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Differentiation of red wines using an electronic nose based on surface acoustic wave devices

M. García, M.J. Fernández, J.L. Fontecha, J. Lozano, J.P. Santos, M. Aleixandre, I. Sayago, J. Gutiérrez, M.C. Horrillo *

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

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Abstract

An electronic nose, utilizing the principle of surface acoustic waves (SAW), was used to differentiate among different wines of the same variety of grapes which come from the same cellar. The electronic nose is based on eight surface acoustic wave sensors, one is a reference sensor and the others are coated by different polymers by spray coating technique. Data analysis was performed by two pattern recognition methods; principal component analysis (PCA) and probabilistic neuronal network (PNN). The results showed that electronic nose was able to identify the tested wines.

Keywords: SAW sensor array; Electronic nose; Pattern recognition techniques; Wine discrimination

1. Introduction

Electronic noses have made their appearance in the market for almost a decade. They are preferred to routine laboratory analysis for chemical vapour detection because they are rapid, simple and easy-to-handle when compared with analytical techniques. Several authors [1–3] reported applications of electronic noses for detection of food flavours. However, due to high cost and complexity in interpreting results they have been confined to food research laboratories. Surface acoustic wave (SAW) devices have shown promising characteristics as chemical vapour sensors due to their small size, low cost, high sensitivity and fast response. The basic principle of SAW sensors is the reversible sorption of vapours by a sorbent coating which is sensitive to the vapour to be detected. The vapour is sorbed by the sensitive layer resulting in a mass increase which alters the surface wave velocity in the device. The velocity changes are measured indirectly with good precision using the device as the resonant element in a delay line (DL) oscillator circuit and measuring the frequency shifts due to the vapour sorption.

To perform an analysis of complex samples it is necessary to use an array of several gas sensors with different sensitive layers and partial selectivities to various gaseous components. The appropriate choice of coatings coupled with an adequate pattern recognition method lead to a selective chemical analysis.

Several materials are used as sensitive layers. The most used are polymers like phtalocianines [4], ciclodextrins [5], organometallic compounds [6] and rubber polymers [7]. Although metals and semiconductors are employed as sensitive layers [8,9].

In the present work rubbery polymer films have been employed as chemical coatings because of their high sensitivity, fast vapour diffusion and reversible responses. A SAW sensor array with different polymers has been used to discriminate several types of wines.

2. Experimental

The devices were fabricated on ST-X quartz substrates ($9\,mm \times 4\,mm \times 0.5\,mm$ of size) to obtain a frequency of

* Corresponding author. Tel.: +34 915 618 806; fax: +34 91 411 7651.
E-mail address: carmenhorrillo@ifa.cetef.csic.es (M.C. Horrillo).
URL: http://www.ifa.csic.es.

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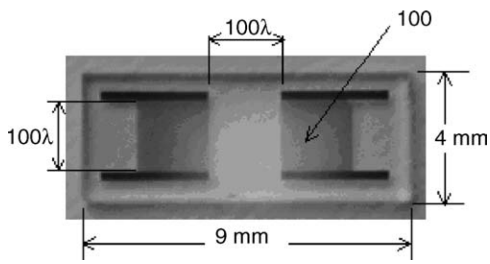

Fig. 1. SAW device.

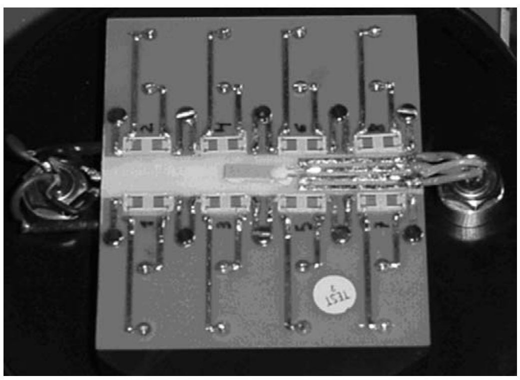

Fig. 2. View of the sensor array in the measuring cell.

157 MHz which means a 20 μm wavelength. The chosen design of the delay lines, optimized previously [10], was λ = 100 for the aperture (W) and for the distance (*L*) between the interdigital transducers (IDTs) and 100 finger pairs. The IDTs were made of aluminium by RF magnetron sputtering, using standard photolithographic techniques. The thickness was 200 nm and the finger width and spacing was 5 μm (Fig. 1).

The sensor array is made up of eight SAW sensors (Fig. 2); one of them is a reference device. Each sensor has its own oscillator circuit.

The polymer films were deposited by spray coating using an airbrush with a solution of the polymer in the appropriate solvent. Four rubber polymers were used: polyepichlorohydrin (PECH), polyetherurethane (PEUT), polybutadiene (PBD) and polydimethylsiloxane (PDMS). They are all commercial polymers for SAW sensor applications with adequate physical and chemical properties in order to obtain fast vapour diffusion and reversible response [11]. The polymer concentrations were as follows: PECH (1.25 mg/ml), PEUT (2.5 mg/ml), PDMS (10 mg/ml), PBD (5 mg/ml).

