

A New Approach To Examine the Relationships between Sensory and Gas Chromatography–Olfactometry Data Using Generalized Procrustes Analysis Applied to Six French Chardonnay Wines

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Six French Chardonnay wines were submitted to both sensory and combined headspace/gas chromatography–olfactometry analyses. The detection frequencies allowed five hierarchical levels to be distinguished: P25, the odorant areas (OAs) having a detection frequency $\geq 25\%$ (the complete olfactogram without the odor noise); P40, $\geq 40\%$; P55, $\geq 55\%$; P70, $\geq 70\%$; and P85, $\geq 85\%$. Moreover, the detection frequencies were analyzed to distinguish 21 discriminative OAs. Wines tested by sensory analysis and the headspace samples analyzed by gas chromatography–olfactometry (GC-O) were described by a heterogeneous vocabulary distributed into nine overall classes of descriptors. The new statistical treatment to examine hierarchical or discriminative OA categories with respect to sensory data used Generalized Procrustes analysis (GPA) from coordinate tables provided by correspondence analysis (CA). The successive data sets supplied by CA were subjected to GPA to yield consensus method maps. The more selective levels of detection frequency (P70 and P85) were responsible for incomplete or distorted information with respect to sensory data. The most appropriate segmentation of the OA distribution (olfactogram) to represent the sensory profile of the six samples would correspond to the intermediate pattern (P40 and P55). The other interest was to study the reasons of distortion due to the dynamic headspace extraction. The highest proportions of the variance were at all times related to the same classes: spicy, herbaceous, and, to a lesser degree, microbiological. This would indicate that the dynamic headspace analysis induces a distortion with respect to sensory data, which systematically affected the perception of both spicy and herbaceous characters of wines.

KEYWORDS: Aroma; wine; Chardonnay; dynamic headspace; gas chromatography–olfactometry; sensory analysis; correspondence analysis; Generalized Procrustes analysis

INTRODUCTION

Two approaches are suitable for wine aroma analysis: sensory analysis and instrumental analysis. Gas chromatography–olfactometry (GC-O) can be considered a combination between sensory and instrumental analyses. From the chromatogram, the target is to display odorant areas likely to be both hierarchically classified using their olfactometric indices and described by an experienced panel. Many methods such as dilution methods and time–intensity methods have been applied to determine the olfactometric indices. The most recently proposed method is

based on the detection frequency observed for each odorant area (1). The success of the detection frequency methods depends on there being no requirement for either extract dilutions or training of the panel, except in odor recognition and ability to generate an accurate vocabulary. On the contrary, dilution methods such as Charm analysis (2, 3) and aroma extract dilution analysis (4–6) require long periods of time for all extract dilutions to be sniffed until no odor is detected. This method cannot be proposed to a number of panelists. In fact, a serial dilution was frequently analyzed by a single sniffer. Time–intensity methods such as OSME analysis (7) and the finger-span method (8) require a training period to evaluate aroma intensity using an intensity scale. Consequently, the detection frequency method has been extensively used to display potent odorants in foods (9–13). Despite all of the studies relevant to GC-O analysis, the procedure of odorant area demarcation requisite to the determination of olfactometric

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indices is never precisely described. Pollien et al. (14) used software to cumulate the individual olfactograms yielding the averaged olfactogram. Individual olfactograms are usually compared using the retention indices (10) of the odorant events, but the limits of acceptance are not given. The final olfactogram is obtained by pooling the individual data by simple compilation (12, 15). This important point must be thoroughly studied. GC-O is a powerful tool for the identification of the odor-active compounds relevant to the main odorant areas (6, 16–18).

The reliability of the results relevant to different procedures of GC-O depends on the odor quality of the extracts. The extraction method must be selected with the aim of producing extracts with odor as close as possible to that of the original product. Several techniques have been applied to wine aroma extraction. All of the extraction methods can be arranged into two groups, the first one producing liquid extracts, therefore likely to be handled for sensory analysis, and the second one producing gaseous extracts. Several techniques obtaining liquid extracts such as solvent extraction, vacuum distillation, demixtion/distillation, or solid phase extraction have been already tested (6, 10, 16, 19–22) using frequently the same approach: first, discriminative tests (triangle tests) are performed both to select significantly different products and to compare extraction methods, and then matching tests are developed to evaluate the similarity of extracts and corresponding samples. In contrast to many methods producing handled extracts, very little information has been reported on the representativeness of the gaseous extracts. Noble et al. (23) had already analyzed the headspace volatiles of wines by GC-O. The selection of the sensorially significant components was particularly based on the intensity aroma rating by GC-O. More recently, static headspace (17), dynamic headspace (9, 14, 24), and nospace (25) have been especially used to display the aroma impact compounds of foods. In no case has the need to evaluate the representativeness of the headspace volatiles been discussed.

The target of the present paper is to propose a statistical methodology to evaluate the relationships between sensory and GC-O data. The new methodology was applied to six French Chardonnay wines. Wines were submitted to sensory analysis. GC-O data were especially obtained by dynamic headspace extraction using the detection frequency method. The lists of terms generated during both the sensory and the GC-O analyses were distributed into nine overall classes of descriptors. The relationships between sensory data and various hierarchical and discriminative categories of GC-O data were displayed by using the numbers of descriptor's classes treated successively by correspondence analysis (CA) and Generalized Procrustes analysis (GPA).

