



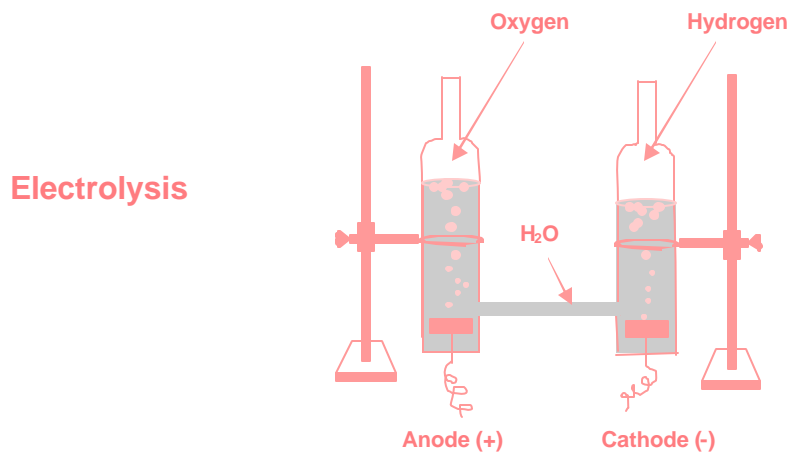
Electrochemical microoxidation of red wine

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- *Oxygen* can be introduced into wine in a variety of ways: 1) through the oak staves and bung in the barrel, 2) in large doses during cellar operations, or 3) slowly, in controlled doses, using microoxygenation. The benefits of wine oxygenation include: changes in astringency through modification of tannin size and structure, decrease of sulfide and vegetative aromas, and stabilization of color through linking of anthocyanins with wine flavanols. This way of introducing oxygen is called **molecular oxidation**, which is the type winemakers are most familiar with.

- An alternative to molecular oxidation is a chemical process called *electrolysis*, which uses electrodes to pass a current through the wine. When this happens, the compounds at the negative electrode –the cathode– tend to be oxidized, and therefore, the process can be called an **electrochemical microoxidation**. The simplest example of electrolysis is the production of hydrogen from water, in which water is split into oxygen –which bubbles at the anode–, and hydrogen –which bubbles at the cathode. In this example, water is “oxidized” to form hydrogen. This is, by the way, how hydrogen gas is industrially produced.



- If you replace water with wine, the result is not hydrogen but instead, *oxidized polyphenols*. A process for electrochemical oxidation of wine in titanium tanks using the passage of small currents was patented in 2002. In this patent, wines treated with microcurrents for 60 days were described as having less free anthocyanins but more color intensity, more anthocyanins present as stable structures, and decreased astringency and bitterness, as judged by wine experts. The advantages of electrochemical microoxidation include: 1) precise control of the applied current to target specific groups of compounds, 2) precise cutoff when desired, and 3) absence of air bubbles in the wine –unlike microoxygenation– which could potentially remove desirable volatile aromas.

• In the current study, the authors used 300-liter stainless steel tanks equipped with a glassy carbon rod as the electrode surface. They passed predetermined currents through a Cabernet Sauvignon wine over a period of 12 weeks. There were 3 treatments: 1) an electrochemically oxidized wine (6144 μA), 2) a microoxygenated wine (4 ml O_2 per liter per month), and 3) an untreated wine (control). The treatments were performed in triplicate. The development of the wines in each treatment was monitored by measuring changes in polyphenols, SO_2 , color, and acetaldehyde. *[Why acetaldehyde? When polyphenols oxidize, a chain of reactions occurs that ends with the oxidation of ethanol to acetaldehyde. Once formed, acetaldehyde has the ability to link anthocyanins with flavanols, forming both unstable and stable pigments. Thus, acetaldehyde is used as a sign of polyphenol oxidation.]*

• **Effect on SO_2 .** Total SO_2 (by aspiration method) did not change significantly in the control wines by Week 12 (30 mg/L). In contrast, SO_2 in the microoxygenated wines declined to 11 mg/L in the same period. Wines treated with electrochemical microoxidation retained the same total SO_2 as the control, but with a considerable portion (63%) in the bound form. The authors attribute this to SO_2 binding to the increased acetaldehyde levels formed in the electrochemical-microoxidation wines. Therefore, a significant amount of the applied current at the electrode went into the direct oxidation of ethanol to acetaldehyde.

• **Effect on acetaldehyde.** Indeed, acetaldehyde (gas chromatography) mostly remained at 1 mg/L in all wines, whereas it climbed to 10 mg/L in the electrochemical microoxidation wines only. Thus, it became apparent to the authors that ethanol was directly oxidized to acetaldehyde in the electrochemical microoxidation treatment, and that this acetaldehyde later bound to SO_2 . The authors do not report on the sensory impact that such elevated acetaldehyde levels may have had on the wines.

• **Effect on polyphenols.** Unlike SO_2 or acetaldehyde, there was little change in polyphenol content. 1) Total phenols increased slightly but similarly in all treatments. 2) Degree of polymerization stayed more or less the same. Therefore, as the authors note, any changes in astringency in the treated wines will likely be due to tannin changes other than changes in average size. 3) As expected, monomeric anthocyanins declined in the treated wines, and this decrease was greatest in the microoxygenated wines. (There was some decrease of individual components, such as caftaric acid and catechin, but the changes were small).

• **Effect on color.** The authors performed 2 spectrophotometric measurements: **SO_2 -resistant pigments** (A520 after adding potassium metabisulfite), and **hue** (A420/A520, after adding acetaldehyde to get rid of variable degrees of left-over SO_2 that would otherwise have an impact on color). 1) Towards the end of the trial, the levels of *SO_2 -resistant pigments* were higher in the treated wines than in the control. The authors believe the buildup of acetaldehyde in the electrochemical microoxidated wines may have contributed to the formation of these pigments (by bonding anthocyanins and flavanols). However, the similar increase in the microoxygenated wines indicates that the formation of these compounds can happen even with less acetaldehyde present.

• 2) There was a steady increase in *hue* in the treated wines, compared to the control, with the highest increase in the microoxygenated wines. The authors believe this increase could be due to the formation of brown polyphenol oxidation products, and increased levels of polymeric pigments (which tend to absorb more at 420 than 520 nm).

In summary, using electrochemical oxidation –passing a current through the wine- the authors were able to achieve results similar to those produced during microoxygenation, such as an increase in SO_2 -resistant pigments, and a decline in monomeric anthocyanins. This came at a cost of a greater buildup of acetaldehyde and bound SO_2 . But the authors believe this problem will be solved with the use of larger-surface electrodes, which will allow working with lower electrode potentials. Electrochemical microoxidation may soon become an alternative technology for aging red wines, with the additional benefit of a more precise control of the rate of oxidation and the timing of treatment cutoff.

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