Wine oxidation profile accessed by voltammetric, antioxidant scavenging and GC-MS techniques

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Introduction

Recently, studies using cyclic voltammetric measurements enable the grouping of both quantitative and qualitative information concerning wine antioxidants (1-5). On the other hand, many aldehydes and other off-flavors, that occurs in wines, resulting from the oxidation of alcohols, sugars and amino acids degradations are described to have an important contribution to the sub-qualities of wine aroma and can be assessed by Gas Chromatography/Mass spectrometry (GC/MS).

Both target and non-target approach strategy can be used to monitor the overall reactions involved in wine oxidation. The non-target methodology includes relevant analytical tools, in order to fuse the information of the used detectors (Cyclic voltammetry and GC/MS) allowing a most comprehensive view of the system and the annotation of interesting compounds.

Material and Methods

Liquid-liquid extraction of wines. Extractions were performed according to the methodology published by (6). **Antiradical activity**. The antiradical activity of wines were determined using the free radical method ABTS (7). **Cyclic voltammetry**. Experiments were performed using a potentiostat (microAutolab Type III with an Autolab Faraday Cage) and voltammograms were obtained with a scan rate of 100 mV with an increment potential of 2.4 mV, between 0 V to 1.2 V. The working electrode was a 3 mm Glassy Carbon disk in combination with a Metrohm tipholder. A saturated calomel electrode was used as a reference electrode in conjunction with a platinum counter electrode. **GC/Mass spectrometry**. Samples were analysed using a Varian CP-450 gas chromatograph equipped with a Varian Saturn 240 MS. The mass range was 33 m/z to 350 m/z, in Full Scan mode, and the column was a FactorFour capillary VF-WAXms 15mX0.15mm ID with DF 0.15 µm from Varian. Raw voltammetric and chromatographic signals were processed using a methodology performed based on R statistical programming (R-Project R, http://www.r-project.org/) and then explored by multivariate analysis, namely, Principle Component Analysis (PCA).

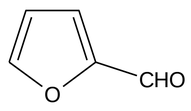
Forced Aging Protocol – 42 days (6 weeks)

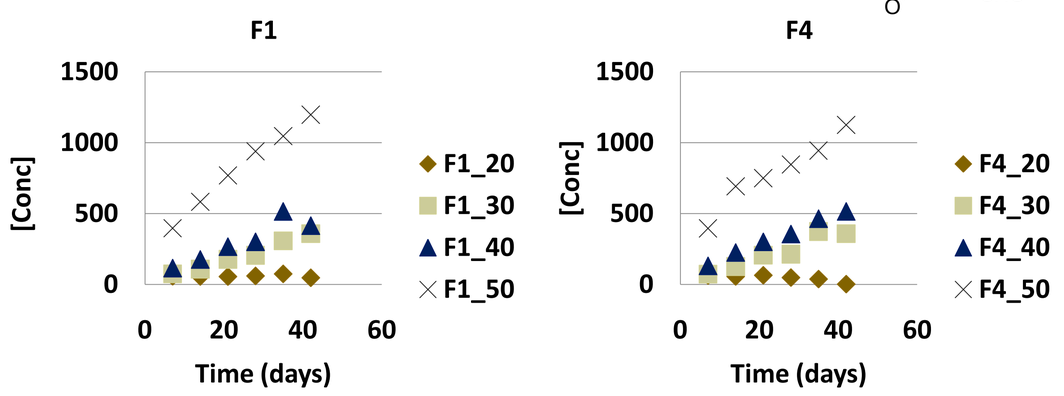
Fourteen litters of white wine (pH = 3.2): 4 oxygen regimes

Treatment I: no oxygen addition (F1)	Treatment II: 2 times saturated (F2)	Treatment III: 3 times saturated (F3)	Treatment IV: saturated every sampling point (F4)
V = 1000 ml, T = 20 ºC	V = 1000 ml, T = 20 ºC	V = 1000 ml, T = 20 ºC	V = 1000 ml, T = 20 ºC
V = 1000 ml, T = 30 ºC	V = 1000 ml, T = 30 ºC	V = 1000 ml, T = 30 ºC	V = 1000 ml, T = 30 ºC
V = 1000 ml, T = 40 ºC	V = 1000 ml, T = 40 ºC	V = 1000 ml, T = 40 ºC	V = 1000 ml, T = 40 ºC
V = 1000 ml, T = 50 ºC	V = 1000 ml, T = 50 ºC	V = 1000 ml, T = 50 ºC	V = 1000 ml, T = 50 ºC

