Discrimination of wine aroma using an array of conducting polymer sensors in conjunction with solid-phase micro-extraction (SPME) technique

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Abstract

A set of 12 polymeric sensors has been tested as an artificial olfactory system for the identification of wines. Three white and two red Spanish wines produced in different locations where analysed by using two alternative sampling methods. A commercial headspace sampler was not successful in concentrating the specific odorants of the different wines, whereas the solid-phase micro-extraction (SPME) technique led to some promising results. By using a selective SPME-fibre, principal component analysis of the data allowed a clear discrimination of the aromas, even for wines that had very similar organoleptic characteristics. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sensors; Conducting polymers; Wine; SPME; Electronic nose

1. Introduction

Aroma is a fundamental organoleptic parameter in the quality assessment procedures for wines. Up to now, this characteristic has been determined by panel test evaluation, a method that requires a group of highly skilled professionals. During the last few years, the so-called 'electronic noses' have been developed as an alternative method to perform this aromatic analysis [1–8]. These systems are based on an array of chemical sensors, which are designed so that, ideally, each one of them responds in a different fashion to a certain aroma. Statistical methods are applied afterwards to the data in order to classify and discriminate different samples. Electronic noses have been previously used for the characterisation of wine aroma [9,10], but certain problems concerning selectivity have risen [11]. This is due to the fact that several of the volatile components relevant to this characteristic of wine are present in minute quantities [12,13].

In order to improve the operation of these systems, we suggest a possible approach based on the use of solid-phase micro-extraction (SPME) for the injection of the aroma. Solid-phase micro-extraction is a well known technique that

has been devised for the preparation of samples for gas chromatography [14]. The method is based on the direct adsorption of analytes, either from the aqueous phase or from the headspace, on an adsorbent fibre, and represents a considerable reduction in the time required for the sample preparation.

The fibre consists of a fused silica frame which is coated with various sorbents: polydimethylsiloxane, polyacrylate, Carbowax®, etc. These sorbents show different affinities to diverse species. Hence, depending on the analytes that have to be detected, a certain sorbent material has to be selected. We have chosen polydimethylsiloxane for our study because this particular material shows a higher affinity towards volatile species that are present in low concentrations than to water and ethanol, the major components in wine. The retained compounds can be released by heating the fibre at high temperatures ($\sim$250°C).

This method has been used in connection with a set of sensors, which have been prepared by electrochemical deposition of various conducting polymers (polypyrrol, poly-3-methyltiophene and polyaniline) [15,16]. The array of 12 sensors, located in a stainless steel chamber, has been exposed to the aromas of Spanish white and red wines from different regions. This system has been able to differentiate among the tested samples.

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2. Experimental

2.1. Samples and conditioning

Different types of Spanish wines were used for the experiments. Three white wines, one from the Rueda O.D., one from Bierzo O.D. and the other produced in the province of Zamora with the Muscat grape variety, and two red wines from the Ribera de Duero O.D., both elaborated following the same procedure and with the same grape varieties, but one of them aged in oak barrels, were tested. For comparison purposes, the effect of deionised water on the measuring system was also analysed. The samples have been prepared following two alternative methodologies, one based on headspace sampling and other based on solid-phase micro-extraction (SPME), both of which are established techniques for their extremely high reproducibility, and as such they have been extensively used in common gas chromatographic analysis.

Constant volumes of the wines (3 ml) were placed in 10 ml vials for the static headspace sampling. The vials are encapsulated and placed in an HP7694e automatic headspace sampler from Hewlett-Packard. The vials are kept at a constant temperature (40°C) for 9 min in order to obtain a homogeneous headspace. The vial is pressurised for 8 s at 1.5 bar. The pressure gradient that builds up permits to fill a 3 ml loop in 9 s, and its content is then injected to the carrier gas that drives the volatiles to the sensors chamber. The carrier gas was high purity synthetic air (99.9990%) and the flow rate was 150 ml min^{-1}.

