Odor Intensity Evaluation in Gas Chromatography−Olfactometry by Finger Span Method

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This paper describes the potential of evaluating odor intensities in a gas chromatographic effluent by cross-modality matching with the finger span (GC-O-FSCM). A simple prototype is described that allows the precise measurement and acquisition of the distance between the thumb and another finger during the analysis. The stimulation of panelists at the sniffing port with ethyl butyrate shows a log−log relation between peak height values obtained from finger span and stimulus concentrations. It also shows that all panelists are able to perform this task but with different precision, which is used to select them. A triplicate evaluation by GC-O-FSCM of the intensity of flavor constituents in synthetic solutions shows that a four-member panel is perfectly able to determine most of the characteristics of the solutions and to create a finger span multidimensional space highly correlated with the theoretical intensity space.

Keywords: *Gas chromatography; olfactometry; odor intensity; cross-modality matching*

INTRODUCTION

In the past 10 years, gas chromatography coupled with olfactometry (GC-O) has been increasingly used by flavor chemists as reviewed recently by Grosch (1993) and Mistry et al. (1997). The success of the method is due essentially to Acree et al. (1984) and Ullrich and Grosch (1987), who both improved and rationalized the protocol of sniffing. The aromagrams they obtained by sniffing successive dilutions of the same extract give valuable information on the number of odor units of each flavor constituent eluted from the column (Acree et al., 1984). This protocol allows the experimenter to obtain reliable results because of the simplicity of the task asked of the panelists and because of a validation of the final result obtained from the multiple detection of the same odor in the different dilutions of the same extract. Nevertheless, the major drawbacks of the dilution approach are, first, the difficulty of using more than one panelist, as is advisable in sensory analysis because the method is very time-consuming, and, second, the results obtained are based on detection thresholds and not on real intensities. To overcome these serious limitations, two different solutions were proposed recently.

The first solution, developed respectively by van Ruth et al. (van Ruth et al., 1995; van Ruth and Roozen, 1994) and Pollien et al. (1997a,b), overcomes the problem of the restrictive number of panelists, thus allowing one to get an aromagram validated on a number of people and also allowing one to calculate statistical differences between aromagrams obtained from the evaluation of different samples.

The second solution, proposed by McDaniel (da Silva et al., 1994), should overcome both problems, because it allows a direct estimation of the intensity of the odors using a reasonable number of panelists. The method, named OSME by its authors, is based on a magnitude estimation of the odor intensity. The panelists make this evaluation using a variable resistor with a pointer moving along a 150 mm long category scale. A simultaneous computerized graphical feedback of the settled position of the cursor helps the panelist to adjust this position to the perceived intensity. Using a synthetic solution, the authors demonstrated in the paper cited above that the estimation of the intensity of odors detected in a chromatographic effluent can be well correlated for each panelist with the concentration of the corresponding constituents, thus proving the feasibility of a GC-O intensity measurement.

The only published application of the method concerns Pinot noir wines of different vintages and maturities (Miranda-Lopez et al., 1992). Surprisingly, the authors interpreted the differences between wine OSME aromagrams using the frequency of detection of the odors as proposed by Pollien et al. (1997b) and van Ruth et al. (1996a,b) but not using the estimation of their actual intensities as originally planned. This limited analysis of the data obtained by the OSME technique is questionable. It could be explained by the conjunction of a large discrepancy observed in the number and quality of the substances detected between panelists, as observed by the same authors in previous papers (da Silva et al., 1994; McDaniel et al., 1989), associated with a reduced number of panelists evaluating the wine extracts. It could also be interpreted as if the OSME analysis was a too difficult task to be performed by the panelists.

The aim of this experiment is therefore to test further the ability of a panel to discriminate samples using a direct estimation of the odor intensity of individual volatile constituents eluted in a chromatographic effluent. Instead of the magnitude estimation, a different scaling method was used, recently tested successfully in GC-O (Guichard et al., 1995): the cross-modality matching with finger span.

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Table 1. Ethyl Butyrate Concentration and Theoretical Odor Intensity Calculated after Stevens Equation of the Solutions Injected

stimulus no.	concn, mg/L	theor intensity
1	67	4.3
2	530	9.0
3	1770	13.7
4	4110	18.4
5	7870	23.1
6	13350	27.8

Table 2. Synthetic Solutions: Constituent Concentrations (Grams per Liter) and Corresponding Odor Intensity Range

	solution no.				theor intensity
compound	1	2	3	4	range[a]
3-methylbutane-thiol (MBT)	0.002	0.514	0.238	0.088	1−6.2
hexan-2-one	10	15	10	15	1−1.2
furfural	15	5.1	15	5.1	1−1.7
benzaldehyde	9	15	9	15	1−1.2
octan-1-ol	7	7	15	15	1−1.2
nonanal	15	5.21	0.4	15	1−2.7
2-methoxyphenol (guaiacol)	0.486	1.61	4.09	0.09	1−6.0
citronellal	15	1	9.36	15	1−2.3
2-phenyl-1-ethanol	0.112	2.16	3.88	0.42	1−6.1
decanal	15	0.6	5.61	5.6	1−2.7
vanillin	0.071	0.273	1.5	0.7	1−5.9

[a] Calculated from the theoretical intensity of C°.

