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Quantitative gas chromatography–olfactometry. Analytical characteristics of a panel of judges using a simple quantitative scale as gas chromatography detector

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Abstract

Some questions related to the ability of gas chromatography–olfactometry (GC–O) to provide quantitative measurements of the concentration of a given odorant in an extract are explored and discussed. A panel of eight individuals has been used to evaluate the intensity of 15 odorants present at different concentrations. The use of very simple scales, such as a 0–3 scale, makes it possible to build calibration graphs based on the different stimulus–response models (Fechner, Stevens, Hill) and, with a proper calibration, up to nine different concentration levels can be discriminated by an eight-judge panel. The signal shows a good long-term stability, and its precision varies between 3.7 and 8% of the whole scale, with 5.7% as average. Sensitivity is extremely dependent on the compound: in the best case a concentration change of 20% can be detected, while in the worst, concentrations must differ more than one order of magnitude. In average, concentrations must differ between 2 and 4.7 times (including calibration error) or between 1.2 and 2.3 (excluding calibration error). The performance of the different judges, the effect of the close elution of two odors and the benefits derived from the use of more complex scales (7-points) are briefly discussed from the perspective of the analytical performance of GC–O methods.
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1. Introduction

The human nose has been used as a gas chromatography (GC) detector almost since the introduction of GC, as the human nose is the most appropriate detector to monitor the presence of an odorant in the effluent of a gas chromatograph [1].

The individual characteristics of this detector, completely different from those from the conventional physical detectors, initially restricted their field of application to qualitative analysis. Its mission in this context was to allow differentiation between those volatile components with a scent, from those that do not have one. Nevertheless, in the last few years a series of studies has appeared in which different GC–O strategies are applied to the evaluation of the importance of one or several odorants in one or several samples, which is clearly a quantitative measurement [2–11]. These studies have had a repercussion in the industry of the aroma, as it is demonstrated by the increasingly greater supply of commercial equipment and prototypes designed to

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extract qualitative and quantitative information on the aromas present in a chromatographic effluent [12–14].

Despite the great number of works that deal with questions related to the quantitative capacity of GC–O systems, the relationship between the concentration of the odorant and the olfactometric signal has been rarely studied. This deficiency can be explained because in GC–O the emphasis is placed on the measurement of the olfactory activity of a component (rather than on its concentration) and by the difficulty and tedium of the GC–O experiments performed with many odorants, judges and concentrations. Until this moment just one author has reported the quantification of a component by means of calibration of olfactometric data [8], although the existence of linear relations between the olfactometric signal (or its logarithm) and the logarithm of the concentration has been reported by several authors [9,11]. Nevertheless, there are no reasons why the GC–O systems should not be evaluated like any other chromatographic detector, in terms not only of the precision of the signal, but also of dynamic range of the response, calibration function, sensitivity and selectivity. This information will allow us to obtain greater knowledge of these techniques, will facilitate the comparison with one another and with more conventional techniques in analytical chemistry and will provide more objective foundations to optimize the operative conditions. The degree of success of this technique should be evaluated, however, not only using conventional analytical criteria, but also in terms of its ability to provide a signal sensitive and precise enough to detect concentrations and concentration changes that can have sensory impact.

The only quantitative method published to date makes use of the different olfactory sensitivities from the judges who integrate the panel [8]. The proportion of people able to detect the presence of a given odorant is related to its concentration. This strategy has the doubtless advantage of its simplicity and requires little training from the judges. Nevertheless, the information that a judge provides is very limited (a binary yes/no answer), which affects the precision of the answer and forces the use of very large panels for more refined methods [14]. An additional refinement, studied in the present work, is for the judge to provide a simple measurement of the intensity of the eluted odorant. The main aim of the present work is, therefore, to study the analytical characteristics of the GC–O signal produced by a panel of judges using a simple ordinal scale for the global evaluation of the aromatic intensity of an odor-peak. Questions such as precision, sensitivity and selectivity of the signal, calibration and dynamic range of work, and the effect of some critical parameters like the number and selection of judges are approached.

