JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

J. Agric. Food Chem. 2009, 57, 11543–11549 11543
DOI:10.1021/jf902109y

Evaluation of Wine Aromatic Compounds by a Sensory Human Panel and an Electronic Nose

Teresa Arroyo,*,† Jesus Lozano,‡ Juan Mariano Cabellos,† Mar Gil-Diaz,† Jose Pedro Santos,§ and Carmen Horrillo§

†Departamento de Agroalimentación, IMIDRA, Finca El Encín, A-2 Km. 38 2, 28800 Alcalá de Henares, Madrid, Spain, ‡Grupo de Sistemas Sensoriales, Universidad de Extremadura, Avenida Elvas s/n, 06071 Badajoz, Spain, and §Instituto de Física Aplicada, Consejo Superior de Investigaciones Científicas, C/Serrano 144, 28006 Madrid, Spain

A comparative study between the perception and recognition thresholds of volatile components calculated for an electronic nose and a human sensory panel is presented. The electronic nose is home-developed for wine purposes and is based on thin film semiconductor sensors. The human sensory panel is formed by 25 tasters with previous experience in wine tasting. Both systems were trained in parallel to detect 17 volatile compounds involved in aromatic and off-flavor notes (grouped under 9 aromatic descriptors) from the threshold concentrations found in the literature (*T*) to increasing concentrations (*T*, 2*T*, and 4*T*). The results showed that the perception level of the human nose is superior in relation to the electronic nose, but the electronic nose gave better results in the recognition threshold of the some aroma. According to these results, it can be concluded that the electronic nose could be a useful complementary tool to sensory human panels.

KEYWORDS: Electronic nose; human panel; odor threshold; aroma; wine

INTRODUCTION

Aroma is one of the main factors contributing to the quality of wines. The aroma of wine is very complex and is the simultaneous result of a great number of aromatic molecules belonging to different families such as alcohols, esters, aldehydes, ketones, fatty acids, and terpenes. The number of odorants that can be found in a wine in a concentration above the threshold is relatively high (up to 50) (*1*−*4*), and the quantitative analysis of some of these components is extremely difficult and expensive (*5*). The contribution of each compound to the entire aroma can be estimated by its odor activity value (OAV). Compounds with OAV ≥ 1 are considered to have an active contribution in the wine aroma (*1*−*3*). Usually, 20 odorants are always present in this group, and in some cases its OAV can exceed 20 aromatic units; this group of aromas is denominated "base aroma". A second aromatic group also present in wine is integrated by 16 compounds with an OAV < 1 aromatic unit; this group is denominated "fine (subtle) aroma" of wine (*6*). Finally, a third group of 20 aromas is present in wines with special characters. This group is designated "impact aroma" (*7*). OAV depends on the concentration and threshold value of the compound in wines. The perception threshold is defined as the minimum concentration of aroma perceived for at least 50% of the members of a sensorial panel. The minimum concentration necessary for odor identification is designated the recognition threshold and is usually higher than the perception threshold. Another term related to the olfactory threshold detection is the difference threshold detection, the minimum amount of an aroma that has to be added to a product already containing this aroma in order to produce an appreciable sensory change. Generally, sensory analysis, based on trained expert panelists, is the most precise approach for wine classification and quality control, because the nose can detect compounds at concentrations that cannot be detected by any other method. Human assessment, however, can be time-consuming and expensive.

In recent years there has been a growing interest in the development of electronics noses (*8*) and their application in the food and beverage industry. An interesting application is the determination of quality because it represents a means of reducing reliance on human judgment, reducing time and cost (*9*).

An electronic nose is usually formed by four elements: a sampling system, an array of chemical sensors, an instrumentation system, and a pattern recognition system. The sampling system extracts a representative fraction of the wine aroma and carries the volatile compounds to the sensor cells. The gas sensors transform the aroma into electrical signals that are measured by the instrumentation and control system. The pattern recognition system processes the data from the sensors with the aim of identifying and classifying the samples in the classes previously learned.

A great deal of research toward the development of electronics noses and their application to wine interpretation has been carried out (*10*−*13*). These systems have been used to analyze the headspace of several foods or beverages (*14*, *15*). In particular, attempts have been made to discriminate wine types and varieties and also to detect wine aging (*15*−*22*) using a variety of chemical sensors, including the use of resistive metal oxide semiconductor (MOS) sensors (*23*−*25*).

*Corresponding author (telephone +34 918879486; fax +34 918879492; e-mail teresa.arroyo@madrid.org).

Published on Web 11/18/2009

Table 1. Aromatic Compounds Used in the Training and Selection of Members of the Sensorial Panel

descriptor	pure standard compound	descriptor	pure standard compound
fruity-like	ethyl octanoate	oxidation	acetaldehyde
	isoamyl acetate		
	hexyl acetate	chemical	isoamyl alcohol
	ethyl cinnamate		3-methylbutanol
	ethyl isobutyrate		decanoic acid
	ethyl hexanoate		sulfur dioxide
	ethyl isovalerate		ethanol
	2-methylethyl butyrate		
		woody-like	β-damascenone
herbaceous	1-hexanol		γ-octalactone
	cis-3-hexenol		γ-nonalactone
	benzaldehyde		δ-decanolactone
			(*E*)-whiskey lactone
spicy	eugenol		2-furanmethanethiol
	2-methyl-3-methoxy-pyrazine		
		off-flavor	ethyl acetate
phenolic	guaiacol		ethanethiol
	4-vinylguaiacol		2,4,6-trichloroanisole (TCA)
	4-ethylguaiacol		
	vanillin		
microbiological	diacetyl		
	butyric acid		
	isovaleric acid		
	octanoic acid		
	acetoine		
	acetic acid		