GC-MS

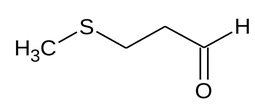
Compounds not modulated by oxygen treatments

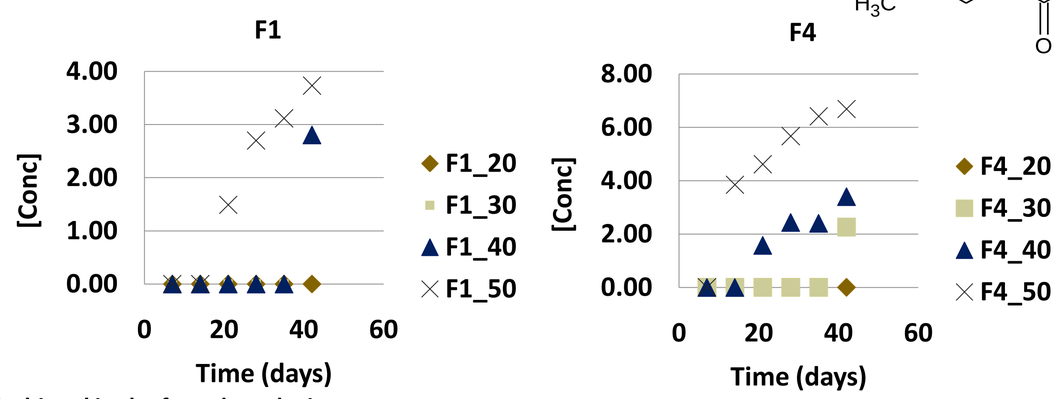




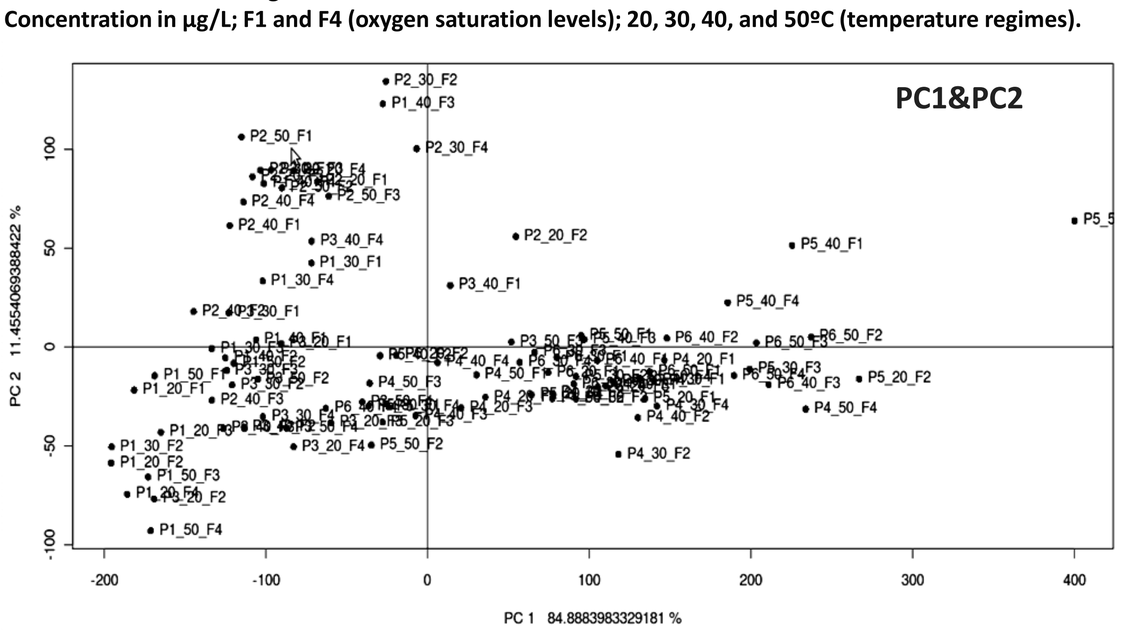
2-Furfural in the forced aged wines.
Concentration in µg/L; F1 and F4 (oxygen saturation levels); 20, 30, 40, and 50ºC (temperature regimes).

