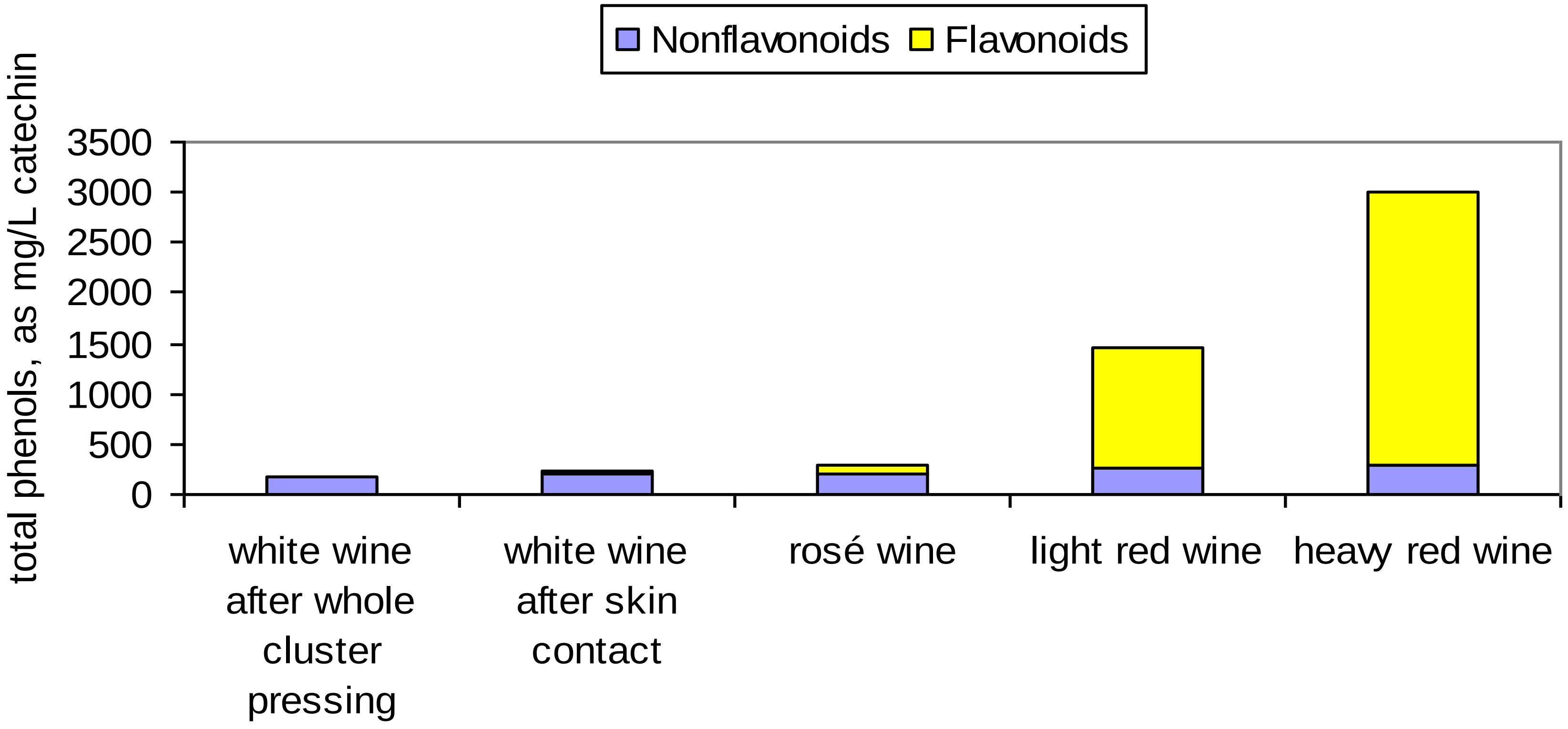
Vinification and Aging of Red Wines

Tannin and Oxygen Management:

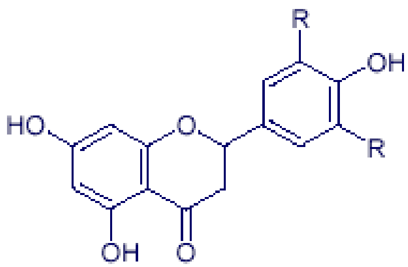
Reactions of tannins with oxygen and their sensory impact

Total phenols of different kinds of wine as made up of flavonoid and nonflavonoid phenols

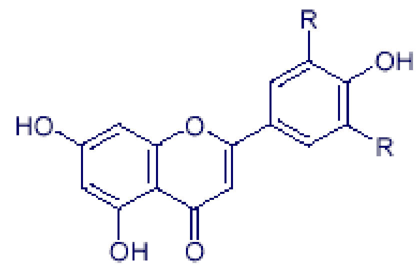


The relatively high amounts of total phenols in red wines are due to their intrinsic tannin including anthocyanins, which is almost absent in white wines. They make the basic difference between white and red wine. Therefore, the content of total phenols is a measure for the intensity of the typical red wine taste characteristics.