MATERIALS AND METHODS

Wines. Six French Chardonnay wines were analyzed. Four of them were made from the Burgundy vineyard (1999 vintage), and the others were elaborated in the south of France (1998 vintage). In Burgundy, Chardonnay grapes (500 kg) were directly pressed (until 2 bar pressure). A mean quantity of SO₂ (60 mg/L) was added to the juice prior to settling (for 14 h at 11 °C). The must was then distributed into four batches. Four commercial yeast strains (*Saccharomyces cerevisiae*) supplied by Lallemand S.A. (Toulouse, France) were inoculated in each batch to perform the alcoholic fermentation. Their registered trademark are CY3079, D522, QA23, and VL1, respectively. Fermentation took place at 20 °C in small-volume tanks (50 L). The wines underwent both alcoholic and malolactic fermentations and were filtered, bottled, and stored for 6 months at 10 °C prior to analysis. The two other Chardonnay wines were produced in Languedoc vineyard (Vins de Pays d'Oc): "les Jamelles" (coded LJ) and "Domaine Loyer Bastié" (coded

LB). They were supplied by a burgundy wine-trader. The two additional white Languedoc wines were chosen to have two separate groups of Chardonnay wines characterized not only by their geographic origin but also by the applied wine-making practices. The Languedoc wines were especially produced by aging in oak barrels for a short time (3 months).

Headspace Sampling. One bottle of every wine was divided into several 30 mL flasks under nitrogen atmosphere. Flasks were stored at 10 °C prior to the headspace sampling. For each experiment, 30 mL of wine was placed into the all-glass system. Headspace volatiles were collected from wine at 20 °C. Nitrogen flow at 50 mL/min for 25 min was provided above the stirred sample. The nitrogen flow was sent through the trap (16 cm length × 0.3 cm i.d.) containing 120 mg of Tenax-TA porous polymer. The Tenax sampling tube was cleaned before use by heating for 30 min at 295 °C under nitrogen flow.

Gas Chromatography-Olfactometry (GC-O). All analyses were performed on a Chrompack CP 9001 coupled to a Chrompack CP-4001 PTI/TCT used in TCT mode (thermal desorption cold trap injector). The Tenax sampling tube was placed on the injection port. The first step was the precool phase in which the cold trap was cooled at -120 °C using liquid nitrogen for 10 min. The second step consisted of a backflush of the Tenax trap using a nitrogen flow at 300 mL/min to remove excess moisture (for 10 min at ambient temperature). Then, the headspace volatiles were thermally desorbed from Tenax-TA for 10 min from room temperature to 250 °C exiting to the cold trap. Finally, the cold trap was flash held at 250 °C, and the volatiles were desorbed from the trap onto the front of the DB-Wax capillary column (J&W Scientific, Folsom, CA; 30 m × 0.32 mm i.d., 0.75 μm film thickness). Helium was used as carrier gas at 1 mL/min. During the desorption period, the oven temperature was heated at 40 °C. Following the injection of the sample, the oven temperature was kept at 40 °C for 5 min then heated to 220 °C at a rate of 4 °C/min. The final temperature was kept for 30 min. The column outlet was connected both to the FID (250 °C) and to a sniffing port equipped with a humidified air make up (30 mL/min).

The solution in pentane of *n*-alkanes (C₇–C₁₆, C₁₈, C₂₀, C₂₂, C₂₄, and C₂₆ at 400 mg/L) was analyzed by FID to determine the linear retention indices (LRIs) of both peaks and odor events. The solution (0.5 μL) was directly introduced through the external port injection in the desorption oven (250 °C) of the Chrompack CP-4001 PTI/TCT.

The sniffing panel consisted of eight judges (four males and four females, average age = 37) already experienced in GC-O. Four of the eight subjects formed an internal jury belonging to the staff of the laboratory, and the four other members of the jury were selected externally out of the laboratory. The judges were chosen for their ability to detect more than 30 odors per GC-O analysis as well as their ability to generate accurate terms. Each panelist carried out a duplicate analysis from each of the six headspace extracts. The order of headspace sampling was established according to the balanced design reported by MacFie et al. (26). Sniffing was performed for 35 min. The odorant perceptions were recorded by pressing a button at the beginning of the stimulus. The yes/no responses and the FID data were simultaneously collected by Maestro software (Chrompack, Middelburg, The Netherlands). The judges were also asked to give a verbal description and the retention time of every perceived odor, even if they did not recognize the odor (descriptor = unknown). The recording of the individual yes/no responses was named odor events recording; 16 odor events recordings were obtained from each dynamic headspace sample. Data from the 16 individual analyses were first analyzed separately. Data were then cumulated to characterize the odorant areas (OAs). The detection frequency of the OAs was calculated by agreement with the method previously described by Pollien et al. (14). Moreover, each OA was limited by two LRIs illustrating the variability of the panel responses. The detection frequencies and the corresponding retention indices can be plotted to establish the averaged olfactogram of the headspace samples. The detection frequencies of the OAs allowed five levels of interest to be distinguished: (1) the OAs having a detection frequency ≥25% (the complete olfactogram without the odor noise); (2) ≥40%; (3) ≥55%; (4) ≥70%; and (5) ≥85% (the major OAs).

Moreover, to compare the six wine headspaces, the detection frequencies of the odorant areas were also used to distinguish the more discriminative OAs.

Furthermore, each OA was described by a list of terms generated by the sniffing panel during the 16 individual analyses. Consequently, wine headspace was described by a heterogeneous vocabulary. The vocabulary was distributed into nine focus groups: chemical, earthy, floral, fruity, herbaceous, microbiological, nutty, spicy, and woody. The scores of the nine classes were determined by numbering the corresponding attributes given by the eight subjects during the duplicate olfactory analyses. The number of the considered OAs depended on the different levels of interest earlier described. The more discriminative OAs were also especially considered to account for the attributes relevant to the nine focus groups.

