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Relationship between Potentiometric Measurements, Sensorial Analysis, and Some Substances Responsible for Aroma Degradation of White Wines

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Oxidative degradation of white wines can be described sensorially as developing from a loss at positive aroma characteristics, through the development of negative aromas to a linel stage of chromatic alterations. This work attempts to relate the oxidation "status" evaluate by potentiometric titrations, with sensorial degradation and the levels of substances responsible for "off-flavors", such as methional and phenylacetaldehyde. The potentiometric titration employed measures the most powerful antioxidants of white wines (e.g., those which more rapidly consume oxygen). Considering that aromatic precedes chromatic degradation, resistance to oxidation (ROX) constitutes a useful indicator of resistance to oxidation. Sensorial degradation (ID), potentiometric measures, and volatiles were determined both in samples submitted to a "forced aging" protocol and normal aged white wines. High correlation values were observed between ROX and the ID, in both sets ($r > 0.87$). ID is better explained by ROX values than by the indicated wine age or by the "degree of browning" (Abs = 420 nm). It was also observed that in samples with ROX values higher than 10, the concentration of methional and phenylacetaldehyde were above their respective odor threshold. Finally, it was observed that there is a relationship between oxygen consumption and the respective ROX. Although these results seem very promising, they needed to be further complemented in order to estimate the shelf life of a white wine using potentiometric titrations.

KEYWORDS: Resistance to oxidation; methional; phenylacetaldehyde; potentiometric measurements; white wines

INTRODUCTION

In wine making, the redox phenomena are responsible for profound changes in the wine's chemical composition. During the fermentation, along with microbial metabolism as well as aging, the action of these mechanisms leads to modifications in the aroma and the color of the wine.

The aromatic degradation is largely caused by these redox mechanisms (*1*). These alterations make up what is commonly known as "oxidative spoilage", a serious fault when it occurs within a period, which can be considered the reasonable shelf life of the specific wine in question. Oxidative spoilage includes alterations such as the rapid loss of fruit and floral aromas, the development of unpleasant aromas, and precocious yellowing or browning. Even between wines, within the dry-white table wine category, which are very similar in style and gross composition, there is a considerable range of susceptibilities for the development of such characteristics. This susceptibility is a function of three main parameters: (i) a wine's redox potential, (ii) the concentration and type of antioxidants—both intrinsic and added—present, and manly on (iii) the concentration of dissolved oxygen.

Various researchers have tried to reproduce in the laboratory, the "aroma degradation" associated with oxidative spoilage (*2*−*5*). The identification of the most important descriptors related to the typical aroma of "oxidative spoiled white wines" was reported as being "honey-like", "farm-feed", "hay", and "woody-like" (*4*). Furthermore, it was observed that wines stored at high temperatures and supplemented with high levels of dissolved oxygen (e.g., saturation) suffered a rapid and pronounced oxidative spoilage aroma, which were related with the presence of 3-(methylthio)propionaldehyde (methional), phenylacetaldehyde, 3-hydroxy-4,5-dimethyl-2(5H)-furanone (Sotolon), and the 1,1,6-trimethyl-1,2-dihydronaphthalen (TDN) (*5*−*7*).

It has been reported that aromatic degradation occurs before chromatic degradation (*3*, *8* ,*9*) resulting manly from the oxidation of phenolic compounds (*10*), which occurs at high redox potentials ($E > +400$ mV) (*11*), leading to changes in wine color and taste. Studies made in beer have demonstrated that neither the removal of flavonoids by PVPP nor additions of flavanols to beer have been found to affect the sensory score and the concentration of trans-2-nonenal compared to control after forced aging (60 °C for 7 days). Furthermore, addition of catechin or ferrulic acid to beer had no effect on the formation of carbonyl compounds (*12*).

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For this reason, it is mostly important to quantify the compounds with a lower potential that was found to be one the most powerful reducing agents (ascorbic acid, SO_2, and some polyphenols), which are largely the wines best defense in removing dissolved oxygen before it produces other effects including oxidative spoilage. Thus, the determination of the "resistance to oxidation", by the potentiometric measurement (*13*) could be useful, as dichlorophenolindophenol constitutes a selective oxidant fitted to measure this first line of defense against aroma degradation. From an industrial point of view, it should be noted that there is no systematic way to predict the shelf life of bottled white wines.