The response of the electronic nose is based on the behavior of the sensors when they are exposed to the wine aroma. The development of electronic noses is focused toward the total or partial substitution of human panels in the evaluation of the quality and aroma of wine. At the moment, no comparative study that connected both sensorial systems had been described for wines. In these sense it would be helpful to determine if an electronic nose can be a valid substitute for human odor panels in the evaluation of the aromatic composition and quality of wine.

To contribute to this knowledge, a comparative study between a human sensory panel and an electronic nose has been carried out in our laboratory. Both systems were trained in parallel with aromatic compounds. Their perception and identification thresholds of volatile components involved in aromatic and off-flavor notes in wine were compared.

MATERIALS AND METHODS

Aromatic Compounds. Thirty-eight aromatic compounds of white and red wines belonging to different chemical families and grouped under nine aromatic descriptors of wine quality were used in the training and initial selection of the members of a sensorial panel. These descriptors were fruity-like, herbaceous, spicy, phenolic, microbiologic, oxidation, chemical, woody-like, and off-flavors (**Table 1**). Finally, a set of the 17 most frequent compounds in wine was selected and used in the training of a final panel. **Table 2** shows these volatile compounds with their odor descriptors and their threshold values (*T*) found in the literature (*1*, *2*, *26*, *27*). These threshold values were used in the initial phases of the training of the panel, in which solutions of pure chemical compounds at different concentrations were presented to the panel.

Sample sets with the 38 aromatic compounds were prepared at three different concentrations: *T*, 2*T*, and 4*T*. When the panel did not perceive the 4*T* concentration, 6*T* and 8*T* concentrations were used in the next session of training. These concentrations correspond to 1, 2, 4, 6, and 8 times the threshold value of detection of the volatile compounds. All compounds were of analytical quality and were provided by Sigma-Aldrich and Merck.

Table 2. Odor Threshold, Odor Description, Perception, and Recognition Threshold of Volatile Compounds (*1*, *25*, *26*)

descriptor	volatile compound	odor threshold (*T*) (μg/L)	odor description
fruity-like	ethyl octanoate	5	fruity, fresh
herbaceous	1-hexanol	8	green, dry
spicy	eugenol	6	clove, balsamic
	2-methyl-3-methoxy-pyrazine	0.002	pepper
phenolic	4-vinylguaiacol	1146	phenolic,
	vanillin	0.2	vanilla, candy
microbiological	diacetyl	100	butter
	butyric acid	173	cheese
oxidation	acetaldehyde	50000	oxidation
chemical	3-methylbutanol	29930	oily, alcoholic
woody-like	β-damascenone	0.1	tinned peach
	δ-decanolactone	88	coconut
	γ-nonalactone	30	coconut, wood
	(*E*)-whiskey lactone	67	flowery, lactone
off-flavor	ethyl acetate	12500	glue, solvent
	ethanethiol	0.1	garlic, onion
	2,4,6-trichloroanisole (TCA)	3	cork, mushroom

Sensory Panel. Twenty-five subjects with experience in wine analysis were selected and subsequently trained in recognizing 38 active aromatic compounds of wine. In the training program all compounds were presented to the panelists at threshold concentration (*T*) in a control synthetic wine. Standard solutions were diluted with water and/or ethanol (adjusting final ethanol content to 12%, v/v) at concentrations typically found in wine. All solutions were amended with 5 g/L tartaric acid, and the pH was adjusted at 3.2 with 1 M NaOH (*28*). The tasters were also trained with increasing concentration levels of the aroma. An experimental young white wine from Airén variety and a young red wine of Tempranillo variety were used as control wines. 1-Hexanol, ethyl octanoate, 4-vinylguaiacol, butyric acid, acetaldehyde, 3-methylbutanol, and ethanethiol, typical of white wines, were added to the Airén wine and eugenol, 2-methyl-3-methoxypyrazine, vanillin, β-damascenone, δ-decanolactone, γ-nonalactone, (*E*)-whiskey lactone, ethyl acetate, and 2,4,6-trichloroanisole (TCA), generally more characteristic of red wines, were presented in the Tempranillo wine. First, the original concentration of the aromatic compounds in these wines was quantified by CG-MS (*29*). The results showed that all compounds were under threshold human detection with the exception of ethyl octanoate and 3-methylbutanol, which presented OAVs > 1. Finally, 7 experimental white wine sample sets and 10 experimental red wine sample sets were obtained, and the only difference from their corresponding test wine was the concentration of one aromatic compound. Each sample set was made of three levels of concentration *T*, 2*T*, and 4*T*. Sensory evaluations were realized under ISO standards related to methodology (ISO 3972:1991), sensory analysis vocabulary (ISO 3972:1991), tasting room (ISO 8589:1988), and selection and formation of tasters (ISO 8586-1 and -2:1993). ANOVA analysis ($p < 0.05$) was applied to the rate of the correct panelist responses after they arranged eight levels of concentration, from *T* to 8*T* of ethyl octanoate (fruity-like) and ethyl acetate (off-flavors) sample sets. The trial consisted of the determination of the perception and recognition threshold by triangular probe (ISO 4120:1983) of each aroma when it was added to synthetic or experimental wines. To avoid a saturation effect in tasters, the training was carried out in ten sessions on different days. Two aromas with six levels each one were performed by session.

