-vinegary, muddy sediment, metallic, and rancid, among others) sensory attributes that are applicable to the organoleptic assessment and classification of virgin olive oil by means of the assessors of a panel test. The method confines all of the virgin olive oil samples into three categories, extra-virgin, virgin, and lampante-virgin olive oils. All of the described samples were subjected to this method implemented by three different panel tests.

RESULTS AND DISCUSSION

Optimization of SPME-SAW Sensor Micro Array Measurements. An optimization process of the measurement variables was carried out because there was not any previous experience in the analyses of virgin olive oil by SAW sensors coupled with a SPME preconcentration system. The optimization process concerned the most significant variables affecting the measurements: the extraction time, the sample temperature, and the flow rate of the carrier gas. Furthermore, a lampante VOO was subsequently analyzed by using PDMS, CAR/PDMS, and DVB/CAR/PDMS fibers to optimize the variables for these three fibers.

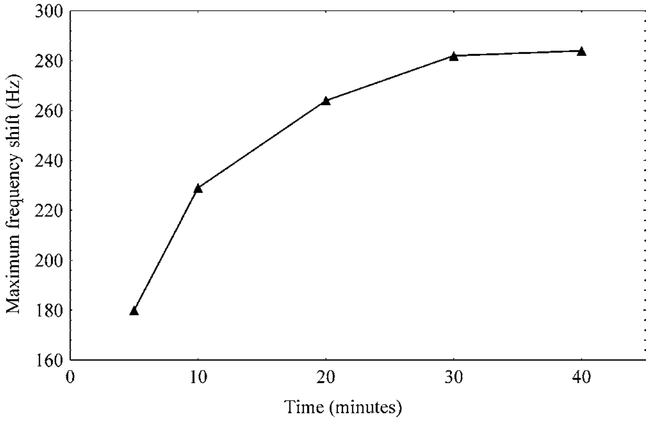

Figure 1. Sensor responses to a lampante virgin olive oil using different extraction times (SPME fiber coating: CAR/PDMS).

Two desirable characteristics were evaluated in the sensor responses: the intensity (maximum) and the velocity of the sensor responses. A high response was required to obtain good sensitivity and repeatability. On the other hand, the sensor response should be rapid enough to allow a fast recovery of the baseline and slow enough to obtain a few data in the steady state because the read-out of the sensor array is one per second.

(a) Optimization of SPME Extraction Time. The coated SPME fiber enriches analyte vapor until an equilibrium is reached between the analyte concentrations in the headspace and on the sorbent material of the fiber, respectively. The higher the concentration and the lower the boiling point of the analyte, the faster the sorbent material will be saturated. The effect of saturation is demonstrated for lampante VOO in **Figure 1**. Different extraction times were evaluated (5, 10, 20, 30, 40 min). At the beginning, the sensor response increases with the extraction time. However, after 30 min of extraction time, the sensor responses do not show a significant increase. Therefore, an extraction time of 40 min was considered as optimum including an extra time of 10 min to ensure that the fibers are saturated in any experiment.

(b) Optimization of Sample Temperature. The samples were preheated for an appropriate equilibration time at a suited temperature. Different values were studied (35, 45, 55 °C). The temperature showed a slight effect on the sensor responses, despite promoting the volatile compound enrichment in the headspace. In previous papers about the analysis of VOO volatile compounds, the authors had established that the sample temperature in headspace studies should not be above 50 °C to avoid the degradation of some volatiles (*17*). In consequence, 35 °C was considered to be the optimum for VOO SPME-SAW sensor analyses.

(c) Optimization of Carrier Gas Flow. To optimize the shape of the sensor response, several carrier gas flow-rates (0.75, 1.25, 1.75, 2.00 mL/min) were tested. A flow-rate of 0.75 mL/min was selected, because the sensor signals obtained with this flow rate showed the longest equilibrium state in the maximum and the highest desorption slope.

