434d Evaluation of Grape Degradation in Must Using an Electronic Nose

Manuel Zarzo, Cruz Garcerá, Ana Isabel Padilla, Abelardo Gutiérrez, and Enrique Moltó

Wine production is an important issue for the economy of many regions around the world. In the winery process, the quality control of the raw material (grape must) is important in order to obtain high quality wines. Some wine cellars own large extensions of vineyards and are able to control the whole process from vine cultivation to wine production, and under this circumstance the quality control of grapes becomes easier. But this is not the normal situation in Spain. Usually a wine cellar is supplied by different wine farmers, and since the period of grape harvest is relatively short, the quality control of grapes becomes difficult: they belong to different cultivars, vines of different ages, not uniform edaphologic or microclimate conditions that affect the maturity state of grapes, etc. And one of the most important quality factors is the phytosanitary state of grapes when they are harvested. So, one of the key points to improve wine quality is the ability to classify grapes when they arrive to the wine cellar.

Must from grapes in the optimum maturity state and phytosanitary conditions, that will produce a high quality wine, has to be fermented apart from must with slight defects of quality, that will become into a mid-quality wine, and apart from grapes that come under degradation conditions. If this classification is not properly conducted, the resulting mid-quality wine will be unable to compete in the market and will suffer a considerably reduction in the price. Most often the only parameters measured in the grape are the content of total acids and sugars. But other quality parameters that might have a strong impact in the final quality, like the ones related with phytosanitary conditions, are not assessed since there are not reliable, objective and fast procedures to obtain this information. For this reason, there is a strong interest in the development of new technologies able to assess the quality of grape must.

Aroma sensors are an interesting choice, since they produce a fast response, do not require a high qualification to be operated, have an affordable price, and some applications with a similar purpose have been reported (Sayago et al., 1999). An aroma sensor consists of a combination of gas transducers of different selectivity working together (transducer array), arranged generally inside a chamber and coupled to a system for gas transferring. Aroma sensors can be used to obtain qualitative and quantitative information about aromatic products if they are automated with procedures for data analysis based on statistical predictive models, previously calibrated with samples characterized by analytical methods or by a sensory panel. For this reason, they are frequently referred as “electronic noses”.

The objective of this work is to check if electronic noses can be useful for the quality control of grape must for winery, specially in the evaluation of grape degradation. With this target, 103 samples of grape must were prepared from vines with different characteristics: two cultivars (tempranillo and bobal), different locations, irrigation schedules, pruning techniques and different dates of vintage (from green to a high mature degree), in order to generate an important variability in the samples. Samples were frozen after obtaining the must and preparing aliquots for the different analyses. For each sample, the following parameters were obtained using conventional analytical procedures: ºBrix, pH, concentration of glucose, fructose, polyphenols, glycerin, anthocyans, catechins, concentration of different acids (acetic, L-malic, L-lactic, gluconic, tartaric), total acids content, colorant intensity and color parameters (L, a, b, c, h).

The same samples were also evaluated by an aroma sensor developed in the Valencian Institute of Agricultural Research (Gutiérrez et al., 2000). This device consists of 14 metal oxide semiconductor gas transducers plus one temperature sensor and one humidity sensor. These transducers are arranged inside an orthoedric sensor chamber, with an inlet for an incoming gas, a gas outlet and an opening to couple a glass flask containing the liquid sample to evaluate (20 ml). Synthetic air was used to clean the chamber and to drag the volatile compounds to the transducers after bubbling into the liquid. The device registers the variation in time of the electric potential in gas transducer electrodes, due to the reaction of volatile compounds. Data were acquired at a frequency of 4 Hz through a data acquisition board and were registered in a computer. The measurement procedure is conducted in different stages: recording the electric base line of each transducer (5 seconds), bubbling the sample with synthetic air (2 min), sensor chamber cleaning (150 s) and return to the baseline (300 s). From each sample, two aliquots were taken, and both of them were measured twice.

Each measurement produces a matrix with the data from the 14 gas transducers recorded at the different instants of time. Data from one transducer were discarded, since it broke down during tests. So, the final data structure is a three-way matrix that has to be properly analyzed with predictive methods in order to calibrate the electronic nose with the information of the analytical parameters. For each transducer, data are characterized by a high autocorrelation. Previous research works (Zarzo et al., 2001) pointed out that values at the last part of the bubbling stage (that will be referred as equilibrium values) are the ones that provide more chemical information, and further analyses with these data seem to confirm this hypothesis. So, these equilibrium values were obtained for each measurement, and the final data matrix contained 412 observations (2 aliquots for 103 samples measured twice) and 84 variables: 13 equilibrium values (one per transducer), the analytical parameters, and others that identify the observations and bring information about samples: date of vintage, date of data acquisition, etc.

Carrying out a Principal Component Analysis (PCA) with the equilibrium values of the 13 transducers, several outliers were detected, and after verifying the characteristics of these samples, it was found that they had a prefermentation of grape juice, or sulfur dioxide added by error. This analysis also revealed that equilibrium values were highly correlated in 10 of the 13 transducers, while the rest provided an orthogonal information. Subsequently, in order to identify the variables with highest correlation to data from the aroma sensor, a PLS (Partial Least Squares Regression) was performed considering the equilibrium values as response variables (Y), and the rest (chemical results and vintage data) as predictors (X). Analyzing the loading plot it turns out that the content of gluconic acid is the X variable with highest loadings, and regarding the Y variables the same applies to the equilibrium value of the transducer SB-15. Once identified the best representatives for the X and Y variables, a linear regression model was conducted with them, revealing a quadratic relation between the logarithm of the gluconic acid and the equilibrium value of SB-15, with a determination coefficient of 0.82. Studying the residuals of this model, two outliers were identified, and after removing these samples, the determination coefficient became 0.87.

The concentration of gluconic acid is a measure of the degradation of grapes, since it appears as a consequence of undesirable fungal fermentations in rotten grapes, and has a negative effect in the final quality of wine. This concentration was reduced for the samples harvested at early stages and increased in samples with a high degree of maturity that had suffered certain degradation. Since a good correlation has been found between the variables from the aroma sensor and one parameter directly related with the must grape quality, these results highlight the potential application of electronic noses to assess the degradation of grapes, that could be used to discard grape must that would produce bad quality wines.

REFERENCES

Gutiérrez, A.; Ramos, P.; Zarzo, M.; Moltó, E.; Juste, F. (2000). A multi-sensor approach for assessing olive oil quality. AgEng Warwich Conference 2000. Warwick, UK, July 2-7, 2000. Paper number 00-AE-013.

Sayago, I.; Horrillo, M.C.; Getino, J.; Gutiérrez, J.; Arés, L.; Robla, J.I.; Fernández, M.J.; Rodrigo, J. (1999). Discrimination of grape juice and fermented wine using a tin oxide multisensor. Sensors and Actuators B 57: 249-254.

Zarzo, M.; Gutiérrez, A.; Ramos, P.; Moltó, E. (2001). Parametrización de la respuesta obtenida con sensores de gases tipo MOS frente al aroma de aceite de oliva. I Congreso Español de Ingeniería de Alimentos; Valencia, 11-15 Marzo 2001. Ref. 5B-06.

Acknowledgements

Authors are grateful to Camilo Chirivella, from the Enology & Viticulture Station in Requena (Valencia), and Mª Luisa Ruiz, from the Agrofood Laboratory in Burjassot (Valencia), for their technical support and collaboration, and also to the Spanish Ministry of Education and Science for the financial support to this work given by the project AGL2002-04450-C02.