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Optimization of an aroma sensor for assessing grape quality for wine making

A. Gutiérrez[1]*, J. A. Burgos[1], C. Garcerá[1], A. I. Padilla[1], M. Zarzo[2], C. Chirivella[3], M. L. Ruiz[4] and E. Moltó[1]

[1] *Instituto Valenciano de Investigaciones Agrarias (IVIA). Ctra. Moncada-Náquera, km 4,5. 46113 Moncada (Valencia). Spain*
[2] *Universidad Politécnica de Valencia. DEIO. Valencia. Spain*
[3] *Estación de Viticultura y Enología de Requena. Requena (Valencia). Spain*
[4] *Laboratorio Agroalimentario de Burjassot. Burjassot (Valencia). Spain*

Abstract

Control of the raw material has considerable influence on final wine quality. The objective of this work was to develop a sensor capable of assessing grape juice quality in the cellar. Sensor response was compared with conventional chemical analysis using multivariate data techniques. The aroma sensor array is composed of 14 metal oxide sensors (MOS) gas transducers plus a temperature and a relative humidity sensor. This work showed that the sensor could detect rotten flavours in grape juice.

Additional key words: degradation, measurement procedure, multivariate analysis.

Resumen

Optimización de un sensor de aromas para la evaluación de la calidad del mosto destinado a vinificación

El control de la materia prima tiene una gran influencia sobre la calidad final del vino. El objetivo de este trabajo es desarrollar un sensor capaz de estimar la calidad del mosto a la entrada de las bodegas. La respuesta del sensor se ha correlacionado con los resultados de distintos análisis químicos convencionales mediante técnicas de tratamiento estadístico multivariante. El sensor de aromas se compone de 14 sensores de gases tipo MOS (sensores de óxidos metálicos) más uno de temperatura y otro de humedad relativa. El trabajo realizado demuestra que el sensor de aromas representa una herramienta adecuada para detectar la presencia de podredumbres en el mosto.

Palabras clave adicionales: análisis multivariante, podredumbre, procedimiento de medida.

Introduction

An important part of Spanish wine production is manufactured in cooperatives, with few controls on the quality of grapes received. However, the control of raw material has considerable influence on final wine quality. For this reason, it is important to include electronic sensors for quality control during wine production. The sensors are needed to detect the concentration of sugars, ethanol, lactic and malic acids and sulphur dioxide.

* Corresponding author: gutierre@ivia.es
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An aroma array sensor consists of a combination of gas transducers with varying selectivity working together (a transducer array). Transducer arrays, generally situated inside a chamber are coupled to a gas transferring system, are devices that give qualitative and quantitative information on aromatic products.

Nowadays, gas transducers, based on metal oxide semiconductor (MOS sensors), have many applications. Information on the concentration of volatiles responsible for aroma perception is extracted through variation in electric resistance of the transducers due to the presence of reducing compounds in the volatiles (Skafidas *et al.*, 1994). The behaviour of MOS sensors has several advantages over other gas sensor technologies:

— MOS sensor signals are stable. Quartz mass balance (QMB) or surface acoustic wave (SAW) sensors

show responses which are highly dependent on the magnitude of the flow of the carrier gas (Hilbert *et al.*, 1994).

— MOS sensors are less affected by temperature and humidity changes than other types of gas sensors as conductor polymers (CP), QMB or SAW sensors (Vlachos *et al.,* 1995).

— MOS sensors have long term stability of more than a year instead of the six months for other technologies.

Wine has been studied by many authors and gas sensors, included in an olfaction and taste system, have been used to identify relevant compounds in red wine through a system devised by Di Natale *et al.* (2000). García *et al.* (2004) have discriminated among several types of wine using an electronic nose and Di Natale *et al.* (2004) analysed wine quality using gas and liquid sensors arrays.

With regard to grape juice, Sayago *et al.* (1999, 2003) demonstrated that it was possible to use a tin oxide multisensor to discriminate between grape juice and fermented 'Albillo' white wine variety, while Mielle and Marquis (2001) developed an olfactometer capable of sorting fresh fruit juices.

