Sensors and Materials, Vol. 15, No. 3 (2003) 165–176
MYU Tokyo

S & M 0518

Tin Oxide Multisensor for Detection of Grape Juice and Fermented Wine Varieties

Isabel Sayago*, María del Carmen Horrillo, Luis Arés, María Jesús Fernández and Javier Gutiérrez

Laboratorio de Sensores, Instituto de Física Aplicada (CSIC)
Serrano 144, E-28006 Spain

(Received September 24, 2002; accepted January 22, 2003)

Key words: multisensor, volatile organic compounds, wine phases, grape juice and fermented wine

A tin oxide multisensor was applied to discriminate between grape juice and fermented wine phases corresponding to different wine varieties. The tested samples belonged to Albillo, Garnacha, Malvar and Tinto Fino varieties produced in the Madrid area. Garnacha and Tinto Fino are red wine varieties and Albillo and Malvar are white wine ones. The response of multisensors was tested in the temperature range of 250–350°C. The maximum responses are reached at 300 and 350°C depending on either the sensor type or the analysed sample variety. At these temperatures, the sensor response to red wines is higher than that to white wines. In all cases, the response to fermented wine was always better than that to grape juice. The detection of the present volatile organic compounds (VOCs) was useful to distinguish between the two wine phases (grape juice and fermented wine).

1. Introduction

Semiconductor gas sensors have a broad spectrum of applications such as in the field of environmental monitoring and in process quality control. There are some significant problems such as poor selectivity, nonlinear response and long-term drift which have prevented the use of these gas sensors when a sensitive and precise detection of various gaseous components is required. Several routes to improve their selectivity have been investigated. These include the use of different metal oxide types, the operation temperature, thickness variation and additives.(1,2)

Efforts to improve the selectivity problem have been focused on for perfecting the performance of a single sensor; however, a more recent research study has begun to exploit

*Corresponding author, e-mail address: sayago@ifa.cetef.csic.es

the usefulness of arrays of sensors, where relationships among the sensor outputs can aid in the discrimination process.[3]

One of the most important purposes for these devices that is currently investigated, consists of flavour identification by a sensor array (electronic nose). An aroma from the chemical point of view is characterized by the presence of a large number of different species, many of them present in very low concentrations. Multisensors have been successfully designed to discriminate among wines, beers, coffees and food flavours.[4–6] The outputs of chemical sensors are related to the totality of the species present in the ambient. In food and cosmetic industries, sensors are used to evaluate the quality of products and to provide a quality control method.[7,8]

The composition and evolution of wines is related to many biochemical phenomena through which some compounds totally or partially disappear, some remain unchanged and some others are finally increased in volume. Wine contains two primary components, water and ethanol. However, its flavor, smell and color depend on additional compounds. The subtle differences that distinguish one varietal wine from another depend on an even larger number of compounds. Employing gas chromatography methods, more than a hundred substances have been identified in wine. Nevertheless, an identity pattern has not been established yet for every type of wine.[9–12]

Tin oxide is currently still the most important semiconductor; it has been used to measure alcohol concentrations in commercial wine[13,14] and it shows good response to volatile organic compounds (VOCs).[15,16]

The volatile substances in wine belong to four groups of compounds: acids, alcohols, aldehydes and esters. Most of these compounds are aromatic and are present in very low concentrations (traces). Detection of VOCs will be used to distinguish among the different phases of wine and will also permit controlling the wine quality. In previous works,[17] a tin oxide multisensor has been utilized to discriminate among grape juice, fermented wine and wine of Albillo white variety. In this study, we analyse the characteristics of this multisensor that is able to differentiate between grape juice and fermented wine phases of different varieties.

2. Experimental

The multisensor consisted of 12 sensing elements formed by thin tin oxide layers deposited by r.f. reactive sputtering. Some of these components were doped with platinum and chromium. These were introduced as an intermediate dotted layer by sputtering in argon atmosphere. The deposition conditions and the thermal treatment have been previously determined.[15,16]

The multisensor was organized into four blocks, each containing three elements (Table 1):

- Block 1 (S1, S2, S3) formed by SnO_2 of different thicknesses (300, 400, 500 nm).
- Blocks 2 (S4, S5, S6), 3 (S7, S8, S9) and 4 (S10, S11, S12) doped with Cr, Pt and Pt respectively. Each element in the block had different dopant contents. (4, 8 and 12 s) Their thicknesses were 300 nm (blocks 2 and 3) and 400 nm (block 4).

