Factors Influencing the Oxidation Phenomena of Sherry Wine

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In this work some of the factors that influence the redox stability of sherry wines of the "fino" type were studied, in particular, dissolved oxygen concentration, container size, temperature, and ferric ion concentration. These factors significantly affect the oxidation process of some types of sherry wines that can occur during post-bottling storage. Due to its special equilibrium, the biologically aged wine of the Sherry zone, if not well stabilized, can suffer oxidation phenomena that impact its organoleptic properties. Temperature and iron content have been shown to influence the kinetic constant of the oxidative process. Initial dissolved oxygen affects initial oxidation rates as well as the final oxidation level. On the other hand, container size determines the total content of oxygen dissolved in the liquid, which can also influence the evolution of the process. The demetallization of wine by application of an ion exchange resin is proposed as a technique to reduce oxidative damage.

Key words: Oxidation phenomena, redox stability, sherry wine

Oxidation of biologically aged wines of the Sherry zone ("fino" or "manzanilla") is one of their main enological problems. Some months after bottling, oxidation can produce remarkable modifications in the aroma, color, and flavor of wines [10,16]. The changes in organoleptic properties mainly consist of continuous browning, a loss of aromatic freshness, and the appearance of precipitates of condensed phenolic material [7,8]. This decay process results in a loss of quality that limits shelf life.

Known factors that strongly influence the redox stability of sherry wines include temperature, dissolved oxygen concentration, quantity and type of polyphenols, and the presence of certain metal ions in the medium that can act as process activators [12,18]. Ferric cation (Fe^{3+}) is the main metallic element capable of producing alterations in wines, followed by cuprous cation (Cu^{+}). However, because the redox potential of the biologically aged wines is in the range of 350 to 400 mV, the normal oxidation states of those elements are Fe^{2+} and Cu^{2+}. The previous redox history of a wine can also influence oxidation phenomena, as it determines redox [11].

Numerous studies carried out in order to suppress the natural oxidation of sherry target the minimization of the above factors. In particular, the separation of metals could constitute a significant stage in the industrial process of sherry winemaking; especially in a situation in which the wine has suffered long biological aging and media is very sensitive to oxidation.

Among the industrial treatments described for the demetallization of wines, the most common with sherry is "blue clarification," or the potassium ferrocyanide method [14]. The dosing of this compound constitutes an effective preventive treatment of the ferric and cuprous turbidity in wines, as the separation percentages of metals usually obtained with this treatment are 65 to 80% for iron and 85 to 97% for copper [19]. However, this technique has the inconvenience of producing solid residuals or wastewater, which are difficult to manage, and has a limited effectiveness in terms of the redox evolution.

At present, the application of ion exchange resins for demetallization of wines is not a widespread practice in the winemaking industry. Recently, certain resins with high adsorption capacity for oxidized polyphenols and unstable proteins have been used in the United States, which also demonstrate demetallization capacity [3,17]. However, at this point they are not specifically used for wine deferrization.

Some studies have shown that iminodiacetic acid has great selectivity with respect to the metallic elements [5,15]. The first applications of metal ion exchange techniques on wine used filters of cellulose-iminodiacetic acid for the separation of lead and copper [4]. Later studies examined the main factors that affect the demetallization of wines using chelating resins with iminodiacetic active groups [6]. The results indicated the effectiveness in removal of iron and copper ions. Moreover, studies using adsorbent polymers of polyvinylimidazol at the semi-industrial scale demonstrate that while they reduce the content in catechins and hydroxycinnamic esters, they also have a certain demetallization capacity [9].

The experimental procedure of this work centers on determining the contribution of each factor to the oxidation phenomena in biologically aged sherry wines. The influence of dissolved oxygen concentration, temperature, ferric cation concentration, and container size in the evolution of the oxidation process are analyzed. Moreover, the effect of the application of ion exchange resins for the demetallization of sherry wine is studied, evaluating the possible changes in redox stability.