Electronic Nose. The electronic nose was developed in the IFA laboratory for wine discrimination purposes. The array is composed of 16 thin film tin oxide sensors, with thickness between 200 and 800 nm, doped with small amounts of chromium and indium to increase their selectivity. Sensors were deposited by reactive sputtering onto an alumina substrate. Details of the preparation can be found elsewhere (*30*, *31*). The array was placed in a 20 cm^3 stainless steel cell, and the temperature operation was kept at 250 °C with a PID temperature controller. The sampling method used to extract the volatile compounds was headspace followed by dynamic injection. Ten milliliters of sample was kept in a Dreschell bottle at 30 °C. The headspace was carried by an inert gas for 20 min to the sensor cells. The carrier gas used was nitrogen, 99.998% purity, at a constant flow of 200 mL/min. A block diagram of the measuring system is shown in refs *9*, *14*, *15*, and *21*. The resistance of the sensors was measured with a Keithley 2700 71/2 digit digital multimeter (DMM) with a 40-channel multiplexer connected to the personal computer through a GPIB interface.

The individual sensor responses (r) were defined as follows with respect to the minimum resistance to 12% (v/v) of ethanol for all measurements: $r = R_{wine}/R_{calibration}$, where R_{wine} is the minimum resistance of the sensor in the measurement of wine and $R_{calibration}$ is that of the sensor exposed to a solution of 12% ethanol. Measurements of this ethanol solution were made to compensate sensor drift. After the feature extraction, preprocessing was performed on the data (centered and scaled). The data collected were analyzed using a commercial software package [Matlab 6.1 for programming the feature extraction and the pattern recognition techniques (principal component analysis, PCA; artificial neural networks, ANNs)].

PCA applies a linear transformation to the data and results in a new space of variables called principal components (*32*). Probabilistic neural networks (PNN) were used for classification purposes. Leave-one-out (LOO) cross-validation method was applied to the network to check the performance of the network (*32*). LOO consisted of training N distinct nets (in this case, N is the number of measurements) by using $N - 1$ training vectors, whereas the validation of the trained net was carried out by using the remaining vector, excluded from the training set. This procedure was repeated N times until all vectors were validated (*33*, *34*).

RESULTS AND DISCUSSION

The first step in the estimation on the detection and recognition threshold of target compounds of wine aroma was to provide a reliable sensory odor panel. Initially, 36 volunteer subjects from investigation groups IMIDRA, IFA, and staff cellars took part in the training program during several months. Sample sets of synthetic wines amended with the 38 compounds grouped under the 9 aroma descriptors (fruity-like, herbaceous, spicy, phenolic, microbiologic, oxidation, chemical, woody-like, and off-flavors) were given to the panelists. Thirty subjects that were able to correctly classify 80% of the compounds continued with the training. In a second stage the tasters were trained to classify and order in decreasing concentration order (8, 6, 4, 2, and 1 times the threshold value) each of the compounds added to the experimental wine. Finally, 25 people were selected to take part in the human sensory panel.

Finally, 17 usual volatile compounds were subjected to sensorial panel and electronic nose evaluation to compare the performances of both systems. These compounds are summarized in **Table 2**, and they were used for the training of the human panel.

Figure 1 shows a typical response of several sensors of the array, operating at 250 °C, exposed to the headspace of one of the samples. The response of the sensors corresponds to several pulses of 20 min of exposure to the tested wine flavor followed by a pure nitrogen purge for 40 min. All samples were measured at least eight times by the sensor system. All data obtained were normalized (mean normalization: $x' = x - \text{av}/\text{SD}$, where av is average and SD is standard deviation of all data) before PCA. The distribution of values for each sensor across the entire database is set to have zero mean and unit standard deviation.

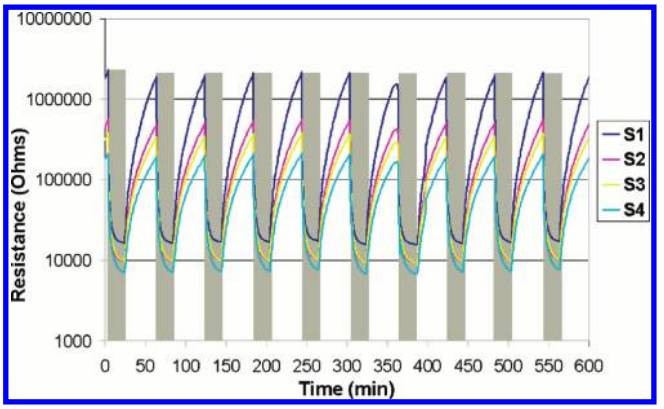

Figure 1. Response of several sensors of the array (S1−S4), operating at 250 °C, exposed toward the headspace of one of the samples.

Threshold Detection. From the results of the olfactory analysis of the tasting panel, the percentages of members who detected the aroma were calculated. A total of 17 aromatic compounds were included in the study and individually added at T, $2T$, and $4T$ concentrations to its correspondent base wine. Sixteen of them were perceived by at least 50% of the members of the panel at T threshold concentration value; only eugenol was detected at $2T$ concentration.