Sensory Analysis. The 14 panelists (five males and nine females, average age = 41) were previously selected for their ability to memorize and recognize common odors, as well as their ability to generate an appropriate and reproducible vocabulary. The judges were regular consumers of white wine and were screened for sensory acuity. Wine samples stored at 10 °C and presented at 15 °C (25 mL) were provided to describe odor and aroma in coded, clear glasses covered with plastic Petri dishes. Wines were randomly assigned, and the order of presentation was established according to the balanced design reported by MacFie et al. (26). The panelists were encouraged to provide their own vocabulary. The procedure of tasting and term-generating was organized in four steps: orthonasal perception (with and without swirling), retronasal perception, and, finally, the smelling of the small quantity of wine remaining once the glass has been emptied. The judges underwent a term-generating period during six sessions. For the first session, the panelists were instructed to taste three wine samples and to describe their odor according to the procedure previously described. During the second one, the six wines were presented to the panelists. For each wine, they were subsequently asked to generate five or more descriptive terms using their own vocabulary. For the third session, the panelists were asked to choose the five or six most significant terms from the previous lists. During the fourth session, the panelists were required to confirm or not the lists of terms. Should they not be satisfied with the terms, they were able to change or add vocabulary. For subsequent sessions, each judge was asked to check his/her list of descriptive terms. At the end of the introspection period, each panelist had a specific list relevant to each wine.

A new heterogeneous list of terms was established from each wine assessed by sensory analysis. The vocabulary was distributed in the nine overall classes already defined about the GC-O analyses. For each wine, the scores of the nine classes were obtained by inventorying the accurate attributes generated by the 14 subjects.

Statistical Analysis. Seven contingency table samples/descriptor classes were obtained: the first one from the sensory data, and six others from the GC-O data. CA was performed using each of the seven contingency tables (27). Each CA provides a plot in which the 9 descriptor classes and the 6 wines are presented as a cluster of 15 points within a unique five-dimension space. The following GPAs were performed to compare the sensory data configuration with each of the six GC-O data configurations. Therefore, it was possible to observe the more similar configuration with respect to sensory data configuration and the nature of descriptors mainly responsible for the distance between the compared configurations.

The statistical procedure is detailed: Seven contingency tables of the nine overall classes of descriptors within the six samples were established. The first one was obtained from the sensory analysis. The six other contingency tables were obtained from the GC-O analyses: five of them corresponding to the hierarchical categories of OAs (1, the OAs having a detection frequency $\geq 25\%$; 2, $\geq 40\%$; 3, $\geq 55\%$; 4, $\geq 70\%$; and 5, $\geq 85\%$; coded P25, P40, P55, P70, and P85, respectively) and the sixth contingency table corresponding to the discriminative OAs (coded 21OAs). The discriminative OAs were selected using the Chi2 test applied to the detection frequencies of the various OAs evidenced within the six samples.

CAs were performed upon each of the seven contingency tables. CA is a multidimensional method close to principal component analysis (PCA), in which the rows (nine overall classes of descriptors) and the

columns (six samples) of the matrix are subjected to a symmetrical treatment. Two clusters of data were analyzed at the same time: ratios were calculated from the total of each row (distribution of overall classes), and ratios were calculated from the total of each column (distribution of samples). The distance between two samples or two classes of descriptors was calculated by the Chi2 method. CA is therefore an analysis of ratios. CA can be regarded as a particular case of PCA in which the two data sets, classes of descriptors and samples, were plotted together. Each sample is defined as the centroid of the nine classes weighted by the nine corresponding ratios described above. Each category of descriptors is defined as the centroid of the six samples weighted by the six corresponding ratios. Finally, the plot is a samples/descriptor class configuration in which samples are located in close proximity to their more specific descriptors. In contrast, a joint category of descriptors is located in the center of the sample's space. Statistical treatments were performed using WinStat2 software (CIRAD, Montpellier, France) and StatBox 2.1 software (Grimmer Logiciels, Paris, France).

Each CA supplied a (15 × 5) table composed of the coordinates of 15 points (the 6 samples and the 9 classes of descriptors) on the 5 axes (number of samples - 1). Subsequently, the seven coordinate tables given by CA were subjected to six GPAs (28). Statistical treatments were performed using Senstools version 2.3.28 (OP&P Product Research BV, Utrecht, The Netherlands).

GPA was suitable for the comparison between two spatial configurations of the same objects (six wine headspaces and nine descriptor classes). Therefore, GPA was especially useful to determine if relationships existed between sensory analysis and each of the six categories of OAs previously displayed by GC-O analysis. At first, GPA was carried out to evaluate the distance between the configuration provided by sensory analysis and each of the five configurations provided by the five hierarchical categories of OAs. Second, the same approach was applied to compare the configuration relevant to sensory analysis and the one relevant to the discriminative OAs.

