Aroma Chemistry of Wine Barrels

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The effect of wine barrels on the taste and aroma of wine aged in them can be profound and make the difference between a good wine and a really great wine. The are many variations in barrel construction and preparation, and their interaction creates a wide array of aroma profiles.

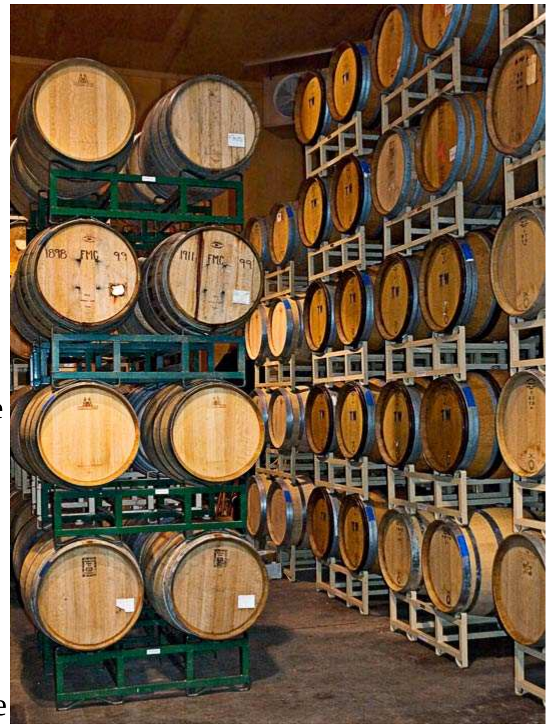


Figure 1- Wine Barrels

There is a need to monitor and characterize the aroma of wine barrels. Conventional instruments such as gas chromatograph/mass spectrometers are too slow and cumbersome to be used to characterize the aroma of wine barrels. However, recent advances in electronic noses based upon high-speed chromatography have led to the introduction and use of instruments such as the zNose® in wineries. The zNose® is a portable battery operated instrument, which utilizes direct column heating (no oven) and a solid-state detector to analyze aroma chemistry. Ambient air within a wine barrel can be directly sampled and analyzed in near real time. Chromatograms are in seconds as compared with conventional instruments, which are in minutes and in some cases hours.

Figure 2- The zNose® is an ultra-fast battery powered gas chromatograph designed to quantify the chemistry of volatile organics over the range C4 to C24.

Chemicals in Wine Barrels

The source of the oak itself is a substantial source of variation. Oak species differ greatly. The French Pedunculate Oak is known for its relatively faint aroma potential compared to French Sessile Oak. American White Oak can have a strong, distinctive aroma, sometimes considered overpowering in certain wines. In contrast, Oregon White Oak seems to have more similarities to the French oaks than to American White Oak. Geographic origin is linked to botanic species, but different species frequently grow in the same forests, and hybridization does occur. Growing conditions, age and genetic variation of individual trees can strongly affect wood structure and composition. Even a stave's position on a trunk has been shown to influence its aroma composition.

Stave seasoning and drying are important. Kiln drying is likely to result in a different aroma character than does air-drying. Air drying conditions (time spent in open air and humidity level) also have a significant influence on wood aroma potential. Finally, the cooperage process adds a considerable layer of variability. Definitions of "light" to "heavy" toasts are subjective and vary among coopers. Difficulty controlling toasting levels creates barrel-to-barrel variation. Stave to stave variation can occur in the same barrel as some staves may toast more rapidly than others.

Figure 3- Toasting wine barrels

Toasting during barrel processing modifies the structure and chemical properties of the oak. This influences the wood aroma composition and consequently, the release of aroma compounds into the wine. Increased toasting diminishes the fresh oak aromas generally attributed to oak lactones. Simultaneously, vanilla and caramel aromas associated with the chemicals

Vanillin (1410)

Furfural (835)
5-methylfurfural (960)

increase. At higher toast levels these compounds decrease and are replaced by spicy

Eugenol (1350)
Isoeugenol (1390)
4-methyl-guaiacol (1201)

and smoky characters

Guaiacol (1090)
4-methylguaiacol (1201)

Oak aroma potential decreases rapidly with barrel use. However, different compounds are extracted from oak at different rates. While a one-year-old barrel will certainly impart less oak character to a wine than a new barrel, the aroma compounds it does contribute are likely to have a different profile than a new barrel. This enforces the need for testing barrel aroma prior to it use.