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Materials and Methods

Influence of dissolved oxygen. In order to study the influence of dissolved oxygen concentration on oxidation phenomena, multiple samples of prebottled industrial sherry wine of the fino type were used (general characteristics noted in Table 1).

Several aliquots of 250 mL of wine were sterilely aerated or gassed with nitrogen to reach various dissolved oxygen levels. Initial oxygen in the samples was determined by the polarografic method [2], and then samples were sealed in Winkler flasks and submitted to an oxidative stability test (OST). This test consisted of incubating the sample in a dark chamber at 45°C for 10 days, and then calculating the difference in the color index between final and initial values. The color index of sherry is normally established by determining the absorbance at 470 nm, in absorbance units (Abu) [16]. As it is expected that the oxidation process directly affects the color of samples, a large increment of the optical density will demonstrate that important oxidation phenomena have occurred. Triplicated samples were used for each oxygen concentration and the average data were studied.

Influence of container size. For this study several samples of the wine were bottled in different containers, using a standard industrial system equipped with an inertization device with nitrogen. The following sizes were tested: 375 mL, 700 mL, 750 mL, and 1000 mL. The average value of the inertization achieved in the headspace of containers was 46% (gas at 54% of air). All samples were sealed and stored at room temperature in a dark chamber for two years. During this time, the change in the optical density at 470 nm in each sample was measured.

To avoid alterations of the samples due to analytical manipulation, multiple flasks of each size were generated, but only three of each were removed from the storage chamber, opened, and analyzed at each time interval. As in previous studies, it was expected that the color of samples would be directly related to oxidation processes and that a higher optical density would demonstrate occurrence of oxidation phenomena.

Influence of temperature. To determine the influence of temperature on the oxidation rate, multiple samples of the wine were sparged with nitrogen to an initial concentration of dissolved oxygen of 4.0 mg/L, sealed in 250 mL Winkler flasks, and then incubated at four storage temperatures (27, 30, 36, and 45°C) in a dark chamber for 10 days. The absorbance at 470 nm was followed as in the other experiments.

Table 1 General composition of sherry wine of the fino type used in the laboratory experiments and ion exchange trials.

Parameter	Value
Alcohol grade (v/v)	15.5
Total sulfurous (mg/L)	94.3
Total acidity (gTH_2/L)	5.25
Volatile acidity (gAcH/L)	0.22
pH	3.35
K (mg/L)	607
Na (mg/L)	21
Ca (mg/L)	66
Mg (mg/L)	56
Fe (mg/L)	3.1
Cu (mg/L)	0.32
Color index (Abu)	0.080
Protein index (mg/L)	0.65

Influence of ferric ion concentration. It is well known that metal ions (such as ferric and cuprous) can influence oxidation processes, and for this reason the influence of ferric ion concentration on the oxidation phenomena of sherry wine was studied. This analysis was divided into two parts: influence on commercial wines and influence on a demetallized wine.

To determine the influence of the ferric content on commercial wines, multiple samples of different sherry wines of the fino type were taken from the market (more than 30 brands). In each case, the content in total dissolved iron was determined by atomic absorption [1]. All samples were aerated until saturation (around 8.6 mg/L oxygen) and sealed in 250 mL Winkler flasks. As in previous experiments, all flasks were submitted to a standard OST (45°C, 10 days).

To determine the influence of the demetallization technique on the redox stability of media, a sample of the wine was percolated through an ion exchange resin until its content in dissolved metal ions was undetectable (Fe2+/3+, Cu+/2+, Zn2+, Hg2+, Pb2+, and so on). The resin used was a complexing type, which presented the iminodiacetic group as active ligand.

Once the samples were demetallized, different quantities of a ferric salt were added (ferrous sulfate) in order to obtain a range of iron concentrations from 1 to 10 mg/L, free from other metal ions. Finally, all samples were aerated until saturated and submitted to a standard OST, as in previous experiments.