Table 1
Multisensor distribution.

Sensor	Semiconductor material	Dopant time
1	SnO_2 [1 layer – 300 nm]	—
2	SnO_2 [1 layer – 350 nm]	—
3	SnO_2 [1 layer – 400 nm]	—
4	SnO_2 [2 layers – 150 nm]	Cr [4 s]
5	SnO_2 [2 layers – 150 nm]	Cr [8 s]
6	SnO_2 [2 layers – 150 nm]	Cr [12 s]
7	SnO_2 [2 layers – 150 nm]	Pt [4 s]
8	SnO_2 [2 layers – 150 nm]	Pt [8 s]
9	SnO_2 [2 layers – 150 nm]	Pt [12 s]
10	SnO_2 [2 layers – 200 nm]	Pt [4 s]
11	SnO_2 [2 layers – 200 nm]	Pt [8 s]
12	SnO_2 [2 layers – 200 nm]	Pt [12 s]

The sensors were numbered considering that the first one, S1 (300 nm undoped) corresponded to the first element belonging to block 1. The last one, S12 (400 nm Pt-doped with 12 s) was the last element belonging to block 4. It was not possible to carry out the resistance measurements in sensor S11 due to problems with the contacts.

The multisensor device was placed in a stainless steel test chamber and the resistance measurements were carried out under a constant argon flow. The sensors were stabilised in argon before their exposure to grape juice or fermented wine vapour. Grape juices and fermented wines were measured by exposing the multisensor to the saturated vapour mixed with argon for a time span of 20 min.

The tested samples were collected in wine cellars and were immediately frozen in order to avoid losses due to component evaporation and to stop the fermentation processes. Before carrying out the respective detections, these samples were defrosted; thus detection processes took place at a constant temperature.

For detection, the following procedure was used: The samples (grape juice or fermented wine) were placed for 20 min in a closed Dreschsel bottle to realize an equilibrium condition between the liquid and the vapour phase (headspace). Later constant argon flow (200 ml·min^{-1}) was bubbled through a Drechsel bottle and introduced into the test chamber. The bottle was placed in a thermostatic bath in order to keep the temperature constant during the detection process. Each experiment was carried out under the same conditions and thc volume of the tested sample was always the same. Detections were carried out at least three times to verify the sensor response.

Preliminary studies carried out with air as the carrier gas[17] showed after the detection processes a sensor resistance increment. The sensor does not recover its initial resistance value despite being purged with carrier gas. This behaviour can be due to the oxidizing-reducing reactions of the samples. During desorption processes, oxygen must be released and it is adsorbed on the sensor surface, increasing its resistance. On the other hand, the oxygen in the air can modify the composition of the samples because it helps to initiate juice fermentation processes and fermented wine oxidizing reactions. As a result of this, it was decided to employ argon as an inert gas which did not alter the sample composition during the detection process.

All the sensors were characterised by resistance measurements from 250 to 350°C, in order to find the optimum detection temperature. The detection of volatile compounds was useful to distinguish among the different wine phases (grape juice and fermented wine). All the measurement steps were automatically controlled through standard IEEE interface boards by a personal computer.

3. Results

The multisensor performed detection in the temperature range of 250–350°C and all the sensors presented high responses. As the temperature increased, their response also increased reaching a maximum value at 300°C or 350°C depending on either the sensor type or the analysed sample variety.

The response values are defined according to the following expression:

$$\Delta R/R_{wine} = (R_{argon} - R_{wine})/R_{wine}$$

The responses shown in this work correspond to the resistance variation average values obtained from the three detection cycles.

These results have been grouped in three sections according to the type of experiment: 1-Detection of grape juice. 2-Detection of fermented wine. 3-Detection of grape juice and fermented wine. All the sensors showed similar behaviour: sensor resistance decreased during detection processes. Therefore, the response curves shown in this work are the most representative ones from the various tested sensors. For an optimal comparison, the values of responses are represented in the same scale.

3.1 *Detection of grape juice*

The tested samples are white wines (Albillo and Malvar) and red wines (Garnacha and Tinto Fino).

