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Influence of metallic content of fino sherry wine on its susceptibility to browning

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Abstract

A study has been conducted on the influence of the content of copper, iron, and manganese on the tendency of a "fino" sherry wine to undergo browning. The concentrations considered cover the ranges found for these metals in this type of wine. The content in copper does not seem to have a significant influence on the susceptibility to browning of "fino" sherry wines. In respect to iron, which does influence this process, there are no significant differences in concentrations ranging from 3 to 9 mg/l. For manganese no differences are observed for concentrations ranging from 0.8 to 1.6 mg/l, but concentrations of manganese below 0.8 mg/l prevent the increase in iron content from being translated into an increased susceptibility to browning.

Keywords: Metals; Sherry wine; Browning

1. Introduction

The "fino" wines typical of the Jerez-Xérès-Sherry and Manzanilla de Sanlúcar Denomination of Origin (SW Spain), which are protected from the action of oxygen by the unusual system of biological ageing under the "flor yeast film" (Casas, 1985), are found to be affected by browning after bottling, as are all other white wines.

It has been known (Macheix, Sapis, & Fleuriet, 1991; Singleton, 1987) for many years that this deterioration in the organoleptic and sensorial characteristics represented by the phenomenon of browning is due to the oxidation of the polyphenolic compounds present in the wine. These alterations in the organoleptic properties lead to the rejection of the wine affected, which causes not only financial loss but also loss of consumer confidence in wine. The metallic content of a white wine appears to play an important role in its browning (Berg, & Akiyoghi, 1956). For this reason, producing wineries have for many years been trying to reduce metallic content by adding various substances to the wine. Notable among these is the use of potassium hexacyanoferrate (II) which causes the elimination of part of the iron content, together with significant reductions in the content of other metals that also participate in the browning and are highly contaminating (Mn, Cu, Zn, etc.; Tarantola, 1963).

The use of this complexing agent carries with it the risk of the possible transformation of the excess quantity into hydrocyanic, a highly toxic compound (Tarantola & Castino, 1964) as well as the production of residuals without utility. In recent years, the search has begun for alternative methods that enable the metallic content of the wine to be reduced without altering its composition.

Iron, copper, and manganese are among the metals most actively participating in the browning of white wines (Cacho, Castells, Esteban, Laguna, & Sagristá, 1995; Makris & Rossiter, 2000; Ruzic, 1998–1999). The quantities in which these metals are present in white wines depend on diverse factors, such as absorption from the soil, contamination by atmospheric emissions, herbicidal treatments, the wine-making process, and the addition of fining agents (De las Infantas & Martín, 1997; Scollary, 1997).

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There have been few studies on setting the optimum degree of reduction of the metallic content of specific white wines in the context of achieving a significant control over its tendency to suffer browning.

This study sought to determinate the degree of participation of iron, copper, and manganese in the browning of "fino" sherry wine. A secondary objective was to study the possible synergic relationships that could result from the coexistence of these metals in the wine, and how these might influence this deterioration that affects white wines.

2. Material and methods

"Fino" sherry wine (ethanol content of 15% v/v) from the Jerez-Xérès-Sherry region (SW Spain) that had been biologically aged for two and a half years was subjected to the addition of iron, copper, and manganese, both individually and in various combinations.

2.1. Samples

Samples of 300 ml volume of wine were prepared, in duplicate, by adding increasing amounts of iron sulfate, copper sulfate, and manganese sulfate. Samples were kept in 0.5-l bottles of topaz glass at room temperature for 5 days until they were analyzed. A total of 128 samples were studied. The final concentrations in the samples were: 3.19, 6.24, 9.20, and 12.23 mg/l for iron; 0.021, 0.042, 0.083, and 0.212 mg/l for copper; and 0.422, 0.821, 1.23, and 1.64 mg/l for manganese. These concentrations cover the ranges found for these metals in this type of wine.

Subsequent tests in which the iron and manganese concentrations were held fixed (9.2 and 1.23 mg/l, respectively) while that the copper concentration was increased in stages from 0.042 to 1.86 mg/l were also carried out.