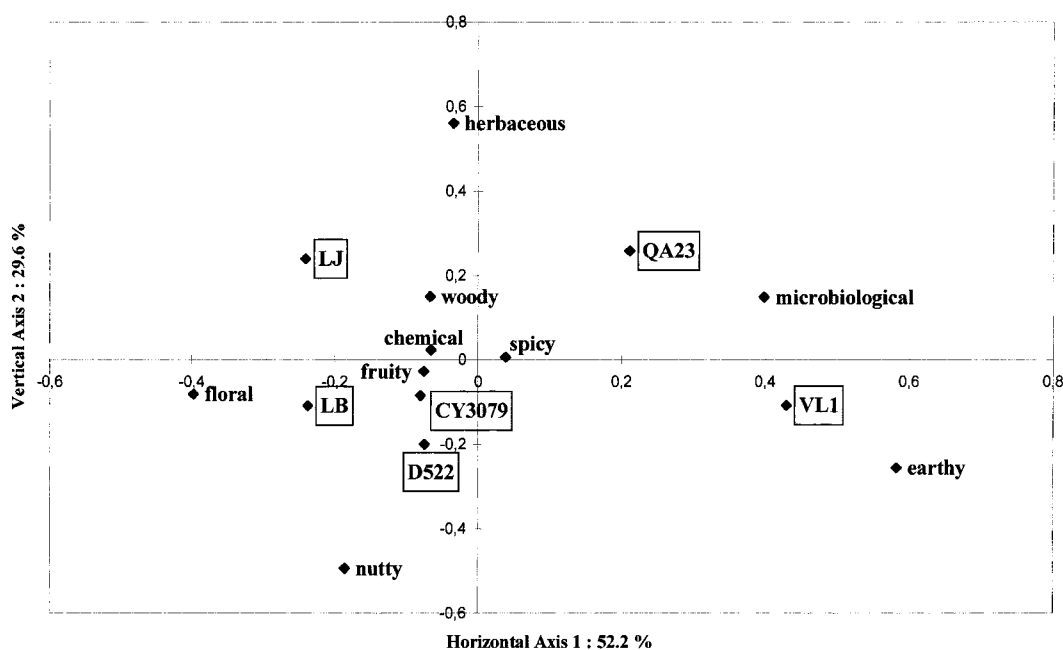
RESULTS AND DISCUSSION

Sensory Analysis. The 14 panelists produced individual vocabularies ranging in size from five to six terms for each Chardonnay wine. In total 447 descriptions were generated by the panelists. The complete list of the vocabulary developed by the jury included 144 different terms. The assessors frequently used the same words. In detail, the number of descriptors suited for a wine included between 47 and 59 different terms for LB and CY3079, respectively. To describe the odor (orthonasal perception) and aroma (retronasal perception) of wines, the panelists did not use exclusively accurate terminology. Three accuracy levels were observed: generic terms (for example, fruity or herbaceous), precise terms (strawberry or hay), and intermediate level terms (berry or dried plant). Noble et al. (29, 30) had previously shown the same requirement to distinguish three precision degrees from a standardized system of wine aroma terminology. To exploit the complete list of terms, including the more general ones, nine overall classes were proposed from the wine aroma wheel (30): chemical, earthy, floral, fruity, herbaceous, microbiological, nutty, spicy, and woody. Thus, all 144 terms generated by the 14 panelists were distributed into the nine classes. The more precise content of each class is detailed in **Table 1**. Despite the experience of the judges, **Table 1** shows that the generic terms were frequently used, especially for floral (floral = 43.6%), microbiological (animal = 43.9%), woody (woody = 33.3%), earthy (mineral = 21.2%), spicy (spicy = 13.7%), and fruity (fruity = 13.4%) classes. This fact justified the use of overall classes. The scores were obtained by numbering the descriptors belonging to each class. The consecutive contingency table was submitted to CA. The results of the CA for each wine and each vocabulary class are presented in **Figure 1**. The first two dimensions accounted

Table 1. Descriptors Developed by the 14 Panelists from the 6 Chardonnay Wines, Content of the 9 Vocabulary Classes,^a and Number of Descriptors Developed by the Panelists for Each Term (in Parentheses)

chemical (42)	earthy (33)	floral (39)	fruity (142)	herbaceous (15)	microbiological (41)	nutty (21)	spicy (51)	woody (63)
alcohol (21)	mineral (7)	floral (17)	fruity (19)	stewed apples (4)	grass cut green (4)	animal (18)	pepper (18)	woody (21)
ether (7)	stone (6)	honey (10)	banana (9)	orange (3)	straw (3)	wild animal (7)	licorice (12)	vanilla (10)
rubbery (5)	undergrowth (4)	rose (4)	grape (Muscat) (8)	peach (3)	herbaceous (2)	rancid (3)	spicy (7)	smoky (8)
iodine (4)	sulfur (4)	white flowers (3)	jam, dried fruit (8)	fig (3)	hay (2)	beer (3)	cocoa powder (2)	toasted (6)
pharmacy (1)	mushroom (2)	syringa (1)	lemon (7)	apple (3)	tobacco (1)	cheese (2)	nutty (2)	oaky (barrel) (4)
varnish (1)	musty (mildew) (2)	lavender (1)	artificial fruit (sweet) (7)	apricot (dried) (3)	sap (1)	butter (2)	hazelnut (1)	clove (3)
menthol (1)	sea (2)	violet (1)	grapefruit (6)	raisin (3)	vegetative (1)	musk (1)	walnut (1)	thyme (3)
plastic (1)	cellar (1)	acacia (1)	quince (6)	tropical fruit (2)	dandelion (1)	vomit (1)	anise (1)	resinous (3)
turpentine (1)	silex (1)	peony (1)	prune (6)	mandarin (2)		dairy product (1)		caramel (3)
	earthy (1)		pear (6)	bergamot (2)		yeasty (1)		roasted (1)
	chalk (1)		apple juice (cider) (5)	berry (1)		leather (1)		burnt sugar (1)
	dusty (1)		citrus (5)	black currant (1)		sweaty (1)		coffee (1)
	ink (1)		pineapple (4)	lychee (1)				cork (1)
			melon (4)	blackberry (1)				
			cherry (4)	raspberry (1)				
			strawberry (4)	passion fruit (1)				

^a All 144 terms are not presented. For example, synonyms, such as apple, Granny Smith, and green apple, were regrouped in one term: apple.

