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Sensor responses to fat food aroma: A comprehensive study of dry-cured ham typicality

Diego L. García-González *, Noelia Tena, Ramón Aparicio-Ruiz, Ramón Aparicio

Instituto de la Grasa (CSIC), Padre García Tejero 4, 41012 Sevilla, Spain

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ABSTRACT

The physicochemical phenomena that explain the sensing mechanisms of gas sensors have been extensively investigated. Nevertheless, it is arduous to interpret the sensor signals in a practical approach when they response to complex mixtures of compounds responsible for food aroma. Thus, the concomitant interactions between the volatiles and the sensor give up a single response affected by synergic and masking effects between compounds. An experimental procedure is proposed to determine the individual contribution of volatile compounds in the sensor response, illustrated with the examples of aroma of dry-cured hams and metal oxide sensors. The results from mathematical correlations and the analyses of pure standards are previously analyzed to describe the behavior of sensors when interacting with individual compounds. A sensor based olfactory detector (SBOD) entailing the use of a capillary column connected to a sensor array as non-destructive detector in parallel with the flame detector served to provide definitive information about the individual contribution of volatile compounds to sensor responses. The sensor responses in this system, which is referred to as sensorgram, were interpreted by taking into account the volatile composition of the samples determined by GC.

1. Introduction

Since most of volatile compounds in fat food products are originated from lipid oxidation, the electronic nose has a significant potential in the odor analysis of fat products. Although systems based on sensor arrays or electronic noses (EN) have proven to be rapid, objective and non-destructive instruments to analyze food aroma [1], this kind of instrument is not being extensively exploited in food industries yet. Thus, despite its capability as on-line screening method and the profusion of literature in recent years reporting promising results, electronic noses are rarely found in routine labs. This delay in its application is partially due to the high difficulty finding an agreement between sensor responses and human odor perceptions, which results in a lack of understanding of the information provided by the sensors. A study of the relation between both kinds of information – chemical, from the compounds, and physicochemical, from sensor signals – requires further analyses on which volatiles are mainly responsible for the overall sensor response as well as to know their contribution to the aroma.

The detection of odors by EN is explained by the presence of volatile compounds that interacts with the sensitive material of sensors. In consequence, whichever the study intended to identify the relations between odors and sensor responses, it should take into account that the aroma is characterized by (i) odor intensity, (ii) odor threshold, and (iii) descriptive sensory notes. On the other hand, the sensor responses depend not only on the presence of compounds interacting with the sensitive material, but also on many other parameters such as the type of sensitive material, the flow and type of carrier gas, and the kinetic of the adsorption/desorption processes.

Some attempts to interpret sensor data in terms of their sensory meaning have been made through correlation studies between sensor signals and the concentrations of volatile compounds quantified by GC [2,3]. An alternative to this method is the sequential analysis of the volatile standards, diluted in odorless oil, corresponding to the compounds that are commonly present in the food headspace [4]. This approach is tough to implement because the food aroma is typically due to the presence of umpteen volatiles. Furthermore, that procedure does not take into account the masking and synergic effects between odorants when interacting with sensor surface. A new approach based on a the previous separation of the volatiles followed by their sequential exposure to sensors would allow weighing the individual contribution of each volatile to the overall sensor response in a single analysis. This approach takes into account the actual concentration of the volatiles in the sample headspace and the possible interaction between them. For this purpose, a silica column could be

* Corresponding author. Tel.: +34 954 61 15 50; fax: +34 954 61 67 90.
E-mail address: dluisg@cica.es (D.L. García-González).

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coupled to a sensor array in order to have a sequential series of sensor responses, each one of them being the result of the interaction between a single compound, or a small group of compounds, and the sensor sensitive material.

The coupling GC-sensor array has been previously used to remove a masking component [5], to correlate the intensity of sensor signals with the structure of volatile compounds [6,7] or to analyze simple mixtures of volatiles [8]. Other research groups are checking pros and cons of micromachined gas chromatographic column in-tandem with sensor arrays [9]. The separation of volatile compounds is apparently incomplete when examining the sensor responses due to the combined effect of the high number of volatile compounds present in the complex aroma of fat products (e.g. virgin olive oils and dry-cured hams) and the slow baseline recovery. Thus, the individual sensor responses to the volatile compounds are partially overlapped resulting in a sequence of adsorption and desorption slopes, henceforth sensorgram [4]. In order to simplify the interpretation of results, the hyphenated technique GC-sensor array requires an appropriate data treatment to extract information even when the peaks eluting from the column are due to more than one compound. Furthermore, the interpretation of the results provided by a coupling GC-sensor array needs a previous in-depth knowledge and experience on the volatile compounds responsible for the aroma.