2. Material and methods

2.1. Chemicals

Five synthetic solutions containing 15 aroma chemicals dissolved in dichloromethane at the concentration ranges given in Table 2 were prepared. The aim was to cover as much as possible the complete range of the proposed intensity scale. Concentration sequences were chosen randomly. Ethylbutyrate and 4-ethylguaiacol were also added to each solution at a constant concentration (120 mg l^{-1} and 16 mg l^{-1}, respectively) as internal olfactometric standards.

2.2. Gas chromatography–olfactometry (GC–O)

A Fisons 8360 gas chromatograph equipped with a polar fused-silica column J&W DB-Wax (30 m×0.32 mm×0.5 μm) was used. One microliter of the test solutions were injected in splitless mode and the compounds were separated using the following oven program: 40 °C (3 min), 5 °C/min, 200 °C (8 min). Eluting compounds were split at the end of the column at a 1:1 rate between the FID detector (250 °C) and the olfactometric port ODO-1 (SGE, Ringwood, Australia). To prevent condensation of high-boiling compounds on the port this was heated sequentially using a laboratory-made rheostat to 90 °C at 80 °C oven temperature, to 140 °C at 120 °C and to 200 °C at 180 °C oven temperature.

A panel of eight judges, five women and three men from laboratory staff, carried out the sniffings. Half of the panel had an extensive experience with GC–O, the rest were novices. Sniffings were performed during all the GC run time (approximately 30 min). Repeatability of sniffers was observed first in

three sniffings. Panelists were trained prior to the first test to use a 4-point category scale (0=not detected; 1=weak, hardly recognizable odor; 2= clear but not intense odor, 3=intense odor) for intensity evaluation. Training was very simple and consisted of a short period of familiarization with the scale and the system. During this period the panelists were asked to run three times analysis of one of the test samples (one per day) and rate intensity of the eluted odor using the scale proposed. They were not instructed about what was the expected intensity of the odors and each one used the intensity category, which in his/her opinion fitted best the intensity of the odor perception caused by the eluted odorant. The panel sniffed afterwards the test solutions successively. Each panelist repeated the sniffing of each test solution three times. In another experiment it was allowed to put + or − signs for the scale points 1 and 2, which were further processed as a half value between the smaller and the greater value. In this way the 4-point scale was extended to a 7-point scale. The scale in use was recalled before each sniffing.

3. Results and discussion

3.1. Precision of the signal

The analytical data of interest in the olfactometric study is the average value of intensity obtained by the panel of tasters, which we will call panel intensity (I). In Table 1 the average of the three panel intensities (for a panel of eight tasters) obtained in the study is shown, as well as the standard deviation obtained in the triplicate analysis of each solution. The existing relationship between this standard deviation and the intensity is shown in Fig. 1. It demonstrates that the standard deviation tends to be smaller at high values of intensity, although the existing relation between both parameters does not become significant ($SD=K-0.044\times I$, $r^2=0.12$). There are two reasons that explain why the standard deviation decreases at high values of intensity. First, when the signal saturation is reached the deviation tends to be smaller. Secondly, at low intensities we can find cases in which members of the panel no longer perceived the component (it is present in a concentration below their personal threshold) while, at the same time, others still perceive the component distinctively. Despite these facts we can assume that the imprecision in the signal is approximately constant in absolute terms in most of the dynamic range of the method. Therefore, a mean deviation for each component—denominated S—can be calculated by combination of the five deviations. This value, which represents the precision of the panel intensity with 10 degrees of freedom, oscillates between 0.11 (case of ethylcinnamate) and 0.24 (case of eugenol), with 0.17 like average value. These values represent 3.7, 8.0 and 5.7% of the total of the scale, respectively. In order that the panel intensities of two solutions of a given compound, in different concentrations, could be considered significantly different, they must differ in at least $2S$. Therefore, and since by definition the value for the panel intensity must be between 0 and 3, an imprecision of 0.17 in the measurement implies that the panel could differentiate a maximum of $3/(2\times0.17)=8.8$ solutions of different concentrations. In the best of cases the panel could differentiate up to 13.7 solutions of different concentration (case of ethylcinnamate) and just 6.25 solutions of eugenol. These data constitute just the first approximation, since the intensity–concentration is not taken into account, nor the possible causes of this imprecision are analyzed, two questions that will be analyzed in a later section.