The mass change of the coating due to the film is detected by a change of the wave velocity and measured as a frequency shift of the oscillation frequency. The film thickness was controlled by measuring the frequency shift with a HP 8510B network analyzer during film deposition. If the film is non-conductive and thin, it can be neglect the electrical and viscoelastic effects and the coating thickness can be calculated from [12]

$$h = \frac{\Delta f}{-(k_1 + k_2) f^2 \rho}$$

where Δf is the frequency shift, f the oscillation frequency, k_1 ($-9.33 \times 10^{-8}\,\mathrm{m^2\,s/kg}$) and k_2 ($-4.16 \times 10^{-8}\,\mathrm{m^2\,s/kg}$) the constants of the substrate and ρ is the polymer density. Table 1 shows the corresponding frequency shifts due to polymer coating for each sensor of the array. This table include coating thickness and attenuations before and after polymer deposition. As it can be seen, in general, the losses are higher when the polymer thickness is higher.

The coated and uncoated devices were introduced into a test chamber of 114 $\mathrm{cm^3}$ in two rows on a printed circuit board (PCB) over a Peltier device, which kept the devices at a fixed temperature (23 ± 0.01 °C). A platinum resistance (Pt100) was glued to the PCB to measure the temperature. The oscillator circuit for each device was connected to the back side of the chamber. The flow rate was 200 ml/min and the carrier gas was nitrogen.

The sensor response, given by the frequency shifts, was measured with a frequency counter HP 53131, connected to microwave switch system, Keithley S46, which allows the frequency display of the eight sensors. The software developed in-house for data acquisition gives the frequency of each device and the frequency difference between each one and the reference. It was used for real-time visualization, storing and analysis of these data. The experimental setup of the SAW sensor system is shown in Fig. 3.

Four bottled wines from the same cellar (Bodegas Centro Españolas, Tomelloso, Ciudad Real) were selected. Wine samples came from the same variety of grapes (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).

Table 1
Frequency shifts, attenuations and coating thickness of the eight devices

	Sensor 0 reference	Sensor 1 PEUT	Sensor 2 PEUT	Sensor 3 PDMS	Sensor 4 PBD	Sensor 5 PECH	Sensor 6 PDMS	Sensor 7 PECH
Δf (KHz)	–	200	300	400	500	200	200	400
h (nm)	0	60	90	120	150	44	60	88
$\lvert S_{12}\rvert_0$ (dB)	19.0	15.4	15.0	14.3	14.1	17.0	14.4	16.3
$\lvert S_{12}\rvert_{pol}$ (dB)	19.0	22.9	24.2	25.1	25.0	20.4	26.3	21.6

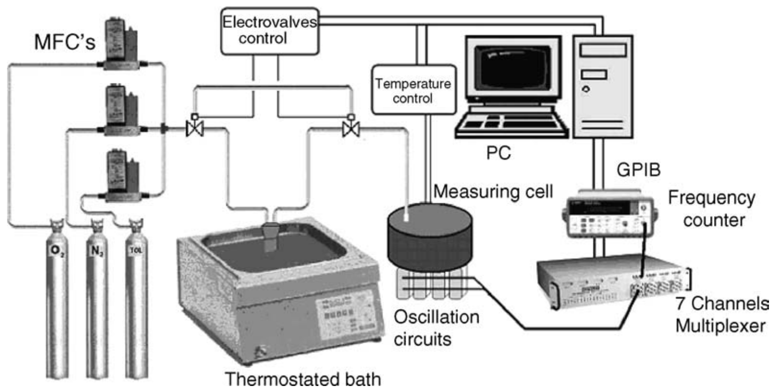

Fig. 3. Experimental setup of the SAW sensor system.

Wine samples (10 ml) were kept at $30 \pm 0.1\,^{\circ}C$ for 30 min in a flask. After that time the headspace was injected in the measurement cell for 10 min. This time was enough for the sensors to reach equilibrium. Measurements were made each 30 s. Experiments were made five times in order to have more data for the later wine classification. The measurements corresponding to each type of wine were conducted in different days to make sure that the differences in response patterns were not due to signal drifts.

3. Results and discussion

The response of each sensor (frequency shift) was subtracted from the reference device frequency shift in order to compensate for temperature and pressure variations. Fig. 4 shows the response of SAW sensors to a sample of *Allozo 2002* young wine. As it is seen in this figure, each sensor shows different response to the wine studied. Response time and recovery time are quite fast, approximately of 2 min.