The potential of a sensor system based on coupling a capillary column to a sensor array is explored in its application as routine analysis of food aroma in contrast with conventional electronic noses. The possibilities of the sensor array as an alternative to classical chromatographic detectors are also studied. Unlike classical chromatographic detectors, which are destructive detectors, the use of a sensor array as detector allows the coupling to other instruments. Furthermore, such a sensor system including a previous GC separation of compounds also allows obtaining a volatile profile based on those compounds that have a major odor impact once the right sensors are selected for a particular purpose. Such methodology would provide more information at first glance than a chromatogram or single sensor responses with a simple interpretation of results. The peculiarities, problems and solutions, and feasibility of this approach will be studied in the frame of particular cases of dry-cured hams.

2. Materials and methods

2.1. Samples

The current variability in dry cured ham features that Spanish and French consumers can find in the market was considered in the sample selection. Thus, nine hams from several geographical origins were purchased from local producers. Three samples were Iberian hams from 'Jamón de Huelva' protected designation of origin – PDO – (Iberian × Duroc-Jersey with a minimum of 75% Iberian pig). Three samples were Serrano Traditional Speciality Guaranteed – TSG – (Large White × Duroc). And three samples were purchased in Aveyron, France (French Landrace × Large White).

The French hams were cured for less than 12 months. Spanish non-Iberian hams were cured for a period between 10 and 18 months, while Iberian hams were cured for more than 18 months. All the hams were processed by local manufacturers using the traditional method of each geographical origin. The samples were stored in vacuum plastic bags at −5 °C until they were required for the sensory and chemical studies.

A fully deodorized olive oil was used to prepare the standard solutions of volatiles compounds. This oil was obtained by steam deodorization under vacuum at the experimental refinery plant of Instituto de la Grasa (CSIC).

2.2. Reagents

The identification of all the volatile compounds were checked with standards purchased from Fluka–Sigma–Aldrich (St. Louis, MO) with the exception of four (2-propanone, 2-ethyl furane, 2, 3-butanodione, ethyl benzene, and 2-methylpropanoic acid) that were identified by GC–MS. The external standard was 4-methyl-2-pentanol.

2.3. Gas-chromatography (SPME-GC)

A sample of approximately 350 g of the part located along and behind the femur was collected from each one of the hams, composed essentially of subcutaneous fat and *biceps femoris*, *semimembranosus* and *semitendinosus* muscles. Three grams representative of the ham portion, previously minced to increase the interface between the ham and the vapor phase during the concentration step, were placed into 20 mL glass vials tightly capped with a PTFE septum and left for 10 min at 40 °C to allow equilibration of the volatiles in the headspace. The septum covering each vial was then pierced with a solid-phase microextraction (SPME) needle and a Carboxen/PDMS/DVB fiber (Supelco, Bellefonte, PA) exposed to the headspace for 180 min [10]. When the process was completed, the fiber was inserted into the injector port of the GC for 5 min at 260 °C using the splitless mode. The temperature and time were automatically controlled by a Combipal (CTC Analytics AG, Zwingen, Switzerland) using the Workstation v.5.5.2 (Varian, Walnut Creek, CA) software.

The volatile compounds were analyzed using a DB-WAX column (J&W Scientific, Folsom, CA; 60 m × 0.25 mm i.d. × 0.25 μm film thickness) installed on a Varian 3900 gas chromatograph (Varian, Walnut Creek, CA) with a flame ionization detector. The carrier gas was hydrogen. The oven temperature was held at 40 °C for 4 min and programmed to rise 1 °C/min to a temperature of 91 °C, and then to rise 10 °C/min to a final temperature of 201 °C, where it was held for 10 min. Each sample was analyzed in triplicate.

The identification of volatile compounds was carried out with standards (Table 1) with the exception of 2-propanone, 2-ethyl furane, ethyl benzene, 2,3-butanodione and 2-methylpropanoic acid that were identified by 5975 Agilent Technologies Series MSD (Santa Clara, CA) coupled to a gas chromatograph (7820A Agilent Technologies), using the WILEY 7 library (John Wiley & Sons Limited, NJ). Odor thresholds were taken from literature [11,12]. Column and analytical conditions were identical to those described for gas chromatography.

The amount of each volatile compound (mg/kg) was computed by relating the peak area of the volatile compound to the area of the standard (1.2 mg/kg of 4-methyl-2-pentanol), and taking into account the sample weight and the response factor of each volatile.

2.4. Response factors

Standard solutions were prepared using a fully deodorized olive oil as matrix. Concentrations in the range 0.1–5.0 mg/g, with the exception of 3-methylbutanol whose range was 0.5–20 mg/kg, were analyzed under the conditions described above. The absolute response factors of the standard compounds were calculated as the slopes of the linear regressions obtained from the ratio of total peak area as a function of concentration. Relative response factors were obtained as the ratio of the absolute response factor of each compound to that of the internal standard (4-methyl-2-pentanol).

