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Electronic nose for ham discrimination

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Abstract

In this paper, we report a specific application of an electronic nose based on a semiconductor thin film sensor array for the discrimination of different hams. The sensing elements of the sensor array were undoped and doped (Cr, Pt) SnO_2 thin films prepared by sputtering process. A system based on a static headspace sampling was used for the injection of the volatile compounds coming from the hams. Data analysis was performed by two pattern recognition methods: principal component analysis (PCA) and probabilistic neuronal network (PNN). The obtained results show that the electronic nose was able to identify the ham samples clearly.

Keywords: MOS thin-film sensors; Electronic nose; Pattern recognition techniques; Ham discrimination

1. Introduction

The quality of ham is influenced by different sensory characteristics. The most important is the aroma. There are a lot of reports where different meat products were studied. It was observed that the more aromatic these products are, the better they are accepted [1,2].

Sensory analysis offers exhaustive information about ham quality, but this method requires a trained team and it is also very subjective. The quality of the hams is currently assessed by ham-flavor experts sniffing small samples taken from the hams. However, the process is tedious and the quality of the hams cannot be monitored at frequent intervals during the curing process.

Usually, the determination of volatile compounds in food is carried out through expensive techniques such as gas chromatography–mass spectrometry (GC–MS) which require complicated extraction methods, but the most important drawback is that these techniques are not able to measure in real time and in on-line process.

Recently, device such as the electronic nose are thought to emerge as a third possibility for aroma profile analysis. The electronic nose consists of an array of gas sensors with different selectivity, a signal collecting unit and a pattern recognition software. It is particularly useful for the analysis of headspace of liquid or solid food samples. The reasons are the possibility of direct measurements with no or very little sample handling, easy to build mobile instruments and the fact that a single instrument might be used in various applications by merely altering the data evaluation setup [3].

Usually, the discrimination among the aromas increases with the number of the sensing elements in the array, provided that these respond with non-identical characteristics and low cross-sensitivity to the range of odours applied. Thereafter, different types of sensors have been used in these arrays to identify various aromas such as quartz crystal microbalances [4], SAW delay lines and resonators [5,6], electrochemical devices [7], etc.

A variety of materials applicable in the sensors array have been proposed, perhaps the most competitive are metal oxide semiconductors, because of their high chemical stability, low ageing, high sensibility, easy manufacturing and low cost [8,9].

In this paper, we focus on an array of 16 metal oxide sensors based on SnO_2 thin films doped with Cr and In.

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Sensor features are based on charge transfer reactions occurring during catalytic reactions of molecules at the surface at high temperature, which cause the change of electrical resistance in the sensor. The measured responses of the array to four different types of hams (three Iberian hams: Fodder, "Montanera" and Spoiled; and one White Large ham: Parma ham) are presented and studied by two pattern recognition techniques: principal component analysis (PCA) and probabilistic neuronal network (PNN).

2. Experimental

2.1. Ham samples

Samples that were analysed came from four different types of hams. Three of them came from Iberian hams and the other one came from White Large ham. Iberian hams differ in the feeding system: Fodder (fed on a concentrated feed), "Montanera" and Spoiled (fed on acorns and pasture both). It can be noticed that Spoiled ham is a "Montanera" ham which has suffered some alterations in its maturation process.

White Large pigs were slaughtered at about 160 kg live weight and the hams were processed and ripened by the conventional technology used at "Stazione Sperimentale per l'Industria delle Conserve Alimentari" [10]. That is an institute with legal status and autonomous administration under the supervision of the Italian Ministry of Production Activities, created in Parma in 1922 to promote the technical progress of the Italian food preserving industry. This type of ham was called "Parma" ham.

Iberian hams were processed according to the traditional method [11].

For all types of hams, a piece of biceps femoris muscle from the hams was taken, vacuum packaged, frozen and kept at −18 °C until analysis.

2.2. Sampling method: static headspace generation

Samples were analysed using a static headspace generation system to extract volatiles.

Ham sample (5 g) was placed into a Dreschel bottle being maintained at a constant temperature (50 °C) in a digital water bath for 20 min. Afterwards, an inert gas (nitrogen) was bubbled at 200 ml/min through the Dreschel bottle (containing the ham sample) to carry the volatile organic compounds into the sensor chamber. In all cases, the exposure time of the sensors to the ham volatile compounds was 15 min.

2.3. Fabrication of SnO_2 thin film sensor array

The multisensor includes 16 sensor elements distributed in circular shape onto an alumina substrate. The tin oxide thin films are grown by reactive sputtering from SnO_2 target under 10:90 oxygen–argon mixture. A detailed description of the complete procedure for the preparation of the sensors has been reported elsewhere [12,13]. Deposition conditions have been fixed during the sputtering process (independent of the target used) and are as follows: substrate holder temperature 250 °C, plasma pressure 0.5 Pa, acceleration voltage 500 V and radiofrequency power 100 W. Some of the sensors have been doped with different amounts of Cr and In, by changing the deposition time during the sputtering process. Dopants are deposited as an intermediate discontinuous layer between two layers of SnO_2 (sandwich structure) or as a superficial and discontinuous layer. Table 1 shows the multisensor distribution. Multisensor is organised in five blocks and each one comprises several sensors: block 1 formed by SnO_2 of different thickness; blocks 2 and 3 doped with Cr and In, respectively, as sandwich structure; blocks 4 and 5 doped with Cr and In, respectively, as a superficial layer. Doping levels are different and were expressed as sputtering time in seconds. The multisensor was thermally treated in air at 520 °C for 4 h to control the material morphology (stoichiometry and grain size of the tin oxide and dopant distribution) and to stabilise the semiconductor electrical resistance before the measurement. Annealing is fundamental in order to obtain a good detection [14,15].

Table 1
Multisensor composition

S 1	SnO_2 200 nm
S 2	SnO_2 400 nm
S 3	SnO_2 600 nm
S 4	SnO_2 800 nm
S 5	SnO_2 300 nm + Cr(8 s) + SnO_2 150 nm
S 6	SnO_2 300 nm + Cr(16 s) + SnO_2 150 nm
S 7	SnO_2 300 nm + Cr(24 s) + SnO_2 150 nm
S 8	SnO_2 300 nm + Cr(32 s) + SnO_2 150 nm
S 9	SnO_2 300 nm + In(8 s) + SnO_2 150 nm
S 10	SnO_2 300 nm + In(16 s) + SnO_2 150 nm
S 11	SnO_2 300 nm + In(24 s) + SnO_2 150 nm
S 12	SnO_2 300 nm + In(32 s) + SnO_2 150 nm
S 13	SnO_2 450 nm + Cr(8 s)
S 14	SnO_2 450 nm + Cr(16 s)
S 15	SnO_2 450 nm + In(8 s)
S 16	SnO_2 450 nm + In(16 s)

2.4. Measuring setup

The multisensor device was placed in a steel test chamber (20 cm^3) and the resistance measurements were carried out under a constant flow (mass flow controllers manufactured by Bronkhorst Hi-Tec) of pure nitrogen (200 ml/min) at 250 °C. A thermocouple was placed in contact with the multisensor to measure the operating temperature, which was continuously recorded. The electrical resistance values of each sensor were measured through digital multimeters (Keithley 2001) with scanner cards connected to a personal computer (PC) by means of an IEEE board. The gas line control system as well as the data acquisition were carried out by a personal computer. The software used to control the measurement process and data acquisition was Testpoint.