The most important part of an aroma sensor is the gas transfer system. A poor transfer of volatiles to the sensor chamber damages the sensitivity of the gas sensors. Mielle and Marquis (1999) studied five different procedures of volatile generation and transfer. The sensitivity and response velocity of gas sensors depend on the nature of volatile and different considerably depending on the procedure used. Thus, the behaviour of many commercial aroma sensors may be poor depending on the nature of the volatiles as its gas transfer system is very rigid.

The *Centro de Agroingeniería* of the *Instituto Valenciano de Investigaciones Agrarias* (IVIA) has now been working on the development of an aroma sensor based on semiconductor gas transducers (MOS sensor) for seven years. This aroma sensor has been demonstrated to be reliable through reproducibility studies and can assess olive oil quality (Gutiérrez, 2002; Gutiérrez *et al.*, 2002). This research group knows the importance of the electronic design, and of adequate sample preparation and the use of the information obtained, to achieve practical results. It is also crucial to consider metrological issues: the transducers must be calibrated and their sensitivity and accuracy verified using statistical techniques applied on natural samples.

The main objective of this work was to develop a sensor to assess grape quality for wine making. To do this the following tasks were performed: i) identification of the relationships between analytical parameters and the presence of anomalous samples through chemical analysis of the grape juice; ii) analysis of the responses of the gas sensors and possible redundancies; iii) determination of the best analytic parameters, with regard to the quality attributes to be graded as related to the sensors signals; and iv) the calculation of simple mathematical estimation models to correlate the sensors signals with analytic parameters related to grape quality.

Material and Methods

Sample preparation

One hundred and three 60 ml samples were prepared from grapes supplied by *Estación Experimental de Viticultura y Enología* of the *Generalitat Valenciana* (Government of *Comunidad Valenciana* autonomous region). Relevant information about the harvest was recorded for all samples:

— Cultivar: 'Tempranillo' (53 samples) and 'Bobal' (50 samples).

— Origin: Rebollar (24 samples), Utiel (9 samples), Quattretonda (37 samples), Estanque (18 samples) and Portera (15 samples), all located in the *Comunidad Valenciana*.

— Training system: vessel (45 samples) and vertical shoot positioning (VSP) (58 samples).

— Pruning level: normal (32 samples), unloaded (24 samples), one retailer (23 samples), two retailers (24 samples).

Each sample was associated with its vintage date and the 100 berry weight from the vintage.

Samples were frozen immediately after vintage due to the instability of grape juice.

Aroma sensor and measurement procedure

The experiments were carried out with an aroma sensor developed at IVIA (Gutiérrez *et al.*, 2000). The device consists of 14 MOS gas transducers from two Fis Inc. (Kitazono, Japan) and Figaro Engineering Inc. (Osaka, Japan), plus a temperature sensor and a relative humidity sensor. The following models were used: TGS-2600, TGS-2602, TGS-2611, TGS-2620, SB-11A, SB-15A, SB-AQ1, SB-AQ4, SB-19, SB-30, SB-31,

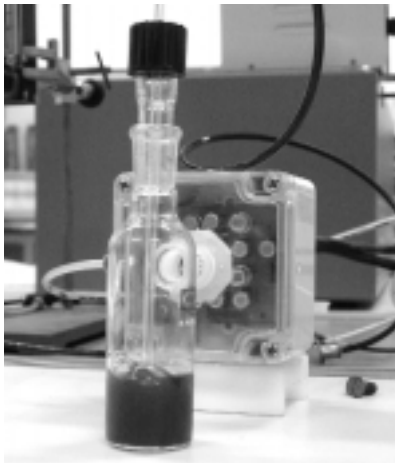

Figure 1. Aroma sensor prototype.

SB-41, SB-42 and SB-95.The transducers are arranged in a circle in an orthoedric sensor chamber with sides $7 \times 7 \times 5$ cm, with an inlet for incoming gas, a gas outlet and an opening to couple to a glass flask which contains the liquid sample for evaluation (Fig. 1). Synthetic air (O_2: 21% ± 1%, H_2O: < 3 ppm, C_nH_m: < 0.5 ppm) was used to clean the chamber and to drag the volatile compounds to the transducers after bubbling through the liquid. Air flow was measured with a rotameter with an accuracy of 1 cm^3 min^{-1}. The device registers variation in time of the electric potential in the gas transducer electrodes due to the reaction of the volatile compounds. Data were acquired at a frequency of 4 Hz through a data acquisition board and were recorded in a computer.