2.5. Sensor based olfactory detector (SBOD)

A sensor system designed in our lab for the analysis of complex aroma [13] was used to study the sensor responses. The

Table 1
Code and relative retention time (Rt), mean concentrations in non-Iberian and Iberian hams and *p* values for classifying the hams by their breeds (Iberian vs. non-Iberian), odor threshold (OT in mg/kg) and sensory descriptors, by GC-olfactometry, qualifying each volatile compound.

Code	Rt	Volatile compound	Non-Iberian	Iberian	*p*	OT	GC-O
1	0.16	Hexane	0.168 ± 0.038	0.092 ± 0.019	0.308	1.50	Spicy
2	0.17	Heptane	0.110 ± 0.033	0.140 ± 0.031	0.496	–	Sweety, alkane
3	0.20	Octane	0.856 ± 0.167	1.858 ± 0.647	0.047	0.94	Sweety, alkane
4	0.21	2-Propanone	2.401 ± 0.251	3.158 ± 0.769	0.230	500[a]	Fruity, apple, pear
5	0.27	2-Butanone	0.355 ± 0.056	0.173 ± 0.029	0.104	40	Ethereal
6	0.29	3-Methylbutanal	0.102 ± 0.017	0.341 ± 0.130	0.003	0.08	Acorn, fruity, cheesy, salty
7	0.31	2-Propanol	0.117 ± 0.026	0.045 ± 0.013	0.160	26[b]	Alcoholic, dry, buttery
8	0.32	Ethanol	1.305 ± 0.599	2.550 ± 1.707	0.393	30	Alcohol, sweet
9	0.34	2-Ethyl furane	0.022 ± 0.003	0.042 ± 0.008	0.007	–	Sweet
10	0.38	2-Pentanone+3-pentanone	0.757 ± 0.116	0.324 ± 0.049	0.061	–	Sweet, fruity, green
11	0.39	2,3-Butanodione	0.154 ± 0.027	0.029 ± 0.028	0.027	–	Vainilla/caramel-like
12	0.46	α-Pinene	0.058 ± 0.009	0.036 ± 0.010	0.242	0.018[b]	Sharp, pine
13	0.51	Methyl benzene	0.148 ± 0.019	0.161 ± 0.009	0.722	0.33	Plastic, glue, strong
14	0.53	2-Methyl-3-buten-2-ol	0.015 ± 0.003	0.043 ± 0.025	0.048	0.48	Earthy
15	0.60	Dimethyl disulfide	0.025 ± 0.011	0.016 ± 0.009	0.640	0.012	Cauliflowers, vegetable
16	0.61	Butyl acetate	0.013 ± 0.002	0.008 ± 0.001	0.106	0.30	Fruity
17	0.64	Hexanal	0.176 ± 0.025	0.669 ± 0.295	0.004	0.08	Green, grassy, fatty
18	0.69	2-Methyl propanol	0.050 ± 0.014	0.269 ± 0.022	0.000	1.00	Wine, penetrating
19	0.75	2-Butanol	0.018 ± 0.009	0.010 ± 0.003	0.614	0.50	Winey
20	0.78	Ethyl benzene	0.135 ± 0.021	0.112 ± 0.021	0.584	–	Dry, glue, unpleasant
21	0.90	Butanol	0.013 ± 0.004	0.356 ± 0.209	0.004	0.038	Fruity, medicinal
22	1.05	2-Heptanone	1.036 ± 0.172	0.298 ± 0.072	0.033	0.30	Spicy, acorn, blue cheese
23	1.06	Heptanal	0.580 ± 0.185	0.960 ± 0.354	0.341	0.50	Fatty, greasy, ham-like
24	1.09	Limonene	0.360 ± 0.110	2.008 ± 0.598	0.000	0.25	Citric, fresh
25	1.21	3-Methylbutanol	2.847 ± 0.422	18.649 ± 3.798	0.000	0.10	Woody, acorn, pleasant
26	1.31	2-Pentyl furane	0.251 ± 0.086	0.288 ± 0.057	0.840	0.10	Green fruity
27	1.43	1-Octen-3-one	2.286 ± 0.023	1.090 ± 0.013	0.000	0.01	Spicy, mushroom, dirty
28	1.46	Pentanol	0.176 ± 0.030	0.237 ± 0.094	0.419	0.47	Pungent, strong, balsamic
29	1.59	(E,E)-2,4-decadienal	0.762 ± 0.203	0.035 ± 0.010	0.071	2.50	Fatty, rancid
30	1.61	2-Octanone	1.001 ± 0.305	0.110 ± 0.025	0.137	0.51	Fruity, floral, green, fresh
31	1.63	Octanal	0.330 ± 0.114	1.489 ± 0.586	0.004	0.32	Meat-like, green, fresh
32	1.84	E-2-heptenal	8.670 ± 5.099	8.433 ± 0.3153	0.426	0.05	Green, fatty, fruity
33	1.89	2-Heptanol	0.173 ± 0.029	0.266 ± 0.076	0.206	0.01	Oily, sweety
34	2.09	Hexanol	0.478 ± 0.067	1.988 ± 0.863	0.003	0.40	Fruity, green
35	2.30	2-Nonanone	0.633 ± 0.105	0.499 ± 0.227	0.569	0.10	Floral, fruity, blue cheese
36	2.33	Nonanal	6.383 ± 1.497	10.121 ± 2.882	0.252	0.15	Rancid, fatty
37	2.55	E-2-octenal	0.059 ± 0.021	0.318 ± 0.165	0.010	0.004	Leaves, pungent, fatty
38	2.76	1-Octen-3-ol	5.555 ± 1.138	1.933 ± 0.494	0.108	0.001	Mushroom-like, earthy
39	3.02	Decanal	0.268 ± 0.045	0.184 ± 0.022	0.339	0.65	Citrus, waxy
40	3.11	Benzaldehyde	1.135 ± 0.129	2.537 ± 0.793	0.006	0.06	Bitter almonds, penetrating
41	3.22	E-2-nonenal	0.749 ± 0.369	0.590 ± 0.305	0.826	0.15	Fatty, waxy
42	3.47	Octanol	0.273 ± 0.040	0.733 ± 0.148	0.000	0.027	Fatty, sharp
43	3.94	Butanoic acid	1.027 ± 0.169	0.492 ± 0.149	0.116	0.65	Cheesy, rancid
44	4.13	Nonanol	0.116 ± 0.015	0.193 ± 0.045	0.048	0.28	Fatty green
45	4.14	2-Methylpropanoic acid	15.670 ± 3.310	14.254 ± 0.302	0.777	8.1[a]	Iron, fishy
46	4.35	Hexanoic acid	0.981 ± 0.148	1.309 ± 0.513	0.399	0.70	Fatty, cheese, sweaty

