Using Electronic Odor Sensors To Discriminate among Oak Barrel Toasting Levels

Pascal Chatonnet*,[†,‡] and Denis Dubourdieu[§]

Seguin-Moreau Cooperage, F-16103 Cognac at the Bordeaux Faculty of Oenology, Victor Segalen Bordeaux II University, 351 Cours de la Libération 33405 Talence Cedex, France; Excell Laboratory, Parc Innolin, 8 rue du Golf, F-33700 Merignac, France; and Faculty of Oenology, Victor Segalen Bordeaux II University, 351 Cours de la Libération, 33405 Talence Cedex, France

Toasting changes both the quantity and the quality of the extractable substances in oak wood of barrels used for the aging of fine wines and spirits. Mastery and repeatability of toasting are vital in the production of quality barrels to be used for aging wines and spirits. Toasted wood components, which can be extracted by the wines or spirits during the aging process, are normally analyzed by maceration in standard alcohol solutions at concentrations adapted to the various products and can be used to control the intensity of the wood toasting. These kinds of analyses are accurate but time-consuming and need specialized laboratories. In this work, the feasibility of monitoring barrel toasting levels using an electronic nose with a metal oxide odor sensor array (MOS) was studied. The results of oak toasting level differentiation obtained via the MOS network were identical to those obtained by analyzing extractable compounds in liquid or gas phase as described in a previous paper. The results presented in this work at the laboratory scale could be used to implement a nondestructive monitoring system based on the analysis of headspace of barrels under industrial conditions.

Keywords: *Oak wood; toasting; electronic nose; metal oxide sensors*

INTRODUCTION

The oak barrels used for aging wines and spirits are heated over a fire to bend the wood into shape. Further heating then toasts the inside, modifying the structure and composition of the inner surface of the staves. Toasting changes both the quantity and quality of the extractable substances in the oak (Nishimura et al., 1983; Dubois, 1989; Chatonnet et al., 1989a,b; Puech, 1987; Chatonnet, 1995; Cutzach et al., 1997). Toasting intensity and duration may be adjusted and adapted to suit oak of different origins and species, as well as different types of wine (Chatonnet et al., 1993, 1997). Mastery and repeatability of toasting are vital in the production of quality barrels to be usef for aging wines and spirits.

Toasted wood components that can be extracted by the wines or spirits during the aging process are normally analyzed by maceration in standard alcohol solutions at concentrations adapted to the various products (10−12% volume for wine, 40−50% volume for spirits) (Puech, 1987; Chatonnet and Boidron, 1989). These analyses are accurate but time-consuming. Several different methods can be used to determine the chemical composition of the toasted wood. In a previous paper, we suggested an alternative method involving headspace analysis by solid-phase microextraction (HSSPME). This method requires neither preparation nor preliminary extraction of toasted wood samples

(Chatonnet et al., 1999). SPME is a very simple method that can be carried out in any laboratory, although it is difficult to obtain good quantitative results. There was no simple, objective technique for assessing oak barrel quality or toasting levels in the average workshop or laboratory.

Five countries worked together on a CRAFT/BRITE-EURAM III European research program to study applications for odor sensors in the agrifood industry and hybrid electronic detection systems combining various technologies. We studied the feasibility of monitoring barrel toasting levels using an electronic nose with odor sensors developed by Laboratoire Excell (Merignac, France). The main components of an electronic nose are a measurement cell and a data processing unit. This data processing system applies various mathematical models, particularly neural networks (Gardner et al., 1992a,b) and multivariate statistical analysis (Gardner, 1991). It can be trained to recognize a characteristic profile.