The measurement procedure is started by extracting two aliquots from a sample of grape juice into glass flasks (20 ml) and leaving them at room temperature (22-24ºC) for one hour. The flask is then coupled to the sensor chamber and the automatic process of signal acquisition begins. One measurement consists of:

1. Measuring the base line for each transducer: 5 s.
2. Bubbling the sample with synthetic air: 120 s.
3. Cleaning the sensor chamber using synthetic air: 150 s.
4. Waiting for baseline recovery without additional air flux: 300 s.

Each aliquot is measured twice, to give four observations for each sample (Fig. 2).

Chemical analysis

Samples were also analysed by *Laboratorio Agroalimentario de Burjassot* of the *Generalitat Valenciana*

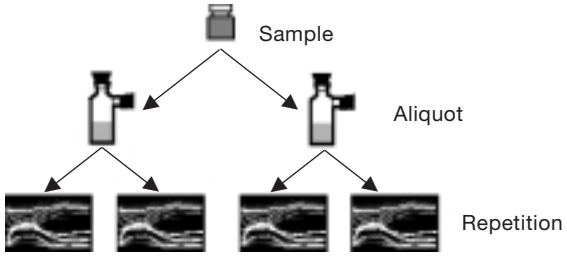

Figure 2. Preparation procedure for a grape juice sample.

(a certified laboratory according to UNE-EN ISO/IEC 17025 regulations), using conventional analytical methods (OJEC, 1990) to determine different chemical parameters related to the maturation state of the grapes, such as sugar content (ºBrix), glucose + fructose (g L^{-1}), acetic (g L^{-1}), malic (g L^{-1}), lactic (g L^{-1}), gluconic (mg L^{-1}) and tartaric (g L^{-1}) acids, polyphenols (mg L^{-1}), glycerine (g L^{-1}), anthocyanins (mg L^{-1}) and catequins (mg L^{-1}). The pH, total acidity (g L^{-1}), colour intensity, probable alcoholic degree and colour parameters (L, a, b, c and h) of the grape juice were also measured.

The relationship between the variation in analytical parameters and the vintage date was addressed by regarding the variance retained by principal components analysis (PCA) on the analytical parameters (1st PC: $r_x^2 = 0.43$; 2nd PC: $r_x^2 = 0.27$), and their relationship with the vintage date. Figure 3 shows that vintage was the major cause of analytical changes in the wine.

Signals obtained with the aroma sensor

All recorded signals corresponding to the gas transducers followed a common pattern (Fig. 4). In the reaction

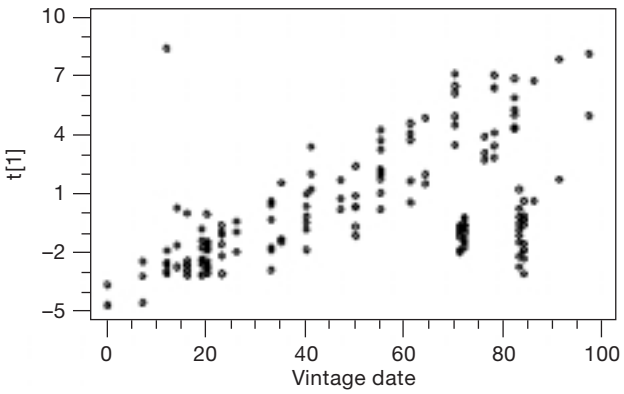

Figure 3. Evolution of the first principal component of the PCA-model *vs.* vintage date.