Hence, the aim of this work was to quantify the white wine fraction with higher antioxidant power, and in what extent this value could be related with white wine oxidative spoilage. For this purpose, three parameters were measured: (i) the index of degradation (ID) evaluated by sensorial analysis, (ii) the resistance to oxidation (ROX) measured by potentiometric titrations, and (iii) the levels of substances responsible for "off flavors" in white wines, such as methional and phenylacetaldehyde. Preliminary experiments were also performed to evaluate the correlation between oxygen consumption with ROX, aiming to gather more information concerning estimation of white wines' shelf life.

MATERIALS AND METHODS

Wine Material. The wines used in this study were separated into three groups. *Wine Group I*. These were wines that came from a forced aging experimental protocol. The experimental design was similar to previous work (*4*). A volume of 2000 mL of white wine, corresponding to 6 year-old vintage, of pH = 3.2 was divided into four portions. The parameters studied were adjusted as follows: (*i*) a first portion was adjusted to pH = 4 by adding Na_2CO_3, (*ii*) a second portion was adjusted to oxygen content of 6.5 mg/L by air bubbling (20/80; O_2/N_2) (Gasin, Portugal), (*iii*) a third portion was adjusted to free SO_2 levels of 50 mg/L (free form by adding sodium metabisulfite), and (*iv*) the last portion corresponds to the untreated wine (control). Each set was kept for 12 days at three different storage temperatures (20, 40, and 60 °C).

Wine Group II. These 24 white wines came from several Portuguese wine regions and from different vintages (between 1 and 20 years old). Winemaking procedures depended on the producers.

Wine Group III. These 35 wines came from several world regions (19 from Portugal, 6 from USA, 6 from Spain, and 4 from France) and were between 3 and 6 years old. Among this group, five samples were submitted to a saturation regime of oxygen (e.g., 6.5 mg/L) and stored at $T = 30$ °C for 10 days. Finally, another subgroup of seven samples, from the same vintage and bottled at the same time, were stored at 15 °C for one year (normal aging) and submitted to analysis.

Sensory Studies. The sensory panel employed in all sensorial measurements in this work was composed of twelve persons: university students, winemakers, and laboratory personnel. The panel is a permanent wine evaluation resource, which receives weekly training sessions. Tests were performed in individual booths, using tulip glasses containing 30 mL of wine at room temperature (20 °C).

Scoring Testing. Previous works have shown that the most important descriptors related to the typical aroma of oxidative spoilage white wines were honey-like, farm-feed, hay, and woody-like (*4*).

Samples were presented to the panel in separate sets ($n = 6$), on different days, to be rated using a discontinuous scale from 0 (absent) to 10 (very intense) for the aroma of each one of the four descriptors described above and "floral" (related with young wine character). Data were treated according to a scoring test and statistical significance was evaluated (*14*).

Similarity Test. The ID was determined by a comparison test of each sample and a white wine that was, in several sessions, unanimously considered as oxidative spoiled. Each coded sample was presented to the panel together with the oxidative spoiled white wine as a pair. The panel was asked to rate the similarity on a discontinuous scale from 0 (no similarity) to 20 (equal) of each sample with the oxidative spoiled white wine. The data obtained were treated according to the ANOVA procedure.

Standards Preparation. The following molecules were purchased from Sigma-Aldrich (Portugal): 3-(methylthio)propionaldehyde (27,746−0) (100% purity), phenylacetaldehyde (10,739−5) (90%), linalool (L260−7) (97%), and 4,5-dimethyl-3-hydroxy-2(5H)-furanone (W36,340−5) (97%). The 1,1,6-trimethyl-1,2-dihydronaphthalen (TDN) synthesis was performed according to (*15*), and the degree of purity obtained was less than 30%.

Quantification Methods. Extraction was performed according to published methodology (*4*). To 50 mL of white wine were added 50 μL of octan-3-ol in hydro alcoholic solution (1/1, v/v) at 466 mg/L as internal standard and 5 g of anhydrous sodium sulfate. The wine was extracted twice with 5 mL of CH_2Cl_2 (Merck, Spain). The two organic phases obtained were blended and dried over anhydrous sodium sulfate. Four mL of this organic extract was concentrated to 1/10 under a nitrogen stream with a 20 L/min gas flow.