3.2. Stability of the signal

Fig. 2 shows the evolution with time of the corresponding olfactometric signal of both aromatic components present at constant concentration in all the solutions analyzed in the experiment. The studied time interval of the experiment was of 15 working weeks (with a total duration above 17 weeks). It can be observed that the response stays stable with time and that there is no visible temporal tendency. Not even the interruption of the experiment for almost 3 weeks (due to winter holidays) between weeks 11 and 12, entailed an apparent change in the panel intensities. The standard deviations of the observed panel intensities in both cases were 0.13 for ethylbutyrate and 0.11 for 4-ethylguaiacol. Both values are well inside the rank of deviations previously observed. We think that this behavior can be

Table 1
Mean and standard deviation of the olfactive intensities obtained in the GC–O analysis of solutions of known concentration by a panel of eight judges (three replicates)

Conc.	Intensity	SD	Conc.	Intensity	SD	Conc.	Intensity	SD
Ethyl 2-methylbutyrate			Ethyl 3-methylbutyrate			4-Methyl-4-mercaptopentanone		
0.032	0.04	0.07	1.25	1.71	0.07	0.00028	1.46	0.19
1.092	0.96	0.19	5.37	2.00	0.13	0.00062	1.83	0.07
3.134	1.54	0.19	20.66	1.83	0.19	0.00068	2.08	0.07
9.880	1.58	0.07	22.10	1.63	0.33	0.00115	2.29	0.19
117.221	2.29	0.19	104.31	2.50	0.13	0.00628	2.58	0.14
		$S=0.15$			$S=0.19$			$S=0.14$
Linalool			Isobutyric acid			Methylbenzoate		
4.97	0.92	0.26	56.42	0.75	0.25	207	1.13	0.22
13.46	1.83	0.14	187.35	1.83	0.14	250	1.75	0.22
29.79	1.92	0.14	309.05	2.13	0.13	327	2.04	0.14
59.00	2.17	0.19	629.35	2.79	0.07	413	2.29	0.19
195.32	2.33	0.19	1250.00	2.71	0.07	538	2.58	0.14
		$S=0.19$			$S=0.15$			$S=0.19$
Isovaleric acid			β-Damascenone			α-Ionone		
0.95	0.67	0.31	0.04	1.42	0.19	0.75	0.38	0.25
2.66	1.54	0.07	0.72	1.75	0.13	4.97	1.58	0.07
4.09	1.88	0.25	1.36	1.88	0.22	14.26	2.04	0.07
5.07	1.96	0.19	3.40	2.17	0.29	28.47	2.25	0.22
27.91	2.75	0.13	39.46	1.79	0.19	61.00	2.29	0.29
		$S=0.21$			$S=0.21$			$S=0.20$
Z-whisky lactone			E-whisky lactone			Ethylcinnamate		
0.10	0.13	0.13	0.11	0.88	0.25	13.86	1.00	0.00
4.55	1.13	0.33	4.77	2.46	0.07	43.20	1.21	0.14
6.27	1.00	0.13	6.58	2.54	0.19	120.65	1.42	0.07
9.95	2.13	0.22	10.44	2.75	0.22	172.13	1.88	0.13
38.25	2.50	0.13	40.14	2.63	0.00	436.60	1.83	0.14
		$S=0.20$			$S=0.17$			$S=0.11$
γ-Decalactone			Eugenol			Sotolon		
0.69	1.29	0.29	10.90	1.50	0.33	0.01	1.96	0.07
10.15	2.46	0.14	46.00	1.83	0.14	0.05	2.25	0.13
48.58	2.71	0.14	64.31	0.92	0.31	0.25	2.35	0.22
226.80	3.00	0.00	79.68	1.88	0.13	0.54	2.54	0.07
1468.72	2.83	0.07	99.49	1.96	0.19	2.39	2.71	0.07
		$S=0.16$			$S=0.24$			$S=0.13$

Concentrations are given in mg l^{-1}.

extrapolated to the rest of the components, and that it is a consequence of the simplicity and the ‘‘naturalness’’ of simple scales of measurement such as the ones used here.