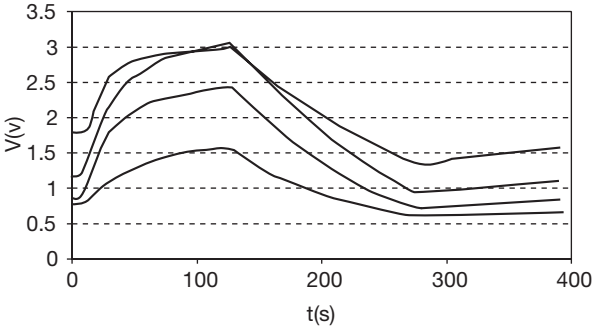

Figure 4. Response of four gas transducers (voltage *vs.* time) to a grape juice sample.

phase, the concentration of volatile compounds increases until final stabilisation around a value related to the global volatile concentrations present in the sensor chamber.

Previous tests with a similar aroma sensor (Zarzo *et al.,* 2001) showed a high autocorrelation with the acquired values for every gas transducer. However, as seen in Figure 4, the signal of all gas transducers tends to stabilize. It is thus possible to define the *equilibrium value* as the maximum signal reached during the bubble stage of measurement.

Drift of gas sensors signals can affect reproducibility as it is cumulative over time. Drift has considerable influence on the calibration frequency of the aroma sensor. Thus it is important to set its magnitude for this application. Some variables related to possible drift of the gas transducer were considered:

— Flask: distinguishes between the two aliquots of the sample.

— Measurement: distinguishes between the first and the second repetition of the measurement of each aliquot.

— Sample order: sampling order in one day of measurement.

— Days since the first day of measurement, determining the first day (21 August 2003) as day 0.

— Order of measurement day: the order of the day in which the measurement was performed.

The data matrix must be elaborated to simplify the analysis. The matrix was divided in a bi-directional structure. Four observations (2 repetitions × 2 aliquots) are made for every sample. Results from one transducer were discarded as it broke down during the tests. In this way, the equilibrium value from 13 transducers, the analytical variables and the vine variables (which were the same for the 4 observations of every sample) were calculated. Finally, a matrix with 412 observations (rows, 103 * 4) and 46 variables (columns, 13 MOS sensor + 1 temperature sensor + 1 relative humidity sensor + 20 chemical + 6 vine + 5 drift) was made.

To study the correlation structure of the parameters from the signals and the chemical analyses, a partial least squares regression (PLS) (Bro, 1996) was conducted using SIMCA-P, version 10.0.2.0 (Umetrics, Sweden) software. A previous study had been done on the statistical distribution of the analytical parameters. As most of the parameters had a positive asymmetric tendency strong, logarithms were applied to them to perform the multivariate analysis.

Results

Firstly, a PCA was performed according to the equilibrium value of the 13 MOS transducers. Loadings of the original variables were included in the two first principal components (1st PC: $r^2_X = 0.74$; 2nd PC: $r^2_X = 0.13$). Transducers were classified into two groups: 10 gas transducers with high loadings in the first component, and the other 3 transducers (SB-AQ4, SB-19 and TGS-2602) with high loadings in the second component. A set of four samples had high values in the projections on the two first dominant components (Fig. 5). After studying these samples, an early fermentation of grape juice was found in all of them. It can therefore be assumed that the transducers were reacting to carbon dioxide.

A plot of projections of the observations on the second and third principal components shows 32 measurements from 4 samples with characteristics differentiated from the rest (Fig. 6). Through verification measurements,

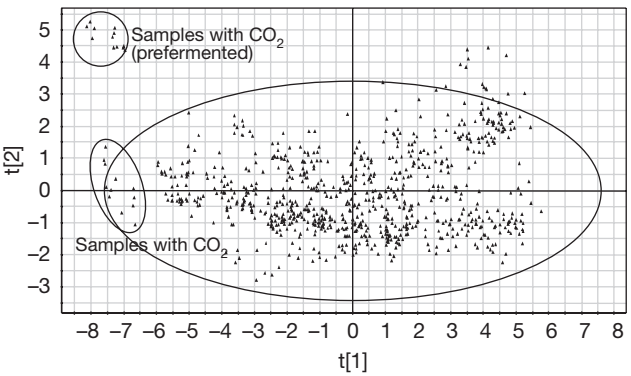

Figure 5. Score plot of the first two principal components (PC) of the PCA model for the equilibrium values of the MOS transducers (95% confidence interval ellipse).