Repeatability Studies. Drift is one of the main problems that must be overcome when working with sensors, and it is caused by changes in the physical properties of the sensors (i.e., aging) or the SPME fibers (i.e., film deterioration). The drift obviously increases, together with the random analytical errors, the relative standard deviation in repeatability. To determine how much of the sensor response is due to the content of the volatile compounds versus the inherent variance of the whole method, a reference standard oil was daily analyzed during 10 days with the aim of obtaining information about the repeatability between days (also called intermediate precision). Three repeatability studies (**Table 1**) were carried out, keeping constant all of the variables excepting the carrier gas for desorbing the volatiles from the SPME fiber and, subsequently, the kind of coating of the SPME fiber. The objective was to check the effect of these two variables (carrier gas and coating) over the method precision. The study of the carrier gas was done with humid and dry nitrogen, while the study on the fiber coating was carried out with CAR/PDMS and DVB/CAR/PDMS.

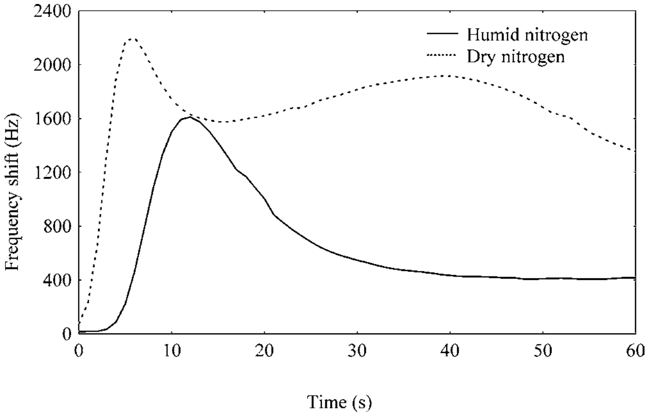

Figure 2. Sensor responses to a virgin olive oil analyzed by using both dry and humid nitrogen.

Table 1. Relative Standard Deviations (%RSD) for the Repeatability Studies Carried Out with Dry (Fiber Coating CAR/PDMS) and Humid (Fiber Coatings CAR/PDMS and DVB/CAR/PDMS) Nitrogen

	dry nitrogen	humid nitrogen	
sensor	CAR/PDMS	CAR/PDMS	DVB/CAR/PDMS
1	3.01	6.45	3.03
2	5.38	9.21	2.64
3	7.82	5.85	3.91
4	2.34	8.16	2.93
5	12.44	6.59	5.87
6	6.05	6.83	5.64
7	5.51	7.87	6.43
8	5.74	6.31	4.26
mean	6.04	7.16	4.34

The effect of the carrier gas (humid nitrogen vs dry nitrogen) on the sensor signal and the repeatability was checked first. **Table 1** shows that the relative standard deviation (%RSD) values were a little lower in the repeatability study with dry nitrogen. **Figure 2** shows sensor signals derived from measurements with pure and humid nitrogen, respectively (constant conditions of all parameters). The signal of measurements with dry nitrogen shows two maxima: the first maximum can be assigned to the VOO, whereas the second broad maximum is ascribed to the humidity in the headspace over the sample. In contrast, the signal of measurements with humid nitrogen shows only one maximum, because the marginal humidity increased by the sample is compensated by the high humidity in the carrier gas. In consequence, the humid nitrogen makes the sensor responses to moisture reach saturation, thus avoiding the effect of humidity on further analyses. Therefore, humid nitrogen was considered to be the optimum carrier gas, despite showing a little bit higher %RSD values.