2.2. Determination of metallic content

In the wine samples, Fe, Cu, and Mn were determined by flame atomic absorption spectrometry (FAAS) using an Unicam Model 939 atomic absorption spectrometer. The following conditions were used for determining Fe, Cu, and Mn in an acetylene–air flame: wavelengths of 248.3, 324.8, and 279.5 nm; lamp currents of 15, 10, and 12 mA; warm-up of 75, 90, and 75%; and bandpass of 0.2, 0.5, and 0.2 nm, respectively. Flow rate of acetylene and air was 1.0 l/min. Accessory for copper: atoms trap (STAT). The iron, copper, and manganese standard solutions were prepared by dilution of 1000 mg/l stock solutions (Merck), using ethanol (15% v/v) and Milli-Q water.

2.3. Determination of the polyphenolic profile

Eighty microlitres of filtered wine (0.45 μm) was analyzed, in duplicate, by HPLC. Mobile phases employed were: solvent A (95% water, 5% methanol) and B (95% methanol, 5% water) at pH 2.5 (super-pure sulphuric acid). Elution phases: gradient elution from 100 to 85% solvent A (5 min), gradient elution from 85 to 50% solvent A (40 min) and isocratic elution (35 min). The analyses were carried out using a C_{18} column (Lichropher 100 RP-18, 250 mm×3 mm, 5 μm particle size) at a flow rate of 0.5 ml/min; and detection at 280 and 320 nm.

The polyphenolic compounds were identified by comparison with a library of DAD spectra and retention times of standards. Commercial standards were purchased from Fluka (Buchs, Switzerland) and East Kodak (Rochester, NY). Caftaric and coutaric acids were isolated by the method described by Singleton, Timberlake and Lea (1978). Each compound was quantified by comparison with a calibration curve obtained with the corresponding standard, except GRP (2-S glutathionyl caftaric acid) that was quantified as caftaric.

2.4. Determination of susceptibility to browning

Each sample was subjected, in duplicate, to a process of electrochemical oxidation using equipment devised by our research group (Barroso & Palma, 1996). Briefly, 120 ml of wine were used for each analysis and 1.5 V was used as the electric potential difference between the sample and the reference solution (distilled water containing 400 g/l zinc acetate). Two platinum electrodes were used. The susceptibility to browning was quantified as the increase in absorbance recorded at 420 nm ("y") against the electrical current ("x") applied (Palma, Barroso, & Pérez-Bustamante, 2000). Previous analytical methods carried out to evaluate the susceptibility of wine to browning are based on heating the sample (Berg & Akiyoghi, 1956), but it has been demonstrated that the reactions due to this high temperature are different to those produced during natural browning (Ferreira, Escudero, Fernández, & Cacho, 1997). This equipment allows, however, that the susceptibility of a wine to browning to be determined rapidly and reliably, without waiting for this phenomenon to evolve naturally (Palma et al., 2000).

2.5. Statistical treatment

Analysis of variance was conducted using the Statgraphics Statistical Computer Package "Statgraphics Plus 3.1″ for Windows 95. In this case the independent variables to be considered were concentration of iron, concentration of copper, and concentration of

manganese; the response variable considered was the increase in browning observed for the wine with the metallic addition, compared with that observed for the wine without addition.

Cluster analyses were performed on color and polyphenolic data from the duplicate samples after 4 months at room temperature. For color, three variables were used: absorbance values at 420, 490, and 520 nm. Polyphenolic compounds used in this study were: gallic acid, tyrosol, *p*-hydroxybenzaldehyde, syringic acid, caftaric acid, GRP, protocatechualdehyde, *cis p*-coutaric acid, *trans p*-coutaric acid, caffeic acid, *cis p*-coumaric acid, *trans p*-coumaric acid, *i*-ferulic acid, ferulic acid, catechin, and epicatechin. In this case, mean values found for each polyphenol and sample were employed.