MATERIALS AND METHODS

Chemicals and Solutions. All aroma substances were purchased from Sigma or Aldrich (Saint Quentin Fallavier, France). Butyrate and synthetic solutions were made by dilution in freshly distilled dichloromethane (pure for synthesis, SDS, Peypin, France).

For ethyl butyrate and each of the 11 constituents of the synthetic solutions, a minimum concentration $C°$ was first determined experimentally as corresponding to an odor just detectable by four people from the laboratory. This estimation was realized by GC-O analysis of a synthetic solution containing the different compounds at concentrations easily detectable and then diluting by a factor of 2 this solution until no more odor could be detected. Higher concentrations were determined theoretically from the minimum detectable concentration $C°$ to obtain a series of solutions with increasing odor intensities following a geometrical progression, as seen in Table 1 for ethyl butyrate. The calculations were made from the Stevens equation $I = (C - C_s)^n$. n, the Stevens's exponent, was obtained from Devos et al. (1998), and C_s, the threshold concentration, was estimated as the experimental value $C°$ divided arbitrarily by a factor of 2. For ethyl butyrate, the threshold value C_s was neglected in the calculation. These estimations of the intensities are characteristic of the GC-O system we used because $C°$ and C_s depend directly on the gas chromatographic parameters and on the sniffing port design.

For the synthetic solutions, each time the calculated concentration was found to be higher than the practical upper limit concentration injectable on the column (saturation concentration), it was replaced by this limit value (15 g L^{-1}). Tables 2 and 3 indicate the final concentrations of the constituents of the different solutions analyzed, and their corresponding calculated intensities.

Gas Chromatography (GC). Gas chromatographic analyses were performed on a Hewlett-Packard 5890 instrument equipped with a split−splitless injector (210 °C; split ratio = 1:3.3), an FID (250 °C), and a homemade sniffing port. Separations were made on a DB-1701 column (J&W Scientific Inc.; 15 m; 0.53 mm i.d.; 1 μm thickness), using hydrogen as a carrier gas (velocity = 57 cm s^{-1}). The column was connected to the FID and to the sniffing port with capillaries of equal lengths by the mean of a Y press fit connector. The transfer line to the sniffing port was heated at 250 °C, and humid air (100 mL min^{-1}) was added concentrically to the chromatographic effluent at the bottom of the glass sniffing cone.

For ethyl butyrate, 1 μL of each of the six different solutions (Table 1) was successively injected every 60 s, and the split was opened 330 s after the first injection. During the whole analysis, the column temperature was maintained at 40 °C. To avoid contamination and errors between solutions during injection, each one was injected with a different and labeled syringe.

For the synthetic solutions, 1 μL of the selected solution was normally injected in the column maintained at 40 °C, and the injector split (ratio = 1:3.3) was opened after 30 s. After 12 min, the oven temperature was raised to 215 °C at 6 °C min^{-1} and then immediately to 220 °C at 10 °C min^{-1} to accelerate the elution of vanillin.

Gas Chromatography−Olfactometry (GC-O). *Hardware and Software.* The distance between the thumb and the major finger, or finger span (Ekman et al., 1967), was measured with the device described in Figure 1. The output signal was sampled simultaneously with the FID signal every 50 ms using a PC-driven four-channel plug-in acquisition board developed in the laboratory (Almanza and Mielle, 1990). The panelists were instructed to match the intensity perceived with the finger span and eventually to describe the quality of the odor detected using a tape recorder with an automatic voice set-off. After the analysis, the data were visualized and processed using software developed in the laboratory (Almanza et al., 1989).

The evaluations were realized in isolated conditions in a quiet room with a natural light and a temperature regulated between 20 and 22 °C.

Panelists. Panelists were volunteers. Four of them (CD, MH, LB, and MJV) participated regularly in descriptive sensory evaluations in the laboratory and two of them (LB and MJV) had previous experience in GC-O. These panelists were paid at the end of the experiment for the number of hours of presence. To stimulate their interest, an extra grant was paid for regular attendance. The panelists were asked to avoid smoking, drinking coffee, or eating food at least 1 h before each experiment. Finally, they were asked not to use perfume or aftershave this particular day.

Among the seven panelists, one was male (OC), four were below 25 years old (OC, CA, LB, and FM), and the other three were between 40 and 50 years old. One of the panelists, CD, stopped the evaluation after the butyrate experiment for personal reasons.

Familiarization and Training Sessions with Ethyl Butyrate. During three preliminary sessions of familiarization, the six ethyl butyrate solutions were injected successively in decreasing concentrations as described above. This series of stimulation was repeated four times in each session. The panelist was informed of the decreasing intensity of the stimulus within each series and was asked to match the different intensities perceived with the finger span using the prototype (high intensity corresponding to a large finger span and weak intensity to a small finger span).