Wine barrel oak can also be a source of chloroanisole contamination in wine. Anisols such as

TCA(1330)
TeCA(1520)
PCA(1720)

are powerful odorants with a musty, moldy, corked smell. These compounds can completely destroy a wine.

Other compounds possessing more desirable properties in roasted barrels can be transferred to the wine during aging. Cinnamon and nutmeg possess both woody and spicy aromas. These characters in oak aroma can be attributed to the combination of woody, coconut oak lactones and spicy compounds such as

Eugenol (1350)
Isoeugenol (1390)

Microbial activity during barrel aging can also influence the taste and aroma of a wine. A red wine lot aged in barrels containing certain yeasts can develop a pharmaceutical, band-aid or horsy, sweaty aroma. The aroma of wine during barrel aging can be tested for compounds produced by yeasts such as

4-ethylphenol (4EP)
4-ethylguaiacol (4EG)

These compounds are byproducts of the yeast Brettanomyces and by periodic monitoring of the wine aroma their concentrations can be controlled with sulphur treatments. In the case of oak shavings, chips or cubes, oak material is soaked for several days in a model solution. The soak solution is then analyzed in a method similar to that described for wine.

Barrel testing before use and periodic testing during again is an important technique for producing high quality wines. Using the portable zNose the aroma chemistry of wine barrels can be quickly and easily tested. Often considering variability of oak aroma composition from barrel to barrel is seen. Thus, a sampling plan is very important. Single barrel samples can be used to evaluate barrel-to- barrel variation.

During aging headspace vapors within the barrel or from representative wine samples from the barrels tested by inserting the zNose™ instrument directly into the bunghole of the barrel. This near real time analytical technique provides great specificity, sensitivity, and is much more cost effective than laboratory style testing. Based upon findings immediate corrective actions can be carried out to control the aging process.

Wine Barrel Aroma

Oak wood used in wine barrels is composed of several classes of complex chemical compounds, each of which contributes its own flavor or textural note to both red and white wines. The complexity of this aroma makes it very difficult for humans using their sensory perception to accurately judge its quality or repeatability. However using an electronic nose like the zNose it is possible to view an olfactory image in which all of the different chemicals are represented. In this diagram the radial direction is proportional to chemical concentration (intensity) and the angular direction is proportional to volatility. The advantage of such a diagram is that the entirety of the aroma is transferred from an olfactory to a visual sense.

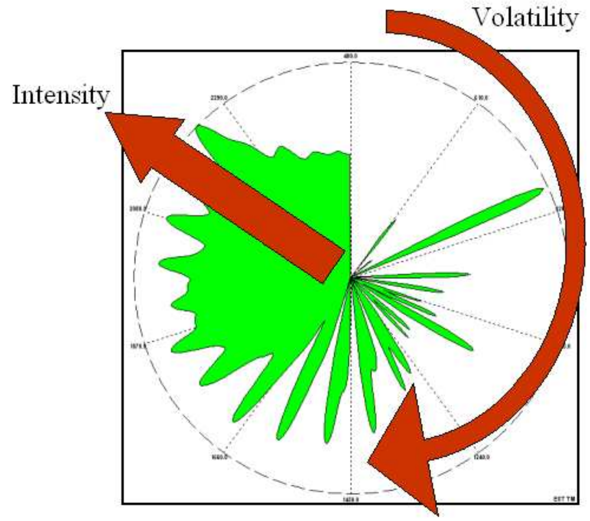


Figure 4- Barrel Aroma Vaporprint® Image.

Wine Barrel Chemistry

Mathematical integration of the aroma diagram allows the zNose® to display the individual chemicals within the barrel aroma as a chromatogram. Chemicals within the aroma are displayed as peaks and the complexity of the aroma is clearly seen in the chromatogram. The chemicals span a wide range of volatility represented by Kovats indices from 400 (c4) to 2500 (c25). The strength or intensity of each peak is proportional to each peak's area. While compounds readily detected by human perception cover a range of 400 to 1600, it is clear there are also compounds of much less volatility present.