Gas Chromatography/Mass Spectrometry. Extracts were analyzed using a Varian CP-3800 gas chromatograph (USA) equipped with a Varian Saturn 2000 mass selective detector (USA) and a Saturn GC/MS workstation software version 5.51. The column used was Stabilwax-Da (60 m × 0.25 mm, 0.25 μm) fused silica (Restek, USA). The injector port was heated to 220 °C. The split vent was opened after 30 s. The carrier gas was helium C-60 (Gasin, Portugal), at 1 mL/min, constant flow. The oven temperature was 40 °C (for 1 min), then increased at 2 °C/min to 220 °C and held for 30 min. All mass spectra were acquired in the electron impact (EI) mode. The ion trap detector was set as follows: The transfer line, manifold, and trap temperatures were 230, 45, and 170 °C, respectively. The mass range was 33−350 *m*/*z*, with a scan rate of 6 scan/s. The emission current was 50 μA, and the electron multiplier was set in relative mode to "autotune" procedure. The maximum ionization time was 25 000 μs, with an ionization storage level of 35 *m*/*z*. The injection volume was 1 μL, and the analysis was performed in full scan mode.

Identification was attempted using mass spectra obtained from the sample with those from pure standards injected in the same conditions, by comparison of the Kovat's index and the mass spectra present in the NIST 98 MS Library Database or in the literature.

Potentiometric Titration. Fifty milliliters of white wine was titrated with 7 mL of a reductant solution (1 mL of $TiCl_3$ 15% in 100 mL of HCl 1M), followed by an oxidation titration with a 0.05% (w/v) dichlorophenolindophenol solution. A combined platinum electrode with a reference system Ag/AgCl in a KCl reference electrolyte (Mettler, Toledo) followed these two titrations in a N_2 atmosphere (100 mL/min). The titrations were carried out by an automatic system Titralab (Radiometer, Denmark). All set points were described in previous work (*13*).

The titrant concentrations employed were determined and adjusted for white wines, the selection criteria being to obtain repeatable curves. The order of sequence titration was imposed by the redox potencial of the wines. An oxidation titration was preceded by a prereduction step in order to ensure the visualization of the end-point indicator of the oxidation titration in all wines. In fact, if a straight oxidation titration were performed, the end-point detection would not be possible.

The pH of analyzed wines decreased during reduction titration (due to the presence of HCl) reaching final values close to pH 1.5. These values do not suffer significant changes with oxidant additions having an overall increment close to 0.2 (dilution effect). Redox species, present in white wine, will be oxidized by the dichlorophenolindophenol in the potential range from −400 to +400 mV.

Considering the formal potential of dichlorophenolindophenol, close to 400 mV, it will selectively pick out the most powerful reducing agents of the wine, which includes ascorbic acid ($E = 210$ mV), to some extent, SO_2, and polyphenols with a triphenol group on the flavonoid B-ring such as flavonol myricetin and anthocyanin delphinidin ($E = 300$ mV), and to some extent, cathecol-containing polyphenols (*11*).

The impact of dissolved oxygen in the reduction titration was reported and quantified in previous work (mmol $TiCl_3 = 2.34$ mmol

Table 1. Coefficients of Correlation between Sensorial Descriptors and ROX Values from Group I and Group II Wines

corr coeff (*r*) with ROX	wine group I forced aging experiment ($n = 13$)	wine group II commercial wines ($n = 24$)
ID	0.8869	0.8725
floral	−0.9068	−0.7728
honey-like	0.8815	0.7826
hay	0.9465	0.8252
woody-like	0.9358	0.8411
farm feed	0.8628	0.8286

of O_2) (*13*). To minimize electrode interference due to the presence of this species, each sample was bubbled with a N_2 flow (500 mL/min) for five minutes before redox titrations. The levels of dissolved oxygen were less than 0.5 mg/L.

The possibility to quantify both oxidized and the total reduced fraction of a wine (base on this methodology) was clearly established, with good reproducibility (CV of 10.87 and 2.65% for reduction and oxidation titrations, respectively) (*13*).

To compare the resistance to oxidation of white wines, a quotient between the oxidized fraction and the total reduced fraction of a wine was calculated (ROX value). Each value was obtained by the millimoles of consumed reductant (mmol Red) and by the millimoles of consumed oxidant (mmol Oxi) using the formula ((mmol Red/mmol Oxi) × 10). This quotient is a status of oxidation of a wine where the mmol Red traduces the already oxidized wine fraction and the mmols Oxi estimates the total range of wine compounds that could be oxidized, characteristic for each wine. The higher the ROX value, the higher susceptibility for a wine to suffer oxidative spoilage.

As an example, ascorbic acid additions to a wine sample will have a direct influence on the consumption of oxidant and no effect on the consumption of reductant. Thus, the quotient value (ROX) will decrease, indicating higher resistance to oxidation.