Training sessions differed from the familiarization sessions by two details. First, the output signal was systematically recorded and afterward processed. Second, the order of the stimuli, which was always known by the panelists, could be different from one series to the other. To help panelists to make a systematic self-calibration of the prototype, they were asked to fit the perception of the first stimulus, which always corresponded to the highest concentration, with their maximum finger span. The number of training sessions varied among panelists from three to nine. Training was stopped when a good discrimination was observed during the three first sessions or when it was considered good enough in the following sessions.

Evaluation Sessions with Ethyl Butyrate. The evaluation sessions were identical to the training sessions. However, the panelists were not informed of the order of presentation of the stimulus concentrations except for the first stimulus, which

Table 3. Psychophysical Characteristics of the Constituents of the Synthetic Solutions

variable	S's,[a] Se	GC-O EDT,[b] kg/L	theor odor intensity			
			solution 1	solution 2	solution 3	solution 4
3-methylbutanethiol (MBT)	0.29	1×10^{-6}	0.16	0.82	0.66	0.49
hexan-2-one	0.42	5×10^{-3}	2.63	3.12	2.63	3.12
furfural	0.47	2.55×10^{-3}	3.57	2.15	3.57	2.15
benzaldehyde	0.36	4.5×10^{-3}	2.21	2.65	2.21	2.65
octan-1-ol	0.28	3.5×10^{-3}	1.72	1.72	2.13	2.13
nonanal	0.27	2×10^{-4}	2.08	1.56	0.78	2.08
2-methoxyphenol (guaiacol)	0.24	2.5×10^{-6}	0.84	1.12	1.4	0.56
citronellal	0.31	5×10^{-4}	2.32	1.00	2.0	2.32
2-phenyl-1-ethanol	0.31	6×10^{-6}	0.51	1.27	1.52	0.76
decanal	0.31	3×10^{-4}	2.32	0.85	1.71	1.71
vanillin	0.30	3.5×10^{-6}	0.45	0.68	1.13	0.9
sum of theor odor intensities			19	17	20	19

[a] Stevens's exponents compiled by Devos et al. (1998). [b] GC-O experimental detection thresholds.

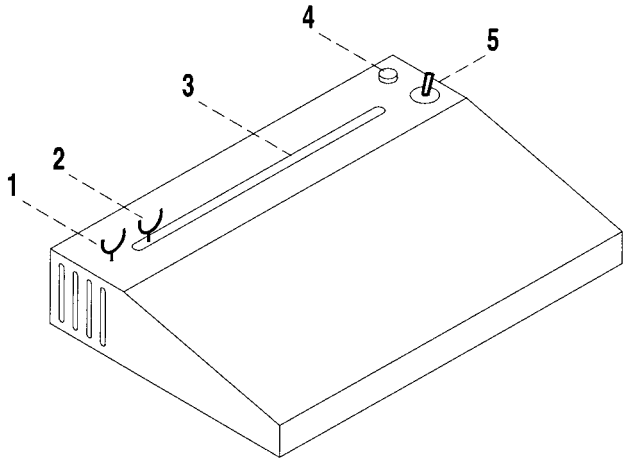

Figure 1. Drawing of the finger span prototype used to measure distance between fingers: 1, fixed ring for the thumb; 2, mobile ring for the major or the index finger connected to a 195 mm long rheostat; 3, cursor track; 4, signal lamp; 5, on/off switch.

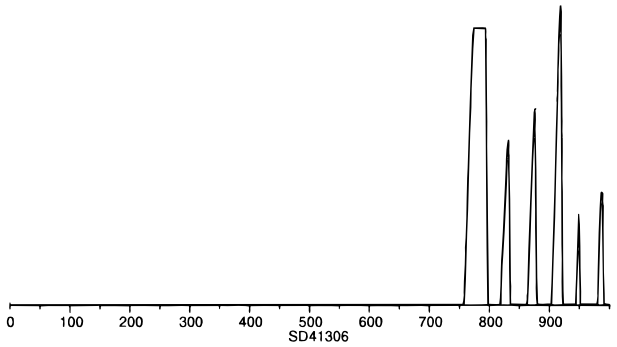

Figure 2. Typical finger span trace obtained after a series of six stimulations with ethyl butyrate at different concentrations in a random order.

was always the highest concentration as described previously. An experimental design balanced on six sessions and five panelists for order and first-order carry-over effects was used. Two panelists (MH and CD) did not participate in each of the six initially planned sessions.

Evaluation Sessions with the Synthetic Solutions. Each session consisted of the analysis of two different solutions among four, separated by a rest period of 8 min. Each panelist therefore evaluated the four solutions in triplicate in six sessions. The order of presentation of the 12 samples was fixed for all panelists as follows: solutions 1 and 2 during sessions 1, 3, and 5; solutions 3 and 4 during sessions 2, 4, and 6. Before the evaluation, the panelists were informed of the temperature of elution of each of the 11 odor active components, and they were allowed to check the temperature of the oven at any moment during the analysis.