**Figure 1.** Correspondence analysis related to sensory data: relative position of six wines and nine overall classes of descriptors in the plane formed by the first two dimensions.

for 81.8% of total variance. The horizontal axis 1 (52.2% of the total information) distinguished the descriptors in two groups, so that they were opposed to each other. Two vocabulary classes were located on the positive part of axis 1: earthy and microbiological. On the opposite, the second group was exclusively constituted by floral. Representation of vocabulary classes on axis 1 clearly separated terms denoting defects and those denoting qualities. The vertical axis 2 (29.6% of the total information) mainly distinguished herbaceous and woody on the positive part and nutty on the negative part. No conclusion can be established from the chemical, spicy, and fruity attributes because they were not well explained in the space confined within the first two axes. Representation of wines allowed VL1 to be associated with earthy and microbiological and QA23 with microbiological and woody. More precisely, VL1 was described by earthy attributes such as mineral, sulfur, and undergrowth. The Chardonnay wine elaborated from the QA23 strain was characterized by woody, toasted, and vanilla attributes, although the alcoholic fermentation was made in a tank. This feature could be explained by the specific effect of the QA23 strain on

the sensory profile. Samples LJ and LB were located together in the negative direction of the first axis. They were mainly characterized by floral descriptors. Furthermore, LJ was associated with fruity, herbaceous, and woody descriptors. LB was also described by nutty as well as woody and secondary fruity descriptors. This displayed the particular aroma profile of these two wines produced in the Languedoc vineyard and the effect of aging in oak barrels. The target to have wines different from those produced in Burgundy from selected yeasts was partially achieved. The scores of D522 and CY3079 had intermediate positions.

Gas Chromatography-Olfactometry Analysis. Eight panelists carried out a duplicate analysis for each headspace sample. For each wine, 16 individual analyses were obtained. First, the odorant events and peak retention times were turned into LRIs to connect the chromatogram and the corresponding olfactogram. Second, the odorant peaks and sometimes the no-peaks were numbered. Finally, each individual datum consisted of the code of the panelist, the numbers of odorant peaks and no-peaks, the LRIs of the odorant events, and the respective descriptors.

Comparison of the 16 individual data allowed the OAs to be distinguished: starting with the headspace sample, the individualization of the OAs was easier when the 16 individual data, especially linear indices and numbers of peaks and no-peaks, were accumulated in the same table. More frequently, each OA consisted of many odorant events detected by different panelists. The main problem was to be sure that different events belong to the same OA. In fact, particularly with the DB-Wax column, the use of relative retention indices was neither sufficient nor satisfactory. In contrast, the morphology of the 16 chromatograms and, especially, the peak numbering were an effective aid. Different descriptors, in agreement or not, relevant to the suggested OAs were displayed. Although the panelists were experienced, the OAs were rarely determined using the descriptors exclusively. On the contrary, the same vocabulary or the same overall-class of terms generated by several panelists contributed to confirm the validity of the segmentation. In some cases, particularly when an odorant event was located between two OAs, the employed term allowed choice. For lack of peak, descriptors were also helpful.

From headspace volatiles of a single wine, the characterized OAs can be classified into five categories: (1) one OA and one corresponding peak, usually slight and well separated; (2) one OA and no corresponding peak; (3) large and heterogeneous OA and corresponding large peak where it was difficult to distinguish different olfactory areas (it was expected that volatile compounds were coeluted but, for lack of consistent descriptors, no olfactory segmentation was possible); (4) one located OA within a large peak (in that case, OA was necessarily described by a list of homogeneous descriptors); (5) one OA and two successive peaks partially separated (in that case, the odorant events were placed both within the first one, the second one, and especially between the peaks). Moreover, descriptors were similar. Therefore, it was difficult to distinguish precisely the area of the chromatogram responsible for the odorant perception. Consequently, in this case, the limits of the OA can include two successive peaks. Only the subsequent mass spectrometry analysis is helpful to identify the volatile compound(s) related to such an OA category. Nevertheless, even if GC-O is considered to be a powerful tool to focus on the areas of the chromatogram from which it is important to identify the responsible compounds, authors such as Escudero et al. (10) did not manage to identify volatile compounds relevant to 6 of the 19 selected OAs in Champagne extracts. This problem is recurrent, but it was interesting to underscore that the unidentified OAs were frequently described by a heterogeneous or generic vocabulary (31). Low concentrations in extracts (second OA category) and coeluted compounds (third, fourth, and fifth OA categories) were mainly responsible for difficult identifications (12, 24).

Finally, the consistent and definitive results of GC-O were obtained when the six final olfactograms were compared. The purpose was to harmonize the data prior to statistical treatment. It was necessary to verify carefully if the same OA was specially detected in only one wine extract or common to some of them. Consequently, the detection frequency of the reliable OAs was calculated. All of the odorant events were considered to calculate the detection frequencies. Subsequently, only the corresponding attributes belonging to the nine overall classes were accounted. The total number of odorant events was included between 608 (LJ) and 682 (CY3079). Every odorant event can be described by one or more terms. The total number of terms was included between 745 (LJ) and 838 (CY3079). It happens that description was not possible and therefore not numbered. The percent of

Table 2. Gas Chromatography–Olfactometry Total Results of Six Chardonnay Wine Headspace Samples

	D522	VL1	QA23	CY3079	LJ	LB
total odorant events	633	618	662	682	608	645
total generated terms	786	775	817	838	745	798
"unknown" (%) ^a	5.1	5.4	4.9	5.8	5.1	5.6
total generated descriptors	746	733	777	789	707	753
discarded descriptors (%) ^b	2.5	1.6	3.5	1.9	1.4	2.5

^a Percentage of total generated terms. ^b Percentage of total generated descriptors (all terms – unknown).

the "unknown" was never more than 5.8% of the total terms. Despite the experienced judges, some of the descriptors generated during the GC-O analyses were removed, given that they did not fall into any of the nine classes (for example, perfume, cereals, flour, cake, freshness, and moisture) or because they had a hedonic (pleasant and unpleasant) or gustatory (sweet, sour, bitter, and acid) character. The discarded descriptors never represented more than 3.5% of the total descriptors. In detail, the results are presented in **Table 2**. Moreover, the OAs having a detection frequency of <25% (detected in fewer than 4 of 16 sniffings) at the same time in the six headspace samples were considered to be odor noise. There were 36 corresponding removed OAs. The 72 remaining OAs are given in **Table 3**.