3. Results and discussion

Fig. 1 shows the mean susceptibility to browning observed for the wine without addition, and for the wine presenting the highest concentration of each metal (12.23 mg/l for iron, 0.212 mg/l for copper, and 1.64 mg/l for manganese). The wine subjected to the addition of metals presented, before the application of the electrochemical test for browning (after five days at room temperature), a more intense color (measured by absorbance at 420 nm) than that observed for the control wine, without addition. After the test for browning, this difference between the two samples continued to be evident, with the wine containing the highest concentration of metals reaching a level of browning clearly greater than that observed for the control wine. This makes evident the catalytic effect that these metals produce on the tendency of a "fino" wine to undergo browning, clearly increasing the susceptibility of this wine to suffer this type of deterioration.

Table 1 gives the results obtained from the multifactorial analysis of variance performed on increment of browning. In the range of concentrations considered for copper (0.021–0.212 mg/l), variations in its concentration do not produce significant changes in the degree of browning suffered by the wine. This would imply that for this range, an increase in the content of copper present in the wine would not increase its susceptibility to browning. This finding was corroborated in subsequent tests in which the iron and manganese concentrations were held fixed (9.2 and 1.23 mg/l, respectively) while that the copper concentration was increased in stages from 0.042 to 1.86 mg/l. The results obtained demonstrated significant increases in the tendency of the wine to undergo browning for the highest concentrations of copper tested (0.621 and 1.86 mg/l), whereas little variation was observed for concentrations in the lower range (from 0.042 to 0.212 mg/l).

Iron and manganese produced significant effects ($p < 0.01$) on the tendency of "fino" wine to suffer browning, with a positive influence on this phenomenon being observed. Tables 2 and 3 present the results obtained from the study of comparison of means using the Tukey's test for iron and manganese. For iron the concentrations within the range from 3 to 9 mg/l did not

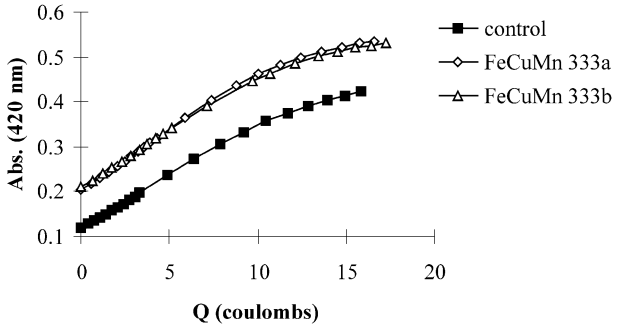

Fig. 1. Susceptibility to browning. Control wine and wine after five days of the addition of iron (12.23 mg/l, final concentration), copper (0.212 mg/l, final concentration) and manganese (1.64 mg/l, final concentration).

Table 1
Multifactorial analysis of variance for increase in browning. Main effects and interactions

Independent variable (factor)	*F*-ratio	*P* value[a]
Fe	50.33	0.000a
Cu	3.70	0.057
Mn	36.11	0.000a
Fe–Cu	1.31	0.254
Fe–Mn	29.70	0.000a
Cu–Mn	0.00	0.962
Fe–Cu–Mn	8.03	0.005a

[a] Values with the same letter are significantly different at $P < 0.01$.

Table 2
Comparisons among the means of Fe, [Tukey's honestly significant differences (HSD) test]

Fe (mg/l)	Fe (mg/l)	Means differences	*P* value[a]
3.19	6.24	−0.0045	0.956
	9.20	−0.0153	0.296
	12.23	−0.0449	0.000a
6.24	3.19	0.0045	0.956
	9.20	−0.0108	0.601
	12.23	−0.0452	0.000a
9.20	3.19	0.0153	0.296
	6.24	0.0108	0.601
	12.23	−0.0343	0.000a
12.23	3.19	0.0450	0.000a
	6.24	0.0452	0.000a
	9.20	0.0343	0.000a

[a] Means with the same letter are significantly different at $P < 0.01$.

demonstrate significantly different effects in terms of the influence on the browning of the wine. Only the highest concentration tested, 12.23 mg/l, was found to be significantly different from the other concentrations. For manganese in the range of concentrations from 0.8 to 1.64 mg/l, no statistically significant differences appear to exist in respect to its influence on the susceptibility to browning.

In respect to the two-factor interactions, only that of iron-manganese appears to produce significant effects on the degree of browning observed for the samples of wine to which the metals were added.