Different types of sensors may be used to detect volatile substances in the gas phase. Metal oxide sensors (MOS) (tin oxide, SnO_2; zinc oxide, ZnO; and tungsten oxide, WO_3), which may or may not be doped with precious metals (especially palladium, Pd, and platinum, Pt), have been used for many years in gas detection and have provided the basis of many new research developments (Seiyama, 1978; Windismann, 1979; Oyabu, 1984; Moseley and Williams, 1987; Oishi et al., 1988; Gardner, 1989; Mosely and Williams, 1991). Their ability to detect aromas and discriminate among them has been tested in many fields, particularly in the agrifood industry (Moy, 1992; Gardner et al., 1992a,b; Moy, 1993; Moy and Chatonnet, 1993). These metal oxides have varying

* Author to whom correspondence should be addressed (e-mail Lab_Excell@compuserve.com).
† Seguin-Moreau Cooperage.
‡ Excell Laboratory.
§ Victor Segalen Bordeaux II University.

selectivity and sensitivity, depending on their oxidation properties and the amount of catalytic additive. This type of sensor is highly sensitive (parts per million to parts per billion depending on the compounds to be detected) to a wide range of chemical compounds. These systems may be used at high temperatures to avoid pollution, are relatively resistant, have a 2−3-year life span, and are relatively cheap, but they are sensitive to humidity.

Surface acoustic waves (SAW) may also be used for gas detection. Adsorption of a substance on the selective coating of the detector causes a frequency variation in an oscillatory circuit. Detection sensitivity is directly related to oscillation frequency. The frequency normally available, 200 MHz, does not provide a high level of sensitivity, whereas a frequency of 433.92 MHz significantly reduces detection limits. However, raising the frequency also significantly increases cost and background noise and causes a considerable decrease in sensor stability. SAWs have gradually been replaced by quartz-crystal microbalances (QCM), using the piezoelectric effect (Ngeh-Ngwainbi et al., 1990; Guilbaut and Suleiman, 1990; Suleiman and Guilbaut, 1991). The sensitive element, a quartz, has a special coating that matches the stationary phases used for gas-phase chromatography. When the gas molecules come into contact with the sensor, they are subjected to an adsorption/desorption balance. Gas adsorption increases the mass of the crystal and decreases the oscillation frequency according to the Saurberey equation (1994). According to this equation, a quartz crystal oscillating at a basic frequency of 9 MHz varies by 400 MHz/μg; a 5 mm diameter crystal oscillating at 15 MHz reacts at 2600 Hz/μg. According to these theoretical calculations, a piezoelectric crystal's detection limit is ~10^{-12} g. QCMs currently available are not very sensitive to humidity but still operate at low frequencies (10 MHz), which does affect their sensitivity.

Polymer conductor-based sensors are not very sensitive to variations in humidity, if at all. This type of sensor is made by coating a very thin layer of polymer conductor, obtained by polymerizing heterocyclic molecules with various counterions (Hodgins, 1995). The most frequently used monomers are pyrrol, indole, thiophen, and aniline. Aniline and indole are the most stable and sensitive to polar molecules. These polymers change conductivity rapidly and reversibly according to an adsorption/desorption balance when they come into contact with the polar molecules in a gas. They are highly sensitive and extremely stable. However, they are significantly less durable than metal oxides and sensitive to poisoning (irreversible adsorption) and, consequently, their life span is often shorter (6 vs 18 months).

After several preliminary studies, we decided to use a network of several MOS-type sensors. In this paper, we present the results of tests to discriminate among different toasting levels used in cooperage. This method is intended for quality control and ensuring the repeatability of specific barrel toasting levels.

MATERIALS AND METHODS

**Barrel Toasting and Preparation of Wood Samples.** Barrels were toasted over a wood fire according to the method and temperature criteria outlined by Chatonnet et al. (1989a,b). The samples of wood toasted to varying degrees were taken by scraping the inside (0−5 mm) of the barrels made from

European sessile oak (*Quercus petraea*). Each sample (four for each toasting level) was homogenized and divided into two parts. The first part was subjected to standard gas-phase chromatography to identify the volatile extractable compounds (after maceration in dilute alcohol solution or direct analysis in gas phase by HSSPME) (Chatonnet et al., 1999). The second sample was analyzed by the MOS network.