For the solid-phase micro-extraction technique, 0.8 ml of the wines were placed in 2 ml vials. The vials were encapsulated and an SPME-fibre coated with 100 μm of polydimethylsiloxane (supplied by Supelco) was placed in the gas-phase of the vial for 30 min at room temperature (22 ± 1°C). In this step, the volatile compounds of the sample were collected in the SPME-fibre. In a final step, the SPME-fibre was placed in a heated injection port (250°C) of a gas chromatograph (8500 GC of Perkin-Elmer). The SPME-fibre remained in the injection port for 5 min, in order to ensure that all volatile compounds present in the sorbent were driven to the sensor chamber. The gas carrier was high purity nitrogen (99.9990%) and the operating flow rate was the same reported for the alternate procedure.

2.2. Preparation of the polymeric sensors

The poly(3-methylthiophene) (PMT) and polyaniline (PAN) films were grown electrochemically onto glass substrates covered with ITO electrodes (electrode spacing 75 μm). Alumina substrates with gold electrodes (electrode spacing 50 μm) where used for the polypyrrole (PPy) sensors. The substrates were cleaned with acetone prior to polymer deposition. A detailed description of the complete procedure for the preparation of the sensors has been reported elsewhere [15,17].

Electropolymerisation and electrochemical measurements were performed using an EG&G PARC Model 263 potentiostat/galvanostat, which was controlled by electrochemical software M270/250 installed in a desktop computer. The reference electrodes were Ag/AgNO$_3$ 0.1 mol l^{-1} (EG&G) for the non-aqueous media, and Ag/AgCl when water is used as solvent. All potentials quoted are relative to the corresponding reference. The counter electrode was a large surface area platinum gauze, which was flamed prior to use. The solutions were prepared and introduced into a cell with a thermostatic jacket (Metrohm) and with a temperature controlled liquid system (Neslab). All the polymeric films were grown at a constant temperature (25°C). The solutions were deoxygenated by bubbling nitrogen for 10 min prior to use.

The poly(3-methylthiophene) sensors were obtained from an electrolytic solution of 3-methylthiophene (0.1 mol l^{-1}, purchased from Sigma), and with 0.1 mol l^{-1} of the corresponding salt in acetonitrile (Sigma-Aldrich, HPLC grade). Lithium perchlorate anhydrous (Fluka), lithium trifluoromethane sulfonate (Fluka), tetrabutylammonium perchlorate (Sigma) and tetrabutylammonium tetrafluoroborate (Fluka) were employed in the polymerisation reaction to check the effects of dopant anions. These polymeric sensors were prepared by chronopotentiometry (CP) at a constant current (0.6 mA for 60 s). Stable oxidised blue films are obtained. In a subsequent conditioning stage, a −0.5 V potential is applied to the films in order to obtain the reduced state, which is more sensible to the gaseous species. The polymer films are finally washed in acetonitrile.

The polyaniline sensors were generated from solutions of aniline (Aldrich) of different concentrations (see Table 1) in deionised water (Milli-Qplus, Millipore), using HCl (2 mol l^{-1}, Panreac) and sodium hydrogensulfate monohydrate (NaHSO$_4$·H$_2$O) (0.5 mol l^{-1}, Fluka) as doping agents. In order to prepare the solution for the deposition of polyaniline with NaHSO$_4$·H$_2$O as doping agent, aniline was added to the background electrolyte and then the solution was acidified with concentrated sulfuric acid until the white precipitate dissolved. These sensors were deposited either by chronoamperometry (CA) or by cyclic voltammetry (CV). The CA films were generated at a constant potential of 0.9 V for 120 s. A 0.0 V conditioning potential was finally applied to the polyaniline films. The films generated by CV were formed by repetitive cycling between −0.3 and 0.9 V at a scan rate of 50 mV s^{-1}. A final conditioning potential of 0.0 V was applied after the 15 cycles required for the deposition of the operative films.

The polypyrrole films were obtained from an aqueous solution of pyrrole (0.1 mol l^{-1}, Aldrich) using tetrasulfonated nickel phthalocyanine (NiPcTs) (0.01 mol l^{-1}, Aldrich) and decanesulfonic acid (DSA) (0.05 mol l^{-1}, Aldrich) as doping agents. These sensors were prepared either by chronoamperometry or by cyclic voltammetry, under the same conditions used for the preparation of PAN films.