The effect of the kind of fiber coating on the sensor response was studied next. Preliminary analyses were performed by using humid nitrogen and three kinds of fibers (PDMS, CAR/PDMS, DVB/CAR/PDMS). The fiber coated with CAR/PDMS provided

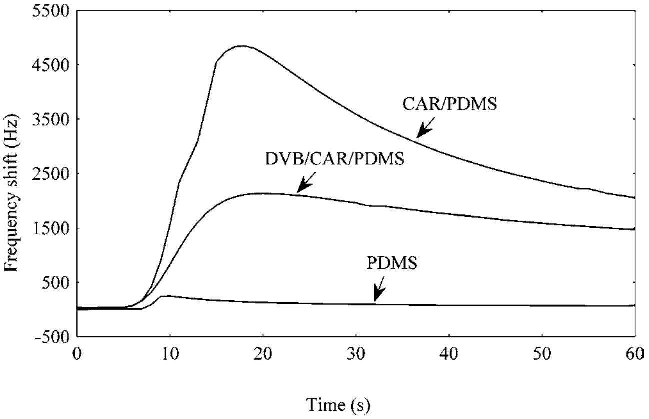

Figure 3. Sensor responses to a virgin olive oil analyzed by using different SPME fiber coatings.

Table 2. Squared Mahalanobis Distances and Number of Misclassifications Distinguishing between Lampante and Nonlampante Virgin Olive Oils[a]

	CAR/PDMS	DVB/CAR/PDMS
squared Mahalanobis distance	6.47	14.08
number of misclassifications	5	1

[a] Studies carried out with two fiber coatings.

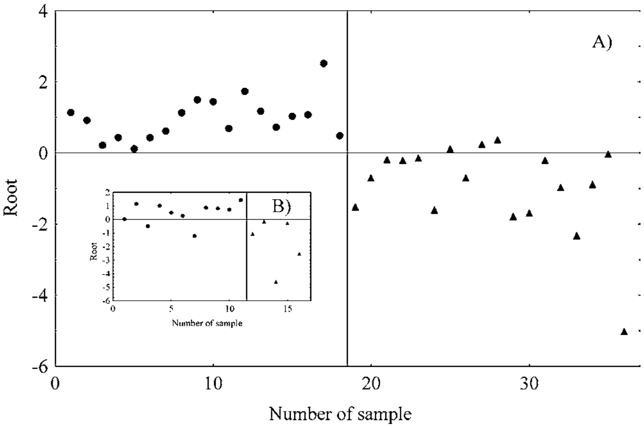

Figure 4. Results of applying the canonical equation to the samples of the training and test sets: nonlampante VOO (●); lampante VOO (▲).

Table 3. Concentration (mg/kg) of the Most Relevant Volatile Compounds Quantified in the Three Misclassified Samples in the Training Set, a Fusty Standard Virgin Olive Oil (VOO) and Nonlampante VOOs

	misclassified samples			fusty	nonlampante
volatile compound	sample 1	sample 2	sample 3	VOO[a]	VOO[b]
ethyl acetate	2.81	1.48	0.90	0.48	0.49
hexanal	2.99	1.19	1.01	0.32	0.62
(*E*)-2-hexenal	1.06	0.52	0.48	1.70	0.18
pentan-1-ol	0.09	0.04	0.11	0.43	0.10
6-methyl-5-hepten-2-one	0.11	0.07	0.05	0.55	0.05
acetic acid	tr[c]	tr	tr	1.60	tr
propanoic acid	tr	tr	tr	15.60	tr
pentanoic acid	tr	tr	tr	2.48	tr
hexanoic acid	tr	tr	tr	0.33	tr

[a] Concentrations reported by Morales et al. (*2*). [b] Means of the concentrations in all of the nonlampante VOOs. [c] Trace.

the highest responses of the sensors (**Figure 3**), while the lowest values corresponded to the fiber coated with PDMS exclusively. These results agree with the conclusions achieved by Vichi et al. (*11*) and Aparicio et al. (*12*) for the analyses of VOO by SPME-HRGC. Furthermore, Vichy et al. (*11*) also reported the poor repeatability of the fiber only coated with PDMS, and, in consequence, it was not used in the following experiments. **Table 1** also shows the %RSD values of the analyses carried out with the fibers coated with CAR/PDMS and DVB/CAR/PDMS. The %RSD values of the fiber coated with DVB/CAR/PDMS were slightly lower than CAR/PDMS fiber, all of the values being lower than 10%. Therefore, the fibers coated with DVB/CAR/PDMS and CAR/PDMS were selected as the most suitable, taking into account their repeatability and response intensity.

