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Oxidation Management of White Wines Using Cyclic Voltammetry and Multivariate Process Monitoring

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The development of a fingerprinting strategy capable to evaluate the "oxidation status" of white wines based on cyclic voltammetry is proposed here. It is known that the levels of specific antioxidants and redox mechanisms may be evaluated by cyclic voltammetry. This electrochemical technique was applied on two sets of samples. One group was composed of normal aged white wines and a second group obtained from a white wine forced aging protocol with different oxygen, SO_2, pH, and temperature regimens. A study of antioxidant additions, namely ascorbic acid, was also made in order to establish a statistical link between voltammogram fingerprints and chemical antioxidant substances. It was observed that the oxidation curve presented typical features, which enables sample discrimination according to age, oxygen consumption, and antioxidant additions. In fact, it was possible to place the results into four significant orthogonal directions, compressing 99.8% of nonrandom features. Attempts were made to make voltammogram fingerprinting a tool for monitoring oxidation management. For this purpose, a supervised multivariate control chart was developed using a control sample as reference. When white wines are plotted onto the chart, it is possible to monitor the oxidation status and to diagnose the effects of oxygen regimes and antioxidant activity. Finally, quantification of substances implicated in the oxidation process as reagents (antioxidants) and products (off-flavors) was tried using a supervised algorithmic the partial least square regression analysis. Good correlations ($r > 0.93$) were observed for ascorbic acid, Folin−Ciocalteu index, total SO_2, methional, and phenylacetaldehyde. These results show that cyclic voltammetry fingerprinting can be used to monitor and diagnose the effects of wine oxidation.

KEYWORDS: White wine; antioxidants; cyclic voltammetry; multivariate process

INTRODUCTION

Oxygen management is one of the most challenging tasks in winemaking. Starting from the grape juice to the maturation process, several critical steps, relating to oxygen exposure, can be found, where the quantities of oxygen supplied will have a major impact on the organoleptic characteristics of the finished wine.

In previous work it has been demonstrated that phenylacetaldehyde, 3-(methylthio)propionaldehyde (methional), and 3-hydroxy-4,5-dimethyl-2(*H*)furanone (sotolon) play a critical role in the perceived oxidized character of wine (*1, 2*). Several mechanisms may explain their formation, but it has been demonstrated that temperature and mainly oxygen at lower pH are synergistic (*3*). Nevertheless, the chemistry of highly electrophilic species presents some particularities. Molecular oxygen (triplet state) needs to be activated to the singlet state to become reactive and then be reduced to water, taking electrons in a stepwise manner (*4*). In wines, this process requires reducing species with a cathecol-like structure and most important, the presence of transition metal ions, iron or copper, which will act as electron "pumps" during the entire mechanism (*4*). The reactivity of oxygen species (ROS) increases dramatically, constituting an escalating risk toward wine instability, from molecular oxygen (singlet state), perhydroxyl radicals, and hydrogen peroxide to the most destructive hydroxyl radical (*4*).

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This species, produced by the Fenton reaction, reacts in a nonselective manner with all organic molecules present in the matrix (*4*).

According to the respective reduction potentials and concentrations, several wine constituents, including antioxidants, will be consumed at different stages of the global oxidation process (*4*). Therefore, in order to optimize wine shelf life, both the quantity and quality of the wine antioxidant fraction needs to be quantified.

Different methodologies have been proposed in the literature to quantify antioxidant activity in foods and biological systems. These assays can be roughly classified into two main groups: methods based on chemical reactions and methods based on the chemical-physical properties of antioxidants (*5*). Methods based on chemical reactions involve hydrogen atom transfer (HAT) and/or electron transfer (ET) (*6*). Methods based on the chemical-physical properties of antioxidants involved electrochemical detection (*5, 7, 8*). ABTS (TEAC-trolox equivalence antioxidant capacity) and DPPH are methods commonly used involving electron transfers (ET).

The knowledge of the total antioxidant capacity as a discrete measure does not have the necessary information to estimate shelf life and correctly manage oxidation. Recently, data concerning wine oxidation monitored by cyclic voltammetric measurements were presented (*9, 10*). This technique enables the grouping of information concerning antioxidants, both quantitative and qualitative. In fact, voltammetric current is a function of concentration and peak position, where the most easily oxidized compounds occur at lower potentials while the less reactive will be detected at higher voltages. Therefore, the pattern of the voltammetric oxidation curve will allow us to better understand both the type and amount of substances possessing antioxidant activity, displayed respectively on the range of potentials and current intensity and implicated on oxidative degradation of wine.

The study of the voltammograms can be extended using multivariate statistical signal processing and multivariate quality control (MQC). These techniques have been widely used in other multivariate signals, such as in spectroscopy (*11*) and image analysis (*12*) or even in process analytical technology (PAT) (*13*). Typically, a pattern recognition model (e.g., PCA, PLS, ANN) characterizes the signal under controlled conditions, and thereafter out-of-control situations are analyzed against the expected behavior by analyzing the *Q*-statistic (square prediction error) and T-hoteling statistic (*14*), being possible to diagnose the cause of quality failures during production (*15*).