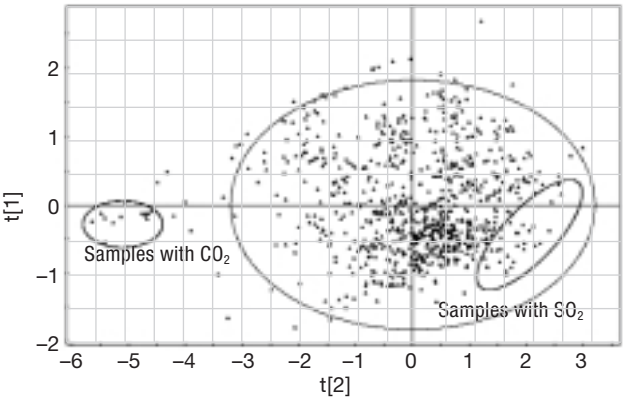

Figure 6. Score plot of second and third principal components (PC) of the PCA model for the equilibrium values of the MOS transducers (95% confidence interval ellipse).

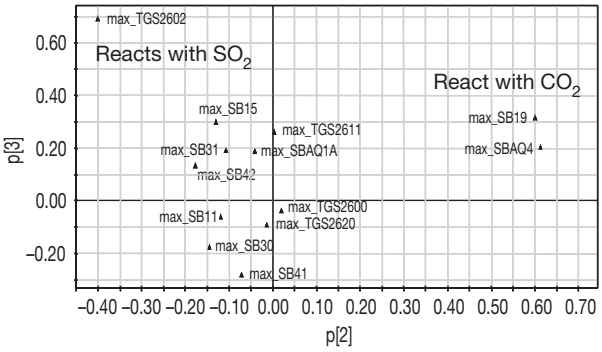

Figure 7. Loading plot of the first two principal components (PC) of the PCA model for the equilibrium values of the MOS transducers.

it was concluded that these samples contained sulphur dioxide, added in error. It can be concluded that the transducers reacted to this compound (Fig. 7).

A PLS analysis was performed considering the equilibrium values of the transducers as independent variables, and the rest as dependent variables (chemical results and vintage data). The results show that the dominant component of the transducers signals in the PLS model was highly correlated with gluconic acid and glycerine concentrations (Fig. 8).

Finally, a linear regression between variables X and Y with greater loading in previous PLS models (the equilibrium value of transducer SB-15 and the gluconic acid content) was calculated. This regression showed a statistically significant quadratic relationship (Fig. 9). A multiple linear regression analysis that incorporated the quadratic effect (square of the logarithm of gluconic acid content), gave a determination coefficient of $r^2 = 0.82$. Among the residuals of this model, there were two samples with abnormally elevated values. When these samples were removed the determination coefficient (r^2) reached 0.875.

If a new multiple linear regression was performed considering the glycerine content and the equilibrium values of the SB-15 transducer, there was a quadratic relationship with a coefficient of determination (r^2) of 0.82.

The analysis showed a clear relationship between gluconic acid and glycerine content in grape juice and the equilibrium values of the gas transducers.

To analyse the drift effect over the signals of the gas sensors, the residuals of the calculated models were plotted against every explanatory variable related to it