Table 1
Conducting polymer sensors formed by electrochemical polymerisation using different techniques: chronoamperometry (CA), cyclic voltammetry (CV) and chronopotentiometry (CP)

No.	Monomer	Electrolyte	Technique	Conditions
S01	3-Methylthiophene 0.1 M	$LiClO_4$ 0.1 M	CP	$i = -0.6$ mA, $t = 60$ s, $E_f = -0.5$ V
S02	3-Methylthiophene 0.1 M	$LiCF_3SO_3$ 0.1 M	CP	$i = -0.6$ mA, $t = 60$ s, $E_f = -0.5$ V
S03	3-Methylthiophene 0.1 M	$TBAClO_4$ 0.1 M	CP	$i = -0.6$ mA, $t = 60$ s, $E_f = -0.5$ V
S04	3-Methylthiophene 0.1 M	$TBABF_4$ 0.1 M	CP	$i = -0.6$ mA, $t = 60$ s, $E_f = -0.5$ V
S05	Pyrrole 0.1 M	DSA 0.05 M	CV	$0/0.9/-0.3$ V, 15 cycles, 50 mV s^{-1}
S06	Pyrrole 0.1 M	NiPcTs 0.01 M	CA	$E_{pol} = 0.9$, $t = 120$ s, $E_f = 0$ V
S07	Aniline 1 M	HCl 2 M	CV	$0/0.9/-0.3$ V, 15 cycles, 50 mV s^{-1}
S08	Aniline 1 M	HCl 2 M	CA	$E_{pol} = 0.9$, $t = 120$ s, $E_f = 0.9$ V
S09	Aniline 0.4 M	$NaHSO_4$ 0.5 M	CA	$E_{pol} = 0.9$, $t = 120$ s, $E_f = 0.9$ V
S10	Aniline 0.4 M	$NaHSO_4$ 0.5 M	CV	$0/0.9/-0.3$ V, 15 cycles, 50 mV s^{-1}
S11	Pyrrole 0.1 M	DSA 0.05 M	CA	$E_{pol} = 0.9$, $t = 120$ s, $E_f = 0$ V
S12	Pyrrole 0.1 M	NiPcTs 0.01 M	CV	$0/0.9/-0.3$ V, 15 cycles, 50 mV s^{-1}

Table 2
Physico-chemical characteristics of the wine samples

Sample	O.D.	Colour	pH	Titratable acidity* (g l^{-1})	Volatile acidity* (g l^{-1})	Malic acid (g l^{-1})	Free SO_2 (mg l^{-1})	Total SO_2 (mg l^{-1})	Residual sugar (g l^{-1})	Alcohol (vol.)	Year
Wine 1	Rueda	White	3.46	5.0	0.38	3.1	51	118	2.4	12.3	1998
Wine 2	Bierzo	White	3.46	5.8	0.41	2.8	50	151	2.0	12.2	1998
Wine 3	Tierra Zamora	White	N.A.	4.8	0.20	N.A.	20	60	48.2	12.7	1997
Wine 4	Ribera de Duero	Red	3.89	4.0	0.59	0.4	55	90	1.6	13.6	1998
Wine 5	Ribera de Duero	Red	3.74	4.8	0.57	0.5	20	77	1.6	13.2	1996

All the polymeric sensors used in this work, as well as the growth techniques and conditions, are collected in Tables 1 and 2.

2.3. Measuring setup

The sensors were mounted in a stainless steel text box with a volume of approximately 15 ml. The connection of the injection port of gas chromatograph to the sensors box is done inside the chromatograph oven with 1/8 in. TEFLON tubing. The test box, which is replacing the chromatographic column, is kept at a constant temperature (30°C) throughout the experiments. An initial flow of nitrogen of 150 ml min^{-1} is set for 1 min to ensure the stabilisation of the baseline, prior to the insertion of the SPME-fibre for the injection of the volatiles. After the response of the sensing units is recorded, the nitrogen flow is kept for 15 min so that the original baseline is recovered.