Other Analytical Measurements. Measurements of *free SO_2* concentration and *chromatic index* (abs 420 nm) were performed (*16*). The *Kovat's index* was calculated according to the literature (*17*), and the concentration of *dissolved oxygen* was measured using a WTW 340 Oxygen Probe. The amount of *total phenolic* was determined according to the Folin−Ciocalteu procedure (*18*).

RESULTS AND DISCUSSION

To correlate the resistance to oxidation, obtained by potentiometric measurements (ROX value), with the oxidative spoilage aroma, groups I and II were submitted to sensorial analysis. The panel has rated both groups according to the above descriptors as well as "floral" (associated with the "freshness" of same non-oxidized white wines) and the ID. The coefficients of correlation between sensorial descriptors and ROX values are shown in **Table 1**.

High correlation values (*r*) were obtained between potentiometric measurements and sensorial analysis, in particular for ID. A high degree of collinearity among descriptors was also observed. Nonexplained variance could be due not only to the intrinsic error of both measurements (ROX and sensorial) but also to the possibility that some wines could have some capacity of resistance to oxidation and simultaneously be perceived as "aroma spoiled".

Results from chemical analysis of the samples from group I, corresponding to forced aging experiment are presented in **Table 2**. Samples kept at 20 °C were rated with lowest values of index of degradation, equal to the control (ID = 1), with the exception of that saturated with oxygen (ID = 4). It is important to note that at this storage temperature, the "degree of browning" (Abs = 420 nm) was similar for all treatments, indicating that no significant chromatic changes had still occurs.

These results corroborate a sequencially sensorial degradation, based on being the the first aroma to be perceived. Remarkably, among the same samples (20 °C), the highest ROX value observed (ROX = 7), correspond to the set saturated with oxygen, which was also considered as the most spoiled by the panel.

A high correlation between ID and ROX values was observed ($r = 0.8869$) along all the treatments. Furthermore, the sample saturated with oxygen was the one that underwent the faster degradation (ID = 18), having the highest ROX value (ROX = 20).

Chemical substances considered as key odorants in oxidative white wine character (*5*) and related with the former descriptors do not, by themselves nor in combination, fully explain the typical spoiled aroma. However, it has been demonstrated that the formation of Strecker aldehydes (methional and phenylacetaldehyde) was highly dependent on temperature and oxygen levels (*4*, *5*, *19*) and that there presence was associated with deterioration. Therefore, these substances can be used as indicators of oxidative spoilage and attempts were made to establish a relationship between ROX, methional, and phenylacetaldehyde. Samples used came from group I, corresponding to the forced aging experiment (**Table 2**).

The concentrations of these molecules, highly dependent on temperature and oxygen levels, were well correlated with ROX values, $r = 0.8430$ and $r = 0.8476$, respectively. Sotolon was only observed on one sample treated with oxygen and stored at 60 °C, which is in agreement with previous work (*5*). Finally, TDN and linalool were also correlated with ROX values, 0.6809 and −0.9026, respectively.

Methional was not detected in samples with ROX values less than 10. The quantities of methional found for ROX values greater than 10 were above the olfactive threshold limit (LDO = 0.5 μg/L) (*7*). The same behavior was observed for phenylacetaldehyde (LDO = 25 μg/L).

Nevertheless, changes in wine composition occurring at high temperatures (forced aging experiment) cannot be directly extrapolated to normal aging processes (*1*). Hence, to validate that ROX values above 10 could be a useful indicator of oxidative spoilage, several commercial white wines from different vintages ($n = 24$) (group II) with different levels of aroma degradation were also submitted to a chemical analysis (**Table 3**).

As shown in **Table 3**, the ranking order based on the resistance to oxidation measured by ROX do not correspond to the respective wine age. For example, sample TF (4 years old) was rated with a higher degradation index and ROX value than sample DVB (9 years old). Assuming similar storage conditions, these results illustrate the different capacity for resistance to oxidation of wines. Index of degradation is better related with ROX values ($r = 0.8725$) than with the respective wine age ($r = 0.7491$) or chromatic index (Abs = 420 nm) ($r = 0.6966$), and no relationship was observed with the total phenolic content (Folin−Ciocalteu). These results corroborate the observations made on forced aging experiments, where the aromatic degradation precedes the chromatic degradation.