Results and Discussion

The kinetic model. Under standard conditions, oxidation phenomena can be considered as oxidation reactions where the two general reactants are the oxidizable matter (polyphenols and others) and the oxidant (dissolved oxygen) and the general product is the oxidized matter (condensed polyphenols and others). It can be described as:

$$\mathrm{OBM} + \mathrm{DO} \rightarrow \mathrm{OXM} \qquad (1)$$

Where OBM is the oxidizable matter, DO is the dissolved oxygen, and OXM is the oxidized matter. The general oxidation rate depends on the concentration of reactants and the oxygen consumption rate (-d[DO]/dt) is the following:

$$-\frac{d[\mathrm{DO}]}{dt} = k\,[\mathrm{OBM}][\mathrm{DO}] \qquad (2)$$

At low oxygen concentrations, it can be assumed that oxygen is the limiting reactant. The concentration of oxidizable matter can be proposed to be much greater than the oxygen concentration and constant. Thus, if it is considered that $k\,[\mathrm{OBM}] = K_{ox}$, the oxidation rate obtained depends directly on the dissolved oxygen concentration. In consequence, integrating the rate expression, the following is obtained:

$$[\mathrm{DO}] = [\mathrm{DO}_0]\exp(-K_{ox}\,t) \qquad (3)$$

Where $[DO_0]$ is the initial dissolved oxygen concentration, at $t = 0$. Equations 2 and 3 suggest a decreasing exponential evolution of the oxidation process.

In the laboratory experiments, absorbance increment has been measured as indicative of oxidized matter, as they are associated. Considering the concentration of the oxidized matter formed (in mg/L) as proportional to the concentration of the dissolved oxygen consumed (in mg/L), $[OXM]_F = \alpha\ [DO]_C$. Moreover, bearing in mind that $[DO]_C = [DO_0] - [DO]$ and applying eq. 3, we have:

$$[OXM]_F = \alpha\ [DO_0]\ (1 - \exp(-K_{ox}\ t)) \tag{4}$$

Finally, if the absorbance increment is considered proportional to the oxidized matter formed ($\Delta Ab = \beta\ [OXM]_F$), eq. 4 can be transformed:

$$\Delta Ab = \Delta Ab_f\ (1 - \exp(-K_{ox}\ t)) \tag{5}$$

Where ΔAbf is the final absorbance increment achieved and is equivalent to $\alpha\beta[DO_0]$. In consequence, eq. 5 can represent the general evolution of the absorbance during the oxidation phenomena.

Of course, eq. 5 is only valid at low oxygen concentrations in comparison with the concentration of oxidizable matter, but these are the normal conditions in the process, where total polyphenols are greater than 100 mg/L and oxygen is not higher than 10 mg/L (total saturation). Another observation in eq. 5 is that K_{ox} must acquire lower values in successive oxygen dosages, as [OBM] diminishes.

Influence of dissolved oxygen. Because oxygen is the basic oxidizing agent in the oxidation process, there is logically a relationship between its concentration in the medium and the resulting oxidation degree in the wine. In the OST carried out at different initial dissolved oxygen concentrations, different absorbances were reached (Table 2).

The temperature conditions and the storage time of the OST suggest that the final kinetic level of oxidation had been reached in all the samples at the end of the tests, so the achieved ratio $\Delta Ab/DO_0$ corresponds to the constant $\alpha\beta$, as is proposed above.

For the test conditions and from the experimental data (Table 2), this ratio has an average value of $12.28 \cdot 10^{-3}$ Abu/mg/L. The test conditions (temperature incubation, storage time, oxidizable matter in the wine tested, Fe content, and so on) influence the changes in absorbance with time and, therefore, this ratio value. However, the standard conditions of the OST described above can be used as a reference for comparative studies with other variables.

Table 2 Absorbance increment at 10 days of storage (ΔAb) for samples with different initial content in dissolved oxygen (DO_0).