The discrimination of the proof wine with respect to the adulterated one was performed in a satisfactory way by the electronic nose, although a 100% correct classification was never achieved; TCA, vanillin, diacetyl, ethanothiol, γ-nonalactone, (E)-whiskey lactone, 2-methyl-3-methoxypyrazine, ethyl octanoate, 1-hexanol, β-damascenone, and acetaldehyde were well classified to T concentration value. In the case of eugenol, butyric acid, and δ-decalactone, the detection level was $4T$ value. The PCA plot of some aromatic compounds is reflected as an example in **Figure 2**. The variance explained by each principal component is in parentheses. The 1-hexanol PCA plot (**Figure 2a**) shows that the blank wine cluster is clearly separated from the wine containing compound clusters. Only the data sets corresponding to 1 and 2 times the threshold concentrations showed partial overlapping. **Figure 2b** shows the PCA plot for acetaldehyde. It can be observed that wine and 1 times the threshold concentration clusters are clearly separated, but there is an overlapping between measurements corresponding to 2 and 4 times the threshold concentration. Saturation in the response of the sensors to this compound has occurred. The PCA plot for eugenol in red wine is shown in **Figure 2c**. The cluster clearly separated from the others is the one corresponding to 4 times the threshold concentration. In this case, the system cannot differentiate the adulteration at low concentrations. The last PCA plot shown in this figure is for ethyl acetate (**Figure 2d**). An overlapping between the clusters of 1 and 2 times the threshold concentration can be observed.

PCA plots showed that the ellipses are separated and differentiated for wine reference in most of compounds. There was an overlapping between the wine and some concentration of the compound in some cases and total concentration confusion in other cases due to sensor saturation even from T concentration value. The PCA results are confirmed with a nonlinear method of classification: PNN analysis. The PNN was trained with the measurement data, and the percentage of answers correctly classified by the network is shown in **Table 3**.

Threshold Recognition. The perception of nondefined variations in wine aroma notes to determine its quality or composition

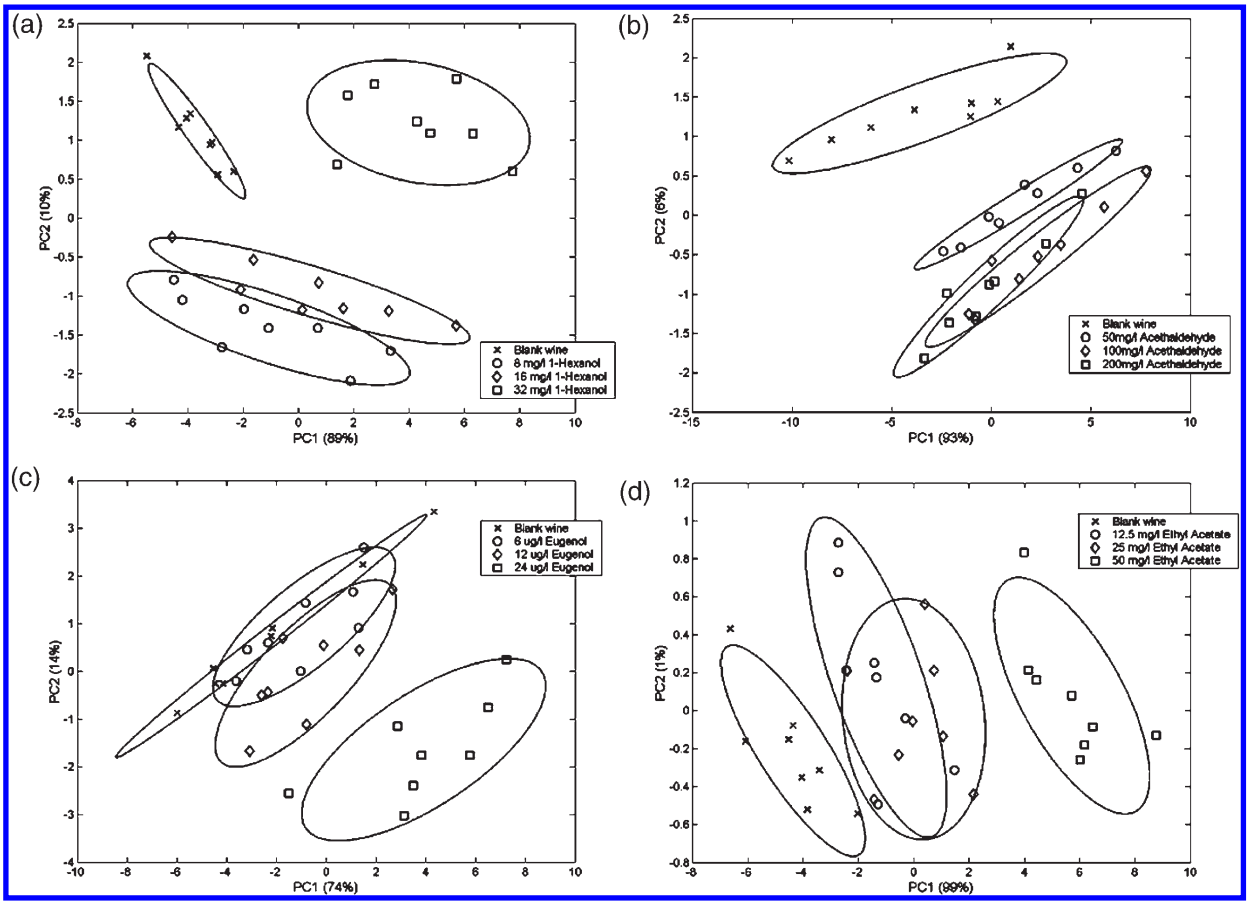

Figure 2. PCA score plot of measurement of several compounds at different concentrations: (**a**) 1-hexanol in white wine; (**b**) acetaldehyde in white wine; (**c**) eugenol in red wine; (**d**) ethyl acetate in red wine.