3.3. Intensity–concentration relationships and calibration

In almost all cases the measured intensity versus

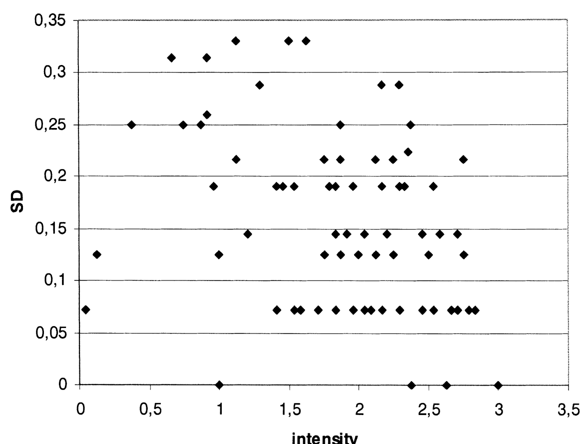

Fig. 1. Intensity–precision (as standard deviation of three replicate measurements made by the whole panel) relationship.

log C relationships followed sigmoidal functions, in agreement with both, the basic psychophysical models and with the results of similar GC–O measurements performed by Audouin et al. [15] and van Ruth and O'Connor [11]. Different calibration approaches were studied. The first one was a normal linear regression (measured I versus log C), which is equivalent to the oldest psychophysical model known as Fechner's law. The second was a regression of log I on log C, which corresponds to the psychophysical model proposed by Stevens 40 years ago. The last calibration approach was a linear regression of the logarithm of the quotient $I/(I_{max} - I)$ versus log C. This relationship derives from Hill's model, recently proposed by Chastrette et al. [16] to model the human olfactory stimulus–response function. According to these authors, the relationship between I and C is:

$$I = \frac{(I_m - I_0)C^n}{C_{ip}^n + C^n} + I_0$$

where I is the calculated intensity of the response, I_m is the maximum value of perceived intensity, I_0 is the perceived intensity with pure air as stimulus, C is the stimulus concentration, C_{ip} is the concentration at the inflection point and n is the exponent of Hill. Taking $I_0 = 0$, this equation can be rearranged to give the following:

$$\frac{I}{I_m - I} = \frac{C^n}{C_{ip}^n}$$

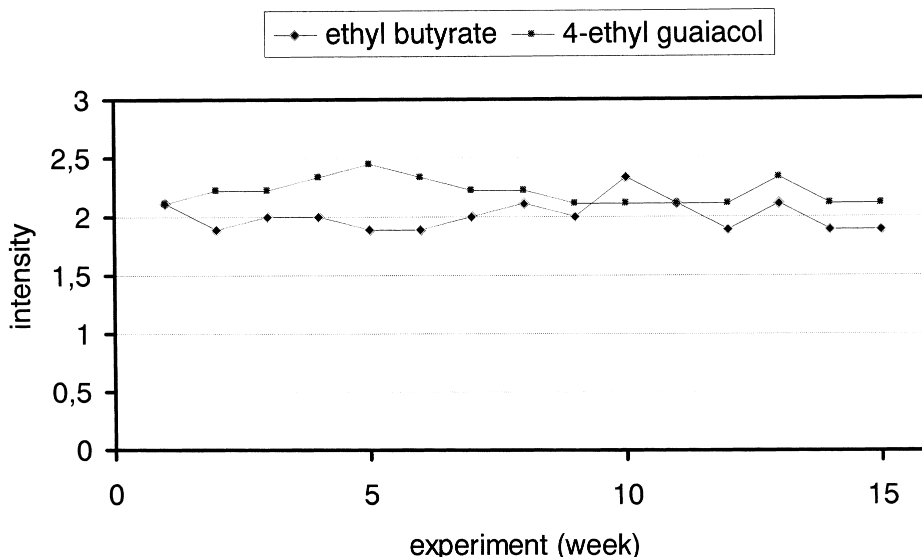

Fig. 2. Evolution of the panel intensities for ethylbutyrate and 4-ethylguaiacol (internal standards) along the 3 months of the experiment.