Analysis of Volatile Compounds by a Network of MOS-Type Sensors. *Operating Principle.* When the aroma sensors of the measurement cell detect a volatile molecule, the electric signal is modified. In this case, the sensors consisted of thin layers (50 μm) of tin oxide-based semiconductors, doped with various precious metals. Tin dioxides (SnO_2) are intrinsically n-type sensors. Oxygen from the atmosphere creates a barrier to potential by decreasing the electron concentration on the sensor surface, as shown by

$$n + {}^1/_2O_2 \rightarrow O\ (s)^- \qquad (I)$$
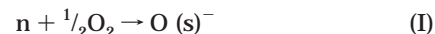
When R volatile compounds are present, the oxygen adsorbed at the sensor's surface reacts as follows (II):

$$R(g) + O(s)^- \rightarrow RO(g) + n \qquad (II)$$
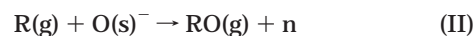
The sensor's resistance drops. The signal curve was digitized and transferred to the computer. Simultaneous use of 24 sensors reacting to different chemicals makes it possible to scan all of the components of the toasted wood aroma. Each sensor presents various answers to the different volatile compounds in relation with its metallic composition and especially the presence of rare earths in the metal oxide. The various sensor responses are combined, and the resulting profile, processed by multivariate analysis or a neural network, makes it possible to distinguish among different toasting levels.

Using an MOS Network To Analyze Headspace. We used a FOX 4000 system supplied by ALPHA-MOS (Toulouse, France) with 18 basic SnO_2 sensors (6 of which were not doped), of a total of 54 available sensors. The system was equipped with an automatic Odorscanner HS50 sampling system. A 0.5 g sample was placed in a 10 mL flask with a PTFE seal. The sample was heated to 80 °C for 10 min. After a 20 min balancing sequence, 2500 μL of headspace was automatically taken using a gas syringe and injected directly into the gas flow (N_2/O_2 80:20, 300 mL/min, constant relative humidity of 20% passing over a $CaCl_2$ solution in a bath maintained at a temperature of 38 ± 2 °C) passing through the three sensor chambers maintained at 175 °C at a rate of 1250 μL/s. Signal acquisition lasted 120 s. The syringe was cleaned by purging it with synthetic air for 3 min. Before each new injection into the detector, the syringe was pumped three times in the headspace to be analyzed. The sensors were purged with synthetic air at a rate of 500 mL/min. Sampling started only once the various sensors had returned to the base signal. All of the sensors had returned to the baseline after 8 min of purging.

Each of the three connecting sensor chambers has six metal oxide sensors (P, flat-plate sensor; T, tubular sensor; SY, nondoped tin oxide), a temperature sensor, and a relative humidity sensor. Patent laws prevent us from revealing full details of the various sensors.

Statistical Analysis of Results. Each sample was analyzed three times. The mean of the results of the three consecutive tests was calculated using the multivariate statistical analysis (Unistat) included in the FOX data processing software. We ran principal component analysis (PCA) and discriminating factorial analysis (DFA) on the centered data after 120 s of data acquisition.

RESULTS AND DISCUSSION

Variations in MOS Response. The changes in resistance R of the sensors compared with the initial resistance ($\Delta R/R_0$) ranged from 1% (T70/1 sensor) to

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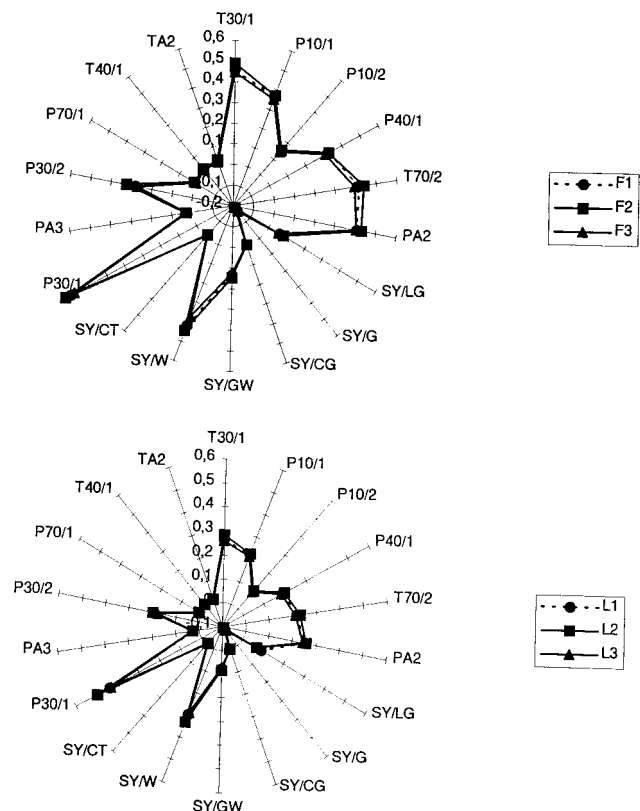*J. Agric. Food Chem.,* Vol. 47, No. 10, 1999 **4321**