DO_0 (mg/L)	ΔAb (Abu)
0.3	0.007
1.3	0.017
2.6	0.023
3.5	0.030
4.5	0.034

Influence of container size. The effect of the presence of oxygen on the stability of wines is well known in the winemaking industry, and several techniques have been implemented at an industrial scale to prevent the action of this oxidant. An operation used frequently in the Sherry zone is sparging deposits and pipes through which the wine passes with nitrogen. However, most of the current bottling systems are not equipped with appropriate devices for the elimination of air that remains in the necks of the bottles after they are filled.

It is necessary to indicate that although the DO in the wine introduced to bottles is relatively low (0.3 to 0.6 mg/L), it is not the value obtained in the wine after bottling. The reason is that the gas present in the internal atmosphere of the flask during the filling operation can oscillate from 30 to 60% of the total saturation concentration. The existence of this oxygen in the gas will allow oxidation phenomena to occur in the wine.

Another important factor that can contribute to the oxidation process is the diffusion of the oxygen through the plugs or caps in the stored bottles, which is why several seals were proposed in the winemaking industry of the Sherry zone. The traditional long plug of cork was used initially, but merchants discarded it due to opening and closing difficulties. A "crown" plug was later proposed, which is shorter, easier to use, and has a polymeric head that provides a seal to the bottle. However, because of an inadequate seal in the crown model, another plug format was tried consisting of an aluminum capsule with hermetic sealing.

Theoretical calculations were performed to determine the quantity of oxygen that could be dissolved in the wine after bottling, based on the four container sizes under study (Table 3). The 375 mL size had the highest quantity of dissolved oxygen after the bottling operation (near to saturation). There was little difference between the 700 mL and 750 mL sizes.

The change in absorbance with time was followed for two different container sizes (Table 4). The 375 mL size displayed the highest oxidation.

Table 3 Theoretical quantity of oxygen in the head space (HSO) for several bottle sizes and oxygen dissolved later in the wine (DO), for head space at 54% of air.

Bottle size (mL)	Head space (mL)	HSO (mL)	DO (mg/L)
375	17	1.9	7.4
700	25	2.8	5.8
750	25	2.8	5.4
1000	25	2.8	4.1

Table 4 Absorbance at 470 nm (Abu) for two bottle sizes (ranges for confidence 95%).

Bottle size	t = 0	t = 6 months	t = 1 year	t = 2 years
375 mL	0.056 ± 0.003	0.077 ± 0.002	0.088 ± 0.002	0.102 ± 0.003
750 mL	0.056 ± 0.002	0.074 ± 0.001	0.081 ± 0.002	0.092 ± 0.002

The shape of the absorbance curves suggests an exponential conversion from the oxidizable to the oxidized matter. The kinetics of the oxidation phenomena can be well approximated by the first-order type proposed in eq. 5. The kinetic parameters have been calculated by iterative linearization of the experimental curves. In the case of the 375 mL size, $K_{ox} = 1.017 \cdot 10^{-4}$ h^{-1} and $\Delta Ab_f = 0.0559$ Abu ($R^2 = 0.998$); and for the 750 mL size, $K_{ox} = 1.139 \cdot 10^{-4}$ h^{-1} and $\Delta Ab_f = 0.0418$ Abu ($R^2 = 0.994$).

These ΔAb_f values confirm the higher oxidation state expected in media rich in oxygen and highlight the conditions of the 375 mL size compared to the 750 mL. Moreover, according to the initial DO values estimated in Table 3, the ratio $\Delta Ab_f/DO_0$ can also be calculated for the conditions of this experiment, resulting in an average value of $7.65 \cdot 10^{-3}$ Abu/mg/L. This ratio is slightly lower than that obtained before due to the dispersion of experimental data. However, when the whole data set of ΔAb_f and DO_0 is computed in a linear estimation, the value of the $\alpha\beta$ constant is $7.85 \cdot 10^{-3}$ Abu/mg/L ($R^2 = 0.944$).