Fig. 2 presents the effect of these interactions on the increase in browning. Each line represents the effect of the content of the first metal, with the points corresponding to identical concentrations of the second metal being joined. If the effects of each metal on the browning were simply cumulative, parallel lines would be obtained for each metal–metal interaction; the clearly absence of this parallelism would lead us to postulate the existence of synergic relationships between the two metals. As can be seen, iron–manganese interaction presented this clear absence of parallelism.

Fig. 3 presents the effect of the iron–manganese interaction for each concentration on the increase in browning. At low concentrations of manganese (0.422 mg/l) no increase is observed in the tendency of the wine to undergo browning when the concentration of iron is increased, whereas for concentrations of manganese equal to or greater than 0.821 mg/l, it is found that there is a strong increase in the tendency to browning, in line with the increase in the concentration of iron.

This could be evidence that, in order for iron to act as a catalyzer of the phenomenon of browning, the presence of manganese is needed. Cacho et al. (1995) found that these two metals intervene as catalyzers of the process of browning, with different actions taking place: whereas the presence of manganese encourages the formation of acetaldehyde, the iron catalyzes the combination of this compound with the polyphenolic compounds to give rise to polymers that readily precipitate out and thus can be easily eliminated from the wine. This would explain the dependence that the iron presents with respect to the manganese when acting as catalyzer of the browning phenomenon.

Fig. 4 shows the results obtained from the study of similarity to which the duplicate samples corresponding to the wine with the combined addition of iron, copper, and manganese, were subjected. The variables considered were the values of absorbance at 420, 490, and 520 nm (a), and polyphenolic content (b) that the samples presented after being kept for 4 months at room temperature. These wavelengths are those that characterize the evolution of the color associated with the phenomenon of browning in white wines while the polyphenolic content is directly involved in the browning reactions. For the first study (A), the samples are grouped in function of the iron content. Two well-differentiated

Table 3
Comparisons among the means of Mn [Tukey's honestly significant differences (HSD) test]

Mn (mg/l)	Mn (mg/l)	Means differences	p Value[a]
0.422	0.821	−0.0489	0.000a
	1.23	−0.0512	0.000a
	1.64	−0.0473	0.000a
0.821	0.422	0.0489	0.000a
	1.23	−0.0023	0.992
	1.64	0.0018	0.996
1.23	0.422	0.0512	0.000a
	0.821	0.0023	0.992
	1.64	0.0042	0.960
1.64	0.422	0.0473	0.000a
	0.821	−0.0018	0.996
	1.23	−0.0042	0.960

[a] Means with the same letter are significantly different at $P < 0.01$.

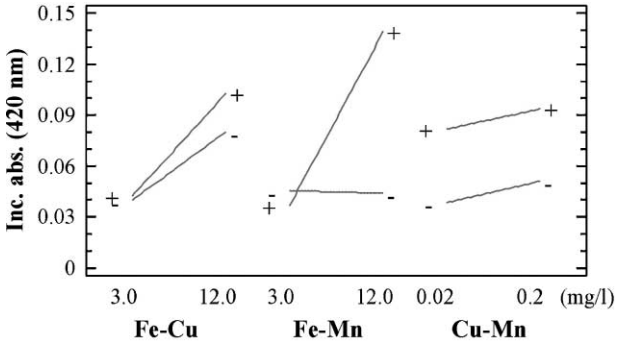

Fig. 2. Two-factor interactions plot for increase in browning (absorbance at 420 nm).

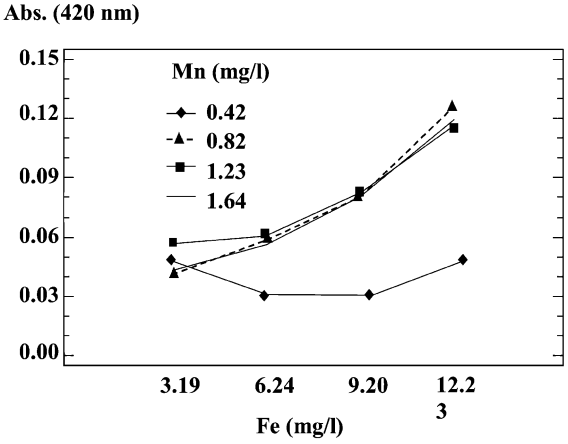

Fig. 3. Fe–Mn Interaction plot for increase in browning (absorbance at 420 nm).