The main objectives of this research are (i) to investigate the fingerprinting potential of cyclic voltammetry by feature extraction and pattern recognition, (ii) to determine the potential of cyclic voltammetry for establishing robust multivariate control charts for monitoring and diagnostic oxidation in white wine, and (iii) to establish the statistical link between voltammograms fingerprints and chemical substances implicated in oxidation.

MATERIALS AND METHODS

Chemicals. All the chemicals employed were of analytical-reagent grade and were used as received from Merck: L-ascorbic acid, sodium metabisulfite, ethanol, L-tartaric acid, NaOH, dichorophenolindophenol, iodine, Folin−Ciocalteu reagent. H_2SO_4 and oxalic acid were purchased from Fluka. The following molecules were purchased from Sigma-Aldrich (Portugal): 3-(methylthio)propionaldehyde (27,746-0) (99% purity), phenylacetaldehyde (10,739-5) (90%).

Wine Material and Antioxidant Additions. *Normally Aged Wines.* Ten white wines from several Portuguese wine regions and from different vintages (between 2 and 10 years old) were used in voltammetric characterization. Winemaking procedures depended on the producers. **Table 1** presents some characterization parameters of these wines as well as their reference codes.

Table 1. Reference Codes of the Normal Aged Wines Analyzed by Voltammetry and Some Characterization Parameters

wine code	age (years)	free SO_2 (mg/L	total SO_2 (mg/L>	Folin−Ciocalteu index	A_{420}[a] (nm)	[AA][b] (mg/L)
Mur_2Y	2	29	163	6.8	0.084	8.9
Borba_2Y	2	39	165	7.2	0.0086	8.2
B_3Y	3	21	114	8.3	0.107	11.0
RSV_4Y	4	14	95	6.4	0.180	6.7
HEsp_4Y	4	20	85	6.4	0.154	8,5
Bairr_6Y	6	18	107	7.5	0.251	8.6
RSD_6Y	6	18	97	7.5	0.361	9.6
FPires_7Y	7	13	59	6.4	0.360	4.6
QCar_9Y	9	8	102	5.4	0.137	6.0
Encr_10Y	10	6	68	5.0	0.151	4.6

[a] A_{420}, absorbance at 420 nm. [b] AA, ascorbic acid.

Table 2. Reference Codes of the Forced Aged Wines

wine code	description control	days of storage	storage temp (°C)
Cp0	control	0	−
O_2p0	oxygen addition	0	−
SO_2p0	SO_2 addition	0	−
O_2p1_15 °C	oxygen addition	15	15
O_2p2_15 °C	oxygen addition	30	15
O_2p3_15 °C	oxygen addition	45	15
O_2p4_15 °C	oxygen addition	60	15
O_2p5_15 °C	oxygen addition	75	15
O_2p1_45 °C	oxygen addition	15	45
O_2p2_45 °C	oxygen addition	30	45
O_2p3_45 °C	oxygen addition	45	45
O_2p4_45 °C	oxygen addition	60	45
O_2p5_45 °C	oxygen addition	75	45
	SO_2p1_15 °C SO_2 addition	15	15
	SO_2p2_15 °C SO_2 addition	30	15
	SO_2p3_15 °C SO_2 addition	45	15
SO_2p4_15 °C	SO_2 addition	60	15
SO_2p5_15 °C	SO_2 addition	75	15
	SO_2p1_45 °C SO_2 addition	15	45
	SO_2p2_45 °C SO_2 addition	30	45
	SO_2p3_45 °C SO_2 addition	45	45
	SO_2p4_45 °C SO_2 addition	60	45
	SO_2p5_45 °C SO_2 addition	75	45
pHp1_15 °C	NaOH addition	15	15
pHp2_15 °C	NaOH addition	30	15
pHp3_15 °C	NaOH addition	45	15
pHp4_15 °C	NaOH addition	60	15
pHp5_15 °C	NaOH addition	75	15
pHp1_45 °C	NaOH addition	15	45
pHp2_45 °C	NaOH addition	30	45
pHp3_45 °C	NaOH addition	45	45
pHp4_45 °C	NaOH addition	60	45
pHp5_45 °C	NaOH addition	75	45

Ascorbic Acid and SO_2 Additions. In order to further evaluate the impact of antioxidant substances on the voltammograms, fingerprint additions were made in a normal aged wine (B_3Y, **Table 1**). The concentrations were 25 and 50 mg/L of ascorbic acid (B_3YAA25 mg and B_3YAA50 mg), 20 mg/L of free SO_2 (B_3Y$SO_2$20 mg), and combined 20 mg/L of SO_2 and 25 mg/L of ascorbic acid (B_3Y$SO_2$20 mg and AA25 mg).