Classification of Olive Oils. Once the method was optimized, the training set samples were analyzed by using both CAR/PDMS and DVB/CAR/PDMS fibers to determine what fiber provided the best performance distinguishing lampante and nonlampante VOOs. Before any mathematical model was designed, results were submitted to PCA to detect multivariate outliers among the data. Thus, this multivariate procedure detected an outlier among cases (a nonlampante VOO). The analysis of volatiles by SPME-HRGC confirmed its singularity as it contained a very high amount of methyl acetate (21 mg/kg) in comparison with the other oils (mean 0.4 mg/kg).

After the outlier sample was removed, a linear discriminant analysis (LDA) was applied to the training set data to distinguish between lampante and nonlampante VOOs. **Table 2** shows the squared Mahalanobis distances and the number of misclassifications for the analyses carried out with both kinds of fibers. The fiber coated with DVB/CAR/PDMS provided the highest squared Mahalanobis distances. Hence, it was selected for building a mathematical model that distinguished lampante VOO from nonlampante VOO by means of stepwise linear discriminant analysis (SLDA). This mathematical procedure selected two out of eight variables (sensors), and the canonical equation, based on the response of sensors 2 and 7, is as follows:

$$y = 0.01 \times \text{sensor2} + 0.05 \times \text{sensor7} + 0.61 \qquad (1)$$

Figure 4A shows the results of the canonical equation when applied to the training set. The *x*-axis shows the sample number, while the *y*-axis points out the quality level of the samples according to the sensor responses. The positive values then correspond to nonlampante VOOs (high sensory quality), whereas the negative values indicate lampante VOO (low sensory quality). The mathematical procedure was able to classify 100% of the nonlampante samples and 83% of the lampante samples, three of them being erroneously classified. This result was similar to that obtained in a previous study carried out with metal oxide sensors (*5*). The diversity of off-flavors (rancid, winey-vinegary, musty, fusty, etc.) and the width range of their intensity explain that the model found more difficulties in clustering the lampante VOOs. In a new sensory evaluation performed at Instituto de la Grasa, the panelists detected the fusty defect in these misclassified samples. Nevertheless, the major volatile compounds commonly present in fusty oils (e.g., propanoic and pentanoic acids) (*2*, *18*) were not identified by SPME-HRGC (**Table 3**). On the contrary, other volatile compounds (i.e., ethyl acetate, (*E*)-2-hexenal, pentan-1-ol) that contribute to characterize the virgin olive oils also contribute to the perception of the fusty defect, although only if they are present at different concentrations. It seems that the concentrations of these volatile compounds in the misclassified samples (**Table 3**) were not high enough to classify them as lampante VOO by the sensors, but they were sufficiently high for the panelists to detect the fusty perception. Anyway, the misclassified samples are placed inside a hypothetical threshold zone between both kinds of olive oil sensory classes.

Once the model was designed, the canonical equation was validated with an external test set of 16 samples. The validation allowed one to check the influence of the olive tree variety (Arbequina, Cornicabra, and Picual vs Hojiblanca) and the sensory evaluation (the panel tests of ACESUR vs Hojiblanca SCA) on the model. The equation classified 88% of the samples (**Figure 4B**). Only two samples were erroneously classified, an extra-virgin and a virgin olive oil (nonlampante samples). The former oil was newly classified by the panelists of Instituto de la Grasa as a nonlampante VOO, although they perceived a slight vinegary defect, probably detected by the sensors that are very sensitive to acetic acid (*19*). However, the second oil was classified as lampante VOO due to the rancid defect (median of defects = 6), which explains its classification as lampante VOO by the sensors.

In summary, the proposed model was able to distinguish lampante VOOs from nonlampante VOOs. SPME-HRGC analysis of the volatile compounds and the organoleptic assessments explain the doubtful classifications (three in the training set and two in the test set). The SAW sensors coupled with the SPME preconcentration technique have proved to be useful in classifying virgin olive oil samples into two classes according to their sensory quality.

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