Statistical Analyses. Experimental designs were obtained using the FIZZ system from Biosystème, France. Univariate statistical analyses were realized using Sigmastat scientific software (version 2.0) from Jandel Corp. (Erkrath, Germany). Multivariate statistical analyses were made with Statbox plus software (version 2.0) from Grimmer logiciels (Paris, France).

RESULTS AND DISCUSSION

Choice of Method and Parameters for Intensity Evaluation. The method used by panelists to evaluate odor intensity during the GC analysis at the sniffing port was rather different from the OSME method described by McDaniel et al. (1989) and da Silva et al. (1994). We observed in the laboratory from 1176 GC-O odor detections that in the chromatographic conditions chosen, the duration of 52% of the detections was <4 s. As a consequence, it appeared unrealistic to use in GC-O a method of evaluation of the odor intensity requiring a systematic feedback of the estimated value, because the panelist has not enough time to adjust or to correct this value before each stimulus ends. Therefore, we chose a cross-modality evaluation, which does not require feedback information to the panelist (Stevens, 1975). Among the numerous sensory functions that were used successfully in cross-modality matching to evaluate the intensity of olfactory stimuli (Stevens, 1975), the finger span was chosen (Stevens and Stone, 1959; Ekman et al., 1967).

The data collected are visualized in Figure 2 as a succession of positive peaks separated by a baseline consisting of zero detection zones. From these data, only the maximum height of each peak was considered because the panelists were instructed to match the intensity of each stimulus with a particular finger span and not to follow the increase and decrease of the intensity of the stimulus with time. The regressions and analysis of variance (ANOVA) applied to peak heights and to peak areas confirmed the better estimation or discrimination obtained with the former, except for the data from one panelist suffering from a metacarpal syndrome (MH, Figures 3 and 4).

Selection of Stimuli and Panelists. The selection and the first measurements were made from series of successive stimulations with ethyl butyrate at six different concentrations in a random order of presentation as described under Materials and Methods. The choice of ethyl butyrate was made because this compound met different requirements, which are as follows: the ab-

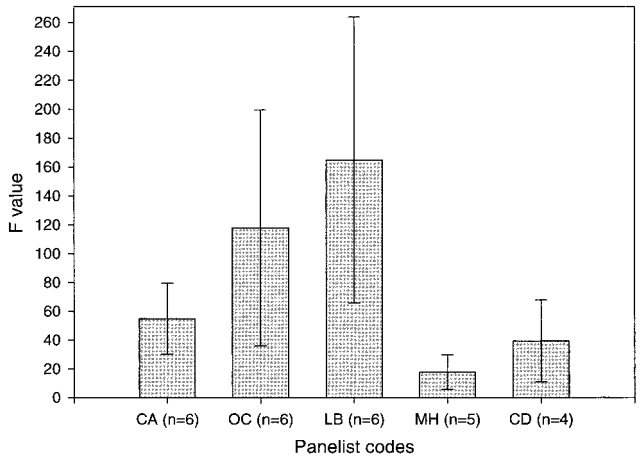

Figure 3. Panelists' ability to evaluate ethyl butyrate intensity.

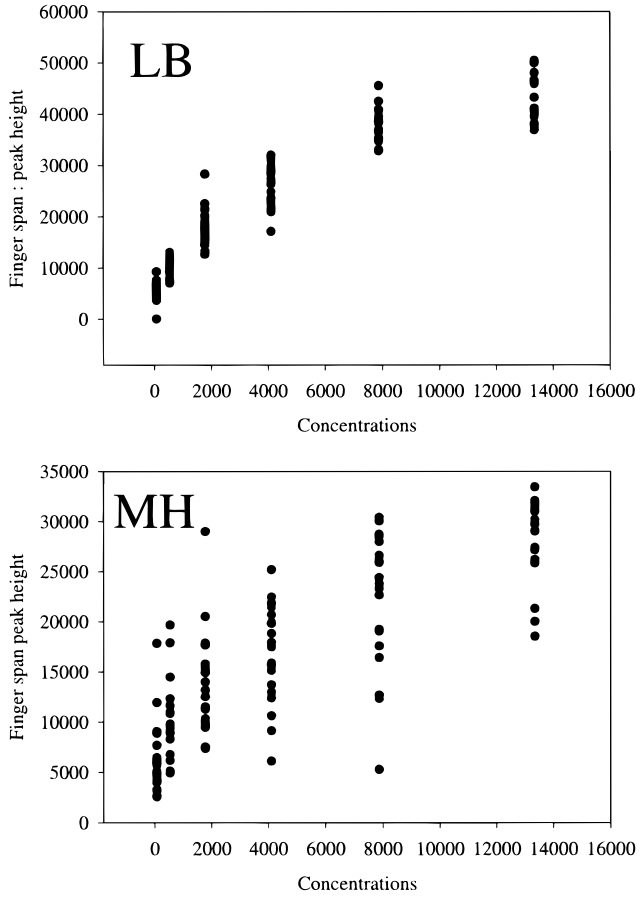

Figure 4. Relation between ethyl butyrate concentration and peak height.