The response variation with respect to temperature shows that grape juice varieties corresponding to red wines present a maximum response at 350°C for any tested sensor. However, for the white grape juice varieties, this temperature is 300°C for undoped sensors and 300 or 350 °C for doped sensors.

Figure 1 shows the responses of the sensors to different grape juice samples at tested temperatures. In all cases, the response to red grape juices is much higher than that to white grape juices. As is seen in the figure, dopant action does not seem to be effective until 350°C, when doped sensors present a higher response than do undoped ones, regardless of the detected sample type (red or white grape juices).

With respect to white wine grape juices, the sensor response to the Albillo variety at

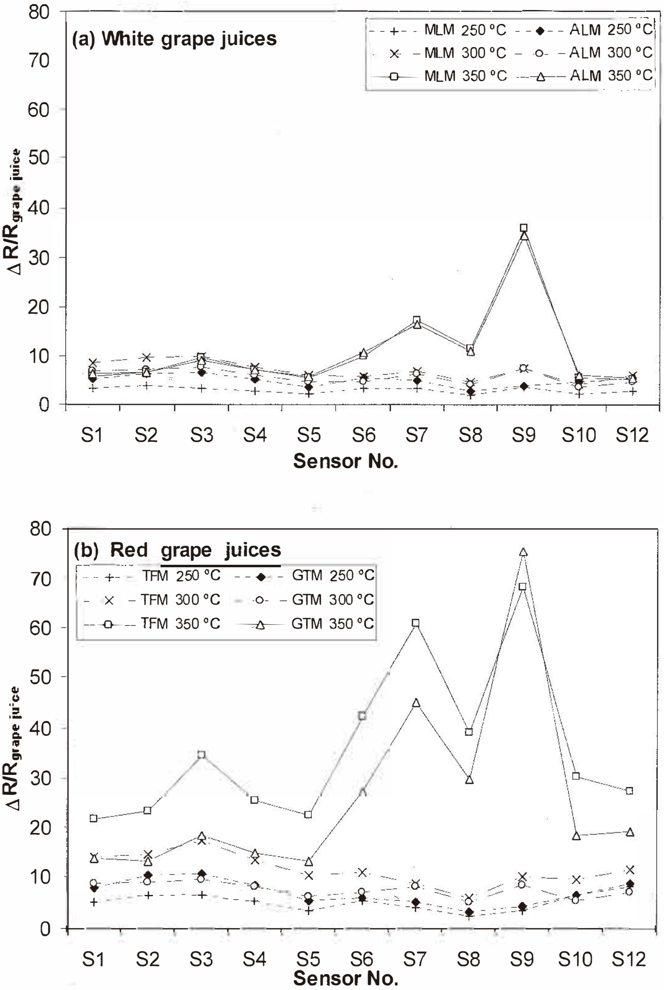

Fig. 1. Multisensor response at 250, 300 and 350˚C for some grape juice varieties: (a) White grape juices: Malvar (MLM) and Albillo (ALM). (b)Red grape juices: Tinto Fino (TFM) and Garnacha (GTM).

250˚C is higher than that to the Malvar one. At higher temperatures (300 and 350˚C), the obtained values are similar in both detection processes (Fig. 1(a)). Concerning red wine grape juices, the sensor response to the Garnacha variety at 250˚C is higher than that to Tinto Fino; however at higher temperatures, the response to Tinto Fino is higher (Fig. 1(b)).

Figure 2 shows an example of the detection curves belonging to the sensor S9 at 300 and 350°C. As is observed in the figure, the resistance variation in the detection processes is useful to suitably discriminate among the different tested grape juice varieties. The resistance modification in a grape juice vapour environment is considerable and becomes higher with temperature. At 350°C, the sensor S9 presents the optimal responses. Dopants do not seem to alter the detection processes since response and recovery times are not modified by the dopant presence.

3.2 *Detection of fermented wine*

The tested samples are: Red wines (Garnacha and Tinto Fino) and Albillo (unfortunately the only fermented white wine variety was tested).