In the static headspace sampling measurements, a flow of 150 ml min^{-1} of dry air is set for 3 min in order to stabilise the baseline. The carrier gas passes then through the sample loop for 1 min, dragging the volatile components of the sample towards the chamber of sensors. In this step no variation in the flow is induced. Finally, the clean air flow is kept for 12 min in order to revert to the baseline.

Up to 16 sensors can be mounted simultaneously in the reaction box. As the polymeric gas sensors produce immediate responses, a fast data collection procedure is required.

This step is performed through an PC-LPM-16 data acquisition card from National Instruments interfaced to a personal computer. The sensors are polarised using a constant voltage of 5 V provided by a Hameg 8142 programmable power supply. The scan rate used to measure the changes of resistance of the 16 sensors is 0.2 s. The data are monitored in real time and the graphs can be followed using Visual Basic software from Microsoft.

The obtained data are exported to the GPES44 program, and the different features of the signals are analysed. The height, full width at half height (FWHH) and area of the signals, as well as the area of the derivative of the responses are routinely determined. Finally, pattern recognition techniques (PARC) were used for the discrimination of the signals. For this purpose, principal component analysis (PCA) has been carried out using the software Matlab, Version 4.2.

3. Results and discussion

The use of micro-extraction as a tool for the injection of wine aroma requires an initial pre-concentration stage for the adsorption of the volatile components, which will be released afterwards by applying a thermal desorption program. The release of the wine aroma that is retained in the fibre is carried out inside the injection port of a chromatograph which is kept at an elevated temperature to promote

the delivery of the aromatic vapours. The injector of the chromatograph was used in order to keep a constant flow, with an elevated rate of 150 ml min^{-1}, so that the operating conditions were comparable to those set for the experiments performed with the headspace sampler.

Once the fibre is inserted in the injection port of the chromatograph, the sensors respond to these vapours in a very fast fashion. The outputs from the sensing units depend on the nature of the polymeric films and dopants; the PMT sensors and those based on PPy doped with DSA experiment increases in the magnitude of their electrical resistance, while those based on PAN and PPy doped with tetrasulphonated nickel phthalocyanine show the opposite effect. An important fact is that the original resistances of the sensors are recovered when the volatiles are extracted from the test chamber. This process is very fast for the sensors based on PMT (approximately 1 min), and somewhat slower for those prepared from PAN (6 min) and PPy (7.2 min). The typical shapes of these curves can be observed in Fig. 1, where the responses of the individual sensors to a red wine from the Ribera de Duero O.D. are shown.

A second sampling method, based on the direct injection of the headspace of the wines using an automatic HP7694e sampler, was also tested. The relative changes of the electrical resistance of the sensors are more intense when this scheme is followed. However, the time required for the complete recovery of the baseline of the sensors is about 40% longer than for the other procedure. Furthermore, as we shall immediately point out, it soon becomes apparent that the selectivity attainable using this method is considerably lower than that achieved by applying the micro-extraction technique.

All the samples were repetitively measured 4 times with each one of the systems for the injection of the aroma. A polar plot of the mean signals of the sensors, expressed in terms of resistance changes for the three white wine samples and for water when the corresponding headspace was directly driven to the test chamber, is given in Fig. 2. The shapes of the graphs are extremely similar, and there is hardly any difference in the response of the sensors towards the various samples. The apparent lack of selectivity of the set of sensors is due to the fact that this injection system mainly collects water vapour and ethanol from the headspace of the wines, whereas those volatiles that are responsible for the characteristic aromas are present in minute amounts. Polymeric chemoresistors are known to be sensitive to water and ethanol [18,19]. Hence, the response to the main two components obscures those specific features, and the differences are negligible.