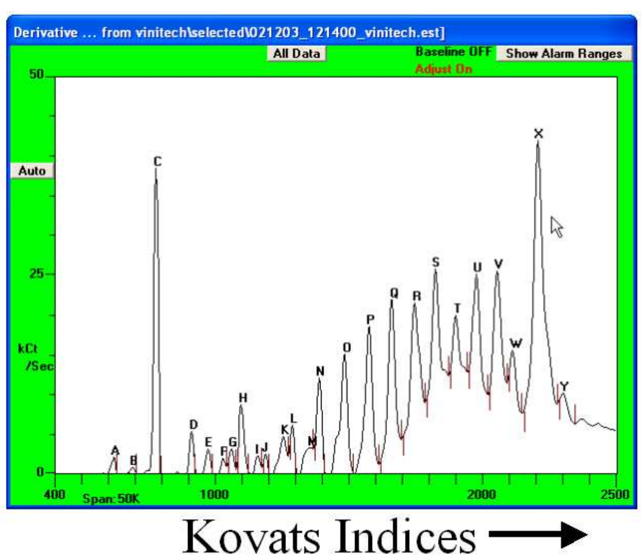


Figure 5-Barrel aroma chemistry C4 to C25

The presence of chloroanisoles in a winery is of major concern and has been traced to bacterial growth (mold) in everything from wine barrels, to corks, and almost everything constructed of wood. Barrels can be sniffed by the electronic nose and aromas chromatograms screened for trichloroanisole, tetrachloroanisole, and pentachloroanisole. These compounds appear as peaks within easily marked alarm bands in chromatograms. TCA contamination can be a serious problem and screening for chloroanisoles should be a standard incoming inspection procedure for corks and other wood products within all wineries.

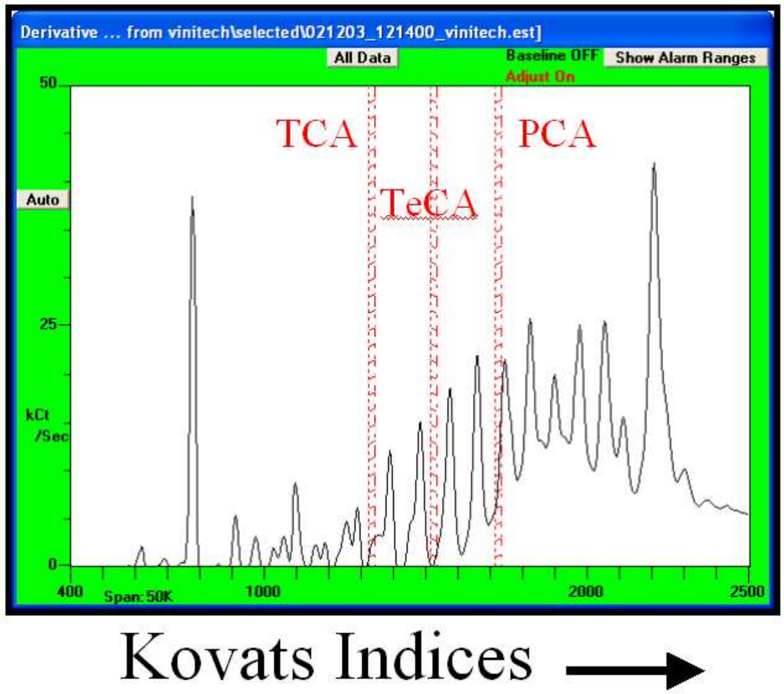


Figure 6- Screening for chloroanisoles

Toasting barrels produces many desirable aroma chemicals which are subsequently released into the wine during aging. Vanilla and caramel notes are important, as are smoky or spicy notes. The concentration of compounds such as methyl furfural, guaiacol, methyl guaiacol, eugenol, and isoeugenol can be quantified in such aromas and even monitored throughout the processing of the wine. These compounds appear in the early part of chromatograms and alarm bands are easily set for monitoring them. Simultaneously, vanilla and caramel aromas associated with the chemicals