[a] [11].
[b] [12].

instrument (Fig. 1) had the following parts: (a) a glass vial (30 mL), with temperature control, where the sample is deposited, with a valve for the carrier gas (helium, 1 mL/min); (b) a chromatography DB-WAX column (J&W Scientific, Folsom, CA; 15 m × 0.25 mm i.d. × 0.25 μm film thickness) coiled in an aluminum piece that is heated with two resistances; (c) the effluent of the column was split 1:1 to the GC detector (FID) and the sensor chamber used as non-destructive detector; (d) a three-way valve that mixes the gas coming from the column and the air in the proportions 1:50 mL/min as the sensors need a higher flow-rate to get their optima responses; and (e) a stainless steel cylinder-shaped chamber with three metal oxide semiconductor (MOS) sensors arranged in line: TGS 2600 and TGS 2620 (Figaro Engineering Inc., Osaka, Japan) and SBAQ1A (FIS Inc., Itami, Japan). The three sensors were composed by SnO_2. This metal oxide showed a good performance in volatile compounds determination in oils [3]. The sensors TGS 2600 and SBAQ1A are typically applied to air control, although it shows a high response to organic volatile compounds present in fat foods [14]. TGS 2620 are applied to detect organic vapors, and it shows high responses to volatiles compounds present in foods [14].

A TC620 temperature sensor (Microchip Technology Inc., AZ) was also installed in the same sensor chamber. The chamber had an inlet and an outlet for the carrier gas and a flow controller.

The sensor signal (henceforth sensorgrams) resulted in a delay in the response of ~7 min in regards to the GC chromatograms from the FID detector due to the slow signal recovery of sensors. The method involved four steps: (i) The sensor chamber was cleaned by circulating humid air with a constant flow (100 mL/min) until the sensors recovered the baseline. (ii) The sample (5 g minced ham) was kept for 10 min in the glass vial at 34 °C to achieve the headspace equilibrium. (iii) The carrier gas (helium, 1.5 mL/min) swept the headspace and the volatile compounds in the headspace were transferred to a chromatography column that is heated at 60°C with a temperature control. (iv) Finally, the volatile compounds were transferred from the column to the sensor chamber. In this step the signals from the sensors were

