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Application of an Electronic Aroma Sensing System to Cork Stopper Quality Control

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Cork odors were characterized using an electronic aroma sensing system. The electronic system is a compact, benchtop instrument comprising a sensor array, signal processing hardware, a measurement algorithm, and a pattern classification system. The sensor array responds to the presence of aroma volatile compounds by changes in their electrical properties. Resistance changes are displayed as a histogram, which is a fingerprint of the aroma being analyzed. Five different cork odors were studied: NE, which is considered as standard cork odor; CO, exhibiting the pleasant boiled cork odor (it is also considered as a good odor); PO, corresponding to rotten odor; and B and BO, representing moldy and very intensely moldy odors, respectively. This electronic aroma sensing system could discriminate quickly and objectively between acceptable odor and the unacceptable taint. Characterization and selection of a subset of sensors were performed. A relation between sensors and specific odors was established. The system, once trained with representative acceptable and unacceptable samples, could be used as a simple quality control tool and incorporated into the normal quality control procedures for each batch of product, by providing real-time analysis of a sample overall aroma.

Keywords: *Cork stoppers; "standard" aroma; off-flavors; electronic aroma sensing system; quality control*

INTRODUCTION

The use of cork for sealing wine bottles is an extremely old practice and still widespread today, especially for quality wines. The cork plays an important role in determining quality because of its peculiar features: impermeability to air and liquids (preventing wine oxidation), ability to adhere to a glass surface, compressibility, resilience, and chemical inertness (Simpson and Amon, 1986).

A specific problem associated with the use of cork stoppers is "cork taint". According to Heimann et al. [as cited in Amon et al. (1989)], 2% of all wines stoppered with corks developed a corky taste, which is considered unacceptable by the consumer to the extent that the product is rejected. The identification of the origin of the off-flavors is a difficult task. The best solution to this problem is for the cork stopper producers to control and certify the odor quality of the cork before dispatching it from the factory. On the other hand, the wine makers may wish to control the quality of the cork stopper they are using, to ensure the quality and the characteristics of their wines.

The economical implications of this problem are quite significant, and several research groups have studied the origins and causes of the corky taints. In the recent years, several studies on cork taint have been published. Cork taint is usually associated with a musty, moldy aroma and taste (Simpson and Veitch, 1993). A large number of compounds have been reported in cork (Mazzoleni et al., 1994; Rocha et al., 1996a,b), some of them with musty and related odors, for example, 2,4,6-trichloroanisole and 2,3,4,6-tetrachloroanisole (Würding, 1975; Tanner and Zanner, 1978, 1983; Dubois and Rigaud, 1981; Rigaud et al., 1984; Maujean et al., 1985) and 1-octen-3-one, 1-octen-3-ol, geosmin, and 2-methylisoborneol (Amon et al., 1989). Other compounds with similar odor characteristics include guaiacol (Amon et al., 1989) and 1-octanol and 3-methyl-1-butanol (Kaminski et al., 1972). The methodologies used by these authors, despite being very informative, are expensive and slow, need the use of a specialist, and are not easy to establish as routine control procedures.

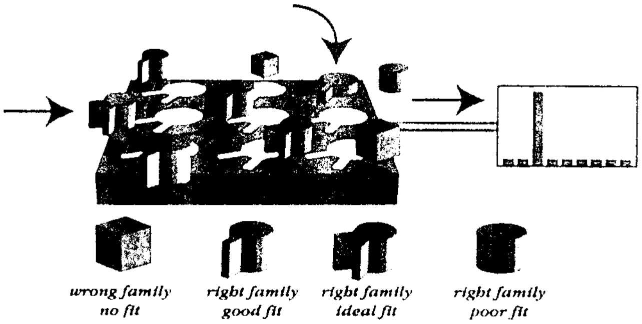

Figure 1. Transient changes in resistance are caused by adsorption and subsequent desorption of volatile chemicals onto the polymer surface.