Forced Aged Wines. In the forced aged wines an attempt to evaluate the impact of some parameters, namely, temperature, oxygen, SO_2, and pH in their oxidative state, was made (**Table 2**) The experimental design, **Figure 1**, was similar to previous work (*3*). A 4000 mL amount of white wine (2-year-old vintage, pH 3.2) was divided into four portions of 1000 mL, and the parameters studied were adjusted as follows: (i) a first portion was adjusted to an oxygen content of 8.2 mg/L by air bubbling (20/80; O_2/N_2) (Gasin, Portugal); (ii) a second portion was adjusted to a SO_2 content of 50.0 mg/L by addition of

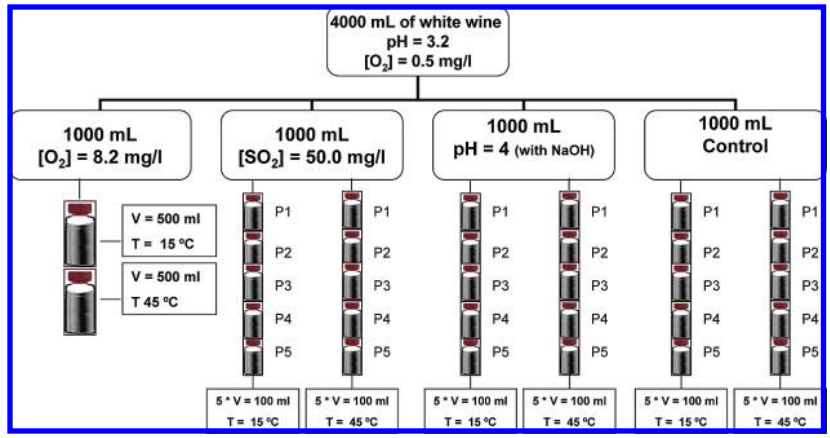

Figure 1. Forced aged experimental design.

sodium metabisulfite; (iii) a third portion was adjusted to pH = 4.0 with NaOH solution; (iv) a fourth portion corresponded to the untreated wine with 0.5 mg/L of dissolved oxygen (control). Subsequently, the oxygen-saturated portion was divided into two 500 mL Shott flasks (Durant, Germany) sealed with screw-caps made of PBT, complete with a PTFE protected seal, to withstand up to 180 °C hot-air sterilization, GL45 (Durant, Germany); one was stored at 15 °C and the other at 45 °C. The last three portions were divided into 10 portions of 100 mL into headspace flasks (headspace <5 mL) sealed with 20 mm crimp caps with septa of silicone/PTFE (Varian). Half of the samples were stored at 15 °C and the rest at 45 °C during storage time. The samples were analyzed by voltammetry at 0, 15, 30, 45, 60, and 75 days of storage. At each sampling time, the samples, initially saturated with oxygen, were resaturated with oxygen. The forced aged experimental protocol was stored in the dark.

Volatiles Quantification. Extraction and gas chromatography mass spectrometry quantification were performed according to published methodology (*2, 3*).

Other Analytical Measurements. Concentration of dissolved oxygen was measured using a "YSI Oxygen Probe - 5010-W", coupled to a 5000 dissolved oxygen instrument. This model is designed to fit directly into the bottleneck for direct measurement of wine bottles. The amount of free sulfur dioxide was determined according to the Ripper method (*16*), the total phenolic was determined according to the Folin−Ciocalteu procedure (*17*), and the ascorbic acid was determined according to the procedure outlined in ref *18*. Measurements of absorbance at 420 nm were made in order to evaluate the "color index" of the evaluated wine.

Voltammetry. Cyclic voltammetry experiments were performed using a potentiostat (Autolab type PGSTAT30, Ecochemie) controlled by GPES 4.9 software provided by Ecochemie. Voltammograms were obtained in the oxidation range of potentials (between ca. 0.2 and 1.2 V) at a scan rate of 100 mV/s using a 3 mm glassy carbon disk electrode (BAS M-2012) working electrode. The electrode surface was cleaned between runs by polishing; otherwise a slight current decrease was observed between sequential scans. This electrode fouling effect was similar for young and aged wines. The polishing was performed with 3 μm alumina powder (PK-4 polishing kit) for 2 min between scans. The polishing time was established as the minimum time for which the current data did not differ by more than 5%. The saturated calomel electrode (SCE) was used as reference electrode in conjunction with a platinum counter electrode. Current data were obtained from the average of three to five determinations, and the presented uncertainty corresponds to the standard deviation. Wine samples were analyzed directly without the addition of supporting electrolyte. Oxygen in wine samples did not interfere with the voltammetric signals (*19*). Therefore, deoxygenation was not carried out in wine samples or model wine solutions prior to voltammogram recording.