The response variation with respect to temperature shows (Fig. 3) that sensor response to fermented wine varieties corresponding to red wines is higher than to white wine (Albillo), as in the grape juice cases. The temperature corresponding to a maximum response value is 300°C or 350°C depending on either the sensor type or the analysed

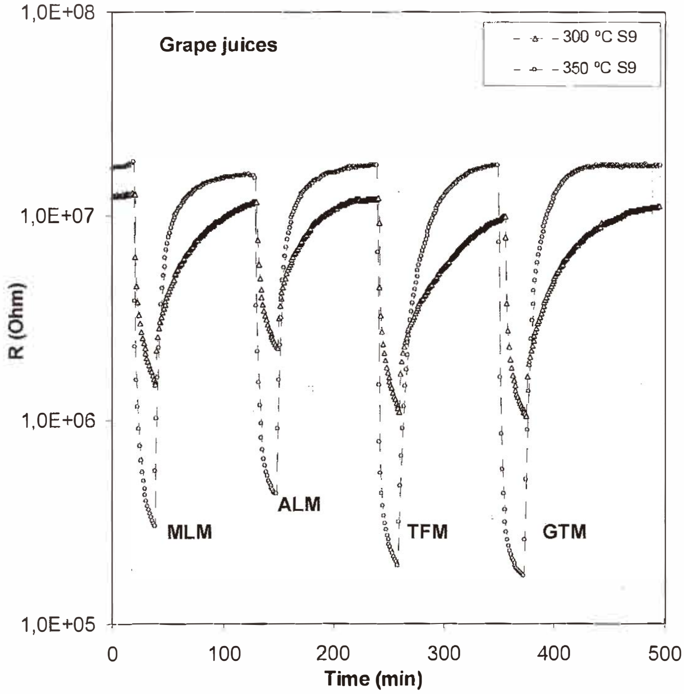

Fig. 2. Detection curves of sensors S9 at 300 and 350°C. The tested grape juices are: Malvar (MLM), Albillo (ALM), Tinto Fino (TFM) and Garnacha (GTM).

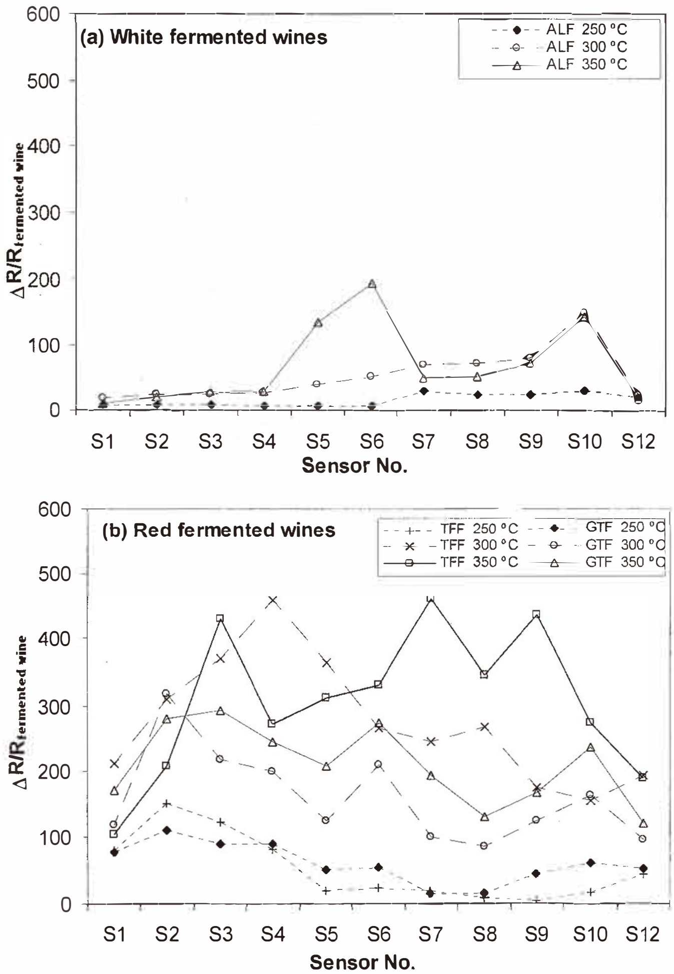

Fig. 3. Multisensor response at 250, 300 and 350°C for some fermented wine varieties: (a) White fermented wines: Albillo (ALF). (b) Red fermented wines: Tinto Fino (TFF) and Garnacha (GTF).

sample variety. In all cases, higher responses are obtained. In the case of the Albillo variety (white fermented wine) at different test temperatures, doped sensors present a higher response than do undoped ones (Fig. 3(a)). On the other hand, in fermented red wines (Tinto Fino and Garnacha) undoped sensors show a higher response than do doped ones. However at 350°C in the case of Tinto Fino detection, some sensors (S7 and S9) offer a higher response than do undoped ones (Fig. 3(b)).