and taking logarithms, the expression is:

$$\log \frac{I}{I_m - I} = n\log C - n\log C_{ip}$$

The results of the linear modeling of data are summarized in Table 2. Eleven out of the 15 tested compounds are shown in the Table. The other four compounds were excluded because it was not possible to build satisfactory models for them, mostly because of the close elution of some other component. Nevertheless, some conclusions drawn from these particular results are presented later.

The following observations can be made on the results presented in the Table:

(1) No single model fits all the compounds. The

Table 2
Linear modelling of gas chromatography–olfactometric data

Compound	Concentration and intensity ranges (mg l^{-1})	Model	r^2	Slope	Intercept	Residuals	Lack of fit	Precision	C_{ip}	$\Delta C/2S_0$
1 Ethyl 2-methylbutyrate	0.02–100	Fechner	0.95	0.62	1.037	0.395	0.165	0.230		8.0
	0–2.3	Stevens	0.85	0.38	−0.208	0.502	0.471	0.031		6.6
		Hill	0.93	0.55	−0.464	0.435	0.313	0.121	7.10	7.5
2 4-Methyl-4-mercapto-pentanone	0.002–0.650	Fechner	0.79	0.79	2.85	0.510	0.301	0.208		6.0
	1.2–2.8	Stevens	0.73	0.17	0.476	0.033	0.021	0.012		5.7
		Hill	0.82	0.61	0.99	0.246	0.083	0.163	0.02	8.1
3 Linalool	2–200	Fechner	0.76	0.83	0.619	0.970	0.605	0.365		4.7
	0.6–2.5	Stevens	0.65	0.24	−0.11	0.133	0.087	0.046		4.3
		Hill	0.76	0.54	−0.583	0.400	0.206	0.194	12	6.5
4 Isobutyric acid	20–2000	Fechner	0.91	1.536	−1.78	0.757	0.518	0.239		5.7
	0.5–2.9	Stevens	0.81	0.43	−0.809	0.142	0.091	0.050		5.2
		Hill	0.88	1.197	−2.54	0.621	0.348	0.273	132	6.1
5 Methylbenzoate	200–800	Fechner	0.86	3.258	−6.24	0.577	0.234	0.343		6.1
	1–2.8	Stevens	0.79	0.80	−1.726	0.057	0.033	0.024		6.1
		Hill	0.87	2.317	−5.51	0.273	0.055	0.218	239	8.2
6 β-Damascenone	0.02–4	Fechner	0.65	0.35	1.88	0.429	0.064	0.365		5.6
	1.2–2.5	Stevens	0.70	0.09	0.269	0.022	0.002	0.020		5.7
		Hill	0.60	0.22	0.24	0.214	0.038	0.176	0.08	6.1
7 3-Methyl butyric acid	1–20	Fechner	0.89	1.355	0.893	0.746	0.288	0.445		5.7
	0.3–2.9	Stevens	0.70	0.41	−0.064	0.239	0.135	0.103		4.1
		Hill	0.90	1.065	−0.48	0.445	0.037	0.408	2.80	7.2
8 α-Ionone	0.8–80	Fechner	0.89	1.040	0.675	0.862	0.456	0.406		5.4
	0.1–2.6	Stevens	0.72	0.46	−0.313	0.528	0.263	0.265		3.2
		Hill	0.83	0.79	−0.684	0.833	0.302	0.531	7.40	5.3
9 (E)-whisky lactone	0.1–10	Fechner	0.96	0.95	1.79	0.305	0.003	0.302		8.7
	0.6–2.9	Stevens	0.93	0.26	0.189	0.040	0.003	0.038		9.3
		Hill	0.87	0.71	0.27	0.591	0.110	0.481	0.42	6.0
10 γ-Decalactone	0.7–200	Fechner	0.87	0.64	1.55	0.623	0.373	0.250		5.8
	1.1–2.9	Stevens	0.81	0.14	0.172	0.049	0.030	0.019		6.3
		Hill	0.93	0.62	−0.005	0.292	0.009	0.283	1.00	8.5
11 Eugenol[a]	11–99	Fechner	0.49	0.46	1.03	0.372	0.007	0.365		
	1.5–2	Stevens	0.50	0.12	0.04	0.025	0.003	0.025		
		Hill	0.49	0.28	−0.28	0.136	0.0006	0.133	10.4	
12 Sotolon	0.01–3	Fechner	0.84	0.30	2.594	0.182	0.019	0.163		7.8
	1.8–2.8	Stevens	0.84	0.06	0.414	0.007	0.001	0.006		7.7
		Hill	0.83	0.28	0.826	0.167	0.027	0.140	0.00	8.4

