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

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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

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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