Figure 4 shows an example of the detection curves belonging to sensor S6 at 300 and 350°C. At these temperatures, resistance variations in detection processes are high (three magnitude orders) and the attained values depend on the tested sample. The detection processes are fast: after 5 or 10 min, the resistance value decreases to 80% of its initial value. The recovery processes are slow (sometimes they take more than one hour). As shown in this figure, response and recovery times depend on the sensor operation temperature and they decrease with it. Response curves can be used as pattern curves to discriminate among the tested fermented wines.

3.3 *Detection of grape juice and fermented wine*

The results obtained at various tested temperatures prove that for the same wine variety, the response to fermented wine is higher than that to grape juice. The behaviour is a predictable one due to the higher quantity of VOCs contained in fermented wines. During the fermentation process, new VOCs are produced, as can be seen in Table 2. As a result,

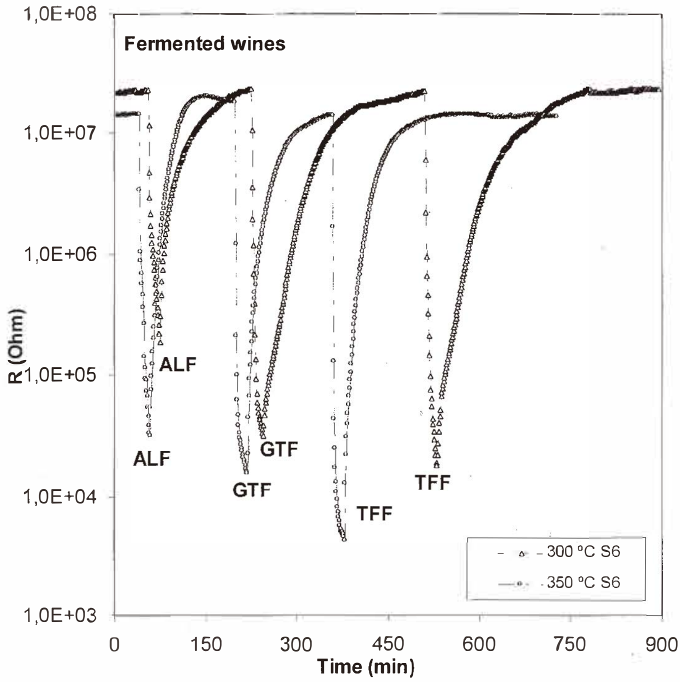

Fig. 4. Detection curves of sensor S6 at 300 and 350°C. The tested fermented varieties are: Albillo (ALF), Garnacha (GTF) and Tinto Fino (TFF).

Table 2
Compounds of wine.[9]

Substances present in wine that previously existed in grape juice	Newly formed substances [during the fermentation process]
Polyvalent alcohols: sorbitol and inositol	Monovalent alcohols: ethanol, methanol, acetylmetylcarbionol and superiors alcohols Polyvalent alcohols: butanediol and glycerine Volatile acids: acetic
Fixed acids: tartaric, malic and citric	Fixed acids: succinic, lactic and superiors grasses
Polyphenols: tannic substances and colorants	
Nitrogenous substances: protides and their degradation products	Esters, aldehydes and acetates Gas: CO_2
Glucides: hexoses and pentoses	
Pectic substances, mucilaginous and rubbers	
Minerals	
Vitamins and enzymes	

the concentration of volatile compounds is higher in fermented wine than in grape juice. The response increase observed in the case of the tested samples is different depending on the wine type (red or white). Tinto Fino and Garnacha varieties (red wines) present a high response increase with respect to grape juice samples. However referring to the Albillo variety, considerably lower response increases are observed. This behaviour could be attributable to the higher alcohol and flavonoid compound content of red wines.