On the one hand, 59 OAs were common to the six headspace samples. Among them, only three odorant areas (no. 16, 18, and 30) were detected in the six samples by the eight panelists during the 16 analyses. OA16 was almost exclusively described by fruity character. OA18 was more heterogeneous, but the fruity character was predominant. Finally, OA30 was described by microbiological, earthy, and herbaceous characters. Among the 59 common OAs, only 11 of them (no. 4, 9, 11, 12, 22, 26, 45, 53, 59, 60, and 69) were characterized in the six samples by a frequency detection >70% (no fewer than 12 sniffings among 16). Moreover, the 11 OAs were mostly focused and described employing a common vocabulary: OAs 4, 9, 11, and 12 were mainly described by fruity terms, OAs 22 and 59 by earthy (mushroom) terms, OAs 60 and 69 by floral terms, and OAs 45 and 53 by microbiological (secondary earthy) and herbaceous, respectively. The number of OAs presented in **Table 3** was included between 64 (LJ) and 69 (D522). Among them, 14 major OAs having detection frequencies >70% can be considered as common and main contributors for the aroma of all the headspace samples. These 14 OAs therefore contributed to the joint sensory quality of samples, but they did not justify the distinctive sensory profiles.

On the other hand, to emphasize the differences between the six wines relevant to the GC-O results, the Chi2 test was carried out using the detection numbers. The results are presented in **Table 3**. Twenty-one odorant areas were responsible for the significant differences among the six samples. The 21 selected OAs and the six wines were plotted in a CA as shown in **Figure 2**. The first two dimensions accounted for 73.2% of the total information. The most interesting information was given by the first axis (46.6% of the information). The first axis clearly distinguished the wines elaborated in the south of France (LJ and LB) from the four regrouped wines elaborated in Burgundy (CY3079, D522, QA23, and VL1). The preliminary choice of two categories of Chardonnay wines was based on different factors: geographic origin (vineyard), vintage, and enological practices. The cleavage of the six wines into two groups was partially demonstrated by sensory analysis. Furthermore, the distribution of the wines into two groups was particularly displayed from the GC-O analysis. Nothing predicted this result.

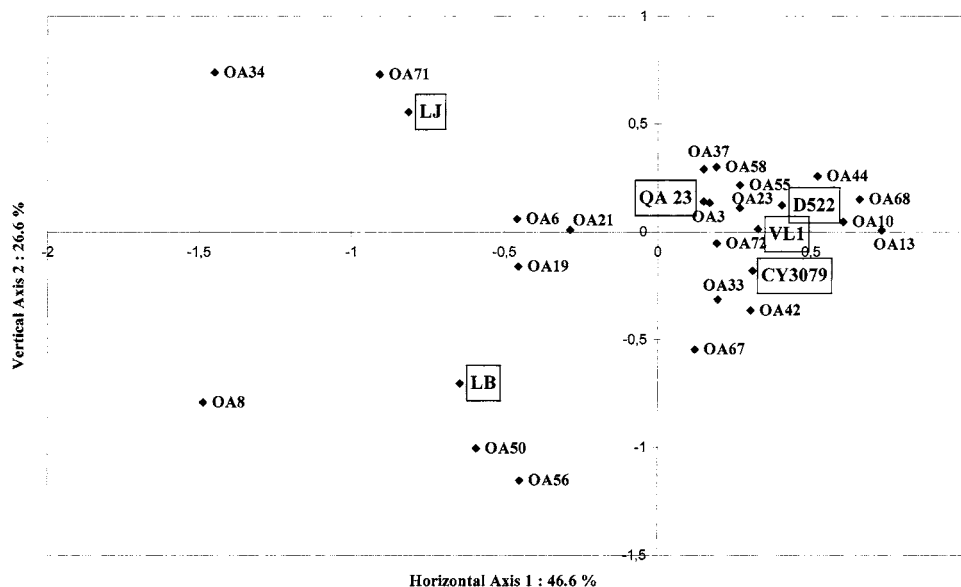


Figure 2. Correspondence analysis related to detection frequencies given by GC-O data: relative position of 6 headspace samples and 21 discriminative OAs in the plane formed by the first two dimensions. The OAs are plotted with their code numbers (see Table 3).

Consequently, it was particularly interesting to show that the 21 discriminative OAs clearly confirmed the consistency of two categories of wines described above. Samples LJ and LB were together located in the negative direction of the first dimension. In detail, OAs 34, 71, and also, to lesser extent, 6, 19, and 21 were more specifically associated with sample LJ. Sample LB was also characterized by OAs 6, 19, and 21 but mainly by three other OAs: 8, 50, and 56. In the first axis and in front of samples LJ and LB, all of the samples CY3079, D522, QA23, and VLI are noticeably regrouped with 13 OAs, especially OAs 10, 13, 44, and 68. Of these 13 OAs, 6 were predominantly characterized by earthy and herbaceous attributes. The descriptors specifically generated to describe the 13 OAs during GC-O from the four samples were distributed as follows: earthy (20.6%), herbaceous (17.3%), chemical (13.7%), microbiological (12.7%), floral (9.8%), woody (9.5%), fruity (9.2%), nutty (4.6%), and finally spicy (2.6%). The descriptors used to qualify the five OAs more specifically associated with sample LJ were distributed as follows: fruity (27.5%), chemical (19.6%), earthy (17.6%), floral (11.8%), woody (7.8%), nutty (5.9%), spicy and herbaceous (3.9%), and microbiological (2.0%). For sample LB, the distribution was fruity (39.1%), chemical (17.4%), floral and earthy (10.9%), woody (6.6%), nutty, spicy, and herbaceous (4.3%), and finally microbiological (2.2%). As shown in Figure 2, the distribution of descriptors into the nine overall classes can be regarded as a corroboration of the sensory data (Figure 1). Nevertheless, even if the volatile compounds responsible for the 21 discriminative OAs were probably specific contributors to the sensory profile of the respective wines, this observation must be interpreted with caution. The sensory profile of the six wines cannot be exclusively explained by various combinations of 21 discriminative compounds.