Samples containing high levels of methional and phenylacetaldehyde, above odor threshold, correspond to those with ROX values close to 10, which is in agreement with results obtained from group I. Conversely, linalool concentration, which imparts floral aroma notes, was not detected in samples with ROX values above 10 (**Figure 1**).

ROX values obtained from these commercial wines (max = 13) were lower than those found in "forced aged" wines (max

Table 2. Relationship between ROX, Sensorial, and Chemical Data, and Chromatic Index from Wine Group I

samples	ROX	ID	methional (μg/L)[a]	phenylacetaldehyde (μg/L)	TDN (nor area)	linalool (μg/L)	Folin–Ciocalteu index	Abs 420 (nm)
T0	3	1	n.d.	12.5	0.9	46.0	7.5	0.099
pH 3, 20 °C	5	2	n.d.	14.1	1.0	40.6	7.1	0.117
pH 3, 40 °C	11	6	10.9	37.2	2.6	9.5	6.4	0.200
pH 3, 60 °C	12	18	26.9	120.2	8.3	11.1	5.5	0.670
pH 4, 20 °C	5	1	n.d.	11.5	0.8	42.3	7.1	0.116
pH 4, 40 °C	13	5	9.3	29.6	0.7	31.3	6.1	0.209
pH 4, 60 °C	18	15	24.0	147.5	1.8	12.4	5.4	0.638
O_2, 20 °C	7	4	n.d.	16.1	0.8	38.5	7.0	0.114
O_2, 40 °C	13	8	28.0	39.8	2.9	8.9	6.1	0.206
O_2, 60 °C	20	18	60.7	189.4	8.9	0.7	5.8	0.643
SO_2, 20 °C	4	1	n.d.	12.2	1.0	40.5	8.4	0.104
SO_2, 40 °C	13	8	9.6	20.5	2.8	16.1	6.5	0.152
SO_2, 60 °C	18	15	25.5	169.0	9.9	1.6	6.2	0.347

[a] n.d. = not determined.

Table 3. Relationship between ROX, Sensorial, and Chemical Data, and Chromatic Index from Wine Group II

samples	age	ROX	ID	methional (μg/L)[a]	phenylacetaldehyde (μg/L)	TDN (nor area)	linalool (μg/L)	Folin–Ciocalteu index	Abs 420 (nm)
DA	18	13	17	4.1	5.9	4.2	n.d.	7.5	0.495
TA	9	12	15	13.0	16.6	8.2	n.d.	7.4	0.292
TODA	7	11	15	0.9	2.8	5.3	n.d.	6.5	0.180
MAS	20	11	15	1.4	7.0	3.3	n.d.	5.5	0.322
CCA	17	10	17	14.5	33.3	5.6	n.d.	6.5	0.433
CB	14	9	17	2.5	6.7	6.8	n.d.	5.4	0.307
CA	17	9	16	1.7	4.6	4.0	n.d.	5.9	0.252
TF	4	9	12	0.8	3.4	5.9	n.d.	6.9	0.171
DA	7	8	12	7.4	10.9	7.0	n.d.	6.5	0.135
CCC	9	8	12	n.d.	3.9	4.4	n.d.	6.6	0.218
MSB	19	8	14	2.4	4.3	4.8	n.d.	5.6	0.314
TE	5	7	7	n.d.	1.8	4.0	n.d.	7.1	0.126
TB	8	7	15	4.7	13.8	9.4	9.2	7.4	0.231
TD	6	5	12	n.d.	4.2	8.5	8.5	6.1	0.215
TC	7	5	13	1.7	4.1	6.2	n.d.	6.9	0.175
DVA	10	3	9	n.d.	0.9	3.2	36.7	6.1	0.167
DQB	4	3	7	n.d.	0.9	2.6	35.2	7.2	0.128
DQA	6	3	7	n.d.	0.9	4.2	4.2	6.4	0.147
DVE	3	2	2	n.d.	n.d.	1.6	146.0	6.7	0.122
DVC	8	2	6	n.d.	2.9	6.9	27.0	6.6	0.326
DVD	4	2	7	n.d.	1.0	3.5	20.4	8.3	0.254
DVF	2	1	4	n.d.	3.6	1.2	44.0	6.1	0.080
DVB	9	1	9	n.d.	n.d.	5.4	68.0	5.8	0.194
DVG	1	1	2	n.d.	2.8	0.1	23.0	6.1	0.054

[a] n.d. = not determined.