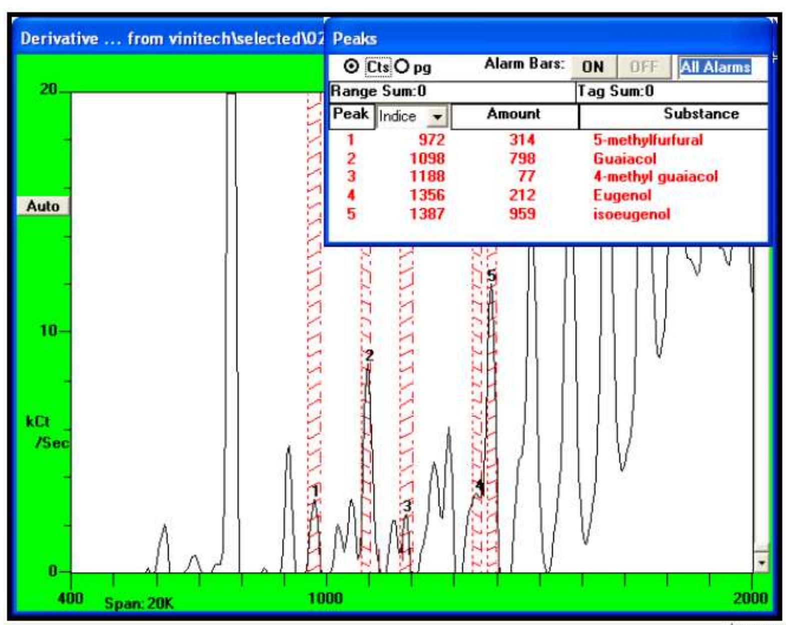
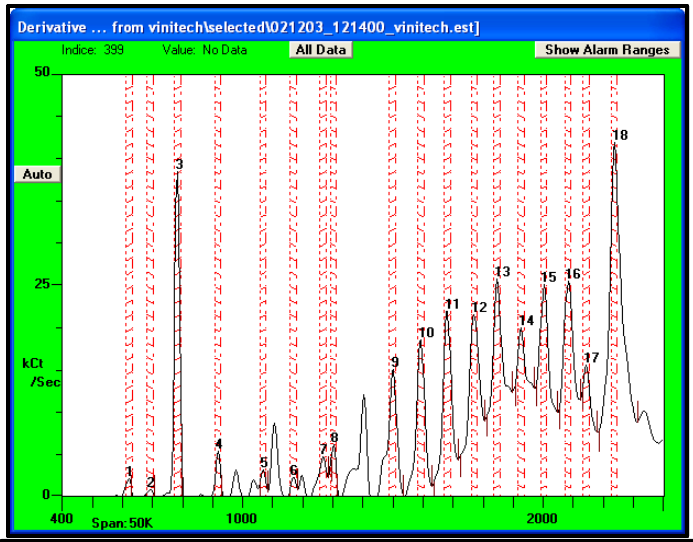


Figure 7- Screening for volatile aromas

Virtually all of the chemicals seen in the aroma from wine barrels can be identified. Most are traceable to the oak used in making the barrel and the toasting process itself. These compounds are identified using their retention indices and software based chemical library. The 'woody' compounds are shown in bands and their relative concentrations listed in the following figure. These included aldehydes, hydrocarbons, ketones, alcohols, esters, acids and many others. In general these are at concentrations of micrograms per kilogram. The most abundant compound detected was 2-methyl propanoic acid. One class of considerable importance are oak lactones. These compounds are responsible for the wood aromas or what is commonly called "oakiness". The cis- and trans-methyl-γ-octalactones, commonly referred to as "whisky lactones" are responsible for the oakiness of wines. Volatile phenols based on guaiacol are released result from degradation in oak .The guaiacol derivatives have a significant impact on the wine flavor. Terpenes are abundant in oak barrels and are very odorous with aromas of resins, violets, lemon and leather. A combination of oak lactones, eugenol and terpenoids are also responsible for the "oakiness" of wines. During roasting of the barrel carbohydrates are degraded producing compounds such as furfural and 5-methylfurfural. These have a sweet butterscotch, light caramel and subtle almond aroma. Volatile organic acids are produced as a result of toasting and the metabolism of these acids by yeasts which produce esters of ethyl acetate. Tannins and other phenolics are also important in giving wine color and astringency, but more importantly to balance the oxidative/reductive reactions of the wine, protecting it from oxidation and lessening the chance of unpleasant reductive aromas. The thermal degradation of lignin results in volatile phenols with spicy, smoky odors.