Relationships between Sensory Analysis and Various Categories of OAs. GPA was used to improve the treatment of GC-O data. At first, the sensory data (SA; coordinate table given by CA) were compared with each of the five GC-O data distributed into the hierarchical categories (five coordinate tables given by CA), corresponding to the OAs regrouped into five levels of detection frequency (P25, P40, P55, P70, and P85). Percentages residual within variance distributed over each pair of methods on the five dimensions of the GPA are presented in Table 4. The total values illustrated the totality of the variation

Table 4. Percentage Residual Variance Distributed over the Two Compared Methods on the Five Dimensions of the Six GPAs

dimension	SA ^a vs 25 ^b	SA vs P40 ^c	SA vs P55 ^d	SA vs P70 ^e	SA vs P85 ^f	SA vs 21OAs ^g
1	16.21	8.42	9.11	10.63	14.17	8.56
2	8.64	10.80	10.78	13.31	9.87	8.31
3	2.98	4.19	4.84	3.33	6.38	1.78
4	2.64	4.37	1.99	1.52	2.62	3.85
5	1.07	1.42	1.98	3.70	1.08	2.18
total	31.54	29.20	28.70	32.49	34.13	24.68

^a Sensory data. ^{b-f} GC-O data: OAs having detection frequencies ≥ 25 , ≥ 40 , ≥ 55 , ≥ 70 , and $\geq 85\%$, respectively. ^g GC-O data: 21 discriminative OAs.

between two configurations. The interpretation of results was therefore independent of the percentage of representation. The lower the value, the lower the distance between two compared methods. The set relevant to the five hierarchical categories of OAs showed the same degree of disagreement with the sensory data. In detail, it was, however, interesting to note that the higher total values were observed for the opposite cases, particularly P85 or P70 but also P25 versus SA. This would indicate that the more selective levels of detection frequency (P85 and P70) were responsible for incomplete or distorted information with respect to sensory data. This result validated the previous GC-O data where each of the 14 OAs having a detection frequency $>70\%$ was both detected and similarly described within the six samples. On the other hand, despite the removal of the OAs infrequently described by the assessors, the less selective level of detection frequency (P25) would provide still odor noise, which disturbed the information. The most appropriate segmentation of the OA distribution (olfactogram) to represent the sensory profile of the six samples would correspond to the intermediate pattern: P40 or P55. An accurate selection of OAs using the detection frequency method depended on the signal above noise level of the group of assessors (32). According to our results, OAs with detection frequencies <30 – 40% (detection by fewer than 3 or 4 assessors of 10) were usually considered to be noise (11, 12, 15, 33). Pollien et al. (14) have reported a method to determine the appropriate number of panelists required to obtain a reliable olfactogram. Indirectly, they have shown that the discarding of OAs with frequency

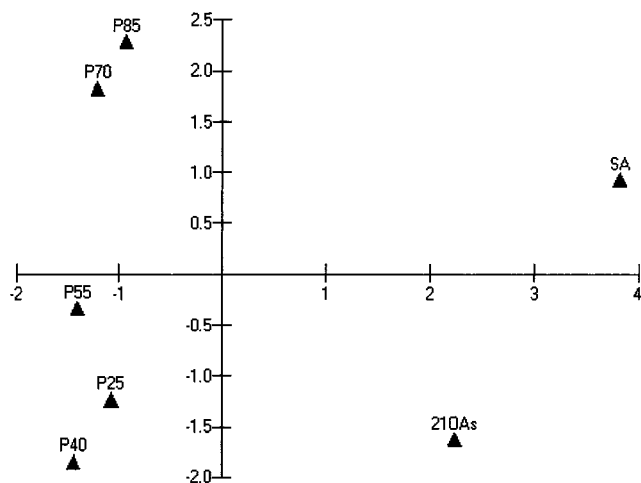


Figure 3. Consensus space from Generalized Procrustes analysis: plot in the plane formed by the first two dimensions. The methods are plotted with their codes (see Table 4 or 5).

detections <30% was permitted when the panel consisted of 8–10 subjects.

As shown in Table 4, the significantly lower variation between two methods was determined for sensory data versus 21 discriminative OA data. This would indicate that there was a connection between the odor description of the six wines by sensory analysis and the sensory description of the more specific OAs evidenced by GC-O in the corresponding headspace samples. The final and complete result of GPA was illustrated by the consensus configuration of the seven methods (SA, P25, P40, P55, P70, P85, and 21OAs). The plot showing the relative position of the seven methods is given in Figure 3, a graphical representation of the first two dimensions accounting for 69.2% of the total variation. The configurations SA and 21OAs were located together on the positive pole of the first dimension (35.6% of the consensus variance) and were behaving differently from the remainder of the configurations. In contrast, the negative pole of the first dimension was characterized by the five hierarchical classes of OAs grouped together. The apparent connection between SA and 21OAs data can be considered as a support of the results mentioned above (Figure 2) and also regarded as a validation of the new methodology using GPA established from coordinates tables supplied by CA to try to correlate sensory and GC-O data.