clusters appear; those wines to which the lower doses of iron (6.24 and 9.20 mg/l) were added constitute the first of these, and the second is constituted by those wines with the highest concentration of iron tested (12.23 mg/l). These last samples had undergone a main evolution in color while the wine without addition of metals presented the least evolution (Table 4). For the study B, the dendrogram obtained reinforced the finding that the iron content of a wine exerts a greater influence on the tendency to oxidation of the polyphenolic compounds present than the other two metals. Two clear clusters again appear: one constituted by the samples with lower concentrations of iron, and a second by all those with iron concentrations close to 12 mg/l, that presented a slight lower polyphenolic content (Table 4). These findings were in agreement with the lack of statistically significant difference, in function of their influence on the susceptibility to browning, for the concentrations of iron in the range from 3 to 9 mg/l.

In summary, for the range of concentrations considered, only iron and manganese appear to influence on the susceptibility of ''fino'' sherry wine to browning. The tendency to suffer this phenomenon increases as the concentration of these two metals increases. For iron, concentrations from 3 to 9 mg/l and for manganese, concentrations from 0.821 to 1.64 mg/l, did not demonstrate any significantly different degree of influence on the susceptibility of ''fino'' sherry wine to browning. The existence of synergism was observed for iron and manganese. It would appear that, for the iron content to act as a catalyst for the process of browning, manganese must also be present. Consequently, in addition to techniques for reducing the iron content, other techniques must also be sought to enable the