It can be established that the overall kinetic constant for the oxidation process (K_{ox}), under the storage conditions of the test, is on the order of $1 \cdot 10^{-4}$ h^{-1}. This low value indicates how slow the process is at room temperature.

Influence of storage temperature. Storage temperature is expected to significantly affect the oxidation process of wines. Table 5 lists the absorbance increments at five different temperatures.

The oxidation degree is much greater at high temperatures than at low ones. At 45°C an absorbance increment of 0.0313 Abu was attained, which is near to the maximum value expected (0.0314) for the DO_0 of the tests (4 mg/L). The kinetic constant K_{ox} has been calculated for each temperature, from the experimental data of absorbance over time (Table 5).

In general, the influence of temperature on reaction rate or chemical process rate is well known and typically of the Arrhenius type. In this case, the form of the equation would be the following:

$$K_{ox} = K^0_{ox} \exp\left(-\frac{E_a}{RT}\frac{T_0 - T}{T_0}\right) \qquad (6)$$

Where K^0_{ox} is the reference value of K_{ox} at temperature T_0, and E_a is the overall activation energy of the process. Those parameters have been calculated by linear regression applied to the experimental data in Table 5. The obtained values are the following: $E_a = 36.92$ Kcal/mol and $K^0_{ox} = 1.86 \cdot 10^{-4}$ h^{-1} at $T_0 = 20$°C ($R^2 = 0.936$). The low value for the activation energy of this process shows how important the storage temperature is in the delay of oxidation phenomena.

Table 5 Absorbance increment at 10 days of storage (ΔAb) and kinetic constant (K_{ox}) for samples stored at different temperatures.

T (°C)	ΔAb (Abu)	K_{ox} (h^{-1})
20	0.0008	$1.08\ 10^{-4}$
27	0.0101	$16.17\ 10^{-4}$
30	0.0121	$20.28\ 10^{-4}$
36	0.0184	$36.74\ 10^{-4}$
45	0.0313	$239.56\ 10^{-4}$

Influence of Fe content. As was expected, the presence of iron in solution contributed decisively to the development of the oxidation phenomena of wines. The final absorbance increment obtained in the standard OST of wines with different Fe content is shown in Figure 1. The conditions of the standard OST were mentioned above (saturated DO_0, 45°C, and storage for 10 days).

As the main difference between samples is the Fe content, this cation exerts an influence on the extent of the oxidation phenomena. The accurate linear variation obtained between the final absorbance increment and the Fe content ($R^2 = 0.907$) must be due to different values of the $\alpha\beta$ constant in each sample.

Developing the kinetic model in eq. 1, if it is assumed that the oxidized matter formed in presence of Fe has a different structure to the one formed in its absence, then we have the following simultaneous oxidation process:

$$\text{OBM} + \text{DO} + \text{Fe} \rightarrow \text{OXM'} \qquad (7)$$

In this case, the new oxidized matter may have different stoichiometry to the other and thereby vary the α ratio (oxidized matter formed to dissolved oxygen consumed). So that now $[OXM]'_F = \alpha' [DO]_C$. By the same token, the new oxidized matter may have a distinct specific absorbance compared to the other and also vary the β ratio (absorbance increment measured to oxidized matter formed). Thus, $\Delta Ab = \beta' [OXM]'_F$. Regardless of whether one or both possibilities occur, the presence of Fe will lead to a different value of the $\alpha\beta$ constant, making this constant proportional to the Fe content. Therefore, the following relationship can be established:

$$\alpha\beta = \alpha\beta_0 + \gamma [Fe] \qquad (8)$$

The values of the parameters $\alpha\beta_0$ and γ have been obtained from the data in Figure 1 by linear regression, resulting $\alpha\beta_0 = 1.17 \cdot 10^{-3}$ Abu/mg/L and $\gamma = 2.29 \cdot 10^{-3}$ Abu/mg/L^2. The slight data dispersion is probably due to the varied nature of samples (content in oxidizable matter and other cations).

