# The Enological and Sensory Significance of Acetaldehyde

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In: Ithaka Journal, Open Access, http://www.ithaka-journal.net/the-enological-significance-of-acetaldehyde?lang=en

Wine contains a large number of aldehydes, and acetaldehyde is the most important among them due to its concentration and enological implications. It is involved in the maturation process of red wines and may be responsible for sensory defects, but can be bound spontaneously with sulfur dioxide ($SO_2$). Its reactivity and binding with sulfites explain to a large extent why normally wines need varying amounts of $SO_2$ and why sulfur dioxide management is important in winery operations and post bottling stability.

**Production and breakdown by yeast**

A microbiological and a chemical pathway produce acetaldehyde. The highest concentrations are formed by yeast metabolism at the very beginning of alcoholic fermentation. The amounts yielded thereby are quite variable and affected by fermentation conditions and the dominant yeast strain involved in (3,5,7). Slow fermentations which might occur after intensive juice clarification or at low temperatures show a tendency to yield more acetaldehyde than fast or regular ones. After a few days of fermentation, there appears a concentration peak which declines gradually as fermentation progresses towards the end. Therefore, sweet wines obtained by stopping the fermentation before completion of fermentation display higher amounts than those fermented completely. This behavior explains the higher need for the combining power of $SO_2$ in wines which are kept sweet by early interruption of fermentation. Sluggish refermentations of partially sweet wines and accidentally occuring fermentations in poorly conserved grape juices, i.e. all fermentations running unintentionally under severely repressive conditions, may yield excessively high amounts of acetaldehyde in no relation to the sugar decrease observed, and which lead to correspondingly high amounts of bound sulfur dioxide when free $SO_2$ is adjusted. When juices are treated with $SO_2$ prior to the onset of fermentation, the initial reaction of the yeast is the production of correspondingly higher amounts of acetaldehyde able to tie up that $SO_2$ (8).

Wines produced by up-to-date vinification methods display fairly low amounts of acetaldehyde at the end of alcoholic fermentation, usually fluctuating in a concentration range from 3 to 30 ppm. Extended postfermentation contact with the lees may cause a further decline that is explained by enzymatical reduction of acetaldehyde to ethanol by the alcoholdehydrogenase contained on yeast cells. This effect is frequently looked for when prolonged yeast contact is carried out. Under practical conditions, however, the enzymatical acetaldehyde reduction is achieved within a couple of days after completion of fermentation and thereafter the concentration can be considered to be of no importance as only a few mg/L remain.

On the other hand, supplementary amounts of acetaldehyde may be produced in completely fermented and yet turbid wines under conditions where oxygen is allowed to be picked up. This behavior is frequently observed in wooden casks, or when tanks are not totally topped. A fraction of the oxygen dissolved is used for the oxidation of ethanol to acetaldehyde. The reaction is driven once more by alcohol ehydrogenase which is still active on the residual, suspended yeast cells in the unfiltered wine. Uptake and dissolution of atmospheric oxygen determines whether yeast synthesizes or reduces acetaldehyde using one and the same enzyme (5,14). For that reason, white wines stored over several years in casks or tanks tend to require more total sulfur dioxide, though they may be stable from a microbiological point of view.

The postfermentation accumulation of acetaldehyde as described above is run to excess when Sherry wine is to be produced. Acetaldehyde is the key impact aroma compound of sherry. Its concentration may exceed far more than 100 ppm in that kind of wine and is achieved by the very specific flor yeasts growing aerobically on the surface of the wine stored with air contact (6).

**Production and breakdown by chemical pathways**

After residual yeast cells suspended in the wine have been removed by filtration, acetaldehyde may also be formed merely by a chemical oxidation of ethanol. This kind of reaction requires the presence of naturally occurring polyphenolic compounds and traces of heavy metals acting as catalysts (16). The extent and speed of this mechanism of acetaldehyde formation depends on the amount of oxygen picked up and consumed (5,13,14). By excluding air during storage, as it is common practice in white wine making, this reaction will be restricted. Free $SO_2$ prevents ethanol from oxidation, scavenging partially the oxygen radicals formed during the oxidation process.

In red wines, a slow decline of acetaldehyde is observed due to its binding with tannins. During storage and maturation of red wines, tannin and anthocyanin molecules bind together in a process called polymerization. In this reaction, acetaldehyde acts as a link or "ethyl bridge" between individual molecule units and is removed from the system (15). The micro-oxygenation of red wines has the purpose of producing additional amounts of acetaldehyde by coupled oxidation of ethanol in order to promote the polymerization and sensory quality of tannins.

**Interaction with sulfur dioxide and sensory implications**

Acetaldehyde is a colorless, highly volatile liquid with a boiling point of 21°C (70° F) and responsible for the typical off-odor of heavily oxidized wines when occuring in its free form. Free acetaldehyde means that it is not bound to sulfur dioxide. Its odor impact reminding one of apple sauce contributes strongly to the traditional bouquet of sherry wines since those wines are aged and bottled without free $SO_2$. In fruity table wines, any free acetaldehyde is rejected as an odor defect distorting the wine's fragrance. Its odor threshold value is only 1-2 mg/L (1).