Many wine and cork industries have developed their own appraisal system for cork odors as part of their overall quality assurance program, reflecting the great

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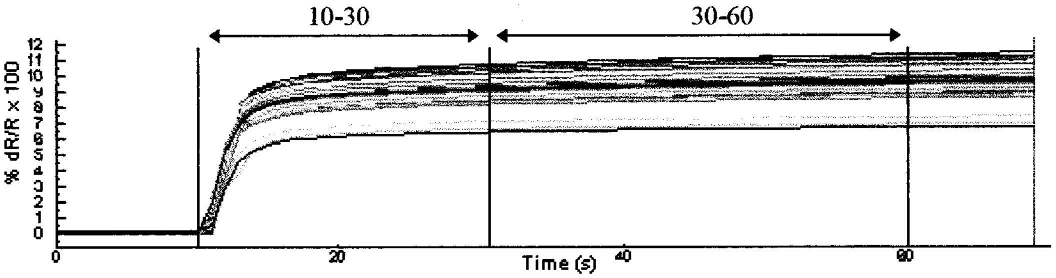

Figure 2. Sensor responses showing sections of data used for mapping (10−30 and 30−60 s).

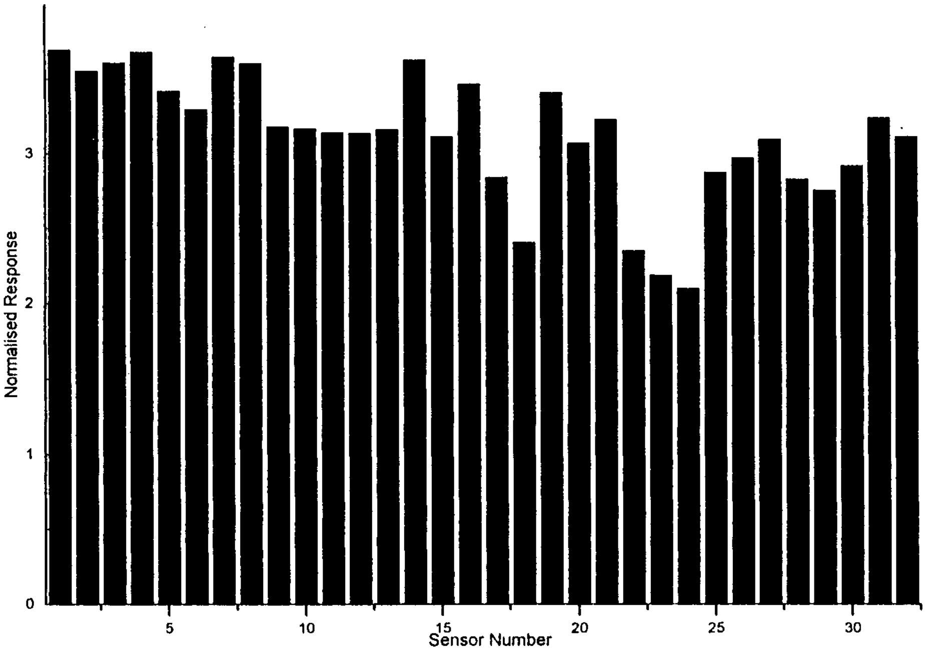

Figure 3. Histogram representing the fingerprint for standard cork odor (NE) region selected corresponding to 30−60 s of the analysis.

importance of this subject. Casey (1990) has also presented a test for tainted corks. The corks are cut in half lengthwise and sealed in a small glass jar with 2−5 mL of sterile, odor-free water. The contents of the jar are then sniffed several times over the next few days. This test is a cumbersome and costly process to be introduced as a routine procedure. The sensory panels are expensive and cannot always consistently identify a taint. Their perception of the aroma of a product will depend on physiological and psychological factors.