On the other hand, as shown in Fig. 3, when the SPME method is used, the plots have a distinct shape for each one of the samples, and the discrimination ability of the array of sensors is enhanced. As previously pointed out, the SPME-fibre here used (coated with polydimethylsiloxane particles with an average size of 100 μm) has a low affinity towards water and ethanol, and tends to adsorb the minority volatile compounds that are responsible for the aromatic differences among the wines.

The SPME method has been shown to be very sensitive to the operating conditions, and any variation of the experimental parameters markedly affects the distribution and the adsorption of the analytes. However, we have observed a higher reproducibility for the signals obtained with this method than with those collected with the automatic headspace sampling technique. For example, for the white wine from Rueda O.D., the mean relative standard deviation ($n = 4$) for the 12 sensors is 8% if the SPME method is used, whereas it increases to 10% with the alternate system.
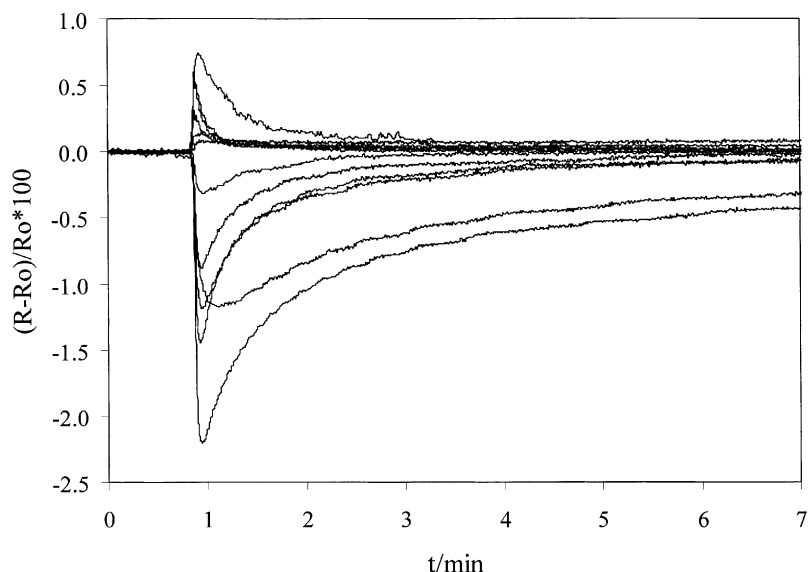