Concentration and intensity ranges and basic results from different models.

[a] Only four calibration points were used for calculations, one was excluded due to a suppressive effect of sooner eluting γ-decalactone.

Stevens' model, however, clearly provided the poorest fits. This can be due to the fact that this model cannot explain the upper curvature of the sigmoids observed at concentrations at which the signal is close to the plateau, as is the case.

(2) In most cases, the models could fit all the points in the concentration range studied. There are some exceptions, however, since for two compounds (β-damascenone and E-whisky lactone) a slight decrease in the signal was noted at higher concentrations.

(3) Results are fairly satisfactory from a quantitative point of view, as it is demonstrated by the high regression coefficients obtained in the different regressions. For five cases r^2 is higher than 0.9 and only in two cases is it below 0.8.

More interesting from a practical point of view is the parameter given in the last column of the table, $\Delta C/2S_0$, where:

ΔC denotes the dynamic range of the method, which is the range of concentrations between those for which the method predicts $I=0$ (or 0.01) and $I=3$ (or 2.99);

S_0 is the average imprecision of a concentration result obtained by interpolation of the measured panel intensity in the calibration graph built with the data obtained in the present experiment (Table 2). S_0 has been obtained with the usual formula:

$$S_0 = \frac{S_y}{b_1}\sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(\bar{y}_0 - \bar{y})^2}{b_1^2 \sum_i (x_i - \bar{x})^2}}$$

in which S_y denotes the residuals variance, b_1 is the slope, m is the number or replicate measurements (1 in this case), and n is the number of pairs of calibration points (15 in the present case).

This parameter $\Delta C/2S_0$ gives an estimation of the number of different concentration levels that the panel would be able to distinguish using the calibration graph built with data in Table 1. According to this parameter, the function of Hill provides the best approach in nearly all cases. In addition, results show that an eight-judge panel is able to quantitatively distinguish approximately eight different concentration levels with the calibration used here.

The analysis of the regression residuals, as shown in the Table, demonstrates that in general there is a balance between the contribution from the lack of fit and the precision, although for some components (E-whisky lactone, 3-methylbutyric acid, eugenol, sotolon), most of the residuals of the models can apparently be attributed almost entirely to high imprecision.

Another interesting parameter to evaluate the capacity of the technique is presented in Table 3. In this Table we can see the factor by which the

Table 3
Factors by which two solutions of a given odorant must differ in order to find significant differences in the GC–O analysis

Compound	Factor to find difference		
	In average	In the area of max. precision	With ideal calibration
Ethyl 2-methylbutyrate	5.4	4.4	2.3
4-Methyl-4-mercaptopentan-2-one	4.0	2.9	1.9
Linalool	7.2	4.7	2.6
Isobutyric acid	2.6	2.4	1.4
Methylbenzoate	1.4	1.3	1.2
β-Damascenone	176	16	13
3-Methyl butyric acid	2.4	2.2	1.7
α-Ionone	5.3	4.6	2.0
E-whisky lactone	2.3	2.2	1.9
γ-Decalactone	3.7	3.3	2.0
Sotolon	19	6.9	3.5