The industry needs a simple, quick, and objective method to classify the odor from the cork, both at the manufacturing stage as a guarantee of quality and at the bottling stage.

The aim of this study was to determine if an electronic aroma sensing system could discriminate quickly and objectively between acceptable odor and the unacceptable taint. It is the first time that this technology has been applied to the quality control of cork odors, and these results suggest that this system has several advantages for the industry.

INSTRUMENTATION

An AromaScan A32S/8S Labstation System (AromaScan plc, Crewe, U.K.) was used during this study. This system comprises an analyzer (A32S) unit with a 32 element sensor array of conducting polymers and a sample station (A8S). The latter generates reference air of known quality and humidity that is used to fill a polyester/polyethylene bilayer pouch containing the sample. The pouch is then left in the temperature-controlled environment (4−35 °C) of the sample station until the required headspace is produced. The equilibrated headspace is then pumped into the A32S analyzer and passed across the sensor array. The sensors are made of a polymer that changes its electrical resistance when a volatile compound adheres (Figure 1). The change in electrical resistance (DR/R) of each sensor element is measured and all responses are converted into a normalized pattern of responses. Each sensor has a different characteristic response. The relative responses of individual sensors reflect the range of volatile compounds given off by a sample.

The system software includes data mapping tools and an artificial neural network (ANN). The mapping software condenses a high-dimensional space into a lower dimensional one by means of a nonlinear mapping algorithm that preserves as much as possible the internal data structure (Sammon, 1969). The results can therefore be displayed in a two- or three-dimensional plot known as a Sammon map. Differences between samples become apparent and quantifiable by measurement of the Euclidean distance. A small Euclidean distance is indicative of similar aromas.

The ANN software is based, among others, on a feed-forward fuzzy algorithm that performs pattern recognition and compares incoming sensor data with the database of previously encountered odors. After training, the ANN can be used