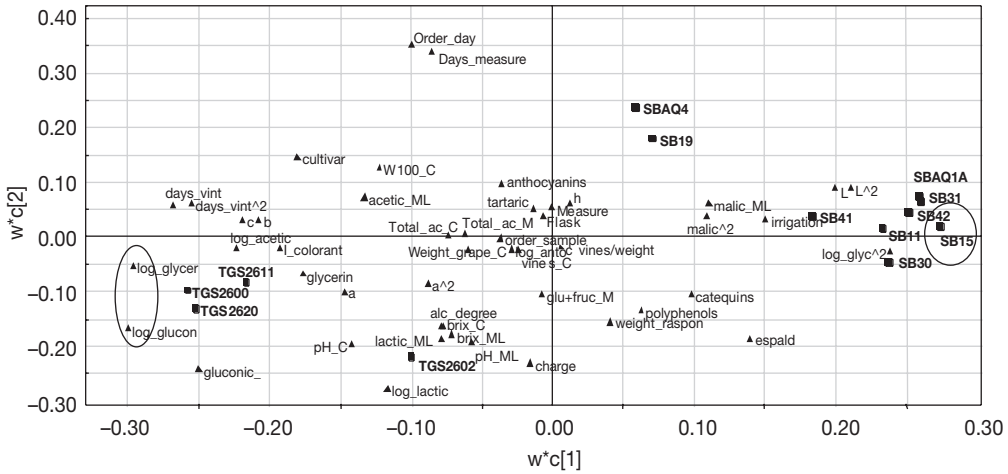

Figure 8. Loading (w *c) plo of the first two latent variables (w * c [1] *vs.* w * c [2]) of the PLS model for the equilibrium values of the fourteen MOS transducers plus chemical and vintage data.

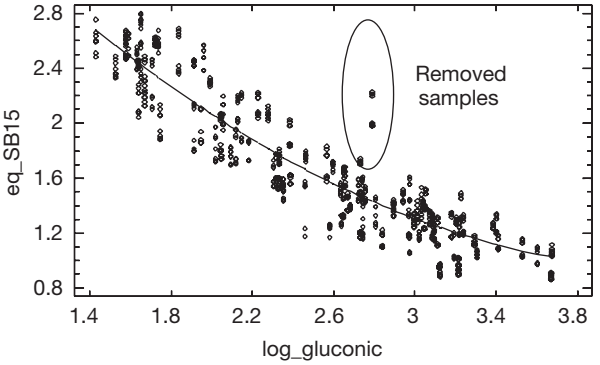

Figure 9. Regression of the equilibrium value of SB-15 transducer *vs.* the logarith of gluconic acid content.

(flask, measurement, order of measurement day, sample order and days since the first day of measurement). Drift influence was not detected in the resultant plots.

To analyze the reproducibility of the gas transducers, the coefficient of variation (CV) was calculated for all sample through the four observations of equilibrium values. In all cases, the CV was less than 8%. This demonstrates the robustness of the measurement procedure and the reproducibility of the gas transducers.

Discussion

The results of this work show that aroma sensors are suitable for the assessment of the grape quality for wine making. The PCA and PLS analysis showed that the sensor can detect the addition of sulphur dioxide to grape juice and the start of the alcoholic fermentation as it is sensitive to the carbon dioxide. Its sensitivity to gluconic acid and glycerine content in the grape juice allow the aroma sensor to detect the presence of rots in the grapes. Thus, the aroma sensor could be calibrated to classify the grape juice according to the level of fungal contamination of the grapes.

The possibility of combining other techniques such as FT-IR and UV spectrometry with the aroma sensor (Roussel *et al.*, 2003) would improve the results obtained with regard to assessing degradation of grape juice. It would also be possible to study other relevant quality parameters such as maturation state. Another approach would be to combine different types of electronic sensor. Di Natale *et al.* (2004) applied two arrays of metalloporphyrins-based gas and liquid sensors for analysis of a red wine. They demonstrate the capability of such systems to be trained according to the behaviour of a taste panel. Mielle and Maquis (2001) proposed to improve the selectivity and sensibility of gas sensors through the variation of their electric parameters. Following this line, they proposed a virtual sensor array capable of giving a pattern of signals from a single sensor. In this work, a PLS and PCA were carried out to study correlations of the parameters obtained from the signals and chemical parameters. Although the results are good, other pattern recognition methods could be tried. García *et al.* (2004) demonstrated the capability of a probabilistic neuronal network (PNN) to discriminate among four varieties of red wine.

The development of this sensor may be a first step in the establishment of traceability systems to guarantee wine quality. Grape assessment is essential in cellars and, over all, in cooperatives as there is a large input of grapes of different origins at the same time during the vintage. Further, the time available to perform analyses is very short.

The aroma sensor developed gives the possibility of a new sensor capable of assessing grape juice quality. Its integration into wine production in cellars is viable because of the low cost of the gas sensors and the rapid response of aroma sensor compared to other methods.

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