Figure 1. Repeatability of the $\Delta R/R_0$ response of different metal oxide sensors [three repeated measurements (1−3) at two toasting levels (L, light; F, heavy)].

Figure 2. Dicrimination of toasting levels (1, light; 2, medium; 3, heavy) of differents samples of toasted oak wood by factorial discriminant analysis of the $\Delta R/R_0$ responses of metal oxide sensors: (a) projection of samples; (b) projection of sensors; (dashed-perimeter circles) repetitions of the analysis of the same sample (DF1 = 94.98% of the total variance; DF2 = 5.01%).

72% (P30/1 sensor). These variations were partly attributable to the sensors themselves but were also due to the samples analyzed (headspace concentration).

Total Analysis Time. Data were recorded for 600 s, or 10 min, after 120 s of injection. After 10 min, all of the sensor readings had returned to the baseline. Total analysis time included the purge time to return to the baseline. It may be reduced at least to 8 min by purging at a higher flow rate, which cleans the sensor surfaces more quickly (1500 mL/min).

Repeatability of Measurements. Samples of lightly (L1−3) and heavily (F1−3) toasted wood were analyzed three times. Figure 1 shows the relatively small difference among the results of three analyses of the same sample. Taking the $\Delta R/R_0$ values into consideration at the maximum variation of each sensor, we obtain a coefficient of variation of 8%.

Discriminating among Wood Toasting Intensities Using the MOS Network. The responses of the various MOS recorded for each toasted wood sample and each repetition were subjected to multidimensional statistical processing. After a stepwise PCA using the score values as variables was run, a discriminant factorial analysis (DFA) optimized the separation of the various toasting intensities. Figure 2a shows a projection of the variables in a space defined by the two principal discriminating axes (DF1/DF2), explaining 100% of the total variance (complete correlation).

The three groups representing different levels of toasting on oak were quite separate in the space being examined. Toasted/nontoasted groups were essentially discriminated on the DF1 axis (94.58% of the variance). It was clear that lightly toasted wood was quite separate from the rest. The distinction between medium and
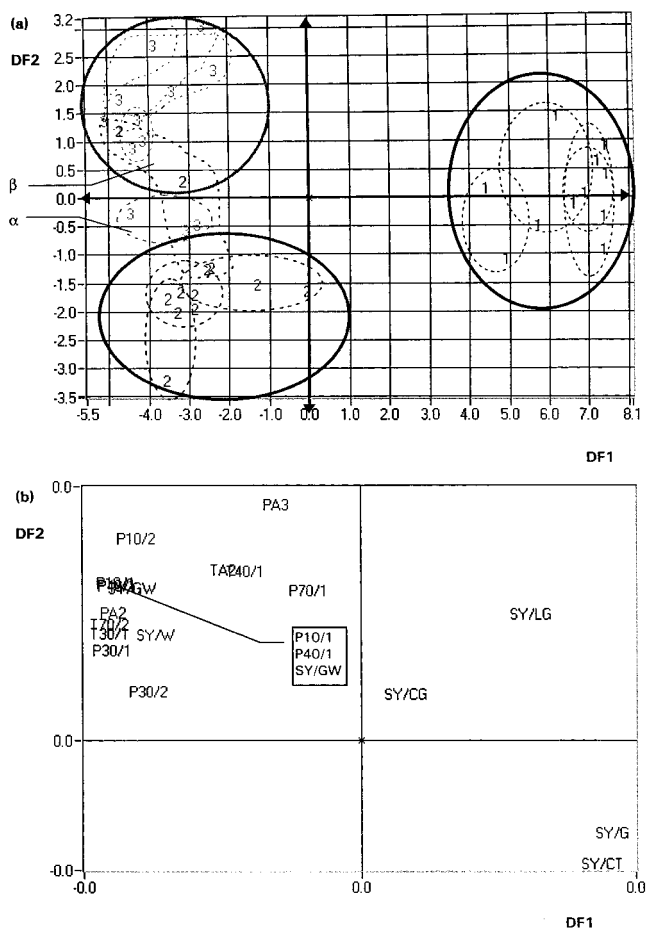
heavily toasted wood, however, plotted on the DF2 axis, accounted for only 5.08% of the variance. Using the Mahalanobis statistic, it was more difficult to distinguish between medium and heavy toasting than it was to discriminate between light and medium toasting or between light and heavy toasting (see Table 1).