Compounds modulated by oxygen treatments





Methional in the forced aged wines.
Concentration in µg/L; F1 and F4 (oxygen saturation levels); 20, 30, 40, and 50ºC (temperature regimes).

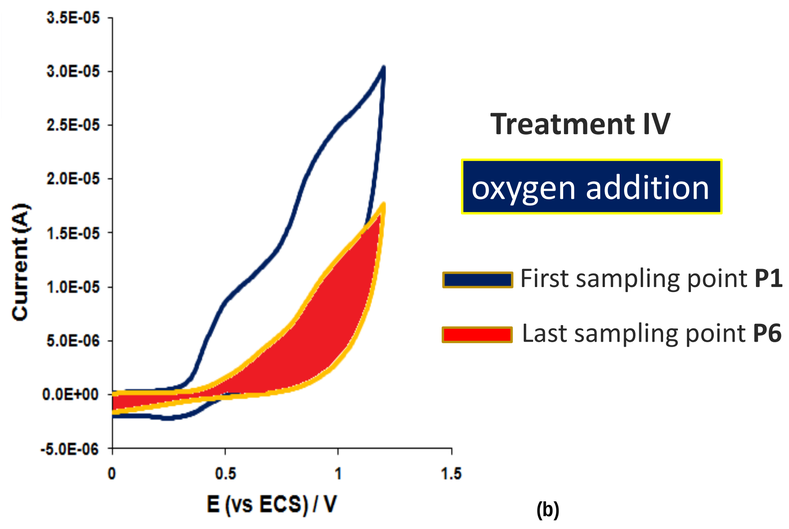


Concerning the GC-MS non-target approach PCA illustrate the global chemical differences of the wines.

Antiradical activity

Results have showed that oxygen consumption and temperature exposure decreases the antiradical activity of the forced aged wine samples, evaluated by the ABTS methodology till 48%, for the IV treatment.

Cyclic Voltammetry



a) Oxidation process and b) Chart control

A supervised multivariate control chart was developed using control wine samples as reference . In this way, when white wines are plotted onto the chart, it was possible to monitor the oxidation status and to diagnose the effect of oxygen and temperature regimes.

Conclusions

Concerning cyclic voltammetry, signal processing techniques were used to decompose the multivariate data sets. Results have showed that oxygen consumption and temperature exposure decreases the antioxidant activity of the forced aged wine samples screening by voltammetric measurements. Furthermore, a supervised multivariate control chart was developed using control wine samples as reference. In this way, when white wines are plotted onto the chart, it was possible to monitor the oxidation status and to diagnose the effect of oxygen and temperature regimes. Additionally, results clearly demonstrate a “convolution” of chemical mechanisms. Same compounds were not modulated by oxygen treatments, like 2-furfural and 5-metil-2-furfural, unlike methional and phenylacetaldehyde that were clearly related to the presence of oxygen. Furthermore, the annotation of interesting compounds can be made and the identification and annotation of the major contributory compounds for samples metabolic variability can be achieve.

1 - Kilmartin, P. A., Zou, H., & Waterhouse, A. L. (2001). *Journal of Agricultural and Food Chemistry*, 49, 1957-1965;
2 - Roginsky, V., De Beer, D., Harbertson, J. F., Kilmartin, P. A., Barsukova, T., & Adams, D.O. (2006). *Journal of the Science of Food and Agriculture*, 86, 834-840;
3 - Rodrigues, A., Silva Ferreira, A. C., Guedes de Pinho, P., Bento, F., & Geraldo, D. (2007). *Journal of Agricultural and Food Chemistry*, 55, 10557-10562;
4 - Martins, R. C., Oliveira, R., Bento, F., Geraldo, D., Lopes, V. V., Guedes de Pinho, P., Oliveira, C. M., & Silva Ferreira, A. C. (2008). *Journal of Agricultural and Food Chemistry, 56,* 12092-12098;
5 - Makhotkina, O., & Kilmartin, P. A. (2009). *Journal of Electroanalytical Chemistry, 633,* 165-174;
6 - Silva Ferreira A. C., Caracterisation du Vieillissement du Vin de Porto (1998). These de Doctorat de L’Université Victor Segalen Bordeaux II. 1998, 593;
7 - Oliveira, C. M., Silva Ferreira, A. C., Pinho, P. G., & Silva, A. M. S. (2008). *Journal of Agricultural and Food Chemistry, 56,* 10326-10331.