Feature Extraction. Singular value decomposition (SVD) is a blind signal technique widely used in multivariate signal processing. When mean centering or autoscaling the signal, SVD performs the principal component analysis (PCA). When the cyclic voltammetry oxidation curve (X) is decomposed in different orthogonal directions in variable space (voltage): $x_{rand} = u \times s \times v^t$ ($u \times s$, scores; v^t, loadings; s, singular values), most variability is captured in the first eigenvectors and noise is captured in the last decompositions (*20*−*22*). The number of relevant decompositions was determined by performing 500 randomizations of x (*23*), rotating the current intensity value at the same voltage among the different samples. Singular values above the first singular value of randomized voltammograms define the number of singular values that capture independent voltammetric features: $\hat{x} = u \times s_{rel} \times v^t_{rel}$, where $u \times s_{rel,t}$ and $v^t_{rel,t}$ are the relevant scores and loadings.

Multivariate Control Chart. A model using only the relevant singular values, using nonoxidized white wines as a training set, was developed: $\hat{x}_t = u \times s_{rel,t} \times v^t_{rel,t}$. Thereafter, the relevant scores were used to determine the 0.90 and 0.95 confidence interval (CI) ellipses (*24, 25*). Wines inside CI are considered similar to those used to develop the control chart ($\hat{x}_t$); otherwise they should be diagnosed for oxidation or antioxidant action by contribution plot analysis.

Feature Extraction Quality. Feature extraction quality can be assessed by the Q-statistic (square prediction error) of the relevant decomposition: $Q = E \times E^t$, where $E = x - \hat{x}$. The Q-statistic CI ($Q\alpha$) is proportional to the $\chi 2$ distribution (*26*−*28*), being computed as described in ref *29*. Samples below $Q\alpha$ are considered with robust feature extractions (*30*). The hoteling T^2h was computed as a measure to the model center. The hoteling T^2 and CI (0.05) are estimated according to ref *31*.

Contribution Plots. These are estimated to determine which variables affect the Q-statistics to diagnose why features were not captured in the fingerprint compression for the reconstructed sample $\hat{x}_i$. Contribution plots for the reconstruction error are estimated by the square error of each variable E^2_{ij} (*32, 33*). All analyses were performed using *R* for Linux (R-project) (*34*).

Fingerprinting Correlations. Electrochemical fingerprint correlations were studied by partial least squares regression (PLSR) (*35*−*37*) to quantify the amount of methional, phenylacetaldehyde, ascorbic acid, Folin−Ciocalteu, and total SO_2 against the oxidation curve.

Cross-Validation. In order to avoid overfitting, a number of selected PLS factors were performed by using cross-validation on the $n - 1$ blocks (90% of data) and tested on the remaining block (10% of total data) to calculate the predicted sum of squares criteria (PRESS). The PLSR confidence intervals were thereafter determined according to ref *37*, and the limit of quantification was assumed 10 times the regression standard error (SE).

RESULTS AND DISCUSSION

The analysis of the voltammograms, obtained by the applied oxidation potential (0.2−1.2 V vs SCE), presented subtle differences that could be related to the oxidation process. These voltammograms showed two broad bands resulting from the electrochemical oxidation of the wine (**Figure 2a**). The first band had a potential position close to 0.7 V, and the second band had a potential close to 1.0 V corresponding, respectively, to the more easily oxidizable compounds, intervenient on the oxygen "activation phase", and to the less easily oxidizable compounds, that will be consumed by the most reactive oxygen

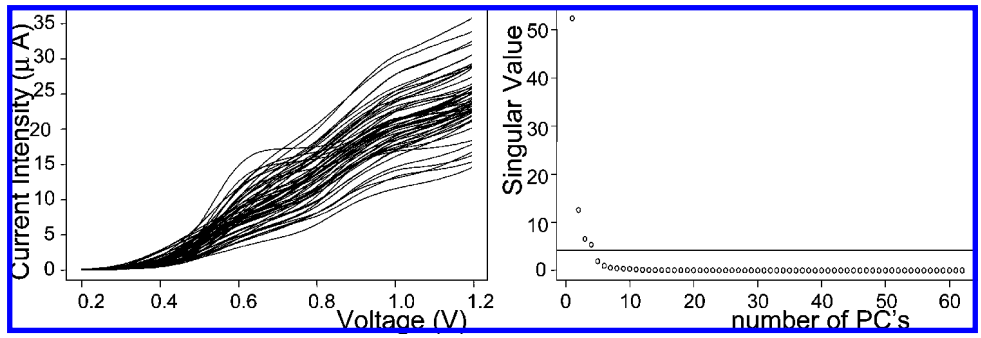

Figure 2. Cyclic voltammetry fingerprinting: (a) oxidation voltammograms; (b) singular value plot with singular value upper limits.