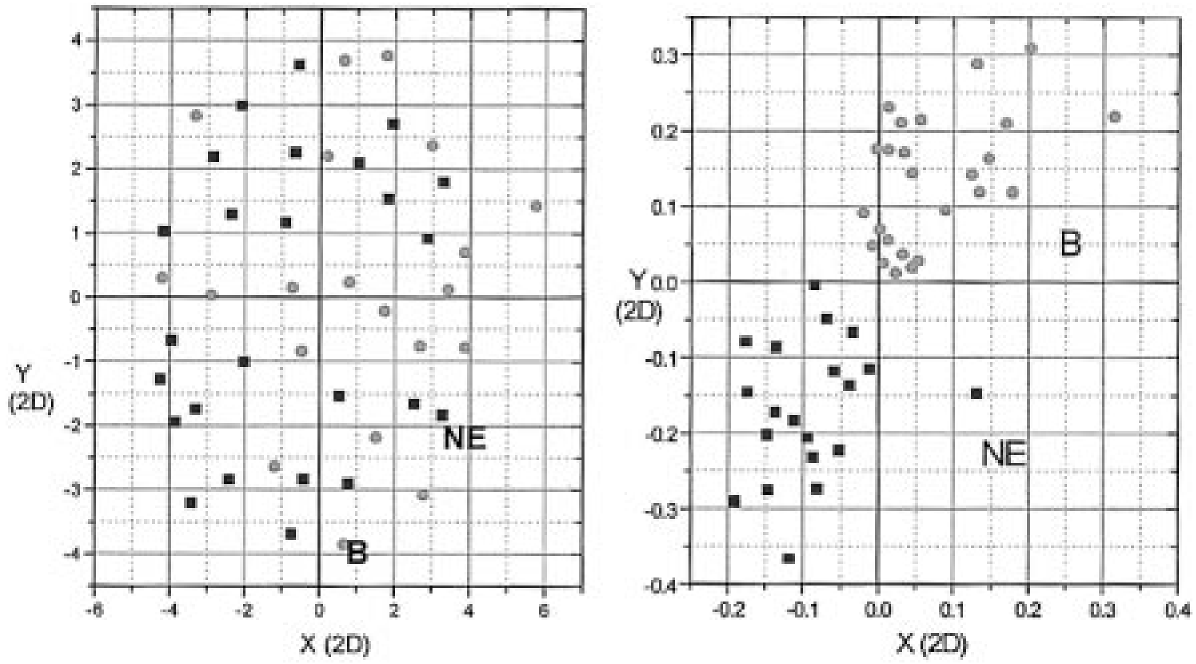

Figure 4. Map of standard (NE) and moldy (B) odors: (a, left) region selected corresponding to 10−30 s of the analysis; (b, right) region selected corresponding to 30−60 s of the analysis.

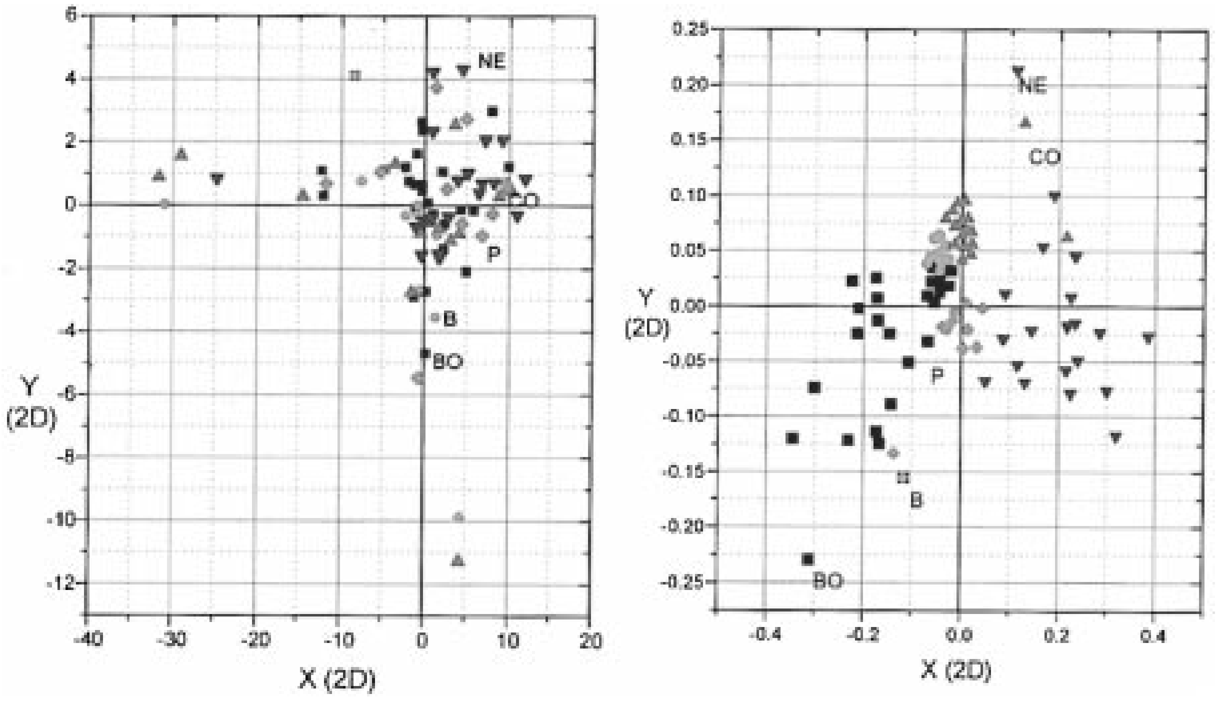

Figure 5. Map of standard (NE), boiled cork odor (CO), rotten odor (PO), and moldy and intensely moldy odors (B and BO, respectively): (a, left) region selected corresponding to 10−30 s of the analysis; (b, right) region selected corresponding to 30−60 s of the analysis.

during data acquisition to perform real-time pattern recognition and aroma identification.