Table 3. Rate of Correct Answers of PNN in Measurement Validation of Detection Thresholds

	% answers correct		
compound	*T*	2*T*	4*T*
ethyl octanoate	75	87.5	75
1-hexanol	50	25	100
eugenol	0	25	37.5
2-methyl-3-methoxypyrazine	50	0	37.5
4-vinylguaiacol	0	22.2	22.2
vanillin	87.5	100	75
diacetyl	75	87.5	75
butyric acid	33.3	66.6	77.7
acetaldehyde	62.5	12.5	62.5
3-methylbutanol	87.5	87.5	62.5
β-damascenone	50	12.5	25
δ-decanolactone	90	50	30
γ-nonalactone	90	50	30
(*E*)-whiskey lactone	100	80	90
ethyl acetate	62.5	62.5	100
ethanethiol	87.5	50	50
2,4,6-trichloroanisole (TCA)	62.5	62.5	100

influence is not sufficient; a clear and specific analysis of its impact in wine odor is necessary. Frequently, the aroma recognition value is higher than the threshold value detection; the panel, as the sensor system, had been trained in the recognition of the 17 aromas (**Table 2**). Each aroma was presented to the panelists in a concentration scale from *T* to 8*T* (only *T*, 2*T*, and 4*T* concentration values are shown in the graphic plots of **Figure 3**). The panelists marked on a taste sheet the concentration level at which they identified the aroma added to test wine.

For the electronic nose responses, a neural network was trained with 53 different classes corresponding to the measurements of 3 test wines and the same wines adulterated with the 17 aromas. To validate the system, a cross-validation was applied and the classification success rate (correct predicted number over total number of measurements) was calculated to evaluate the performance of the system.

To compare the success rate of the panel's aroma recognition with the electronic nose answers, a univariate general linear model analysis with the measurement system (human panel and electronic nose) as fixed factor and concentration level (*T*, 2*T*, and 4*T*) as a random factor was used (SPSS 16). It allowed the effect of the variability of the studied factors on the rate of correct aroma classification to be quantitatively established. It was found that the influence of the fixed factor was not statistically significant ($p > 0.05$) except for the volatile compound ethyl octanoate. However, the interaction between the system and the concentration factor was statistically significant ($p < 0.05$) for the compounds ethyl octanoate, 2-methyl-3-methoxypyrazine, vanillin, diacetyl, β-damascenone, δ-decalactone, and ethyl acetate. This means that the rate of correct answers is dependent on the level of the aroma concentration. **Figure 3** shows the bar charts of success rate of classification for the different compounds grouped under the nine descriptors. The *p* statistical value of the significance level of the measurement system has been included. There is significant difference between the human panel and the electronic nose when the *p* value is < 0.05.

Fruity-like Character. Ethyl octanoate is an important fruity-like and base aroma character with aromatic units > 20. The electronic nose achieved a correct classification above 50% with *T*, 2*T*, and 4*T* concentrations; on the contrary, the human panel