concentrations of two solutions of a certain odorant must differ so that the GC–O method can find significant differences. The first column produces this factor from the average standard deviation obtained when calculating the concentration from the corresponding regression lines. The second gives the same factor but in the proximities of the centroid. Finally, the third column shows the factor obtained when calculating in concentration terms—using Hill's equation—the factor $2S$, where S is the average deviation of the signal (not of the concentration) calculated in Table 1. This last value represents, therefore, an ideal situation in which the calibration does not introduce additional uncertainty to that from the signal. It can be observed that in the three cases strong divergences between the different components exist. β-Damascenone is the component for which GC–O offers less sensitivity, and in the best of cases the panel only seems to be capable of perceiving differences when the difference in concentration is above one order of magnitude. This is a consequence of the small slope of the regression line, and of the high uncertainty of the signal. On the opposite side lies methylbenzoate, for which the method allows to differentiate two solutions whose concentrations differ only by a factor of 1.3. It could be thought that this data are poorer than those other attained with conventional GC detectors. However, the ability of the GC–O panel to detect differences is related to the existence of real effective sensory differences between the products being analyzed. Therefore, precision should be likely enough to detect a concentration difference with real sensory impact, which is one of the most important objectives of flavor analysis.

3.4. Sources of imprecision and method optimization

The global imprecision of the signal measured in Table 1 can be decomposed into the more elementary contributions of panel variability and personal variability. This decomposition is shown in Table 4. It is possible to appreciate that most of the signal variance is due to personal rather than panel variability. The explanation is not that the latter does not exist, even though in some cases it has not been possible to calculate it, but that the personal variability is very high. This is due to several reasons. First, due to the nature of the GC–O signal, it is not infrequent that a judge "loses" an odor, mainly if the olfactometric operation is long and tedious. The second reason is caused by the own nature of the scale. Given that it is a very limited scale, a difference in one unit causes a very pronounced deviation. This result is in agreement with the decomposition of regression residuals shown in Table 2. An interesting point is that there is no correlation between the variability of the signals given for one judge to the different compounds in a given run (data not shown). This is to say, it seems that the judge's day to day variability is random which means that precision cannot be improved by using olfactometric internal standards.

Table 4
Decomposition of the variance of the signal in its two basic components, judge and panel

Compound	S	S_{judge}	S_{panel}
Ethylbutyrate	0.15	0.34	0.24
Ethyl 2-methyl butyrate	0.15	0.42	0.13
Ethyl 3-methyl butyrate	0.19	0.44	0.32
4-Methyl-4-mercaptopentanone	0.14	0.40	0.08
Linalool	0.19	0.53	0.09
Isobutyric acid	0.15	0.41	0.09
Methylbenzoate	0.19	0.50	0.16
Isovaleric acid	0.21	0.52	0.29
β-Damascenone	0.21	0.55	0.22
α-Ionone	0.20	0.56	0.13
Z-whisky lactone	0.20	0.52	0.22
E-whisky lactone	0.17	0.46	0.18
4-Ethylguaiacol	0.09	0.40	–
Ethylcinnamate	0.11	0.55	–
γ-Decalactone	0.16	0.32	0.33
Eugenol	0.24	0.79	–
Sotolon	0.13	0.39	–

The performance of the different judges was determined by a comparison of the individual scores with those obtained for the whole panel. Some results are given in Table 5. As shown in the Table, it is not easy to classify judges as "good" or "bad" according to their performance, since all of them showed a special ability to quantify some components and certain ineptitude to quantify others. From these observations one can conclude that a selection of the judges is decisive if the objective of

Table 5
A comparison of individual precision (measured as maximum, minimum and mean SD obtained by one judge) and individual ''accuracy'' (measured as maximum, minimum and mean correlation between individual intensity/concentration curves and the curves provided by the whole panel) of the eight judges employed in the study