Peaks

Cts ppm — All Alarms

Range Sum:0 — Tag Sum:0

Peak	Indice	Amount	Substance
1	622	210	2-methyl-1-propanol
2	693	88	2-pentanone
3	785	3,099	2-methyl propanoic aciddd
4	920	486	Pentanoic acid
5	1070	137	Hexanoic acid 2-propenyyyl este
6	1169	171	naphthalene
7	1268	401	2-methyl naphthalene
8	1304	199	1-methyl naphthalene
9	1504	2,615	triacetin
10	1596	2,839	3-4-5-Trimethoxy-phenolll
11	1684	2,842	dodecanoic acid 1-methyyylethyl
12	1772	2,368	Tetradecanoic acid
13	1848	2,237	tetradecanoic acid 1-meeethylet
14	1928	832	Z-9-hexadecenoic acid eeethyl e
15	2004	1,691	hexadecanoic acid ethylll ester
16	2084	2,254	Octadecadienoic acid meeethyl
17	2144	335	9-12-octadecadienoic acccid
18	2240	7,476	Octadecanoic acid

Figure 8- Wood aromatics

Summary

Wine barrels have a major impact on the taste and aroma of wine aged in them and can make the difference between a good wine and a really great wine. The is a wide diversity in barrel materials, construction techniques, and preparation, and they all interact to create the aroma of chemicals within a barrel e.g. the aroma profile. Wood has a profound influence on the flavor profile and characteristics of a wine. There is an interaction between the wood and the wine, and certain substances are extracted directly from the wood to the wine, while other substances interact with yeasts and bacteria in the wine to form flavors different to the original flavors. Some substances that are extracted in large amounts may influence the organoleptic properties of the wine. Some of the extractives can influence the bouquet, while others may influence the mouth feel.

There is a need to easily and quickly monitor the aroma chemistry of wine barrels in near real time. Conventional instruments such as chromatograph/mass spectrometers are too slow, not portable, too costly, and too cumbersome to be used to characterize the aroma of wine barrels. However, recent advances in electronic noses based upon high-speed chromatography have led to the development of an instrument, which is specifically designed for wineries. Using this handheld instrument ambient air within a wine barrel can be sampled and chemically analyzed in seconds. Typical chromatograms are in seconds as compared with conventional instruments, which are in minutes and in some cases hours.

Barrels are recognized as valuable aids to the winemaking process. For white wines, primary fermentation in oak barrels not only increases the range of flavors, but also prepares the wine for battonage, which softens and integrates the flavors from the wood and lightens the color. For both red and white wines, malolactic fermentation (a secondary fermentation that converts malic acid to softer lactic acid) in barrel, or in contact with oak, adds richness and length of flavor on the palate.

Barrel testing before use and periodic testing during again is important for producing high quality wines. Using the portable zNose® the aroma chemistry of wine barrels can be quickly and easily tested. Often considering variability of oak aroma composition from barrel to barrel is seen. Thus, a sampling plan is very important. Single barrel samples can be used to evaluate barrel-to- barrel variation.

During wine aging, headspace vapors within the barrel can simply and easily be tested by inserting the zNose® instrument directly into the bunghole of the barrel. This analytical technique is fast and provides great specificity, sensitivity, and is much more cost effective than laboratory style testing. Nevertheless because chromatography is used, the results can readily be validated by laboratory testing. Based upon screening tests immediate corrective actions can be carried out. Screening on a routine basis for chloroanisole contamination, flavor chemicals, and quantification of chemical groups such as oak lactones, phenols, and terpenes can be cost effective and at the same time produce superior wines.