The reason for the split in the pattern can be explained by the examination of the percentages residual variance distributed over both the nine overall classes of descriptors and the six samples on the five dimensions of the six GPA where each category of selected OAs was compared with sensory data (Table 5). The residual variances were uniformly distributed over the nine classes of descriptors, showing that the distances between sensory data and various categories of OAs were homogeneous. Thus, the residual variances of total descriptors were comparable. Consequently, the total variation between each pair of methods previously discussed (Table 4) was not relevant to the nine overall classes of descriptors. In detail, it was very interesting to note that the highest proportions of the variance were at all times related to the same classes: spicy, herbaceous, and, to a lesser degree, microbiological. These were evaluated to differ from the others. This can be therefore attributed to the dynamic headspace extraction method, which would indicate that the headspace analysis induced a distortion with respect to sensory data that systematically affected the perception of both spicy and herbaceous characters of wines. All wines strongly

Table 5. Percentage Residual Variance Distributed over the Nine Overall Classes of Descriptors and the Six Samples on the Five Dimensions of the Six GPAs

	SA ^a vs P25 ^b	SA vs P40 ^c	SA vs P55 ^d	SA vs P70 ^e	SA vs P85 ^f	SA vs 21OAs ^g
chemical	0.56	0.45	0.56	0.59	1.25	0.18
earthy	1.43	1.61	1.74	1.88	1.94	1.09
floral	0.58	0.49	0.62	1.61	1.71	0.67
fruity	0.77	0.82	1.02	0.69	0.27	1.50
herbaceous	5.90	3.99	3.50	2.30	2.67	4.07
microbiological	2.57	1.27	1.51	3.52	1.77	0.47
nutty	0.55	0.88	1.12	0.58	1.08	1.73
spicy	5.34	3.08	3.71	3.54	2.35	3.96
woody	0.62	0.95	0.93	1.57	1.74	2.39
total descriptors	18.32	13.54	14.71	16.28	14.78	16.06
CY3079	0.92	2.62	1.95	1.35	1.05	1.56
D522	4.35	3.28	1.85	1.93	1.65	2.47
QA23	1.17	1.10	1.03	1.67	1.28	1.78
VL1	1.89	2.68	2.58	5.68	7.33	0.29
LB	3.75	4.95	5.48	4.50	5.86	0.40
LJ	1.14	1.03	1.10	1.08	2.18	2.12
total samples	13.22	15.66	13.99	16.21	19.35	8.62
total	31.54	29.20	28.70	32.49	34.13	24.68

^a Sensory data. ^{b–f} GC-O data: OAs having detection frequencies ≥ 25 , ≥ 40 , ≥ 55 , ≥ 70 , and $\geq 85\%$, respectively. ^g GC-O data: 21 discriminative OAs.

exhibited a spicy character evenly perceived by the assessors during the sensory analysis, whereas the six corresponding headspace samples were never characterized by numerous spicy OAs. Among 72 OAs given in Table 3, only 3 of them (OAs 62, 66, and, to some extent, 70) were more particularly described using spicy attributes. Thus, the number of spicy attributes generated during GC-O was low, independent of the hierarchical categories of OAs. In addition, the infrequent OAs responsible for spicy character were systematically detected at the end of chromatograms. Other research has investigated the combination between headspace volatiles of five wines and sensory evaluation of GC effluents (23) and found only two spicy OAs in the last part of chromatograms. This would confirm that the distortion of the balance between the volatile constituents is especially induced by the conditions of the dynamic headspace sampling. This phenomenon seems to affect more particularly the ability of the dynamic headspace to reproduce the spicy character of wines. In contrast, the herbaceous attributes were recurrently used to describe various OAs, whereas the six wines did not exhibit a herbaceous note. The emphasis of herbaceous character in GC-O data with respect to sensory data was probably due to the isolation of various volatile compounds from the matrix, responsible for herbaceous character when these compounds were separated but without predominant effect on the overall sensory quality of wines. Consequently, the coupled headspace/GC effluents analysis involved a distortion promoting the perception of herbaceous OAs. This persistent fact was observed independent of wines and various categories of OAs, more particularly for the less selective level of detection frequency. The higher percentage residual related to total descriptors was determined when sensory data were compared with P25. Herbaceous showed highest proportion of the total variance. The herbaceous note was therefore more associated with the OAs with lower detection frequency. Consequently, the distortion related to the perception of herbaceous character especially affected the comparison between sensory and P25 data.

As shown in **Table 5**, no configuration (couple of methods) had a total descriptors residual that was consistently greater than the others. Thus, the contrast between each pair of methods was mainly attributed to the total wines residual variance. As previously discussed, the higher agreement was obviously obtained when sensory data were compared with 21 discriminative OA data. This resulted from the consensus relevant to both VL1 and LB samples. In contrast, in the other cases, VL1 and LB showed high proportions of the total variance, more particularly when sensory data were compared with P85. The residual sample variance was evenly distributed over wines QA23, CY3079, LJ, and, to a lesser degree, D522, showing that these were judged not to differ on the six configurations.

The new statistical treatment to examine hierarchical or discriminative OA categories with respect to sensory data successfully used GPA from coordinate tables provided by CA. It was the first application of GPA to such data. Furthermore, the interest of the methodology was to display the reasons of distortion due to the dynamic headspace method. However, to fully explain the influence of extraction method on the degree of representativeness, other investigations will be required to validate the new statistical approach.

ABBREVIATIONS USED

CA, correspondence analysis; FID, flame ionization detector; GC, gas chromatography; GC-O, gas chromatography-olfactometry; GPA, Generalized Procrustes Analysis; OA(s), odorant area(s); PCA, principal component analysis; SA, sensory analysis; LRI, linear retention index.

ACKNOWLEDGMENT

We are grateful to the Bureau Interprofessionnel des Vins de Bourgogne for providing wine samples.

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Received for review May 13, 2002. Revised manuscript received October 13, 2002. Accepted October 13, 2002. This work was performed with the financial support of the Conseil Régional de Bourgogne and Lallemand S.A., Project 00/5112/E6/03111.

JF0205458