sence of pungency and toxicity at the concentrations tested; an experimental detection threshold sufficiently lower than the maximum injectable concentration to allow a large variation of the concentration; the knowledge of its Stevens exponent; a pleasant and not too persistent odor; and a rapid elution after the solvent from the gas chromatograph. To minimize adaptation, the time lag between two stimulations was kept to 60 s (Köster, 1968).

The evaluation of the performance of each panelist was made from an analysis of variance, with concentration as the only factor. It was performed after each session on the peak height values obtained from the evaluation of the six concentrations injected four times.

Table 4. Training Sessions: Number of Ethyl Butyrate Consecutive Concentrations Significantly Different in Perceived Intensity

panelist code	session no. 1	2	3	4	5	6	7	8	9	median
OC	4	3	2	4	4	3	/	/	/	3.5
FM	0	4	2	3	0	1	1	0	/	1
CA	2	3	5	4	3	2	5	5	/	3.5
CD	4	3	4	5	/	/	/	/	/	4
MH	4	5	4	/	/	/	/	/	/	4
LB	4	3	4	4	3	3	5	/	/	4
MJV	2	4	3	3	1	0	3	4	0	3

Because all panelists succeeded in the test at each session (not shown, mean peak heights increasing with concentration and $H°$ rejected at $p = 0.05$), a Newmans−Keuls test was then performed to determine the number of pairs of consecutive concentrations (CPC) that were significantly discriminated at $p = 0.05$. The number of the different stimulus concentrations was six. Consequently, the maximum possible CPC score was 5. These five possible pairs of stimulus are theoretically identical with a difference of intensity approaching 5 units (Table 1). The task to distinguish CPC should therefore have been of similar difficulty, independent of the level of concentration.

Table 4 shows a large difference in the performances of the panelists. Because they were informed of the order of presentation of the stimulus intensities before the beginning of each series, we considered arbitrarily that they should be able to discriminate more than three CPC among five. The results from two panelists, FM and MJV, were consequently discarded.

Panelists' Ability To Evaluate Odor Intensity. The panelists' ability to evaluate the odor intensity was estimated as previously from an analysis of variance of the results obtained from each evaluation session, on 6 × 4 odor estimations with concentration as the only factor. As previously (not shown), mean peak height values obtained within each session were always increasing with concentration.

The average F values determined individually for the null hypothesis of equality of the six mean peak heights, and the variance associated, are given in Figure 3. Depending on the initial performance of the panelists and on their progress, the number of sessions varied from one panelist to the other from four to six as indicated along the x-axis.

As for training, the F value calculated for each session and each panelist is always much higher than the critical value at $p < 0.05$, $F(5,18) = 2.77$. It is therefore concluded that all panelists were able to evaluate differently the six different stimulus intensities, using the prototype provided. A large variation is, however, observed between panelists and also between sessions for each panelist. The latter variation seems to be random as a function of time, indicating that it is not correlated with training. Concerning the former variation, the F values obtained for LB are significantly higher ($p < 0.05$) than those obtained for MH and CD. This different performance of the panelists to discriminate between stimuli is visualized in Figure 4, in which all of the evaluations made by LB and MH for the six different concentrations are plotted.

This figure shows first that the results from LB are much more reproducible than those from MH in the estimation of the perceived intensity, independent of the concentration. It also shows that the relation between