Judge→	A	C	JA	JO	L	M	N	R
SD max[a]	0.73 (3)	0.63 (4)	0.63 (6)	0.86 (8)	0.73 (7)	0.52 (9)	0.73 (7)	0.77 (4,5)
SD min[a]	0.00 (1,4)	0.00 (10)	0.26 (2,8,10)	0.26 (4,9)	0.00 (8)	0.00 (11)	0.26 (1)	0.26 (10)
Mean SD	0.46	0.51	0.43	0.50	0.44	0.34	0.51	0.56
r^2 max[a]	0.98 (8)	0.96 (1)	0.98 (10)	0.99 (4)	0.98 (4)	0.98 (10)	0.99 (8)	0.98 (9)
r^2 min[a]	0.01 (6)	0.31 (6)	0.35 (6)	0.17 (2)	0.00 (11)	0.46 (11)	0.00 (6)	0.00 (3)
Mean r^2	0.61	0.70	0.78	0.75	0.75	0.74	0.79	0.75

[a] Numbers in brackets are codes for compounds and are given in Table 2.

the analysis is quantification of a single compound or of a small number of compounds. In this case the selection should prove the judge's capacity to quantify the particular component. On the contrary, if the objective of the analysis is to determine a large number of components, the number of judges becomes more important than their selection. In the present experiment, the ''a posteriori'' elimination of the results from the worst judges only brought about a marginal benefit on the results. Another observation is that experienced judges did not show a significantly higher performance than novel ones.

The effect of using a more complex scale (7-point scale) was investigated in an independent experiment and in a lower concentration level. The panel of tasters used was also different, which can explain part of the contrasting differences. The results are shown in Table 6 where the standard deviations assigned to the panel and to the individual tasters are compared for similar concentration points. While the use of a 7-point scale improved the precision of the individual measurements of the judges in most cases (variance decreased for 40% in average), the variance due to the panel (excluding the variance for the individual judges) remained unchanged. On the whole, the use of the 7-point scales reduces the confidence intervals of the measured concentrations by a factor between 5 and 30%, which implies a clear improvement over the previous situation, although the scale becomes slightly more complex.

3.5. Interferences and selectivity

The presence of interferences has a deep but partially predictable impact on the signal. The most remarkable case is that of ethyl 3-methylbutyrate. The measurement of its intensity is strongly affected by the previous close elution of ethyl 2-methylbutyrate (20 s before). A satisfactory model could be found for the former taking into account the intensity of the latter: ($I_{3Mbut} = 1.78 + 0.445 \log C - 0.261\ I_{2Mbut}$; $r^2 = 0.71$). That is, in this case the intensity of the first odorant exerts an approximately linear effect on the intensity of the second. A very different case is that of eugenol, already presented in Table 2. In this case, its olfactometric intensity is affected by the previous elution from γ-decalactone (eluting 30 s before), but this component only exerts its effect when it is present in high concentrations (1000 p.p.m.). Below this value the signal obtained from eugenol conforms with the previous models.

Table 6
Comparison of two types of intensity rating scales while considering standard deviations of judges' and panel's responses

	4-Point scale		7-Point scale	
	S_{judge}	S_{panel}	S_{judge}	S_{panel}
Ethyl 2-methylbutyrate	0.46	0.31	0.47	0.56
Ethyl 3-methylbutyrate	0.43	0.64	0.24	0.48
Linalool	0.53	0.40	0.37	0.38
Isobutyric acid	0.41	0.49	0.39	0.52
Methylbenzoate	0.53	0.68	0.44	0.48
Isovaleric acid	0.52	0.45	0.34	0.52
β-Damascenone	0.55	0.60	0.15	0.89
α-Ionone	0.54	0.35	0.46	0.41
E-whisky lactone	0.47	0.63	0.39	0.48

4. Final considerations and conclusions

The signal produced by a panel of judges using simple scales can be treated as the signal from any other chromatographic detector. Although it is obvious that the GC–O detector cannot match the precision attained with other well-established GC detectors, it outperforms almost any other detection system in terms of sensitivity and selectivity for powerful odors, such as 4-methyl-4-mercaptopentan-2-one, ethyl 2-methylbutyrate, β-damascenone or sotolon. In these cases, analytical methods based on quantitative GC–O can provide simpler and cheaper alternatives to conventional GC–MS determination, particularly in the cases in which complex samples with a large number of odors must be analyzed.

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