Sample α (Figure 2a), considered by the cooper to be heavily toasted, was not properly classified by the statistical model, as it falls between medium and heavy toasting. Sample β, which was analyzed three times, shows a significant dispersion in the measurements. The first measurements were probably erroneous as some sensors had not returned to the baseline.

Selecting the Most Discriminating Sensors. The sensors were projected onto the previously calculated discriminating functions to determine which were most efficient in discriminating among the three toasting intensities (Figure 2b). Table 2 shows each sensor's contribution toward distinguishing among the different toasting levels in DFA.

Table 1. Mahalanobis Distance Calculated between the Different Groups of Toasting Levels

groups	distance
heavy/medium	2.82
medium/light	9.35
heavy/light	10.28

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Table 2. Capacity of Different MOS Used in a Network To Distinguish among Three Toasting Levels

MOS	discrimination power[a]	MOS	discrimination power[a]
T70/2	34.80	SY/GW	30.09
P10/1	34.34	P30/2	24.00
T30/1	34.24	SY/W	23.29
PA2	34.04	SY/LG	16.96
SY/G	33.93	TA2	13.69
P40/1	33.89	PA3	10.71
P30/1	33.15	T40/1	10.67
SY/CT	32.38	P70/1	4.28
P10/2	31.32	SY/CG	1.31

[a] Square of the determination coefficient.

We can see that some nondoped, tin oxide-based sensors (SY/G, SY/CT, SY/CG) are well correlated with the light toast. The other sensors, doped with precious metal, were highly influenced by the volatile compounds emitted by the more heavily toasted wood. The best light/medium or light/heavy toasting discrimination was obtained on the DF1 axis with the SY/G, SY/CT, T30/1, P10/1, P10/2, and SY/GW sensors. Fewer sensors were able to distinguish between medium and heavy toasting on the DF2 axis. The most discriminating sensors were PA3, P30/1, and P30/2. P70/1 and SY/CG sensors were inefficient. Furthermore, P70/1 had a tendency to be contaminated because it never returned to the baseline as quickly as the other sensors. These last two MOS can thus be eliminated without altering the quality of group separation.

CONCLUSION

On the basis of results obtained in this laboratory work, it is possible to envisage using a network of MOS to monitor the quality and toasting homogeneity of oak wood used to make barrels for aging wine and spirits. The results of oak toasting level differentiation obtained via the MOS network, as described above, were identical to those obtained by analyzing extractable compounds in liquid or gas phase as described in a previous paper (Chatonnet et al., 1999).

It should be possible to implement a nondestructive monitoring system based on the analysis of headspace in barrels, under conditions to be defined at a later date. This will, however, require the development and regular updating of a toasting database, customized for each workshop and each toasting level.

Work is currently in progress to examine the technical feasibility of this type of control method under industrial conditions.

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