



## Title: “Effect of microoxygenation on anthocyanin and derived pigment content and chromatic characteristics of red wine”

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In: Am. J. Enol. Vit. 57(3):325-331. 2006

The authors applied microoxygenation to Mourvedre, the second most cultivated variety in Spain (better known there as Monastrell or Mataro). Then they investigated how the anthocyanin profile and the chromatic characteristics changed with microoxygenation, as compared to a Control.

- Anthocyanins are unstable compounds that tend to react during fermentation with other phenolic compounds, particularly with flavanols. Several mechanisms have been proposed for the formation of these interactions: 1) direct reactions between anthocyanins and flavanols, 2) reactions involving acetaldehyde, with the formation of complexes linked by an ethyl bridge, and 3) formation of pyranoanthocyanins (anthocyanins attached to a pyran ring), in which acetaldehyde is also involved. Acetaldehyde is a natural compound in wines, where it is produced either by 1) yeast metabolism during fermentation, and by 2) ethanol oxidation. Of the three mechanisms of phenolic interaction described above, only those involving acetaldehyde (the last two) are expected to be favored by the presence of oxygen (microoxygenation).

- Microoxygenation is a technique that, as the authors point out, has existed for as long as vintners have put wine into barrels. In its more modern sense, it refers to the treatment of a wine with well-controlled doses of oxygen over short periods of time. This normally involves the use of a diffuser that injects minuscule amounts of oxygen into the wine, producing microbubbles which rise and dissolve as they travel upwards to the surface. Microoxygenation can start at any point during winemaking, although it is more effective at the end of alcoholic fermentation and before malolactic fermentation is completed (addition of SO<sub>2</sub> greatly decreases its efficacy). Microoxygenation can have the following beneficial effects in a wine: 1) improve structure and body, 2) remove sulfides and reductive aromas, 3) stabilize color, and 4) reduce herbaceous characters. But the technique is not risk-free. Too much oxygen can 1) form molecules that become too large, causing precipitation of polymeric material, 2) leave the wines with reduced color, 3) cause irreversible oxidation of a wide range of substrates that can be detrimental, and 4) have adverse effects on microbial activity (mainly increased VA).

- During harvest 2003, the authors compared a commercial-scale (4,600 gallons) control wine with two microoxygenated wines, one receiving twice the dose of oxygen of the other. Microoxygenation began just after alcoholic fermentation finished, and was discontinued when malolactic fermentation started. It then resumed at a lower rate after malolactic fermentation ended, and one month later, the dose was reduced again for a final two weeks of treatment.

	ml/l/month of O <sub>2</sub>		
	<i>31 Oct-21 Nov</i>	<i>21 Jan-25 Feb</i>	<i>26 Feb-12 Mar</i>
Control	0	0	0
Low dose	5	3	1.5
High dose	10	5	2.5

- The wine was analyzed at two stages, 1) before microoxygenation started, and 2) 15 days after it stopped (last oxygen applied takes about 10 days to dissolve). The authors measured **anthocyanins** using high performance liquid chromatography (HPLC), and further confirmed peak identity with HPLC-mass spectrometry. **Color determination** was by absorbance (A420, A520, A620, and percentage of yellow, red and blue) and CIELab parameter determination (L\*=measure of lightness, a\*=measure of chroma, b\*=measure of hue angle). They also used the method of Levengood and Boulton to calculate the following **color parameters**: *total color* (adding HCl to convert all anthocyanins to the flavylium form), *total color of pigments* (adding acetaldehyde to release all anthocyanins attached to SO<sub>2</sub>), and *color due to derivatives resistant to SO<sub>2</sub>* (adding SO<sub>2</sub> before measuring absorbance). And here is what they found.

- **Effect on anthocyanins.** In their chromatograms, the authors detected 4 main categories of “anthocyanins” (peaks), or anthocyanin-derived pigments. This is how microoxygenation affected these peaks. 1) **Microoxygenation caused a decrease in the monoglucoside anthocyanins.** These compounds also decreased with time, even in the Control. Pyranoanthocyanins are important in the color of a wine because they incorporate a ring that strongly increases their stability. Some of the more important pyranoanthocyanins are called *vitisins*. Vitisins increased in the microoxygenated wine, the highest dose having the greatest increase. Because some pyranoanthocyanins other than vitisins decreased in the microoxygenated wines, 2) there was no overall difference in pyranoanthocyanins between the microoxygenated wine and the Control. 3) **The concentration of ethyl-linked compounds increased in all of the microoxygenated wines.** Finally, 4) there was no difference in the compounds formed by direct reaction of anthocyanins with flavanols between the microoxygenated and the Control wines. (Sorry we are diving anthocyanins into a zillion types, but these peaks represent anthocyanins in different condensation states, and we do need to understand how microoxygenation affects each of them).

- **Effect on chemical composition.** A greater increase in pH, and a greater decrease in TA, were observed in the Control wine compared to the wines that had been microoxygenated. So microoxygenation seems to have protected –or added to- the natural wine’s acidity. No increase in volatile acidity, or acetaldehyde accumulation, was observed in any of the microoxygenated wines.

- **Effect on color.** The microoxygenated wines had higher color intensity (by absorbance). As for the CieLab parameters, light (L\*) and hue angle (b\*) decreased in the microoxygenated wine. The decrease in hue might be due to the formation of ethyl-linked compounds, which are purplish in color. *Total color of pigments* (color after converting colorless anthocyanins and bisulfite complex into the red form) was not affected by microoxygenation. But this parameter decreased significantly with time. This decrease was correlated with the loss of monomeric anthocyanins over time. The authors interpret this as the rate of formation of anthocyanin-derived pigments not being able to compensate, or “catch up”, with their natural degradation rate.

- **Correlations.** Color intensity by absorbance did not correlate with the concentration of monomeric anthocyanins –and very little with ethyl-linked compounds. But there was a **very high and significant correlation between color intensity and pyranoanthocyanins. This emphasizes the importance of these compounds in stable wine color.**

In conclusion, microoxygenation of Mourvedre wines on a commercial scale favored reactions that led to a greater formation of pyranoanthocyanins and ethyl-linked compounds. This, in turn, caused an increase of color intensity. Wine microoxygenated with the highest dose showed the highest color intensity. The wines will continue to be monitored to determine whether the improved color of the microoxygenated wines is maintained during barrel aging and bottling.

*Author: Bibiana Guerra, Editor: Kay Bogart. This summary series funded by J. Lohr Vineyards & Wines.*