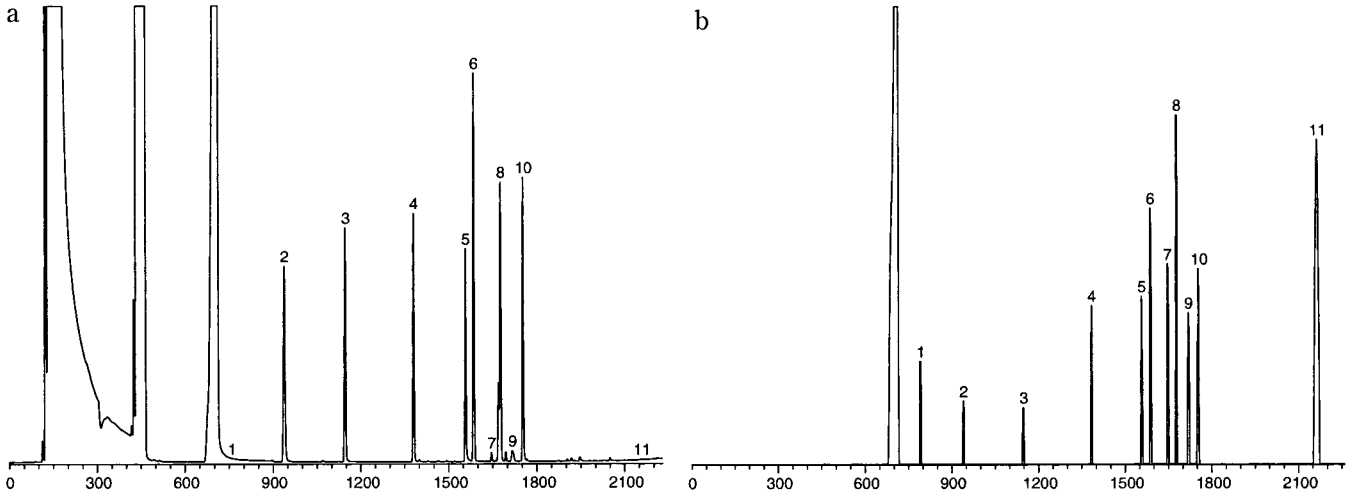

Figure 5. Analysis of synthetic solution 1: (a) FID trace; (b) finger span trace. Peak identification: (1) 3-methylbutanethiol (MBT); (2) hexan-2-one; (3) furfural; (4) benzaldehyde; (5) octan-1-ol; (6) nonanal; (7) guaiacol; (8) citronellal; (9) 2-phenyl-1-ethanol; (10) decanal; (11) vanillin.

the concentration of the solutions injected and the evaluation made with the finger span is obviously log−log. This result fits the psychophysic law that foresees a linear matching function in log−log coordinates between intensity and finger span (Stevens and Stone, 1959; Köster, 1991; Zamora, 1995). In our experiment, if

(1) log(perceived intensity) = n_1 log (finger span peak height) and as

(2) log(perceived intensity) = n_2 log (concentration), then

(3) log(peak height) = n_2/n_1 log (concentration) as observed in Figure 4

These data clearly confirm the conclusion given by da Silva et al. (1994) about the ability of trained panelists to evaluate the intensity of odors eluted during a GC analysis from a capillary column. Nevertheless, the task given to the panelist was simplified in our experiment because the stimulus was repeated at regular intervals and the quality of the stimulus was constant.

To test the ability of our trained panelists to evaluate odor intensity in conditions more similar to those met in a flavor extract analysis, synthetic solutions were therefore prepared and evaluated.

Odor Intensity Evaluation of 11 Constituents in a Synthetic Solution. Eleven substances were chosen mainly for their published Stevens's exponent (Devos et al., 1998) and their different volatilities and chemical functionalities, and also because they were detected at the sniffing port by all panelists at a concentration <15 g/L, the GC saturation concentration (Table 3).

The distribution of the concentrations of individual compounds in the four solutions (Table 2) was made arbitrarily to equilibrate the sum of the intensities in the solutions and to alternate intense and weak stimulations during the analysis of each solution (Table 3).

A typical FID trace of solution 1 is given in Figure 5, with the corresponding odors detected and their intensities. It shows that the time elapsed between two odors varied from a minimum of 35 s to a maximum of 407 s, which is a typical situation in GC-O analysis. The only difference with a real situation is that panelists were informed of the elution temperature of each compound and were instructed to smell the effluent 2° before their elution, until no more odor could be detected.

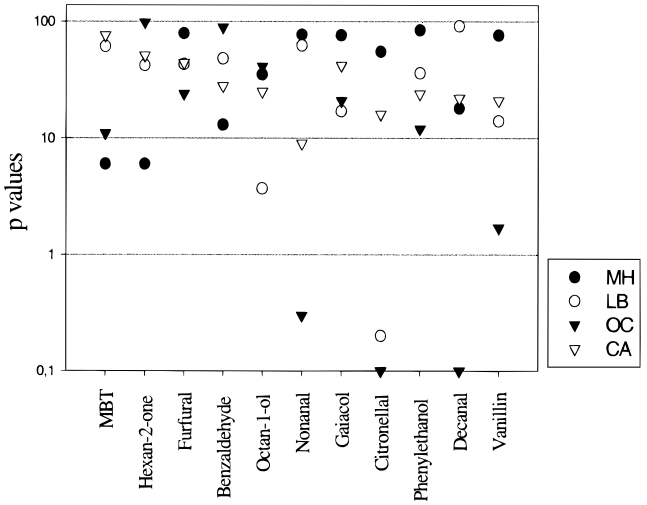

Figure 6. Evaluation of the synthetic solution: ANOVA on the concentration factor per panelist and per variable.