The response to the four types of wine was also tested (Fig. 5). The sensor responses to four wines are normalized to response of *Allozo Gran Reserva 1997*, due to this wine exhibits the maximum response. This polar plot shows the differences among the studied samples. The variation in response intensity is due to different headspace composition

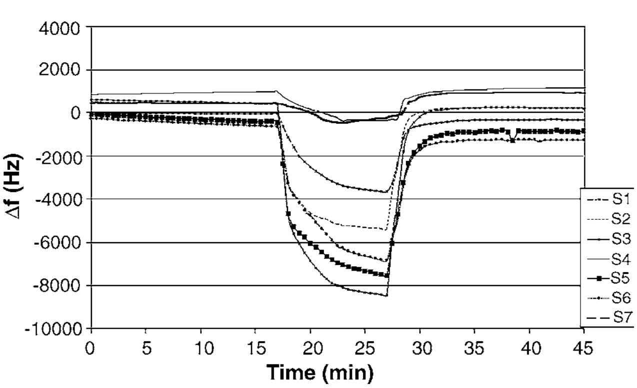

Fig. 4. Response of SAW sensors to a sample of *Allozo 2002* young wine.

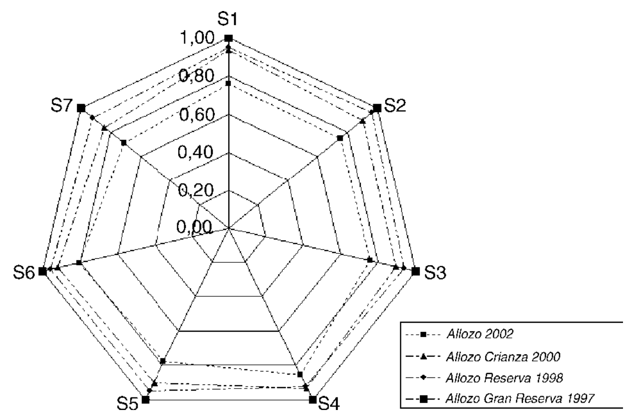

Fig. 5. Polar plot of SAW sensors to the studied wine samples.

of samples wines. Each sample has its characteristic organic volatile compound profile.

The data obtained were pre-processed by centering about the mean and scaling with the standard deviation before performing a principal component analysis (PCA). The PCA results of the four types of wine are illustrated in Fig. 6. It can be seen that all types of wines are well separated.

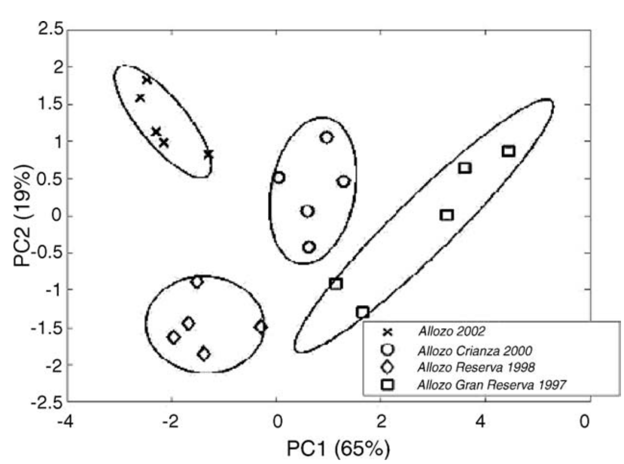

Fig. 6. Principal component analysis plot for the four wines: *Allozo 2002*, *Allozo Crianza 2000*, *Allozo Reserva 1998* and *Allozo Gran Reserva 1997*.

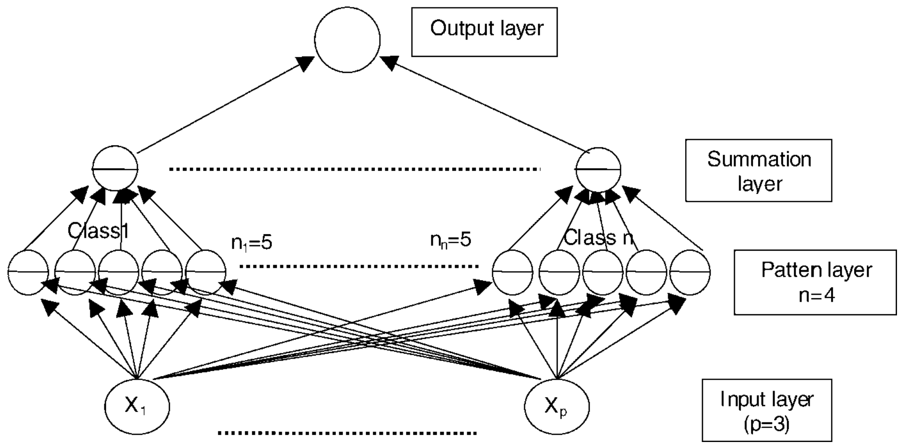

Fig. 7. A probabilistic neuronal network (PNN) with 3 input variables, 4 classes and 20 training examples (5 belonging to each class).