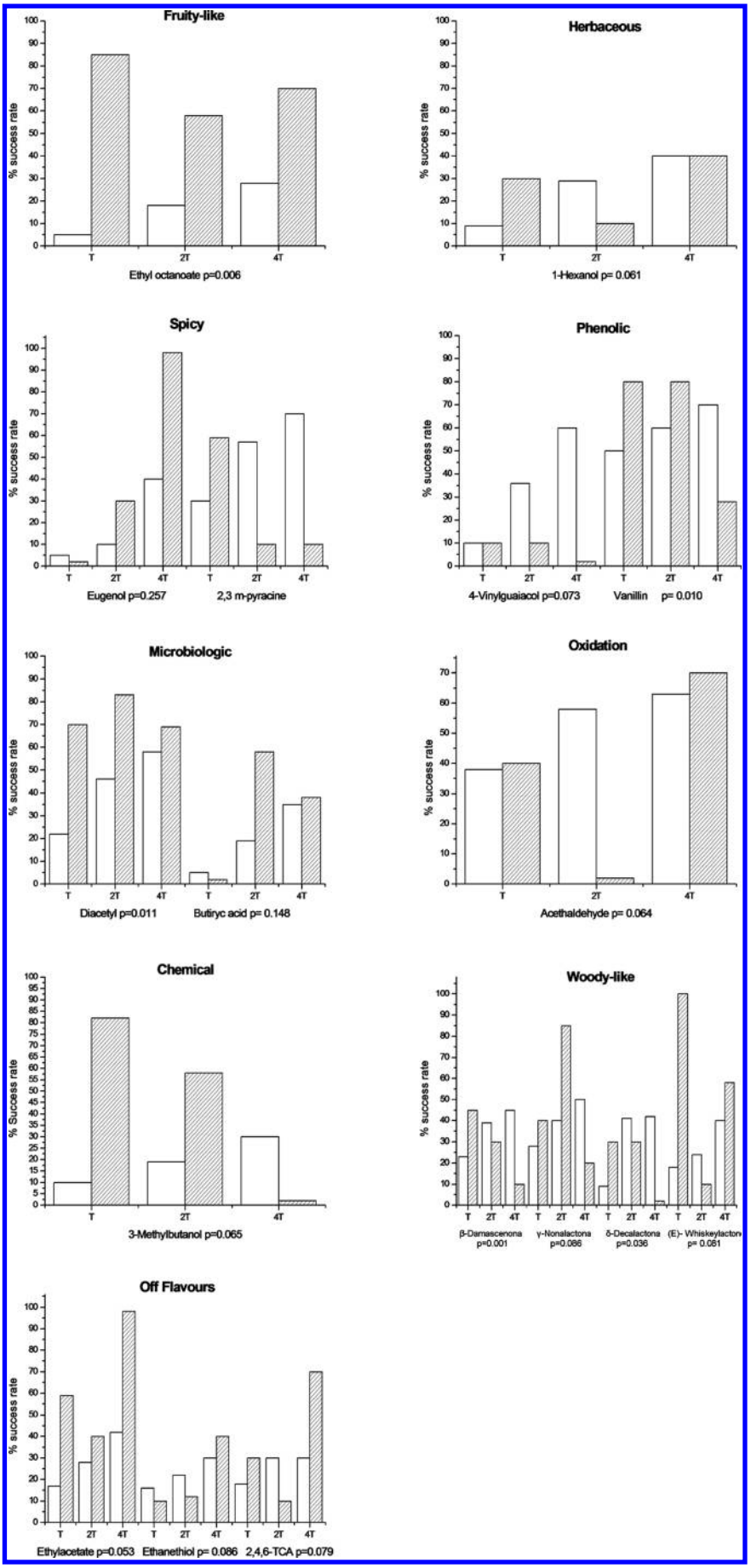

Figure 3. Bar charts of success rate to correct answers of the human sensory panel (solid) and electronic nose (lined) in the identification of aromas at T, 2T and 4T concentrations.

was not able to identify this aroma; the addition of 8 times the *T* value is not relevant to find differences with the control wine.

Herbaceous Character. The odor of herbs or grassy character in wine is well represented by 1-hexanol. This compound, in general, does not exceed 1 OAV in wines. 1-hexanol was not identifed by either system at the concentration levels assayed.

Spicy Character. Notes such as eugenol and 2-methyl-3-methoxypyrazine, impact aromas present in wine of special characters, was only detected by the electronic nose at 4*T* level and *T* concentration, respectively. Eugenol can be detected in aged wines. 2-Methyl-3-methoxypyrazine is described as a typical aroma of Cabernet sauvignon grapes.

Phenolic Character. Vanillin, a phenolic aroma also grouped under impact note, comes from the oak barrels in which wines are aged; it was well classified by 52% of panel members when it was present at threshold value (*T*). The electronic nose is under saturation when the concentration is increased; in fact, the system is not able to differentiate 4*T* from *T* and 2*T* values.

Microbiological Character. Diacetyl, a fine (subtle) butter aroma of malolactic fermentation, was identified by the human panel at 4*T* value, whereas sensor response was correct to *T* and 2*T*; at 4*T* value the system is saturated. Butyric acid, a microbiological compound of yeasts and bacterial metabolism, is an aroma base of wines and usually is >5 times its aromatic units. This compound was not appreciated by the panel; the electronic nose correctly identifies only it at 2 times the threshold value.

Oxidation Character. Acetaldehyde at low levels can contribute pleasant fruity aromas to a wine; however, at higher levels the aroma is considered to be a defect and is reminiscent of rotten apples. In this study, it was detected by 50% of the panel at or over the 2*T* level; the electronic nose required the 4*T* concentration.

Chemical Character. In the case of 3-methylbutanol (fusel alcohol), although its concentration in the test white wine was higher than the OAV value, the panel did not find differences in the triangular probe. The electronic nose was saturated to 3-methylbutanol at 4*T* value.

Woody-like Character. In general, the compounds selected to study the woody-like aroma were best detected by the electronic nose. Lactones of wine, δ-decalactone, γ-nonalactone, and (*E*)-whiskey lactone, have very sweet odors that resemble coconut, peach, and wood, and their contribution may show some additive effect.

The aldehyde β-damascenone is not well classified at the concentrations used; both systems needed concentrations above to 4*T* to detect it. β-Damascenone has a distinctive aroma and has been found in red wines and in white wine of Macabeo; suppression studies had indicated that this compound is fundamental in the aroma of this wine (*7*). β-Damascenone is an enhancer of fruity-like character, and it comes from the grapes, although it is also originated from carotenoid degradation and from the hydrolysis of specific precursors. This compound offers a tinned peach aroma, and it could be extracted from the wood. β-Damascenone is somehow linked to wine maturation because it is found at high intensity in aged wines, in which its levels increase with time (*35*).