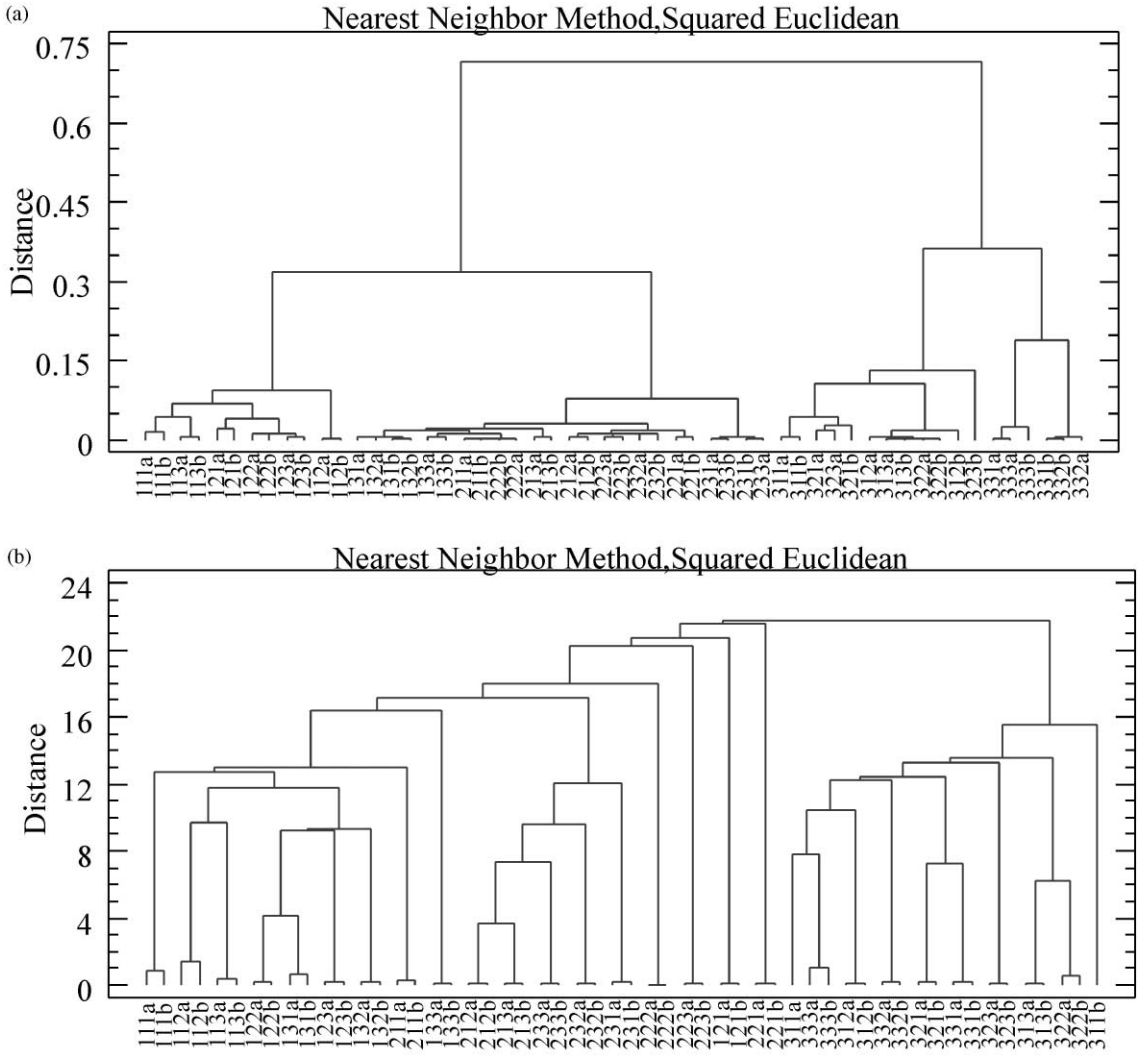

Fig. 4. Cluster analysis performed on color (a) (absorbance at 420, 490 and 520 nm) and polyphenolic compounds (b) of samples after 4 months at room temperature. First number = iron content (1: 6.24 mg/l; 2: 9.20 mg/l; 3: 12.23 mg/l); second number = copper content (1: 0.042 mg/l; 2: 0.083 mg/l; 3: 0.212 mg/l) and third number = manganese content (1: 0.821 mg/l; 2: 1.23 mg/l; 3: 1.64 mg/l).

Table 4
Mean values of polyphenolic compounds (mg/l) and color for samples corresponding to the wine with the combined addition of iron, copper and manganese