Evaluation of Panelist Performance. A first analysis of variance was realized for each stimulus on the factor "solution" to evaluate the performance of each panelist. The results of this analysis are summarized in Figure 6, in which the probability associated with the *F* value was plotted for each compound and each panelist. This figure shows that the individual performance of the panelists is low, despite their being trained and informed about the elution time of each compound. If we reject H0 at $p < 0.1$, then each panelist is considered to evaluate the difference in odor intensity by GC-O-FSCM on a maximum of 1−4 constituents of 11. This result could appear disappointing, but it is a general fact that when a panel is asked to score the intensity of odor descriptors by sensory descriptive analysis, each descriptor is demonstrated as discriminant between samples only for a few panelists (Molimard, 1994). It is therefore the cumulative information obtained by these individuals that allows finally a good description or discrimination of the samples assessed.

If we go back to Table 2, it is clear that the fact that some compounds were found different in intensities

Table 5. Two-Factor ANOVA of the Peak Heights Obtained from GC-O-FSCM of the Synthetic Solutions

variable	*F* values[a]		
	panelist effect	solution effect	interaction effect
3-methylbutane-thiol (MBT)	8 ***	19.9 ***	0.8
hexan-2-one	3.3 *	10 ***	0.9
furfural	1.7	14.9 ***	0.7
benzaldehyde	0.5	15.7 ***	1.2
octan-1-ol	4.9 **	5 **	1.6
nonanal	7.8 ***	9.6 ***	1.4
2-methoxyphenol (guaiacol)	0.9	70 ***	1.8
citronellal	17.4 ***	12.3 ***	1.3
2-phenyl-1-ethanol	2.9 *	18.3 ***	0.4
decanal	5.3 **	6.7 ***	0.8
vanillin	4.4 *	67.4 ***	1.7

[a] ***, $p < 0.001$; **, $p < 0.01$; *, $p < 0.1$

among the four solutions, and others not, is not due to the different ranges of their theoretical intensities because hexan-2-one and octan-1-ol, which were found to be different, varied in a 1−1.2 theoretical range and guaiacol and 2-phenyl-1-ethanol, which were not found to be different, varied in a 1−6 range. The lack of difference observed at $p < 0.1$ in the estimation of the different concentrations of 4 of the 11 constituents (furfural, benzaldehyde, guaiacol, and 2-phenyl-1-ethanol) cannot be a simple consequence of cross adaptation. Citronellal and nonanal intensities are, for example, found to vary between solutions, although the compounds were eluted, respectively, 35 and 41 s after guaiacol and octan-1-ol. Conversely, the odor of benzaldehyde was not found to be significantly different in the four solutions, although eluted 233 s after furfural.

It is therefore concluded from these relatively poor individual performances that it is necessary to use a panel of several individuals to perform such an analysis.

Evaluation of the Panel Performance. To evaluate the agreement of the panel, a two-way analysis of variance was realized by taking into account two factors with interaction (panelist × solution), with panelist as a random factor. The solution effect is here obvious for the group (Table 5), because the mean peak heights evaluated for each compound by the panel are found to be significantly different ($p < 0.01$).

To visualize these very encouraging results, a PCA was made on the raw data. The plot along the two first principal components (PC), representing 64.2% of the variance, mainly shows the panelist effect noticed previously (not shown), as it is commonly the case in sensory descriptive analysis. To eliminate this effect, the data were centered for each panelist and each compound by subtracting the general mean from each of the 12 raw values obtained (4 solutions × 3 repetitions).

Figure 7 is a biplot representation of the location of the solutions evaluated by each of the four panelists and of the 11 variables (finger span odor estimation of the 11 solution constituents) along the two first PCs, which explain 56% of the variance. This figure visualizes clearly the solution effect, which was somehow masked in the PCA realized on the raw data. Solutions 1 and 4 are well separated from solutions 2 and 3 along the first PC and solutions 1 and 2 from solutions 3 and 4 along the second PC.

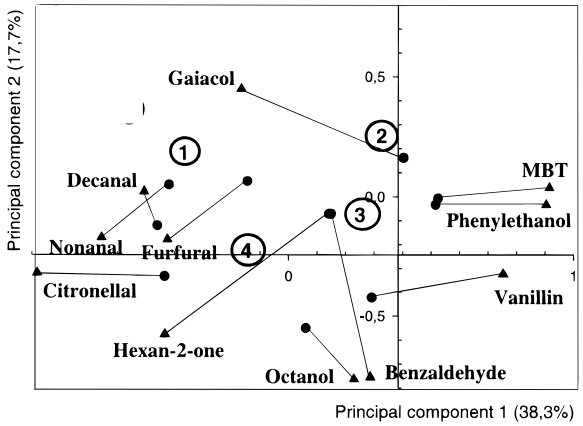

Figure 7. PCA biplot representation of the synthetic solutions along the two first components: (1−4) solutions 1−4; (solid triangles) finger span variables; (solid circles) theoretical intensity variables (illustrative).