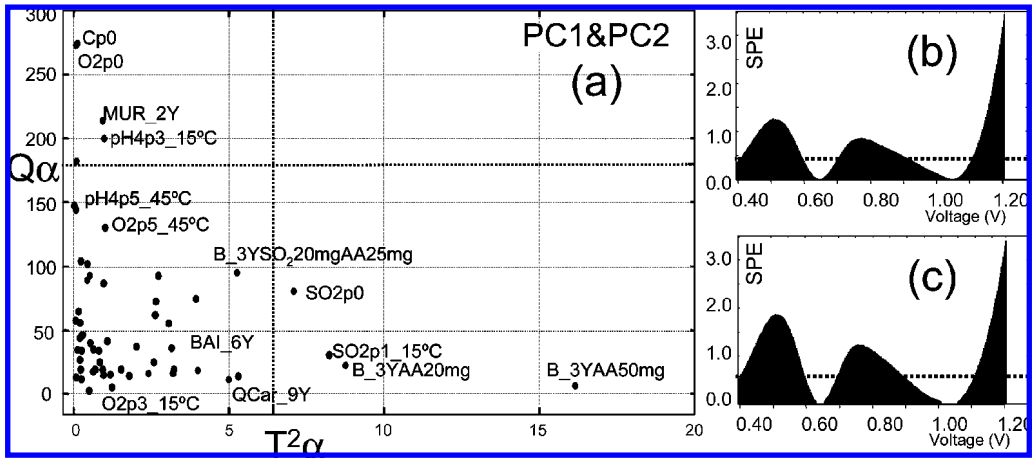

Figure 3. Voltammograms featuring extraction diagnosis: (a) Q-Th diagnostic plot; (b) contribution plot for Cp0; (c) contribution plot for Mur_2Y. Mur_2Y, normal aged wine (**Table 1**); Cp0, control forced aged wine (**Table 2**).

species (*4*). In fact, in previous work, good correlations were observed between the current intensities measured at 0.7 V potentials with ascorbic acid and at 1.0 V with the Folin−Ciocalteu index used for the colorimetric assay of phenolic and polyphenol antioxidants (*19*).

In order to understand how the shape of the curve could provide information concerning oxidation, blind signal decomposition techniques, SVD, were chosen. This procedure allows the determination of the data structure of the voltammograms (**Figure 2b**), which is indispensable for the robust application of quantifications later on, such as PLS. The variance captured in the relevant principal component contains the features in the voltammograms that discriminate wine samples, allowing the analysis and the reconstruction of the relevant voltammetric fingerprints.

The voltammetric fingerprint is structured into four main principal components, compressing 99.73% of total variance, four nonrandom singular values (**Figure 2b**): PC1 (73.32%), PC2 (21.49%), PC3 (2.65%), and PC4 (2.27%).

The relevant component structure can be studied by accessing the diagnostic plot. Thus, by plotting it for the two first components, it filters the effect of the third and fourth component (**Figure 3a**). These two orthogonal directions are capable of capturing the main features of voltammograms with the exception of (i) Cp0 (**Table 2**), (ii) O_2p0 (**Table 2**), and (iii) Mur_2Y (**Table 1**). In **Figure 3a** these samples are above $Q\alpha$, and the main features cannot be reconstructed with the two first principal components, their fingerprint being distinguishable from the rest of the voltammograms. In order to understand this behavior, the corresponding contribution plots were studied (**Figure 3b**,**c**). The procedure displays the variables (V) that contribute to the error when using a given number of components. The contribution plots of Cp0 (**Figure 3b**) and O_2p0 (figure similar to 3b, not showed) displays an interesting pattern. In fact, the uncompressed features in these wines are due to voltage ranges of 0.40 to 0.60 V, and 0.70 to 0.90 V. It is also clear that Cp0 has a higher contribution in the range of 0.4 to 0.6 V, when compared to Mur_2Y (**Figure 3c**), and the latter presents higher contributions in the region of 0.85 to 0.95 V. The contribution plot analysis allows the assessment of the possible chemical cause of distinct fingerprints, clearly indicating that there is a distinct voltammetric fingerprint for these wines, which is not present in other samples. In fact, the 0.40−0.60 V potential interval represents the most powerful reducing agents of the wine, mainly ascorbic acid, SO_2 to some extent, and polyphenolic compounds with a triphenol group on the flavonoid B-ring (e.g., flavonol myricetin, anthocyanin delphinidin, and to some extent cathecol-containing polyphenolic compounds) (*9*).