Figure 5 shows the sensor S3 detection curves for the different samples (fermented and grape juices). The sensor S3 is a 400 nm undoped one with high responses to all the detected samples. In white wine response curves (Fig. 5 (a)), the sensor reaches saturation during its exposure time to grape juice vapours (20 min), this does not happen in the case of red wine detections (Fig. 5(b)). On comparing the fermented response curves, similar behaviour can be observed: the sensor practically reaches the saturation level during its exposure time to Albillo, but it is far from the saturation level for red wines samples. All the undoped sensors exhibit this behaviour while the doped ones, as shown in Figs. 2 and 4, do not reach the saturation level during the exposure time. This can be due to a higher dopant reactivity at these temperatures.

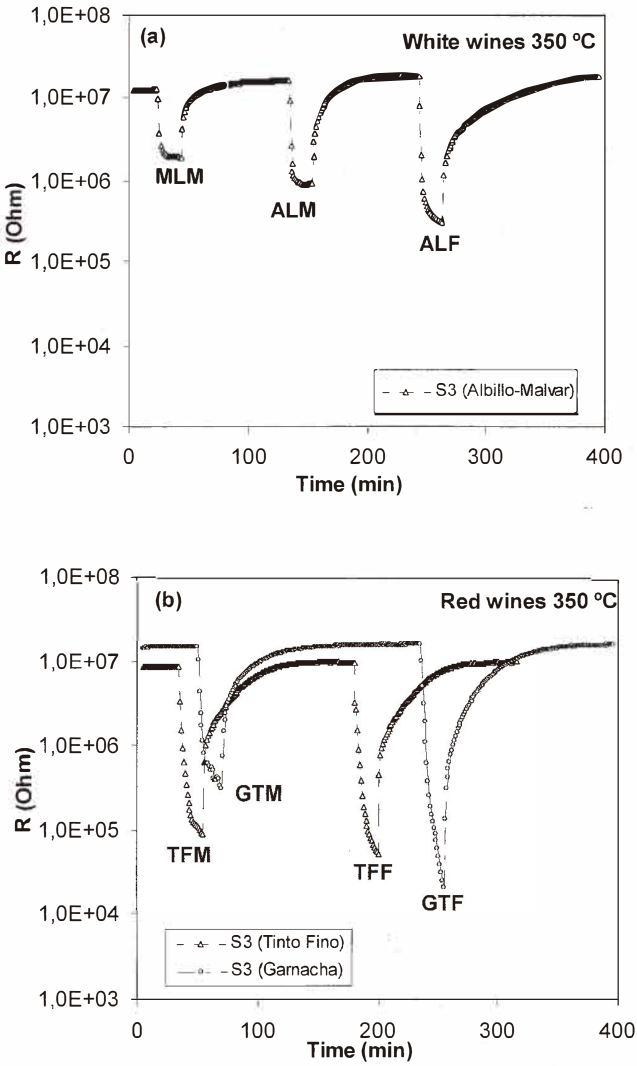

Fig. 5. Detection curves of sensors S3 at 350˚C for white wine (a) and red ones (b). The grape juices tested are: Albillo (ALM), Malvar (MLM), Garnacha (GTM) and Tinto Fino (TFM). The fermented wines tested are: Albillo (ALF), Garnacha (GTF) and Tinto Fino (GTF).

4. Conclusion

Every phase of wine (grape juice, fermented wine and wine) contains some sugars, acids, salts, phenolic compounds, aromatic volatile substances and many others compounds in very low concentrations. The sensor responses are related to the totality of the volatile species present in each wine process (alcohols, aldehydes, esters, acetic acid...).

The multisensor detection is performed in the tested temperature range and high responses are obtained with all the sensors. In every experiment, the resistance of the sensors decreases because the wine vapours (VOCs) are reducing gases. Detection of volatile compounds can be useful to distinguish among wine varieties and wine phases. VOCs detection also allows controlling the wine quality because it is possible to detect anomalies in some steps of the elaboration process.

Sensors present high resistances at various temperatures in the reference atmosphere (argon). These resistance values confirm that the thermal treatment applied to the sensor before the detection permits the oxygen adsorption on the sensor surface. The oxygen reacts with the volatile substances to enable their oxidizing reaction. Under these conditions, the reaction products must release oxygen which is adsorbed again on the sensor surface resulting in that oxygen is available to react with the substances to be detected. After detections and despite the inert atmosphere, the oxygen on the surface is not consumed and the sensor recovers its initial resistance value.

The influence of thickness and dopant is as follows:

- In undoped sensors, the response increases with thickness, though variations are not considerable.
- The dopant action is only effective at higher temperatures with the exception of Albillo fermented wines. In this last case, at all detection temperatures, doped sensors present a higher response than undoped ones.