A probabilistic neuronal network (PNN) has been trained with the above data in order to perform the classification. This network is composed by four layers. In the input layer there are three elements that correspond with the first three components of the PCA. The next layer is the pattern layer. This layer has a number of neurons equals to the training pattern vectors, grouped by classes, where the distance between the test vector and a learning pattern is assessed. The purpose of this layer is to measure and weight with a radial function the distance of the input layer vector with each training set element. The third layer, the summation layer, contains one neuron for each class. This layer adds the outputs of the pattern neurons belonging to the same class. Finally, the "output layer" is simply a thresholder that seeks for the maximum value of the summation layer. Then the highest one is selected and takes one as result. The others outputs are set to 0. It has been validated with the leave-one-out method. In Fig. 7 a schematic diagram of the PNN network is shown.

The plot for the neuronal network is shown in Fig. 8. The success rate (correct predicted number over total number of measurements) was 95%. All the samples corresponding to *Allozo 2002*, *Allozo Crianza 2000* and *Allozo Reserva 1998* are well classified. The network only confuses 20% of *Allozo Gran Reserva 1997* samples with *Allozo Crianza 2000* samples.

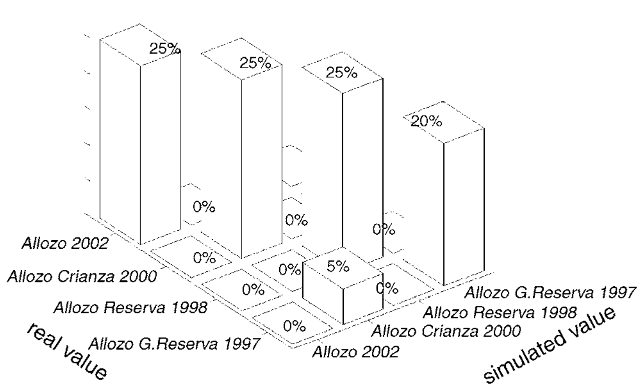

Fig. 8. Classification with the PNN network of four types of wine: *Allozo 2002*, *Allozo Crianza 2000*, *Allozo Reserva 1998* and *Allozo Gran Reserva 1997*.

4. Conclusions

A SAW multisensor has been developed in order to detect volatile organic compounds (VOCs) coming from different wines. Samples coming from the same cellar (same grape variety and same geographical region), although they have been subjected to different evolution after fermentation. Samples differ in the time passed inside the oak and bottle.

Chosen polymers as sensitive layers showed goods properties to be used as adequate coatings, due to their high and fast response. PCA showed a good discrimination among the different wines. As well, the classification performance by PNN was satisfactory (95% success rate).

References

[1] A. Stephan, M. Bücking, H. Steinhart, Food Res. Int. 33 (2000) 199.
[2] T. Nakamoto, Y. Isaka, T. Ishige, T. Moriizumi, Sens. Actuators B 69 (2000) 58.
[3] M. Costa Freitas, C. Pariera, L. Vilas-Boas, J. Food Compos. Anal. 14 (2001) 513.
[4] W.P. Jakubik, M.W. Urbanczyk, S. Kochowski, J. Bodzenta, Sens. Actuators B 96 (2003) 321.
[5] DeQuan Li, Min Ma, Sens. Actuators B 69 (2000) 75.
[6] M. Penza, G. Cassano, A. Sergi, C. Lo Sterzo, M.V. Russo, Sens. Actuators B 81 (2001) 88.
[7] F. Bender, N. Barié, G. Romoudis, A. Voigt, M. Rapp, Sens. Actuators B 93 (2003) 135.
[8] D. Rivera, M.K. Alam, W.G. Yelton, A.W. Staton, R.J. Simonson, Sens. Actuators B 99 (2004) 480.
[9] S.-Y. Chu, T.-Y. Chen, W. Water, J. Cryst. Growth 257 (2003) 280.
[10] M.J. Fernández, J. Fontecha, M.C. Horrillo, I. Sayago, L. Otero, M. García, R. Gómez-Espinosa, J. Gutiérrez, C. Cané, I. Gràcia, Proceedings of the Eighth International Symposium on Olfaction and the Electronic Nose (2001) 134.
[11] M.C. Horrillo, M.J. Fernández, J.L. Fontecha, I. Sayago, M. García, M. Aleixandre, J.P. Santos, L. Arés, J. Gutiérrez, I. Gràcia, C. Cané, Thin Solid Films 467 (2004) 234.
[12] H. Wohltjen, Sens. Actuators B, Chem. 5 (1984) 307.