All sample voltammetric fingerprints that are below the $Q\alpha$ limit are well reconstructed by the relevant model and, therefore, possible to analyze in terms of the first and second decompositions. **Figure 3a** shows that samples (i) B_3YAA50 mg, (ii) B_3YAA20 mg, (iii) SO_2p1_15, and (iv) SO_2p0 are above the $T^2\alpha$ limit. This means that these samples generally present scores very different than the average scores of the white wines. Therefore, one can conclude that the effect of ascorbic acid and SO_2 provokes a very distinct voltammetric fingerprint pattern that can be analyzed by understanding the variance captured in the first two orthogonal directions (eigenvectors). Generally, forced aged and normal aged wines present the highest scores in the first component. As this effect appears in the first component, it is also a very visible pattern in the voltammetric fingerprint. Older wines generally present smaller current intensities in the oxidation voltammogram, which is in good agreement with the expected consumption of antioxidants over time. In fact, if the normal aged wines were ordered according

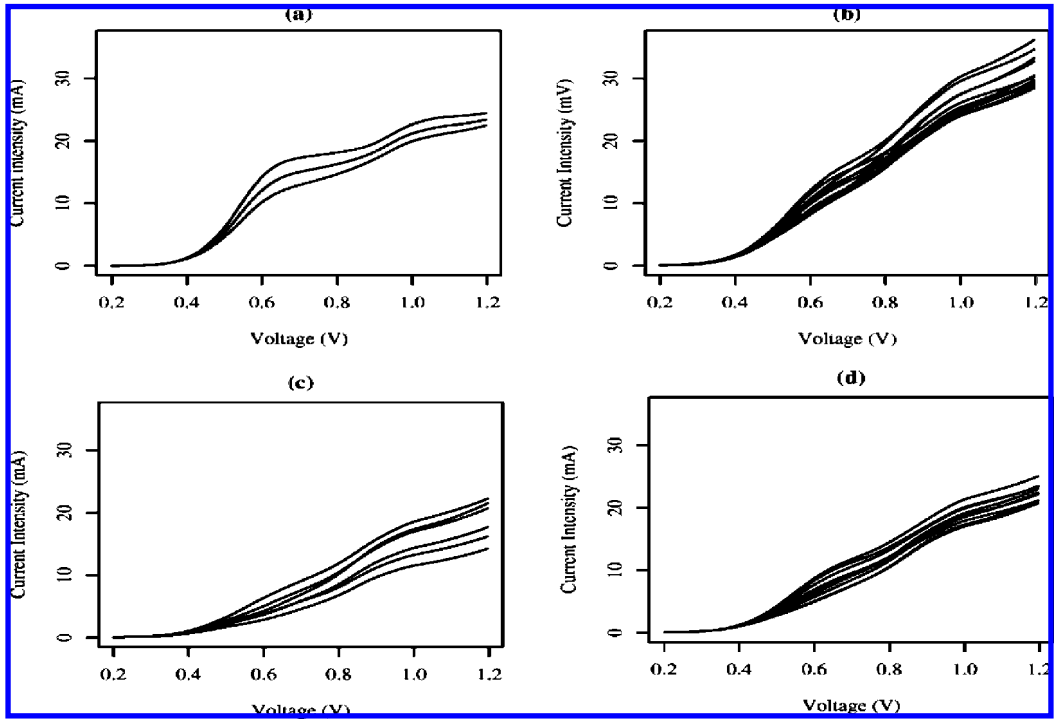

Figure 4. Cyclic voltammetry recognized fingerprints: (a) ascorbic acid; (b) SO_2; (c) aged wine; (d) oxygen supplemented samples.

the respective score in PC1, the ascending ranking would be sequentially HEsp_4Y, BAI_6Y, RSD_6Y, Encr_10Y, and QCar_9Y, which is relatively similar to the age of each wine. The second orthogonal decomposition PC2 (21.49%) captures the large variation in the voltammogram shape, especially the curvature patterns, where ascorbic acid and SO_2 are very distinct. Ascorbic acid attains very large positive score values, attaining very low resistance in the voltage range of 0.55 to 0.70 V. This is observable in the higher concentrations of ascorbic acid in the voltammogram with the curve presenting very high currents in this range (**Figure 4a**) The inflection point in this region has been used to quantify ascorbic acid in white wines. Nevertheless, SO_2 shows a completely different voltammogram shape, without the curvatures of ascorbic acid or the rest of the studied wines. Although the resistance in the voltage is lower, high concentrations of SO_2 lead to wine voltammograms without abrupt curvatures in the studied voltage range (**Figure 4b**). The rest of the wines present curvature patterns between the ascorbic acid and SO_2 patterns.

More detailed features could be extracted from the original voltammograms in the third and fourth relevant orthogonal decompositions. Using PC3 (2.65%) and PC4 (2.27%) it is possible to discriminate between samples: (i) nonoxidized wines: Cp0, O_2p0, Mur_2Y; (ii) pH4 samples; (iii) oxygen supplemented and kept at 45 °C. Analysis of the third and fourth eigenvectors allows the understanding that lower oxidation wines exhibit higher intensities in the range of 0.7 to 0.8 V, whereas oxidized samples (protocol at 45 °C) are more influenced by 0.5 to 0.6 V and 1.0 to 1.2 V. The exclusive features of the nonoxidized wines allow the construction of a multivariate control chart to diagnose oxidation of white wines. Fifty true replicates of Cp0 were used as a training set for developing a fingerprinting model of this wine. The fingerprint was compressed into two relevant principal components, containing 99.44% of the original Cp0 features. Afterward, the control limits and the rest of the remaining samples were projected into the Cp0 scores space, as described in Materials and Methods, and the control chart in **Figure 5** was produced. This chart can now be used as a monitoring and diagnostic tool for oxidation management of white wines. All wines that fall outside of the confidence intervals present a different fingerprint. Furthermore, the distance to the center is an indication of the degree of difference, and the position is due to interpretable features that enable rapid diagnostic and management actions, such as (i) high concentrations of antioxidants, (ii) characterization of the oxidation "status", and (iii) follow-up of oxidation mechanisms.