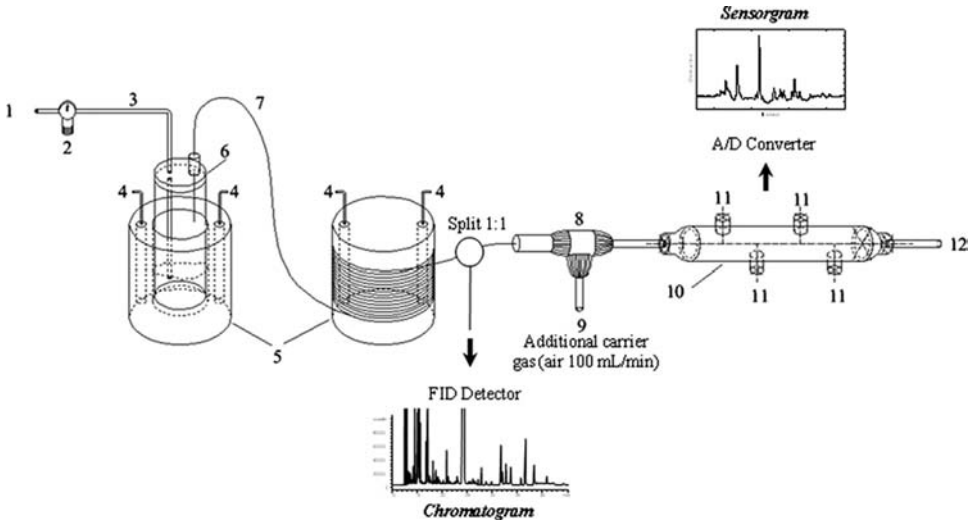

Fig. 1. Sensor Based Olfactory System (SBOS). (1) Gas input (He); (2) adjustable valve; (3) tube connecting to sample vial; (4) heating resistances; (5) heated aluminum holders; (6) sample vial with gas output to capillary GC column; (7) polar capillary column; (8) 3-way connector; (9) gas input (air); (10) stainless steel cylinder-shaped sensor chamber; (11) sensors (3 metal oxide semiconducting sensors and 1 temperature sensor); and (12) gas output (He+air).

recorded on a computer using an A/D converter PCI-1200 with eight analog inputs (National Instrument, Madrid, Spain). Sensor responses were processed to obtain the fractional resistance change $(R_0-R)/R_0$ (R is steady state resistance and R_0 is baseline resistance).

2.6. Data processing and statistical analysis

Data management and statistical analysis was carried out by means of Statistica 8.0 (Statsoft Iberica, Lisbon, Portugal). Correlation was used to determine the relationship between the concentration of volatile compounds and sensor response. The relationship between both concentration values and sensor signals was also examined by principal component analysis.

In order to establish clear relationship between sensor responses and volatile compounds the first derivative was computed and the smooth algorithm of Savitzky–Golay [15] was applied to the whole sensorgram with Omnic 7.3 (Thermo Electron Corporation, Marietta, OH). The resulted plot was similar to that of the corresponding FID chromatogram and the volatile identification was based on the similarities between two signal profiles.

3. Results and discussion

The responses of MOS sensors are typically curves with adsorption and desorption slopes that correspond to the deposition and subsequent combustion of the volatiles on the hot metal oxide semiconducting film of the sensor. This characteristic signal does not explain to which volatiles the sensor is sensitive since the response is the result of the concomitant adsorption processes of all the volatiles that occur as soon as they reach the sensor chamber. Although mathematical algorithms such as windowed time slicing – WTS – [16], allow extracting more information from the raw response obtaining better classification rates, they still do not provide chemical knowledge about why some sensor are directly related to sensory attributes. Thus, a quality classification by means of sensors may not be based on the volatiles that actually contribute to aroma unless a further study check the sensor sensitive to those compounds with major sensory impact.

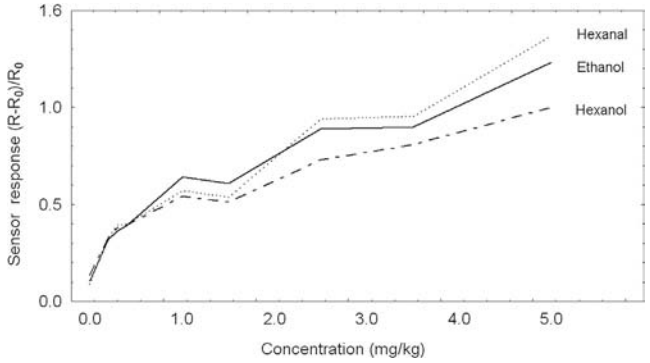

Fig. 2. Responses of a TGS 2620 sensor to different concentration of volatile compounds diluted in a fully deodorized olive oil.

3.1. Analysis of the volatile composition from the sensor responses

An approach to determine the sensitivity of sensors to the volatile compounds present in the sample headspace involves a correlation study between the concentration of volatiles and the sensor responses. Fig. 2 shows the response of a sensor to different concentration of three compounds diluted in the fully deodorized olive oil (0.2, 0.3, 0.4, 1.0, 1.5, 2.5, 3.5, and 5.0 mg/kg). The results show the responses are not fully linear with a sensitivity of ~129 (average of slope of calibration lines). Table 2 shows the responses of the sensors to volatiles identified in dry-cured hams diluted in the fully deodorized olive oil (at 5 mg/kg). The responses have been normalized in order to compare the relative sensitivity between compounds. The volatiles that induce the highest responses in the sensors are: ethanol, 2-methyl-propanol, 3-methyl-butanal, 3-pentanone, hexanal, 3-methyl-1-butanol, pentanol, hexanol, and 1-octen-3-ol.