One milligram acetaldehyde binds 1.45 mg $SO_2$. The reaction product formed hereby is odorless. The reaction between acetaldehyde and sulfite is more or less spontaneous with the reaction equilibrium shifted to the side of the bound form (9). Therefore, the off-odor disappears within 2-5 minutes upon $SO_2$ addition to the wine. Only when acetaldehyde is tied up totally by sulfur dioxide, can there be $SO_2$ left in its free form. In the reverse situation, the off-odor is produced when free $SO_2$ is consumed completely by oxidation and the first mg/L acetaldehyde set free.

In fruity wines made from sound grapes, the amount of total $SO_2$ they require depends essentially, but not exclusively, on their acetaldehyde content. In sweet dessert wines, however, other compounds able to bind $SO_2$ as sugar and keto acids may be more predominant as sulfite reaction partners (2).

Free acetaldehyde and free $SO_2$ exclude one another. For that reason, a wine containing free $SO_2$ cannot display the off-odor generated by acetaldehyde, but it may show other sensory forms of oxidative or non-oxidative aging (12). In this context, free $SO_2$ is the amount exceeding other reducing agents (normally 4-8 mg/L in white wines) which are measured as $SO_2$ thereby interfering in the common, routine determination of $SO_2$ using iodine titration. The sum of free and bound $SO_2$ corresponds to total sulfites.

Wines with a high acetaldehyde content need more sulfur dioxide to totally bind the acetaldehyde and, furthermore, to make sure the presence of free $SO_2$ required to protect them against oxidation. In doing so, the legally fixed limit of total sulfites may be exceeded sometimes. The problem of such wines, known as "sulfite eaters", cannot be resolved by any means of desulfitation. Upon desulfitation of a wine, free $SO_2$ is removed first, and the odor of free acetaldehyde appears. Total sulfite is lowered at the same time. However, the concentration of compounds responsible for binding $SO_2$, especially acetaldehyde, is not affected. Thus, when $SO_2$ is added again to achieve a certain level of free $SO_2$, the original content of total $SO_2$ will be obtained once more. In such a situation, the problem cannot be overcome using desulfitation by one another technique, but with a reduction of compounds responsible for binding $SO_2$. In the absence of any other means, blending with another wine will be the only solution.

**Sensory definitions and misunderstandings**

Free sulfite is an anti-oxidant, but it is not able to protect the wine totally against oxidation by molecular oxygen that is absorbed to a variable extent through bottle closures. Therefore, in fruity white wines known for their sensitivity towards oxidation, the phenomena of oxidative aging may occur even in the presence of free $SO_2$ and without any free acetaldehyde involved. This kind of oxidative aging can be described by the French term *rance* or the German term *firn* for moderate oxidation, or *maderization* in the most severe form. It is characterized by odor attributes reminiscent of straw, hay, walnuts, honey, black garden soil, canned mushrooms etc. (11). Simultaneously, fruity and floral aroma compounds as responsible for the typical fragrance of most cultivars tend to disappear. The term *oxidized*, often used to describe the sensory profile of aged white wines and to justify their rejection by quality control panels, is not as precise as it should be. A difference has to be made between the odor of free acetaldehyde and that of moderate aging. The first one is reversible, the latter one not. However, both of them may occur at the same time since the absence of free $SO_2$ accelerates oxidative aging.

The apple sauce-like off-odor generated by free acetaldehyde is often misleading and confounded with other similar off-aromas from which it must be differentiated properly by the use of correct linguistic terms and adequate sensory training. Especially ethyl acetate and acetone, both of them of microbial origin, belong to this category.

**Non-sulfite wines**

The low amounts of sulfite commonly found in wines are not known to affect human health in any way, but some producers around the world have specialized for ethical reasons in the production of wines without any $SO_2$ added. In order to protect these wines against the formation of the off-odor caused by free acetaldehyde, its production by microbiological and chemical pathways has to be reduced to a minimum (4,10). Basic requirements to achieve this aim are the use of suitable yeast strains for alcoholic fermentation as well as fining, cold stabilization, storage, and bottling operations using all means of protecting the wine against oxygen uptake from the atmosphere. Usually, and especially for sensitive white wines, it is necessary to run all winery operations after filtration using careful blanketing with inert gases like carbon dioxide, argon, or nitrogen, if consumer demands for sensory stability and shelf life are to be fulfilled.

**Health considerations on acetaldehyde**

As any other substance like bread and milk, acetaldehyde may be harmful to health or even carcinogenic if it is consumed in excess. In some brandies as well as in certain sherry and port wines, acetaldehyde concentrations as high as 1,000 mg/L have been found and reported with alarm in the consumer press (17). However, acetaldehyde is formed also as an intermediate compound in the human body when alcohol is broken down by alcohol dehydrogenase. Since wine contains about 100 g/L ethanol, the human organism is able to metabolize considerable amounts of acetaldehyde in comparison to which the amounts taken up directly from wine are negligible. Furthermore, acetaldehyde in current wines does not occur in its free form, but bound to sulfur dioxide making up a completely new compound called *hydroxy ethan sulfonate*. No health implication has been found in this compound.

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