The chart presented in **Figure 5** is reasonably intuitive, it being possible to diagnose features in three main quadrants: (i) high values of PC1 and PC2: diagnose high values of SO_2 (pathway 1); (ii) high values of PC1 and low values of PC2: diagnose high values of antioxidants such as ascorbic acid (pathway 2); (iii) low values of PC1 and PC2: diagnose the extent of white wines oxidation (pathway 3). Scores with combinations of low values of PC1 and high values of PC2 are nonexistent, and therefore any new sampling found in this area should be considered an aberration and should be investigated further. In fact, when the model was used to reconstruct in silico samples belonging to different regions of the Multivariate Chart Control, the reconstructed samples were in good agreement with the real observation, with the exception of scores predicted in axe1 positive and axe2 negative (figure not shown). These last reconstructed samples presented negative current intensities at the 0.4 to 0.8 V potential ranges. **Figure 6** represents the control chart contribution plots for (a) SO_2p3_15 °C, (b) HEsp_4Y, (c) Cp5_45 °C, (d) B_3YAA50 mg, (e) QCar_9Y, and (f) O_2p5_45 °C.

By direct observation of **Figure 6a**, it is very simple to diagnose the effect of SO_2. As SO_2 has low resistance and curvature, it presents high values of both PC1 and PC2. Adding SO_2 to white wines only increases their conductivity and diminishes the curvature effects in the voltammetric fingerprint. The SO_2 fingerprint is detectable because of a wide range increase in current intensity, presenting high contributions at 0.4 to 0.6 V, 0.7 to 0.8 V and 1.0 to 1.2 V (**Figure 6a**).

Oxidation is also monitored in the control chart. In fact, in samples submitted to high regimes of oxygen it is possible to

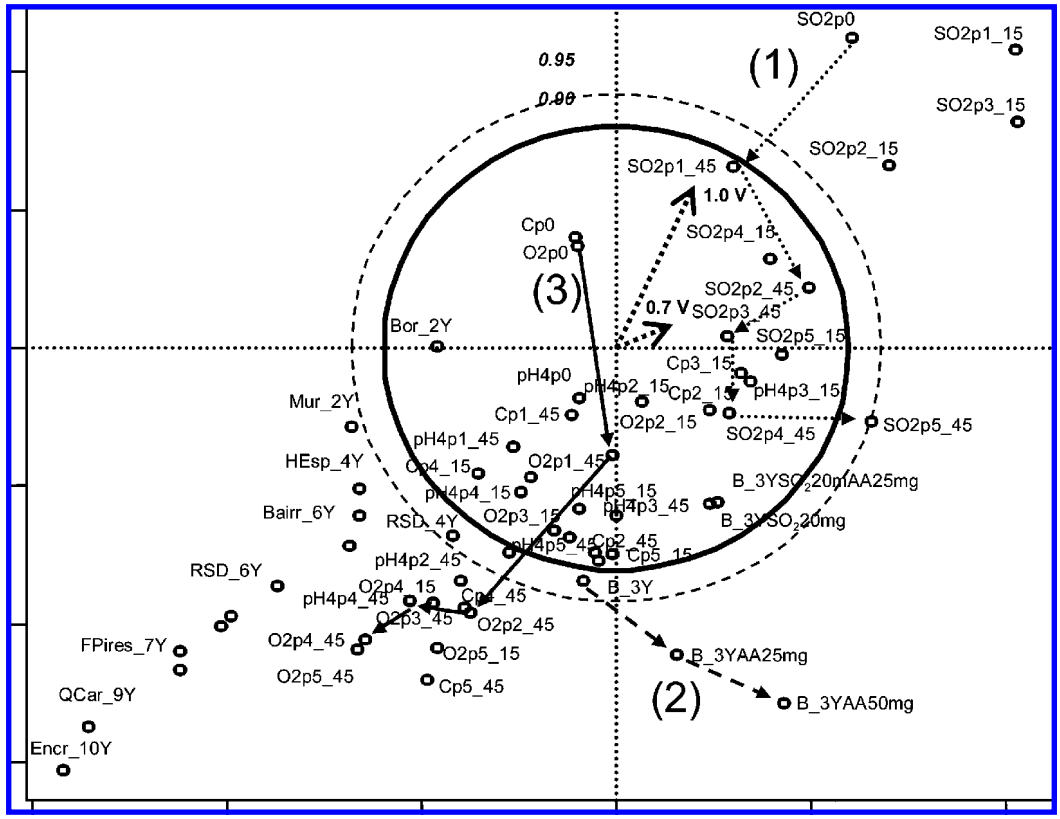

Figure 5. Oxidation management. Cyclic voltammetry multivariate control chart and pathways: (1) SO_2, (2) ascorbic acid, and (3) oxidation.