These studies are not, however, valid for foods with complex aroma because they do not consider the effect of masking and synergy effects between compounds interacting with the sensors. Furthermore, the volatiles that better interact with the sensitive material may not be necessarily significant from a sensory viewpoint since only those volatiles with odor thresholds lower than their concentrations in dry-cured hams are perceived by the human nose [17]. Therefore, in order to provide an appropriate sensory interpretation of sensor responses, the relation between

Table 2
Normalized responses (V) of the sensors to dilutions (5 mg/kg) of standards in a fully deodorized olive oil. *Note*: Figures in bold and italics correspond to values higher than 0.90.

Volatile	TGS 2600	TGS 2620	SBAQ1A
Octane	–	0.76	–
3-Methylbutanal	***0.91***	***0.92***	***0.94***
Ethanol	0.80	***1.00***	***1.00***
3-Pentanone	***0.98***	0.89	***0.90***
Hexanal	***0.95***	0.80	0.83
2-Methyl propanol	0.86	***0.95***	***0.90***
Ethyl benzene	–	0.73	–
3-Methyl butanol	0.75	0.89	0.83
Pentanol	***0.92***	0.87	0.85
Hexanol	***0.86***	0.76	–
1-Octen-3-ol	***0.94***	0.77	0.74
Decanal	0.78	–	–

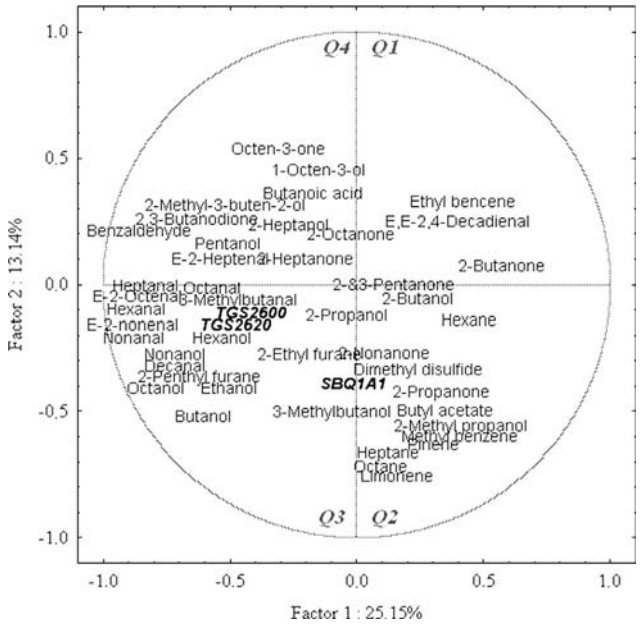

Fig. 3. Projection of the sensor response on a PCA plot of volatiles.

the concentration values and odor thresholds expressed as odor activity values (OAV) should be considered; OAV is the ratio between their odor thresholds and their concentration in the sample, and it is higher than 1 for volatiles that contribute to aroma. Table 1 shows the concentration ranges of volatile compounds quantified in dry-cured hams and their odor thresholds. The highest concentrations of volatiles correspond to the aldehydes hexanal, octanal, nonanal and the alcohol 3-methylbutanol, all of them being quantified in Iberian dry-cured hams at higher concentrations.

In addition to correlation studies between concentration values and sensor responses, the exploratory analysis of data by principal component analysis (PCA) also provide useful information to determine the most significant volatile compounds interacting with the sensors. This procedure offers the advantage of studying the relation of sensors responses with a high number of volatile compounds in a single step. Fig. 3 shows the result of projecting the response of the sensors on the principal component analysis (PCA) of volatiles. The sensors are near 3-methylbutanal that is one of the markers of Iberian dry-cured hams. The regression coefficient (R) of the sensors TGS 2600 and TGS 2620 with the concentration of this compound oscillates between 0.91 and 0.94 (Table 2), which indicates their high sensitivity with 3-methylbutanal. The value is higher (R=0.90) when the concentration corresponds to the volatile presents in the subcutaneous fat exclusively. On the other hand, the sensor SBAQ1A are near to 3-methylbutanol and not far from octanol and limonene which are important contributors to dry-cured aroma (Table 1) [18].

3.2. An approach to chemical explanation of sensor signals by in-tandem GC-sensor array

The relations between sensors and volatiles observed in the previous studies are based on mathematical correspondences and require an additional procedure with an experimental basis to corroborate these relationships. In fact, the correlation between the concentration of volatiles and the responses of the sensors reports certain useful information to know the sensitivity of the sensors to some volatiles but that may be the result of an apparent correlation between two series of data. The implementation of a previous step of separation of the volatiles by a GC column would help to make sure that the compounds are individually transferred to the sensors at the actual concentrations that they are in the samples.