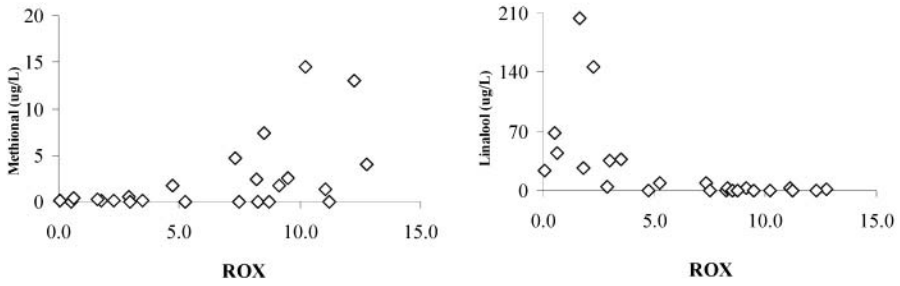

Figure 1. Relationship between methional and linalool concentrations with ROX from Group II wines.

= 20). Furthermore, levels of methional were also lower in group II than those in samples from group I. This fact could be due to the extreme conditions applied to forced aged samples, knowing that the reactions due to high temperatures are different from those produced during natural browning (*1*).

The resistance to oxidation was also determined on a third set of wines, group III (n = 35), with a similar age range (3−4 years old). The ROX values observed ranged from 0.4 to 4.4. Furthermore, sensorial analysis did not find oxidative spoiled white wines.

Considering that ROX preferentially quantifies the wine fraction more readily oxidized by dissolved oxygen, it was attempted to relate, for the same wine sample, the oxygen consumed over time, with the respective ROX values. The aim was to determine to which extent the ROX measurement could be useful as an indicator of the shelf life of a white wine. For this purpose, five samples from group III were saturated in oxygen and stored for 10 days at 30 °C (closer to real conditions), and a second sub-group of seven samples, from the same vintage and bottled at the same time, were stored at

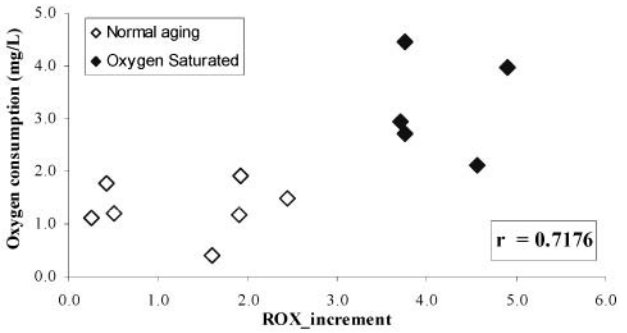

Figure 2. Relationship between ROX increments and oxygen consumption in normal-aged and oxygen-saturated samples.

15 °C for one year (normal aging) and submitted for analysis. The oxygen saturation treatment leads to an alteration of the aroma of all samples.

Two populations can be observed in **Figure 2**. The first one, composed of the normal-aged wines, had smaller ROX-increments (<3) than the second one, which correspond to those samples saturated with oxygen and stored at 30 °C. The increments on ROX were also more important among these samples. Considering the number of samples analyzed, it was not possible to construct a more elaborate mathematical model. Nevertheless, increments between ROX values for each sample after oxygen consumption was significant, and a positive impact of oxygen consumption on ROX values was observed between all samples ($r = 0.7176$).

Although these results seem very promising, they needed to be further complemented in order to estimate the shelf-life of a white wine using potentiometric titrations.

CONCLUSION

To establish a relationship between the degree of oxidation of a wine and the presence of molecules responsible for off-flavors, this work tried to correlate sensorial data and chemical measurements with potentiometric data. A method to quantify the resistance to oxidation of wine, based upon a sequence of redox titrations, reduction followed by oxidation using $TiCl_3$, and dichlorophenolindophenol was employed.

ROX values obtained were strongly correlated with the index of degradation attributed to samples by the sensorial panel, both in normal aged wines and in samples submitted to a forced aged experiment $r = 0.8725$ and $r = 0.8869$, respectively.

ID is better explained by ROX values than by the indicated wine age in the bottle or by the chromatic degradation. Assuming similar wine ages, these observations illustrate the differences of resistance to oxidation between wines.

It was also observed that for ROX values higher than 10, linalool was not detected, and the concentration of methional and phenylacetaldehyde were above 10 μg/L and 50 μg/L, respectively. Finally, a relationship between consumed oxygen and the respective ROX was observed. These last results needed to be further complemented in order to estimate the shelf life of a white wine using potentiometric titrations.

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