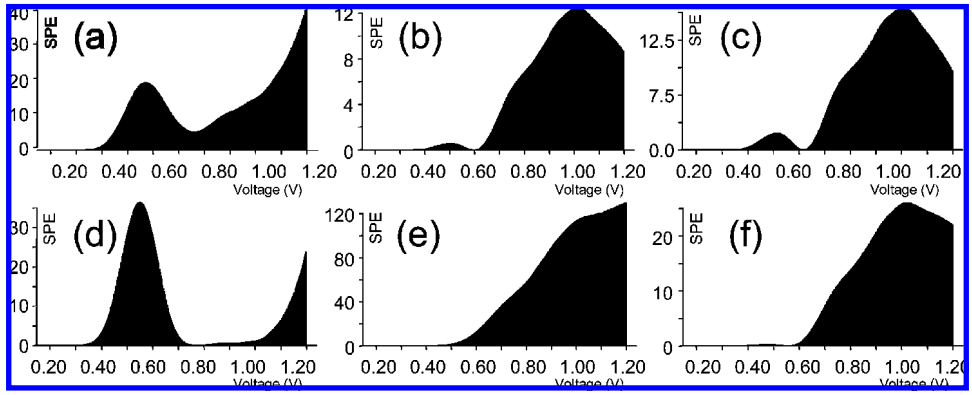

Figure 6. Control chart contribution plots: (a) SO_2p3_15 °C; (b) HEsp_4Y; (c) Cp5_45 °C; (d) B_3YAsc50 mg; (e) QCar_9Y; (f) O_2p5_45 °C.

follow the successive steps of oxygen consumption, displaying a rapid decrease both in PC1 and PC2 score values (**Figure 5**). These samples present a similar pattern to normal aged wines, with all the curvatures but with less current intensity for all the voltage range. Nevertheless, normal oxidized wines present an interesting difference: they do not show the rapid increase of current at the voltage range of 0.4 to 0.6 V as in the forced aged wines. Normal aged wines present a voltammetric fingerprint with an exponential shape and the forced aged wines a logistic-like shape in this region. This observation is easier to interpret in the older wine (FPires_7Y, Qcar_9Y, and Encr_10Y) scores that are highly distinguishable from the forced aged protocol (**Figure 5**).

The performance of a diagnosis is also possible in the normal aged wines. For example, Borba_2Y is well inside the confidence intervals as expected, being in the same class of the control samples. Mur_2Y, although this is a 2 year-old wine, shows higher traces of oxidation than Borba_2Y. After the inspection of its contribution plot (not shown), higher contributions at 0.7 to 0.9 V and 1.0 to 1.2 V were possible. The chart also shows three other intermediate groups of wines with different states of oxidation. Wines such as HEsp_4Y, Bairr_6Y, and RSD_4Y are in an intermediate state of oxidation, while RSD_6Y and FPires_7Y present higher oxidation levels.

Table 3. PLS-1 Regression Statistics

PLS-1 model	variance (%)	*R*-adj	PRESS	MSE	R^2	error
phenylacetaldehyde	99.93	0.9769	907.111	3.913	0.9919	1.739
(nPC = 5)	98.39					
SO_2	99.76	0.9367	164.43	5.332	0.9717	2.167
(nPC = 10)	94.42					
AA	98.91	0.9579	3.016	0.1037	0.9524	0.2935
(nPC = 8)	95.51					
Folin	99.87	0.9515	0.5424	0.0208	0.9817	0.1246
(nPC = 11)	96.36					

Table 3 presents the PLS-1 regression statistics. Results show that there is a direct relationship between cyclic voltammetry and the studied compounds. All models also passed the lack of fit test (*F*-test, $\alpha = 0.05$), and R^2 are all above 0.97. Furthermore, PLS-1 models present low quantification limits in (i) methional:

2.6 μg/L, (ii) phenylacetaldehyde: 17.4 μg/L, (iii) ascorbic acid 2.9 mg/L, (iv) Folin−Ciocalteu 1.2 index, and (v) total SO_2 21.7 mg/L.

Cyclic voltammetry proved to be useful as a fingerprinting technology, being possible to be used as a method for diagnostic and oxidation management in white wines. Feature extraction also showed that this technique may be used for following and quantifying dynamic changes in the composition of white wines. More efforts in signal processing may turn this technology into an interesting tool for managing wine production. Voltammetric measures proved to be a valuable tool for monitoring oxidative reactions, contributing to an increase in the knowledge on fundamental mechanisms of oxidation in white wines.

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