The experimental results show that SnO_2 (undoped or doped) can be used to distinguish between grape juice and fermented wine phases of different wine varieties depending on the multisensor operation temperature.

1– Grape juice varieties:
  - At $T \geq 350$°C: $\text{Response}_{(\text{Tinto Fino})} > \text{Response}_{(\text{Garnacha})} >> \text{Response}_{(\text{white grape juices})}$
  - At $T = 250$°C: $\text{Response}_{(\text{Garnacha})} > \text{Response}_{(\text{Tinto Fino})} > \text{Response}_{(\text{Albillo})} > \text{Response}_{(\text{Malvar})}$

2– Fermented wine:
  - At $T = 300$°C: $\text{Response}_{(\text{Tinto Fino})} > \text{Response}_{(\text{Garnacha})} >> \text{Response}_{(\text{Albillo})}$

3– Grape juice and fermented wine:

In order to differentiate among wine varieties (Garnacha, Tinto Fino, Malvar and Albillo) and wine phases (grape juice and fermented wine) it is necessary to make the following considerations:
  - For the same variety, response to fermented wines is always higher than to grape juices.
  - Response to red fermented wines is always much higher than to the rest of the tested samples.

Considering the above-mentioned remarks, grape juices and fermented wines could be identified according to the sensor operation temperature as was previously stated.

The number of conducted measurements (three detections per sample) is not sufficient to employ the pattern recognition methods as principal compound analysis (PCA) in sample discrimination. Nowadays, more measurements are being carried out and the initial results are satisfactory because they permit the differentiation of wine phases (grape juice, fermented wine and wine).

Acknowledgement

Comunidad Autónoma de Madrid has supported this work. The authors wish to thank the Consejo Regulador de la Denominación de Origen de Vinos de Madrid for the wine samples.

References

1 T. Seiyama: Chemical Sensor Technology (Kodansha LTD, Vol. 3, 1991 Elsevier).
2 P. T. Mosely, J. Norris and D. E. Williams Eds.: Techniques and Mechanisms in Gas Sensing (Adam Hilger, Bristol, 1991).
3 H. Ulmer, J. Mitrovics, G. Noetzel, U. Weimar and W. Göpel: Sensors and Actuators B **43** (1997) 24.
4 E. Schaller, J. O. Bosset and F. Escher: Lebensm.-Wiss.-Technol **31** (1998) 305.
5 J. W. Gardner, H. V. Shurmer and T. T. Tan: Sensors and Actuators B **6** (1992) 71.
6 T. Nakamoto, K. Fukunishi and T. Moriizumi: Sensors and Actuators B **18** (1998) 473.
7 M. Schweizer-Berberich, S. Vahinger and W. Göpel: Sensors and Actuators B **18–19** (1994) 282.
8 Bourrounet, H. Talou and A. Gaset: Sensors and Actuators B **26-27** (1995) 250.
9 Emile Peynaud: Enología Práctica (Ediciones Mundi-Prensa, 1996).
10 C. S. Ough: Winemaking Basics (Editor Food Products, New York, 1992).
11 F. Oreglia: Enologia Teorico-Práctica Vol. 1. Ed. Instituto Salesiano de Artes Gráficas (Buenos Aires, 1978).
12 R. S. Jackson: Wine Science Principles and Applications (Academic Press 1996).
13 L. Promsong, M. Sriyudthsak and M. Sriyudthsak: Sensors and Actuators B **24–25** (1995) 504.
14 C Di Natale, F. Davide, A. D'Amico, P. Nelli, S. Groppelli and G. Sberveglieri: Sensors and Actuators B **33** (1996) 83.
15 M. C. Horrillo, J. Getino, J. Gutiérrez, L. Arés, J. I. Robla, C. García and I. Sayago: Sensors and Actuators B **43** (1997) 193.
16 J. Getino, M. C. Horrillo, J. Gutiérrez, L. Arés, J.I. Robla, C. García and I. Sayago: Sensors and Actuators B **43** (1997) 200.
17 I. Sayago, M.C. Horrillo, J. Getino, J. Gutiérrez, L. Arés, J. I. Robla, M. J. Fernández and J. Rodrigo: Sensors and Actuators B **57** (1999) 249.