Electronic nose for wine discrimination

M. García, M. Aleixandre, J. Gutiérrez, M.C. Horrillo *

Laboratorio de Sensores (IFA-CSIC), Serrano 144, 28006 Madrid, Spain

Abstract

An electronic nose based on metal oxide semiconductor thin-film sensors has been used to characterize and classify four types of red wines of the same variety of grapes which come from the same cellar. Two different systems for the injection of the volatile compounds coming from the wine, based on static and dynamic headspace sampling, were used. Sensor response generates a typical chemical fingerprint of the volatile compounds present in the wines. Data analysis was performed by two pattern recognition methods: principal component analysis (PCA) and probabilistic neuronal network (PNN). The results show that electronic nose was able to identify the above wine well.
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1. Introduction

Wine consists of two primary components, water and ethanol. However, the basic flavor of wine depends on 20 or more compounds. The subtle differences that distinguish one varietal wine from another depend on an even larger number of compounds with a wide concentration range from a few ppm to much higher quantities up to 10–15% in weight. Several compounds have been identified in the aroma profile of a wine. The most important are alcohols, esters, acids, ketones, aldehydes, ethers, terpenes, lactones, sulphur compounds, nitrogen compounds, carbonyl compounds, phenolic compounds, etc. [1]

All aroma compounds play a role in the characterization of the aroma pattern of a specific wine. The discrimination of the wines is not an easy task due to the complexity and heterogeneity of their headspace. The complete analysis of wine aroma is extremely complex and expensive. The best example of such analysis can be found in the work carried out by Guth [2].

Currently, there are two basic techniques available to assess the aroma quality of wine. The first is the sensory analysis based on the trained expert panel test. It is useful in the wine classification, but the panel may be affected by problems concerning the standardization, the training quality of the panel members and the stability and reproducibility of the evaluation. The second method is based on instrumental analytical techniques such as gas chromatography which has higher reliability, longer processability, low in situ measurableness and higher costs. This technique enables identification and quantification of volatile compounds in most food and beverages but the drawback of this method is the time required for a single analysis.

Electronic noses 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 pattern recognition software. They have been developed since the 1980s [3] principally using metal oxide semiconductor sensors, surface acoustic wave (SAW) sensors and quartz resonators. In the case of metal oxide semiconductors (MOS) sensors, adsorption of volatile molecules on the sensor surface induces oxide-reduction reactions, which affect the electric resistance of the sensors.

The electronic nose device has the advantage of high portability for in situ and on-line measurements with lower costs and good reliability. They are particularly useful for the analysis of headspace of liquid or solid food samples [4,5]. During

* Corresponding author. Tel.: +34 91 5618806; fax: +34 91 4117651.
E-mail address: carmenhorrillo@ifa.cetef.csic.es (M.C. Horrillo).
URL: http://www.ifa.csic.es.

the last years, numerous attempts using the electronic nose for classification wines have been reported [6–11].

The analysis of wines with semiconductor-based electronic noses is a difficult challenge due to the non-specificity of the sensor arrays and principally to the presence of high ethanol and water concentrations in the wines. In fact, in a wine sample, the aroma compounds amount represent only to about 1 g/l, while water and ethanol amount are about 100 and 900 g/l, respectively. These compounds contribute to the shortening of the sensor life and mask the presence of the other volatile compounds [12]. To overcome this problem in this work, a trap and purge method has been proposed in order to remove ethanol and water.

In this paper, the aim was to develop an electronic nose based on semiconductor gas sensors for the detection of volatile organic compounds (VOCs) coming from different types of wine, using two different extraction sample methods.

2. Experimental

2.1. Wine samples

Four bottled wines from the same cellar (Bodegas Centro Españolas, Tomelloso, Ciudad Real) were selected. Samples wines came from the same variety of grape (Tempranillo) and the same geographic origin (Castilla-La Mancha). They differ in the different evolution which took place after the fermentation. Studied samples were: *Allozo 2002* (young wine), *Allozo Crianza 2000* (aged for a year in American oak barrel and 6 months in bottle), *Allozo Reserva 1998* (aged for 18 months in American and French oak barrel and 18 months in bottle) and *Allozo Gran Reserva 1997* (aged for 24 months in American and French oak barrel and 36 months in bottle).

2.2. Sampling methods

Samples were analysed using two different techniques to extract volatiles, one is based on a static headspace generation and the other one is based on an automatic purge-trap concentrator system.

2.2.1. Static headspace generation
Wine sample (10 ml) was placed into a Dreschel bottle being maintained at a constant temperature in a digital water bath for 30 min. Afterwards, an inert gas (nitrogen) was bubbled at 200 ml/min through the Dreschel bottle (containing the wine sample) to carry the volatile organic compounds into the sensor chamber. In all cases, the exposure time of the sensors to the wine volatile compounds was 20 min.

2.2.2. Dynamic headspace generation: purge and trap
Each sample (1 ml) was placed into a flask for the volatile compound extraction. The extraction was carried out using a Tekmar 3100 purge and trap concentrator. The sample headspace was swept onto the Tenax/silica gel/charcoal

trap using a Helium stream of 40 ml/min. Conditions were as follows: sample temperature 30 °C, preheat time 2 min and purge time 15 min. The volatile compounds were desorbed by heating the trap at 225 °C for 5 min and they were immediately transferred to the sensors chamber. The transfer line to the sensors chamber was held at 150 °C to avoid condensation of volatile organic compounds.

2.3. Multisensor preparation

The multisensor includes 16 sensor elements distributed in circular shape onto an alumina substrate of 1 in. of diameter. Sensor elements are 1 mm width and 8 mm length. Electrical contacts (Pt) are deposited in circular shape of 1.5 μm thickness. The tin oxide thin films are grown by reactive sputtering from a SnO_2 target under a 10:90 oxygen–argon mixture. A detailed description of the complete procedure for the preparation of the sensors has been reported elsewhere [13,14]. Deposition conditions have been fixed during the sputtering process (independently of the target used) and are as follows: substrate holder temperature 250 °C, plasma pressure 0.5 Pa, acceleration voltage 500 V, radio frequency 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 are deposited as a superficial and discontinuous layer. Table 1 shows the multisensor distribution. Multisensor is organised in five blocks and each one comprises several elements: block 1 formed by SnO_2 of different thickness; blocks 2 and 3 doped with Cr and In, respectively, as sandwich structure and 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 [15,16].

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(8s) + SnO_2 150 nm
S 6	SnO_2 300 nm + Cr(16s) + SnO_2 150 nm
S 7	SnO_2 300 nm + Cr(24s) + SnO_2 150 nm
S 8	SnO_2 300 nm + Cr(32s) + SnO_2 150 nm
S 9	SnO_2 300 nm + In(8s) + SnO_2 150 nm
S 10	SnO_2 300 nm + In(16s) + SnO_2 150 nm
S 11	SnO_2 300 nm + In(24s) + SnO_2 150 nm
S 12	SnO_2 300 nm + In(32s) + SnO_2 150 nm
S 13	SnO_2 450 nm + Cr(8s)
S 14	SnO_2 450 nm + Cr(16s)
S 15	SnO_2 450 nm + In(8s)
S 16	SnO_2 450 nm + In(16s)