Off-Flavor Character. Compounds such as ethyl acetate, ethanethiol, and TCA, which are impact compounds that can be the cause of wine alteration, were not identified by the panel at the assayed values; on the contrary, the electronic nose classifies properly ethyl acetate and TCA at and above the 4*T* concentration level.

Generally, the ability of a given compound to affect the aroma of wine is due to specifically the aromatic note and the concentration of such a compound; this is certainly the case for diacetyl, vanillin, eugenol, 2-methyl-3-methoxypyrazine, and TCA (*1*, *3*).

A study by Escudero et al. (*7*) reveals that compounds such as fusel alcohols, acids, esters, and some volatile phenols, even having a high OAV, are not able to affect individually the aroma in wine even if they are present at concentrations well above their odor threshold. This may explain why the individual addition of components such as 1-hexanol, butyric acid, 3-methylbutanol, β-damascenone, and ethyl acetate to the base wine does not bring about a clear increase in its odor note to the human nose. In other cases it is not the aroma of individual components that is perceived, but the aroma of its mixture; it has been demonstrated that wine lactones, in addition, can have odor activies of >1(*35*).

These results of the behavior of electronic nose versus a human panel have shown that the perception level of the human nose was superior in relation to the electronic nose, although the electronic nose yields better results in the recognition threshold of the aroma components; however, more studies are needed to understand the relationships between the compounds of wine aroma.

Conclusion. According to these results, it can be concluded that the electronic nose could be a complementary tool to sensory human panels, useful in the early detection of possible damage compounds such as TCA and ethyl acetate, in the elaboration and conservation of wine.

ACKNOWLEDGMENT

We thank the panelists for participating in the tastes and the reviewers for their comments.

LITERATURE CITED

(1) Ferreira, V.; Ortín, N.; Escudero, A.; López, R.; Cacho, J. Chemical characterization of the aroma of grenache rosé wines. Aroma extract dilution analysis, quantitative determination and sensory reconstitution studies. *J. Agric. Food Chem.* **2002**, *50*, 4048–4054.

(2) Guth, H. Quantitation and sensory studies of character impact odorants of different white wine varieties. *J. Agric. Food Chem.* **1997**, *45*, 3027–3032.

(3) Ferreira, V.; Lopez, R.; Cacho, J. F. Quantitative determination of the odorants of young red wines from different grape varieties. *J. Sci. Food Agric* **2000**, *80*, 1659–1667.

(4) Ferreira, V.; López, R.; Aznar, M. Olfactometry and aroma extract dilution analysis of wines. In *Analysis of Taste and Aroma*; Jackson, J., Ed.; Springer-Verlag: Berlin, Germany, 2001; pp 89−122.

(5) Tominaga, T.; Murat, M. L.; Dubourdieu, D. Development of a method for analyzing the volatile thiols involved in the characteristic aroma of wines made from *Vitis vinifera* L. cv. Sauvignon Blanc. *J. Agric. Food Chem.* **1998**, *46*, 1044–1048.

(6) Cacho, J. La percepción de notas aromáticas del vino y el efecto de ciertas moléculas volátiles. *ACE, Rev. Enol.* **2006**, , 66.

(7) Escudero, A.; Gogorza, B.; Melús, M. A.; Ortín, N.; Cacho, J.; Ferreira, V. Characterization of the aroma of a wine from macabeo. Key role played by compounds with low odour activity values *J. Agric. Food Chem.* **2004**, *52*, 3516–3524.

(8) Gardner, J. W.; Bartlett, P. N. *Electronic Noses*; Oxford University Press: Oxford, U.K., 1999.

(9) Santos, J. P.; Arroyo, T.; Aleixandre, M.; Lozano, J.; Sayago, I.; García, M.; Fernández, M. J.; Arés, L.; Gutiérrez, J.; Cabellos, J. M.; Gil, M.; Horrillo, M. C. A comparative study of sensor array and GC-MS: application to Madrid wines characterization. *Sens. Actuators B: Chem.* **2004**, *102*, 299–307.

(10) Persaud, K. C.; Travers, J. P. In *Electronic Noses. Handbook of Biosensors*; Kress-Rogers, E., Ed.; CRC Press: Boca Raton, FL, 1997; p 563.

(11) Di Natale, C.; Macagnano, A.; Davide, F. A. M.; D'Amico, A.; Paolesse, R.; Boschi, T.; Faccio, M.; Ferri, G. An electronic nose for food analysis. *Sens. Actuators B: Chem.* **1997**, *44*, 521–526.