MATERIALS AND METHODS

Cork slabs and stoppers without any treatment were collected in the cork factory and were chosen to represent five different odors: NE, which is considered the standard cork odor; CO, exhibiting the pleasant boiled cork odor (it is also considered as a good odor); PO, corresponding to rotten odor; and B and BO, representing the moldy and very intensely moldy odors, respectively. All of the samples were carefully selected by a group of five professionals experienced in recognizing cork odors for quality control purposes. In this study were used only the samples resulting from a unanimous odor evaluation among the five professionals. These aromas represent the most frequent cork odors at the industrial level. The selected samples were divided in two groups: a group of 82 samples that was used to build the five databases to train the ANN and another group of 460 samples to validate the method.

Two cork stoppers or 17.5 g of cork slabs (the same mass as two stoppers) representing different odors were cut in pieces of about 2 cm × 2 cm and were sealed into the sample pouch, which was filled with charcoal and molecular sieve filtered air at approximately 10−12% relative humidity (RH). The headspace above the cork was left to equilibrate for 30 min at 35 °C in the A8S sample station. This procedure was repeated for all samples. The samples were then analyzed on the A32S unit, using the 32 sensors. The following protocol for the valve sequence was established: reference 10 s, sample 60 s, wash 10 s, and reference 30 s. The reference consisted of 10−12% RH air passed directly from the A8S sample station to the analyzer (A32S). The wash part of the cycle consists of passing over the sensor air that had been passed over a 2% water/butanol solution. The purpose of this part of the cycle is to avoid cross-contamination between successive samples. The effectiveness of the wash with butanol/water in the reduction of the cross-contamination of the sensors is controlled during the second reference step, when the response of the sensors has to return to zero. The sample station provides a wash (vapor) source through the wash line at the rear of the instrument. The wash source is generated from the headspace above the wash liquid (2% butanol/water). The time of washing should be chosen adequately to the sample analyzed. In this case 10 s was considered enough to obtain the return to zero.

The analysis of each cork sample took 110 s, including the reset time of the instrument to be ready to run another sample. As shown in Figure 2, two data sets were produced at different periods of acquisition (10−30 and 30−60 s from the start of the acquisition).

Sensor Selection. The data set of 82 samples that comprised the five odors studied (inputs to the neural network) were used to select the sensors most related to specific odors.

The selection of these sensors was performed by means of a variable reduction using Procrustes rotation (Krzanowski, 1987) coupled with a genetic algorithm as an optimization method. The Procrustes rotation method selects a subset of sensors that better describes the variability on the initial data set, removing, therefore, those sensors that are not very important. An optimization technique was necessary since one had an array of 32 sensors, representing, therefore, 2^{32} possible combinations of sensor subsets.

RESULTS AND DISCUSSION

Cork Odors Discrimination. Figure 2 represents the variation of the relative resistance change of each sensor with time. The responses of the different sensors were extremely rapid. The first response was obtained at ~11 s and a plateau within 16 s. The kinect profiles are similar for all of the sensors. The intensities of the sensors, normalized by the sum of the sensor responses over all of the sensor elements and averaged over a fixed time range in the acquisition cycle, define a histogram, which is the fingerprint of an aroma. Figure 3 shows a histogram representing the "standard" cork odor fingerprint; the region selected corresponds to a time interval from 30 to 60 s into the analysis.

Only an adequate selection of a region corresponding to a specific period of the analysis (Figure 2) will permit the discrimination between different kinds of samples. Thus, before the region is selected, a couple of factors have to be taken in account: The sensors may take some time to stabilize. On the other hand, it will be during the first second that the rich volatile fraction from the sample reaches the sensors. As the sensors are sensitive to humidity, it is also important to control this parameter.