Fig. 1 shows the scheme of the sensor system used in this work, in which a GC column separates the compounds by their polarity (according to their Kovats Index) and they are sequentially released into a sensor chamber. As a consequence, the sensors react to each volatile individually. The sensor system is also connected to a FID detector at the end of the chromatographic column. This strategy provides information about the relative sensitivity of each sensor for each volatile.

The sensor response (sensorgram) recorded during all the experiment is the results of the interaction of volatiles with the sensor grid which means a variation of the sensor resistance (Fig. 4). Thus, the sensor response, in regards to both the height and the breadth of each peak, represents the sensor sensitivity to the volatile compound. Both variables (height and breadth expressed in the time domain) match with those variables determined in the peaks of the chromatogram obtained from the FID output.

As the sensor response is slower than the output of the FID detector, the response consists on a series of adsorption and desorption slopes, caused by the volatiles that are released by the GC column in a short time frame. Furthermore, the sensor response is relatively slow compared with a FID detector and it does not allow a complete baseline recovery in the experiments till the end of the process. In order to individualize the contribution of each volatile – a peak can be the result of the contribution of several volatiles – the first derivative is calculated for the whole sensorgram after applying the smooth Savitsky–Golay algorithm. Thus, the resulting sensorgram is much easier to compare with its corresponding chromatogram to assign most of the peaks to the volatile compounds that are being released by the column, as shown in Fig. 4. This figure shows a delay in the retention time of the sensorgrams in comparison with the GC detector as a consequence of the lengthy desorption of the volatiles deposed at the sensor surface. This delay makes the sensor response much more complicate to explain when identifying the volatile compounds in the sensorgram by comparing the signal to the chromatogram. Thus, Fig. 4 shows the sensorgrams of the TGS 2620 sensor to a sample of Iberian dry-cured ham, and two non-Iberian samples. In all the cases, the first change in the response of the sensors was observed at ~24 min due to 3-methylbutanal. The previous studies based on correlation and PCA also reported a high sensitivity to this compound (Table 2 and Fig. 3). 3-Methylbutanal is one of the most significant aldehydes characterizing Iberian hams (Table 1), and it means 25% of aldehydes quantified in semitendinosus muscle [19]. This compound explains the acorn,

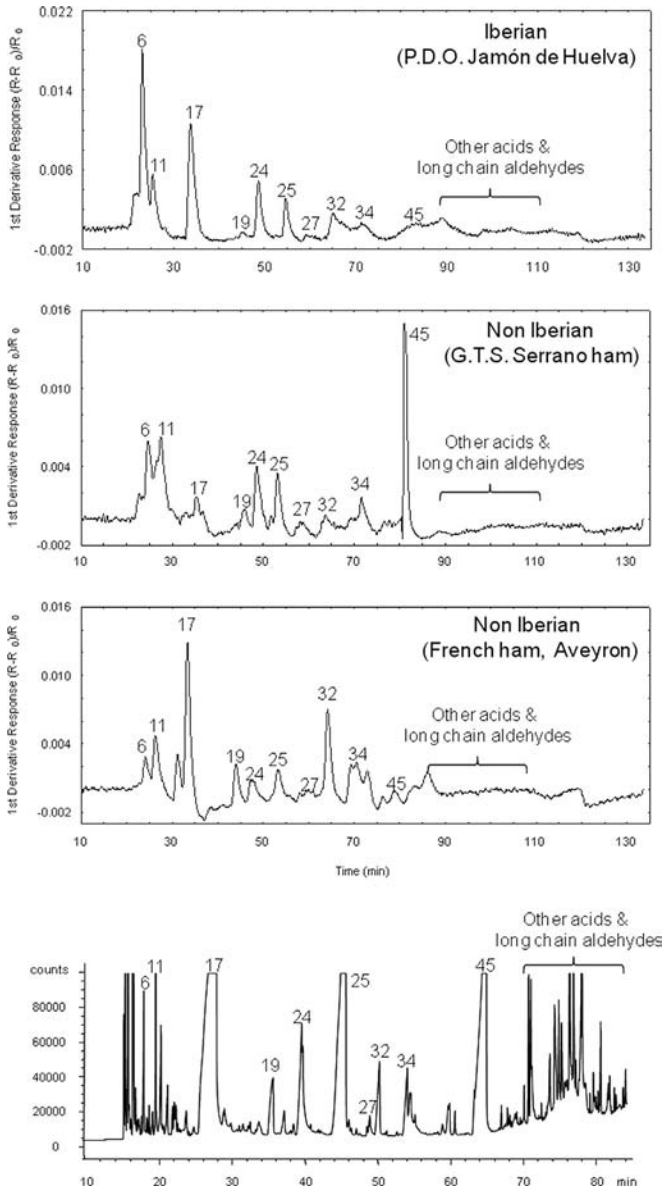

Fig. 4. Responses of the sensor TGS 2620 to a sample of Iberian dry-cured ham (PDO 'Jamón de Huelva') and non-Iberian hams from Spain (GTS Serrano) and France. The chromatogram of volatiles of the Iberian sample is also shown. *Note*: numbers corresponds to the codes of Table 1.