Samples	Polyphenolic compounds and color (absorbance at 420 nm)																
	Color (420 nm)	Caftaric acid	PTALDH	CPCT acid	TPCT acid	Caffeic acid	CPCM acid	TPCM acid	*i*-Ferulic acid	Ferulic acid	GRP acid	Gallic acid	Tyrosol	Syringic acid	Catechin	Epicatechin	OHBEAL
111	0.210	39.64	1.36	4.44	10.71	5.15	1.52	2.58	2.19	3.80	3.29	4.49	31.33	0.82	10.33	13.87	0.94
112	0.202	39.31	1.43	4.03	10.76	4.95	1.47	2.52	2.19	3.65	3.00	3.67	29.08	0.54	9.24	13.18	0.87
113	0.211	39.23	1.48	4.13	10.73	4.93	1.44	2.48	2.24	3.64	3.90	3.57	28.84	0.78	9.88	13.29	0.81
121	0.228	39.97	1.42	4.56	10.59	5.02	1.48	2.51	2.38	3.78	3.03	3.75	35.78	0.80	10.21	13.78	0.89
122	0.223	39.24	1.34	4.21	10.82	5.07	1.49	2.57	2.17	3.88	3.08	3.84	30.01	0.74	9.54	14.00	0.83
123	0.226	39.83	1.51	4.30	10.86	5.13	1.48	2.60	2.18	3.76	2.98	3.99	31.77	0.60	10.52	12.06	0.89
131	0.247	39.85	1.45	4.19	10.98	5.10	1.47	2.60	2.14	3.84	2.88	3.87	30.87	0.71	9.74	14.01	0.84
132	0.249	39.63	1.55	4.06	11.57	5.31	1.50	2.69	2.18	3.94	3.14	4.02	31.27	0.87	9.57	14.17	0.89
133	0.252	39.96	1.35	4.12	11.34	5.23	1.50	2.65	2.20	3.89	3.35	3.81	35.82	0.77	9.93	14.54	0.95
211	0.253	38.16	1.49	4.27	10.93	5.10	1.51	2.59	2.12	3.86	3.04	4.45	30.51	0.96	10.22	13.45	0.85
212	0.255	39.39	1.57	3.99	11.44	5.22	1.49	2.39	2.14	3.90	3.26	4.55	30.20	0.45	9.74	13.73	0.90
213	0.248	38.68	1.62	3.97	11.56	5.22	1.49	2.45	2.14	3.94	3.28	4.46	30.30	0.31	9.63	13.54	0.93
221	0.266	39.71	1.52	4.29	11.27	5.23	1.62	2.38	2.18	3.96	2.80	4.74	29.85	0.35	10.97	13.53	0.88
222	0.254	39.39	1.69	4.08	12.00	5.33	1.57	2.44	2.23	4.07	3.84	4.95	30.70	0.53	10.16	13.79	0.93
223	0.259	39.64	1.65	4.09	11.82	5.27	1.58	2.42	2.19	4.09	3.21	4.69	30.43	0.45	9.81	13.92	0.66
231	0.283	39.21	1.55	4.17	11.35	5.25	1.55	2.39	2.26	4.06	3.40	4.69	31.51	0.48	10.09	14.25	0.94
232	0.263	38.33	1.59	4.00	11.45	5.15	1.55	2.38	2.14	3.94	3.02	3.72	29.12	0.47	10.45	13.23	0.86
233	0.281	38.43	1.53	4.06	11.39	5.15	1.48	2.42	2.10	3.86	3.26	3.93	29.59	0.37	9.25	13.64	0.93
311	0.296	38.23	1.38	4.01	10.64	5.07	1.41	2.31	2.13	3.90	3.96	4.49	29.63	0.42	9.12	10.50	0.87
312	0.275	39.23	1.52	4.14	10.41	4.99	1.40	2.39	2.18	3.94	3.98	5.05	31.07	0.36	9.05	10.92	0.93
313	0.267	38.64	1.52	4.17	10.05	5.01	1.40	2.31	2.18	3.84	3.98	5.05	38.11	0.35	9.37	11.84	0.92
321	0.307	39.54	1.47	4.06	10.24	4.82	1.43	2.29	2.29	4.03	3.47	5.44	32.43	0.44	9.25	12.99	1.01
322	0.279	38.90	1.60	4.21	10.46	4.88	1.42	2.38	2.19	3.97	3.68	4.87	38.05	0.40	9.11	12.80	0.95
323	0.304	38.72	1.40	4.37	10.07	4.93	1.42	2.34	2.16	3.88	3.63	4.87	30.93	0.37	9.25	12.84	0.92
331	0.333	39.57	1.35	4.07	10.06	4.97	1.45	2.35	2.27	3.83	3.30	5.02	31.10	0.46	9.21	12.91	0.97
332	0.323	39.92	1.55	4.08	10.92	4.97	1.44	2.31	2.23	3.87	3.45	5.01	30.70	0.57	9.33	11.49	0.87
333	0.333	38.05	1.40	4.07	10.81	4.94	1.44	2.37	2.18	3.90	3.41	4.48	30.37	0.50	9.26	10.25	0.75
control	0.167	40.01	1.56	4.57	12.48	5.24	1.50	2.58	2.25	3.87	3.36	4.55	30.96	0.75	10.91	14.56	0.89

First number = iron content (1: 6.24 mg/l; 2: 9.20 mg/l; 3: 12.23 mg/l); second number = copper content (1: 0.042 mg/l; 2: 0.083 mg/l; 3: 0.212 mg/l); and third number = manganese content (1: 0.821 mg/l; 2: 1.23 mg/l; 3: 1.64 mg/l). PTALDH = protocatechualdehyde; CPCT = *cis p*-coutaric; TPCT = *trans p*-coutaric; CPCM = *cis p*-coumaric; TPCM = *trans p*-coumaric; GRP = 2-*S* glutathionyl caftaric acid; OHBEAL = *p*-hydroxybenzaldehyde.

content of manganese present in "fino" sherry wine to be reduced. The content of both metals needs to be reduced in order to achieve the successful reduction of the tendency of this wine to undergo browning.

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