Two region sets were studied: 10−30 s, which corresponds to the time when the rich volatile fraction from the sample reaches the sensors but the sensors are not completely stabilized, and between 30 and 60 s, which represents the section when the sensors are stabilized and the humidity is acceptable. After 60 s, the humidity attains 100% and the sensors are saturated, responding inadequately.

Figure 2 displays the sensor response and shows the two sections used for mapping (10−30 and 30−60 s). Figure 4 shows the cluster analysis from two different corks, the standard odor (NE) and the moldy odor (B), which correspond to the most frequent cork odors and constitute a simple system to begin the present study.

Figure 4a shows a map of samples of NE and B with a time interval of 10−30 s. No discrimination is evident. The map (Figure 4b), which represents the 30−60 s region, clearly shows the distinction between the two populations of cork samples.

Panels a (10−30 s region) and b (30−60 s region) of Figure 5 show the maps of cork presenting five different odors: standard odor (NE), boiled cork odor (CO), rotten odor (PO), and moldy and intensely moldy odors (B and BO, respectively). The map in Figure 5a does not allow any classification of the different cork odors and increases the dispersion already observed in Figure 4a. Figure 5b shows a map demonstrating that the samples are discriminated by the system. The organoleptic assessment of these samples, showing that they have different aroma characteristics, is confirmed by the electronic aroma analysis. The map (Figure 5b) clearly shows five populations of cork samples, showing discrimination between the moldy and intensely moldy odors. This map can be split into two distinctive sections corresponding to acceptable (NE and CO) and unacceptable odors (PO, B, and BO).

These results clearly indicate that the region of 30−60 s should be chosen to build the databases. Five databases were therefore prepared: base NE (25 samples), base CO (18 samples), base PO (14 samples), base B (25 samples), and base BO (20 samples).

For this work neural network pattern recognition software was used to distinguish among different cork aromas, with the intention of detecting unacceptable odors. The information from each database was fed into the neural network software separately to create a recognition file. After this period of training, the sensor array was able to differentiate different cork odors by reference to a database of previously encountered odors. The neural network was trained with the five databases and was used to classify "unknown" samples.

To validate this method, 460 cork samples were analyzed. All of the samples were previously evaluated by the mentioned group of five tasters. The results of the identification of the cork odor using an electronic aroma sensing system are shown in Table 1.

Table 1. Identification of Cork Odor Using an Electronic Aroma Sensing System (All Samples Were Previously Submitted to a Sensory Panel Evaluation)

sample		identification[c]			identification[d]		
type[a]	no.[b]	corr	incorr	error (%)	corr	incorr	error (%)
cork NE	110	105	5	4.5	107	3	2.7
cork CO	90	84	6	6.7	86	4	4.4
cork PO	80	74	6	7.5	75	5	6.3
cork B	90	87	3	3.3	88	2	2.2
cork BO	90	83	7	7.8	87	3	3.3

[a] Cork classification done according to sensorial analysis. [b] Number of samples analyzed. [c] Identification was considered correct (corr) or incorrect (incorr) according to the sensorial analysis. [d] Identification was considered correct (corr) or incorrect (incorr) according to the following classification: acceptable (acc), if corresponding to the NE and CO odors, and unacceptable (unacc), if corresponding to the PO, B, and BO odors.