cheesy and salty sensory notes [20] and it is also related to the acceptability of Iberian hams by consumers [21]. The second response in the sensorgram corresponded to 2,3-butanodione, which are present at a higher concentration in non-Iberian (Table 1). The next broad peak was due to hexanal, which is among the most significant aldehydes, and it even represents 64.2% of all the aldehydes in the particular case of subcutaneous fat [19]; it results from the oxidation of free and esterified linoleic acid. After the response assigned to hexanal there was a small change in the slope caused by 2-butanol. However, the high odor threshold of this compound (0.50 mg/kg) pointed out that the contribution of this compound was not as relevant as for others. Next to this peak it was located the response assigned to limonene at approx. ~50 min; the highest concentrations of this compound was found in pigs fed with acorns [22]. The next compound that was observed in the sensorgrams was 3-methylbutanol at 55 min, which is the most abundant alcohol of dry-cured hams [19]. Another response assigned to 1-octen-3-one was observed in all the sensorgram, although in all cases the intensity was very low compared to other volatile compounds. This low response was followed by a higher response due to E-2-heptenal. This compound was characterized by a very low odor threshold (0.05 mg/kg) and contributes to the aroma with a green-fatty attribute. The alcohol hexanol was also responsible for changes in the response of sensors. This compound is the major volatile in subcutaneous fat [22] and contributes with a fruity and green aroma. The last part of the sensorgram was due to the action of 2-methylpropanoic and other acids like hexanoic acid, nonanoic acid, etc., together with some long chain aldehydes such as decanal and E-2-nonenal [22].

The concentrations of these compounds varied between Iberian and non-Iberian hams and, in consequence, the profiles of volatiles determined by SPME-GC were different (Table 1). Similar differences were also found in the sensorgrams (Fig. 4). The most significant difference was based on the higher concentration of 3-methylbutanal in Iberian hams compared to non-Iberian breeds. Other remarkable differences were observed in the peak intensity assigned to hexanal, which were higher in Iberian and French non-Iberian hams, this compound being less relevant in the sensor response to Serrano ham aroma. Other compounds showing a clear difference in sensor response were 2-butanol, E-2-heptenal, 1-hexanol, 2-methylpropanoic acid, and the rest of acids.

4. Conclusion

Since the aroma analyzers based on gas sensors apply a non separative principle and they are equipped with non selective sensors, the results classifying samples are questioned because they may be only due to a distinction of samples by total concentration of volatiles, and not to a different profile of volatiles. Therefore, a true characterization of aroma by sensor systems must be supported by an experimental approach that allows exploring the individual contribution of each volatile to the whole sensor response. Such study would ensure that the results can be directly related to the quality of the samples, and it would allow predicting the sensor responses for other samples with a different profile of volatiles, so providing a chemical basis to the electronic nose analyses.

Besides the mathematical correlation and the sequential analyses of pure compounds, the procedure based on a sensor system including a previous separative step gives definitive and univocal information about which compounds are the main responsible for the sensor responses. The sensor system described in this work (SBOD) makes advantage of this procedure and it has been designed for analyzing complex odors such as food aroma. This instrument opens a new line to explore the possibilities of aroma sensors in real applications. The resulting sensorgrams allows identifying the volatile compounds that have a major impact on sensor responses. In addition to the application of SBOD for identifying the most relevant volatiles compounds eliciting the sensor responses, we have observed clear differences in sensorgrams of Iberian and non-Iberian hams, which suggests the ability of this sensor system for aroma characterization (Fig. 4). In consequence, the equipment used in this work can be applied to the chemical interpretation of sensor responses, and to the routine analysis of food aroma in a larger extent than conventional electronic noses do. Other application of this system is to provide an experimental criterion to select sensors that are sensitive to the compounds with major odor impacts for a given application. Today there are many gas sensors that are commercially available and the kind of metal in the composition may drastically change their sensitivity, hence the analyst should carry out a selection of sensors based on their responses to real samples to search an optimized sensor array. Finally, this sensor system and the proposed data processing based on derivative and smoothing of the

signal can be an alternative non-destructive GC detector that allows the coupling to other instruments. Furthermore, a sensor array used as GC detector would provide sensorgrams that can be easily correlated with the human odor perception once the appropriate set of sensors are selected. The micromachined GC columns, whose application in sensors has been recently reported [9], can improve the performance of these systems without significant diminishment of the more advantageous properties of sensing instruments, the speed reporting results, low cost, and the options of portability and automation.

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