Fig. 1. Electrical response of the polymeric sensors towards the aroma of a Ribera de Duero O.D. wine, as collected with a SPME-fibre.
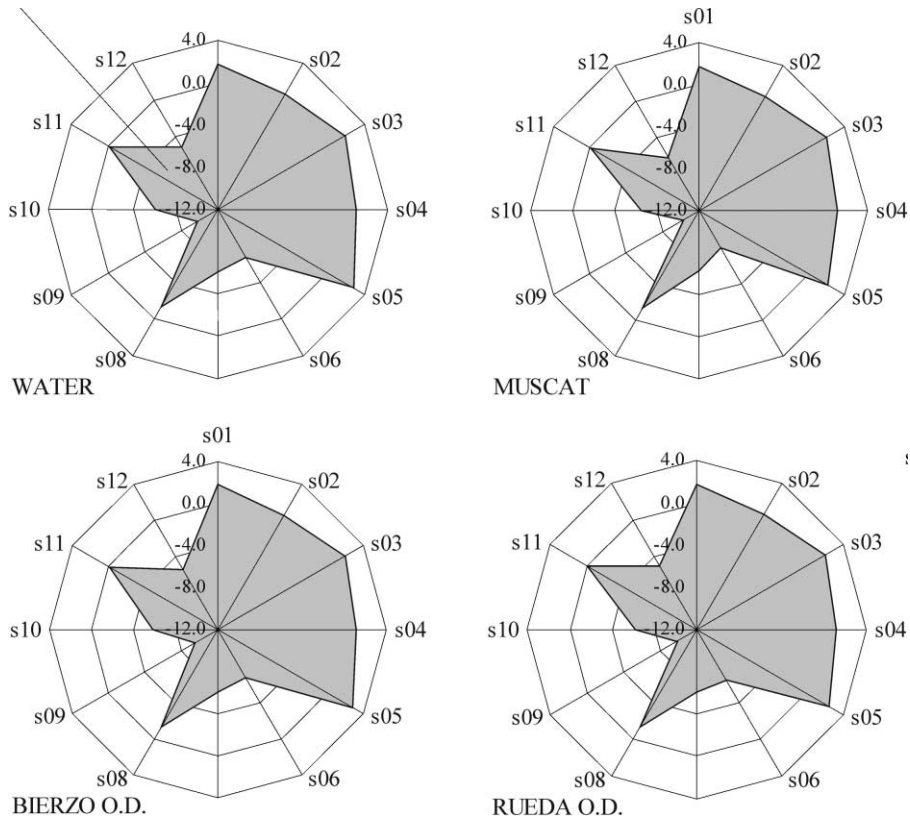
Fig. 2. Polar plots of the percentage variation of the resistance of the sensors when using the automated headspace sampler.
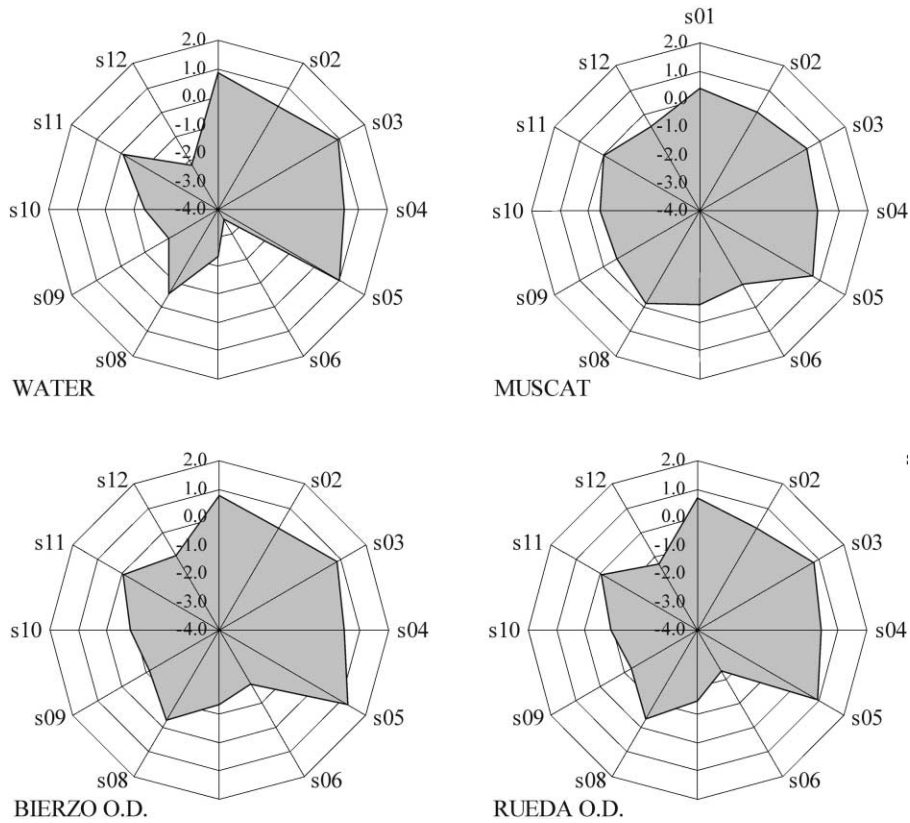