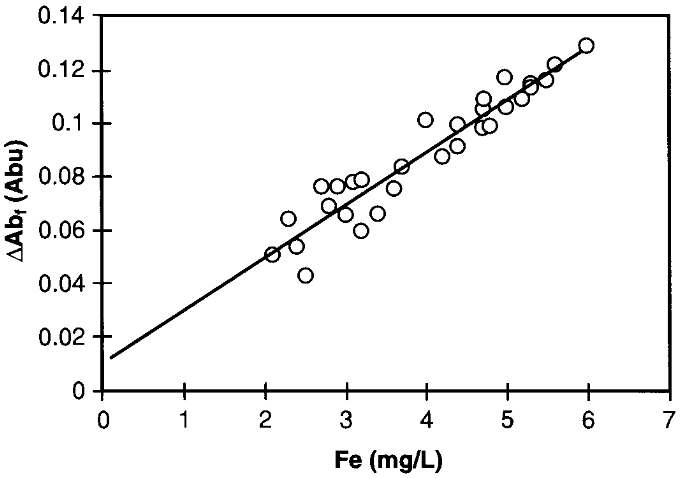

Figure 1 Relationship between the final absorbance increment of the OST (ΔAb_f) in absorbance units (Abu) and the Fe content of the wines in mg/L.

Table 6 Final absorbance increment in the standard OST (ΔAb_f) for samples with different Fe content.

Fe (mg/L)	ΔAb_f (Abu)
0.5	0.009
1.0	0.015
2.0	0.020
3.0	0.028
4.0	0.031
5.2	0.046
8.4	0.067
10.2	0.084

To define the influence of the Fe content and to isolate it from the other cations, a study with demetallized samples was carried out. After demetallization, the samples were supplemented with different Fe contents as described above (Table 6). In this case, the linear parameters obtained are $\alpha\beta_0 = 0.60 \cdot 10^{-3}$ Abu/mg/L and $\gamma = 0.88 \cdot 10^{-3}$ Abu/mg/L^2 ($R^2 = 0.993$).

First, the strong linear dependence obtained again confirms the influence of the Fe content in the oxidation process. Moreover, the lower values of γ obtained for the demetallized samples confirm the possible influence of other cations in the same way as iron. In consequence, the general oxidation phenomena can include different processes like the ones shown in eqs. 1 and 7, but with different oxidizable matter or cations. The observed value of the $\alpha\beta$ constant may be the result of all these processes, and so it could be difficult to establish a unique value for all the sherry brands. Nevertheless, the very low value obtained in both experiments for the $\alpha\beta_0$ constant (Fe absence) demonstrates that the extent of the oxidation process will be lower in iron free samples and even lower in totally demetallized samples.

The complexity of the overall oxidation process leads us to consider the influence of the redox history of the samples as an important factor. According to the proposed kinetic model, different final absorbance values will be obtained in wines aerated and stored in the same conditions, but with a different kind of oxidizable matter, as this leads to different values of k and therefore K_{ox}. Similarly, the final absorbance will be different in samples with different concentration or distribution of metal cations, as this condition determines the value of $\alpha\beta$. Different absorbance increments will be obtained if we submit the same sample to successive identical aeration processes, as the sample has a lower concentration of oxidizable matter each time, which leads to different K_{ox} values.

Conclusions

In general, it has been demonstrated that the main factors that influence the oxidation phenomenon of sherry wine of the fino type are the content of oxidizable matter, level of dissolved oxygen, container size, storage temperature, and iron concentration. These factors can be numerically evaluated following the kinetic model proposed. The model can also explain the complex influence of the redox history of samples in the evolution of the process.

It has been shown that other metal cations distinct from iron can influence the extent of the oxidation process. Therefore, ion exchange technology is suggested as an effective procedure for demetallization of biologically aged sherry wines and for the redox stabilization of these products.

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