(12) Bartlett, P. N.; Elliot, J. M.; Gardner, J. W. Electronic noses and their applications in the food industry. *Food Technol*. **1997**, *51*, 44–48.
(13) Penza, M.; Cassano, G.; Tortorella, F.; Zaccaria, G. Classification of food, beverages and perfumes by WO_3 thin-film sensors array and pattern recognition techniques. *Sens. Actuators B: Chem*. **2001**, *73*, 76–87.
(14) Lozano, J.; Santos, J. P.; Gutierrez, J.; Horrillo, M. C. Comparative study of several sampling methods combined with an electronic nose applied to discrimination of grape varieties in wines. *Sens. Actuators B: Chem*. **2007**, *127*, 616−623.
(15) Lozano, J.; Santos, J. P.; Horrillo, M. C. Classification of white wine aromas with an electronic nose. *Talanta* **2005**, *67*, 610–616.
(16) Parra, V.; Arrieta, A.; Fernández-Escudero, J. A.; Iñiguez, M.; de Saja, J. A.; Rodríguez-Méndez, M. L. Monitoring of the ageing of red wines in oak barrels by means of an hybrid electronic tongue. *Anal. Chim. Acta* **2006**, *563*, 229–237.
(17) Apetrei, C.; Apetrei, I. M.; Nevares, I.; del Alamo, M.; Parra, V.; Rodríguez-Méndez, M. L.; De Saja, J. A. Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods: correlation between electrochemical signals and analytical parameters. *Electrochim. Acta* **2007**, *52*, 2588–2594.
(18) Chatonnet, P.; Dubordieu, D. Using electronic sensors to discriminate among oak barrel toasting levels. *J. Agric. Food Chem*. **1999**, *47*, 4319–4322.
(19) Rodríguez Mendez, M. L.; Arrieta, A.; Parra, V.; Bernal, A.; Vegas, A.; Villanueva, S.; Gutierrez-Osuna, R. Fusion of three sensory modalities for themultimodal characterization of red wines. *IEEE Sens. J*. **2004**, *4*, 348–354.
(20) Aznar, M.; López, R.; Cacho, J.; Ferreira, V. Prediction of aged red wine aroma properties from aroma chemical composition. Partial least squares regression models. *J. Agric. Food Chem*. **2003**, *51*, 2700–2707.
(21) Lozano, J.; Arroyo, T.; Santos, J. P.; Cabellos, J. M.; Horrillo, M. C. Electronic nose for wine ageing detection. *Sens. Actuators B: Chem*. **2008**, *133*, 180–186.
(22) Di Natale, C.; Davide, F. A. M.; D'Amico, A.; Nelli, P.; Groppelli, S.; Sberveglieri, G. An electronic nose for the recognition of the vineyard of a red wine. *Sens. Actuators B: Chem*. **1996**, *33*, 83–88.
(23) Ampuero, S.; Bosset, J. O. The electronic nose applied to dairy products: A Review. *Sens. Actuators B: Chem*. **2003**, *94*, 1–12.
(24) Baldacci, S.; Matsuno, T.; Toko, K.; Estella, R.; De Rossi, D. Discrimination of wine using taste and smell sensors. *Sens. Mater*. **1998**, *10*, 185–200.
(25) Di Natale, C.; Davide, F. A. M.; D'Amico, A.; Sberveglieri, G.; Nelli, P.; Perego, C. Complex chemical pattern recognition with sensor array: the discrimination of vintage years of wine. *Sens. Actuators B: Chem*. **1995**, *24*−*25*, 801–804.
(26) Peinado, R. A.; Moreno, J.; Bueno, J. E.; Moreno, J. A.; Mauricio, J. C. Comparative study of aromatic compounds in two young white wines subjected to pre-fermentative cryomaceration. *Food Chem*. **2004**, *84*, 585–590.
(27) López, R.; Aznar, M.; Cacho, J.; Ferreira, V. Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection. *J. Chromatogr., A* **2002**, *966*, 166–177.
(28) Ortega, C.; López, R.; Cacho, J.; Ferreira, V. Fast analysis of important wine volatile compounds. Development and validation of a new method base on gas chromatographic-flame ionisation detection analysis of dichloromethane microextracts. *J. Chromatogr., A* **2001**, *923*, 205–214.
(29) Gil-Díaz, M.; Cabellos, J. M.; Arroyo, T.; Prodanov, M. Characterization of the volatile fraction of young wines from D.O. "Vinos de Madrid" (Spain). *Anal. Chim. Acta* **2006**, *563*, 145–153.
(30) Horrillo, M. C.; Getino, J.; Gutiérrez, J.; Arés, L.; Robla, J. I.; García, C.; Sayago, I. Measurements of VOC's in soils through a tin oxide multisensor system. *Sens. Actuators B: Chem*. **1997**, *43*, 193–199.
(31) Getino, J.; Horrillo, M. C.; Gutiérrez, J.; Arés, L.; Robla, J. I.; García, C.; Sayago, I. Analysis of VOC's with a tin oxide sensor array. *Sens. Actuators B: Chem*. **1997**, *43*, 200–205.
(32) Duda, R. O.; Hart, P. E.; Stork, D. G. *Pattern Classification*; Wiley-Interscience: New York, 2001.
(33) Derks, E. P. P. A.; Beckers, M. L. M.; Melssen, W. J.; Buydens, L. M. C. Parallel processing of chemical information in a local area network−II. A parallel cross-validation procedure for artificial neural networks. *Comput. Chem*. **1995**, *20*, 439–448.
(34) Bishop, C. M. *Neural Networks for Pattern Recognition*; Oxford University Press: Oxford, U.K., 1999.
(35) López, R.; Ferreira, V.; Hernández, P.; Cacho, J. Identification of impact odorants of young red wine made with Merlot, Cabernet sauvignon and Grenache grape varieties: a comparative study. *J. Sci. Food Agric*. **1999**, *79*, 1461–1467.

Received for review March 13, 2009. Revised manuscript received October 9, 2009. Accepted November 02, 2009. We thank the Spanish Science and Technology Ministry and Regional Government for supporting the Projects TIC2002-04588-C02-01/02 and OLFACTOSENSE (S-SEM-0255-2006).