Fig. 3. Polar plots of the percentage variation of the resistance of the sensors when using the SPME method.
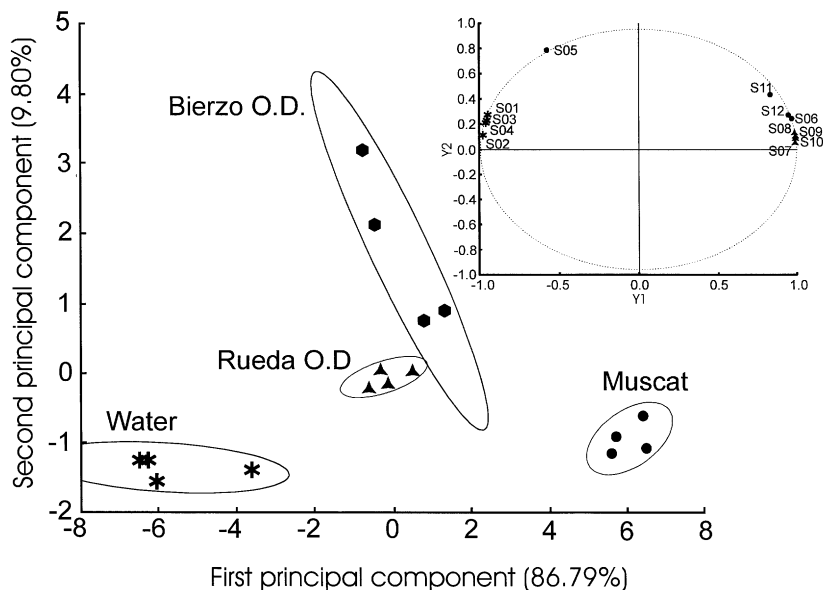
Fig. 4. PCA of the signals obtained with the SPME system for white wines and water. The inset show the circle of correlation where the individual sensors have been labelled.

The enhancement in the selectivity and reproducibility observed when the SPME is used, is expected to lead to a better discrimination of the data when using multivariate analysis. The principal component analysis (PCA) for the three white wines and water is shown in Fig. 4. This measuring system permits to classify the signals in separate clusters, and to discriminate one set from the others. There is a clear differentiation of the water cluster from those of the wines, that reveals the adequate performance of the SPME technique for this application. For the white wine clusters, a better resolution is observed for the Muscatel sample. This wine has a medium–high aromatic intensity, with the typical lemon-like and sweet notes of this grape variety. The two other white wines are both characterised by green fruit primary aromas (mainly apple), as well as a medium aromatic intensity. Some vegetative and floral notes that are not present in the Bierzo O.D. wine become apparent for the Rueda O.D. wine, that has a more complex aroma. These minor differences could be the reason for the slight separation between the two corresponding clusters.

The correlation circle for the multivariate analysis performed with the white wines has also been calculated and is shown at the inset of Fig. 4. This type of representation gives further information about the performance of the individual sensors for this set of aromas. There is a clear separation of the sensors that experiment increases in the electrical resistance from those that show the opposite, i.e. a net reduction of their resistances when exposed to the vapours. More precisely, the sensors form groups which are directly related to the polymeric species, thus, sensors S01, S02, S03 and S04 (all based on PMT) are arranged close to each other, while sensors S06 and S12, prepared from PPy doped with nickel phthalocyanine, are superimposed. All the PAN

sensors (S07, S08, S09 and S10) gather at the right-most region of the circle, close to the Y2-axis.

The results obtained when applying the automatic head-space sampler to measure the aromas from the white wines lead to an unsatisfactory outcome. As it can be clearly observed in Fig. 5, no separation among the different sets of data was achieved, and hence, it was impossible to classify the samples. This further confirms our previous statement that this method is unsuccessful if directly applied to the measurement of wine aroma with this array of sensors, as vast amounts of water and ethanol are indiscriminately led into the sensing chamber and they interfere with and hide the other aromatic substances. As a matter of fact, the
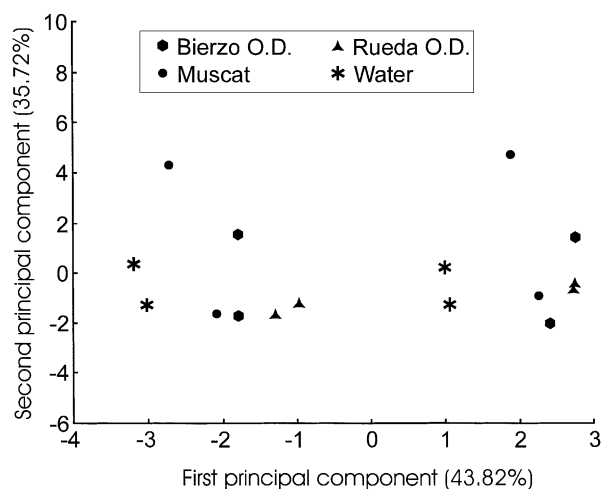