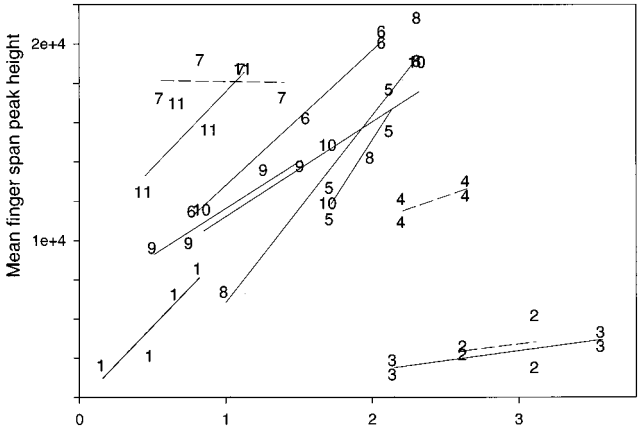

Figure 8. log−log regressions between finger span peak heights and theoretical intensities. Dashed lines correspond to insignificant relations ($p > 0.1$); for better visualization, scaling is linear and only mean values are shown: (1) MBT, $R^2 = 0.55$, $F = 17$, $p < 0.001$; (2) 2-hexanone, $R^2 < 0.1$, $F = 0.3$, $p = 0.57$; (3) furfural, $R^2 = 0.35$, $F = 8$, $p = 0.01$; (4) benzaldehyde, $R^2 < 0.1$, $F = 0.8$, $p = 0.39$; (5) octan-1-ol, $R^2 = 0.41$, $F = 9.7$, $p = 0.008$; (6) nonanal, $R^2 = 0.48$, $F = 13$, $p = 0.003$; (7) guaiacol, $R^2 < 0.1$, $F = 0.06$, $p = 0.82$; (8) citronellal, $R^2 = 0.63$, $F = 24$, $p < 0.001$; (9) 2-phenyl-1-ethanol, $R^2 = 0.61$, $F = 22$, $p < 0.001$; (10) decanal, $R^2 = 0.4$, $F = 9$, $p = 0.008$; (11) vanillin, $R^2 = 0.38$, $F = 8$, $p = 0.01$.

Relation between Theoretical and Estimated Intensities. To check if these results fit the theoretical sensory characteristics of the solutions, the logarithm of the individual mean peak heights obtained from the evaluation of each solution were regressed according to eq 1 on the logarithm of the corresponding theoretical intensities. The quality of each regression was evaluated from the coefficient of determination R^2 and from the F statistic gauging the contribution of the peak height variable in predicting the theoretical intensity. Figure 8 gives the results of this analysis with a graphical representation of the regressions. It shows that except for hexan-2-one, benzaldehyde, and guaiacol, for which the correlation between the two variables was very low and not significant (dashed lines), 8 variables among 11 show a significant ($p < 0.05$) log−log relation between the two cross-matched sensory modalities.

Looking back to Figure 7 and Table 3, it is clear that the panel was able to find most of the characteristics of the different solutions including (i) a highest intensity for 3-methylbutanethiol, 2-phenyl-1-ethanol, and vanil-

lin in solutions 2 and 3; (ii) a highest intensity for nonanal and citronellal in solutions 1 and 4; (iii) a highest intensity for octanol in solution 3 and 4; and finally (iv) a highest intensity for decanal and furfural in solution 1 and of hexan-2-one and benzaldehyde in solution 4. However, some characteristics of the solutions are difficult to find from this analysis such as the high content of hexan-2-one in solution 1, of furfural in solution 3, of benzaldehyde in solution 2, and finally of guaiacol in solution 3.

This interpretation was further tested by comparing on the same plot the correlations of the finger span variables on the two first PCs with those of the theoretical intensity variables considered as illustrative in the analysis. It shows that the correlations of 3-methylbutanethiol, phenyl-2-ethanol, vanillin, octan-1-ol, citronellal, nonanal, decanal, and even furfural with the two first components of the PCA are not very much different when the theoretical or the experimental values are considered. This means that the previous conclusion given on the odor intensity of these compounds in the four solutions is probably very close to the real fact. Conversely, the correlations for hexan-2-one, benzaldehyde, and guaiacol are clearly different, giving for the three compounds a different estimation of the intensity using the cross-matching estimation or the calculation. This different estimation cannot be only due to a smaller intensity range of the stimulus because guaiacol varied theoretically from 1 to 6, a much wider range than for citronellal, which was better estimated (Table 2). It cannot also be due only to a phenomenon of cross adaptation because 2-hexanone and benzaldehyde were eluted, respectivey, after a period without any stimulation of 178 and 233 s, theoretically sufficient for the panelists to recover from the previous stimulus. Because the estimation of the other compounds appeared to be better, we therefore postulate that the Stevens exponents used to determine the theoretical intensities for these three compounds were much lower than the exponents corresponding to our panelists.

These experiments confirm the real interest of a finger span method to evaluate the intensity of odors in a GC effluent. They also demonstrate the necessity of using a panel of several trained people to determine all of the intensity characteristics of complex solutions or extracts.

The next logical stage will consist of a validation of these results on a real flavor extract and the determination of the role of training on the quality of the estimation of the intensities.

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