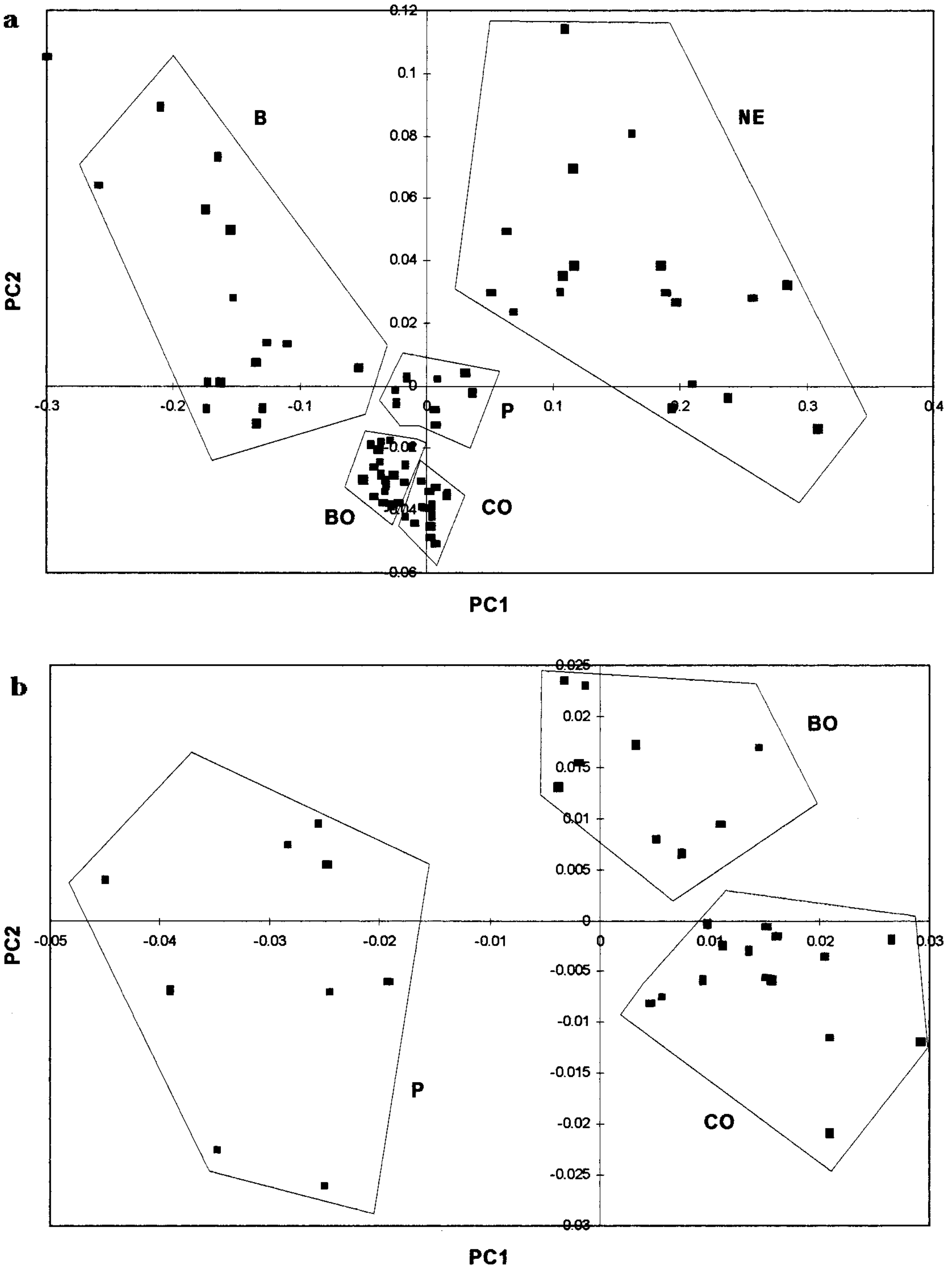

Figure 6. Score scatter plot PC1 vs PC2: (a) all odors; (b) BO, P, and CO odors.