Fig. 5. PCA of the same set of wines in Fig. 4, collected with the automated headspace sampler.
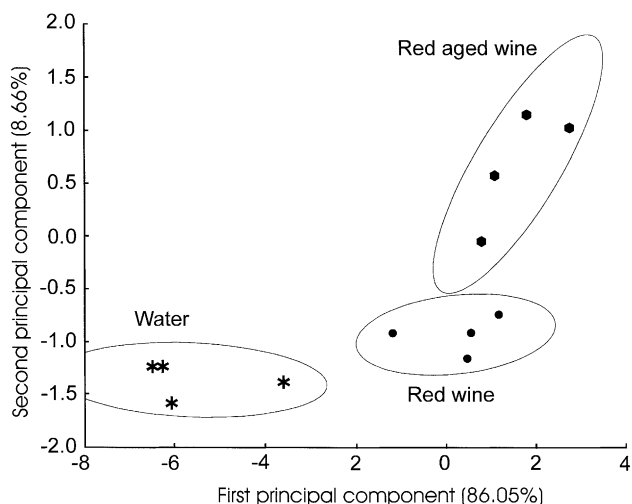
Fig. 6. PCA for the red and the red aged Ribera de Duero O.D. wines as desorbed from the fibre.

differences measured as the changes in the mean responses of the sensors towards the various samples are comparable to or even smaller than the standard deviation in the data for a certain wine. Hence, the variances corresponding to the individual sensors are very similar (as previously stated, about 10%), so that the PCA is not very efficient in concentrating information on the first principal components (variance on PC1 + PC2 = 79.54%).

In another set of experiments, two red wines produced from the same grape variety and at the same location, one of which had been aged in an oak barrel, could be successfully clustered, as shown in Fig. 6, when using the SPME method. From an organoleptic analysis, primary aromas (mature red and black fruits, and some vegetative notes) dominate in the wine that did not undergo the ageing process. This type of aromas is less intense for the aged wine, while certain tertiary aromas (vanilla, cinnamon and liquorice) reveal the treatment in the oak barrel.

4. Conclusions

A set of sensors for volatile compounds have been prepared by electropolymerisation of 3-methylthiophene, pyrrole and aniline with different salts. The sensors, thus, prepared were mounted on a box and subsequently exposed to a variety of wine vapours.

Solid-phase micro-extraction has been demonstrated to be a reliable and reproducible method for the injection of the aromatic volatile components of wines into a sensing device based on the array of polymeric chemoresistors. The system gives a fast and consistent response to the analysed samples. The utilisation of the SPME-fibre leads to noticeable differences in the responses of the sensors towards different wines, that reveal a degree of selectivity that could not be attained

by using an automatic headspace sampler, which only led to slight variations in the signals for the same set of wines.

The SPME technique, associated with multivariate analysis methods, facilitates the clustering and differentiation of the examined wines. The results reveal the selective adsorption of the fibre, that modifies the composition of the headspace by increasing the concentration of the minority compounds responsible for the specific aroma of the wines and, therefore, permits a better discrimination of the samples.

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M. Íñiguez received her degree as a technical engineer in Chemistry from the University of Zaragoza. She has been working at the Enological Station of Haro (Rioja) since 1976. At present, she is the head of the Department for Quality Control and Instrumental Analysis. The Station is credited since 1999 for the quality system she implemented according to the standard 45001. She has participated in research projects and has given conferences and published several articles in the field of enology.

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Jose Antonio de Saja is full professor and head of the Department of Condensed Matter Physics at the University of Valladolid. His present research interest is at the intersection of materials science, physics, physical chemistry and device engineering and focus on novel nanos-tructured materials (mainly from LB monolayers). He is author or co-author of over 140 publications and has edited seven books.