Two criteria were used to identify the cork odor. According to the first criterion the cork samples were classified into five databases (NE, CO, PO, B, and BO), and this identification was considered correct or incorrect relative to the previous sensory panel evaluation. According to the second criterion the cork samples were classified into two groups: acceptable odors corresponding to NE and CO aromas and unacceptable odors corresponding to PO, B, and BO aromas. For the first criterion the identification error varied between 3.3% and 7.8% (Table 1), with the lowest errors corresponding to the larger sample set. The databases NE and B contain more elements and give the lowest identification errors, 4.5% and 3.3% respectively. It was observed that some cork samples that were classified as NE by the sensory panel were identified as CO odor by the electronic aroma sensing system. The same happens with the PO, B, and BO cork odors. This incorrect identification may be explained, at least in part, by the small number of different odor types, which may not represent the high variability of natural cork odors. Nevertheless, the fuzziness between NE and CO odors and PO, B, and BO odors does not have a great practical significance and indicates that this electronic system finds some affinity within the two groups (NE and CO; and PO, B, and BO). Therefore, it appears adequate to classify the cork odors into acceptable and unacceptable groups. The error associated with this classification is considerably smaller, ranging from 2.2% to 6.3% (Table 1). The highest error (6.3%) corresponds to the PO type that contains the smallest number of elements. This system is self-learning: the more data submitted, the more discriminating the system becomes. It is important to include a large number of representative measurements in each database to take into account the most variability possible and, therefore, to increase the confidence in the identification.

Sensors Selection. As it has been seen in this study, the response of the sensor array was very sensitive to different odors. The results obtained were based on the response of the complete sensor array, and therefore, the properties of each sensor were not taken into account as potential information for a given odor or a set of odors. Therefore, it was important to select a set of sensors that were most related to a set of odors; that is, they better described the variability of the initial data set.

Using the method of variable selection (Procrustes rotation), from the 32 initial sensors, a subset of 17 sensors was selected as the most related to the five odors in study. This subset described nearly 94% of the variability in the data set, and from Figure 6, one can see that it was possible to discriminate among the different odors.

The subset included sensors 1−4, 7, 8, 11, 12, 18−21, 23, 25, 28, 29, and 32. From this subset it was possible to relate these sensors to specific odors. It was found that sensors 1−4, 7, 8, 11, 12, and 21 were related mainly with NE; sensors 18, 23, 25, 28, 29, and 32 with B; and the odor CO was highly related to sensor 19 and anticorrelated to sensor 23. The odors P and BO were characterized by sensors 18 and 20. To highlight the discrimination among BO, CO, and P odors, a principal component analysis (PCA) was performed using the samples and the sensors previously selected for these odors (18−20 and 23). As can be seen from Figure 6b, a good discrimination is obtained.

The sensors selected increase the discrimination power between NE and the other odors, as can be seen in Figure 6.

CONCLUSIONS

The electronic aroma sensing system used in this work enabled cork odors to be stored in digital form and to be displayed as visual aroma maps that allowed a suitable interpretation.

This electronic aroma sensing system coupled with the ANN can, in real time, characterize the cork quality with respect to odor. The objective nature of the analysis increases the confidence of evaluation. It provides consistent, low-cost, and quick classification of the samples (±2 min). The same equipment and accessories allowed the study of samples at all stages during the manufacturing process, without any prepreparation.

This system has many potential uses in the cork stopper industry, in which problems of odor management are critical and objective measurements need to be applied. This particular application demonstrates its use in monitoring the aromas from the cork during the stopper manufacture and thus as an indicator for final product quality.

It can be also used by both the supplier and the customer to enable agreed odor profiles to be matched against ungraded stoppers. The wine makers can also control the odor quality of the stoppers used to seal the wine, thereby preventing waste through the early detection of “nonstandard” odors.

The sensor characterization and the relation between their proprieties and the odors were studied, and it was found that there is a specific subset of sensors that are related to specific odors. From these results, it seems clear that the sensors that are related to the normal odors are different from the ones related to other types of odors. This difference in the sensor proprieties can be used to establish a better training method for the neural network, increasing, therefore, the confidence on the characterization of odors.

Results indicate that this electronic aroma sensing system can be a perfect complementary tool to sensory panels to assess extremely quickly the quality of cork.

Exhaustive work must be carried out to characterize all of the potential odors that may be associated with the cork samples in any manufacturing or storage stages.

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