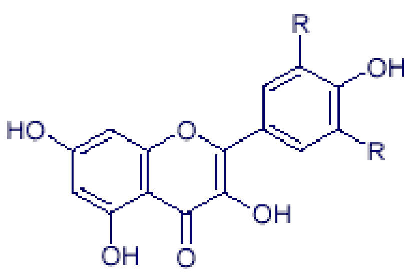
Molecular structures of monomeric flavonoid phenols



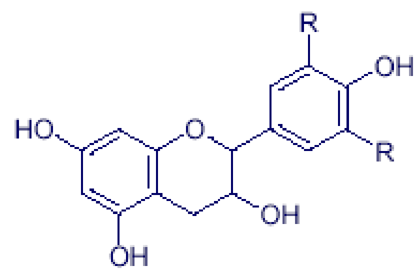
Flavanone



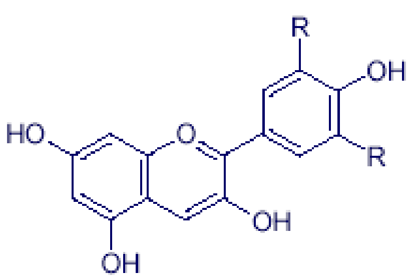
Flavone



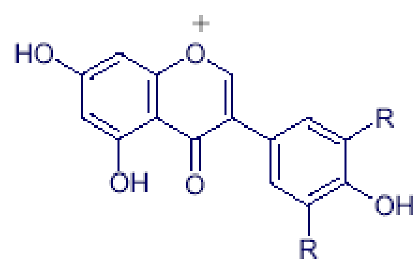
Flavonole



Flavanole



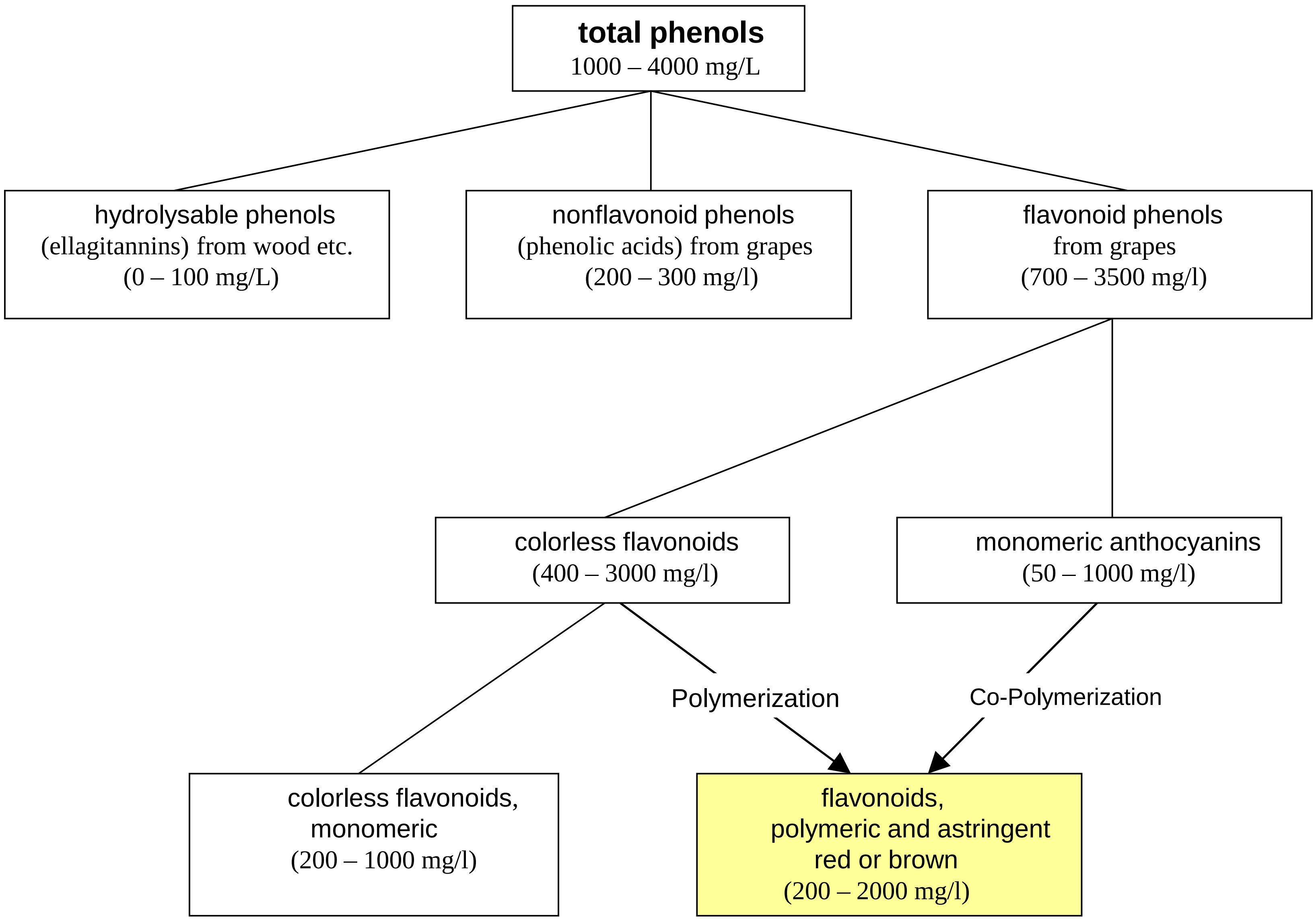
Anthocyanidine



Isoflavone

Monomeric flavonoid phenols are the constituents of grape-derived tannins and display the basic structure C_6-C_3-C_6

Total phenols in red wine. Fractionating for quality control purposes.



Correlation coefficients (r) between phenolic fractions and taste qualities in cool climate red wines

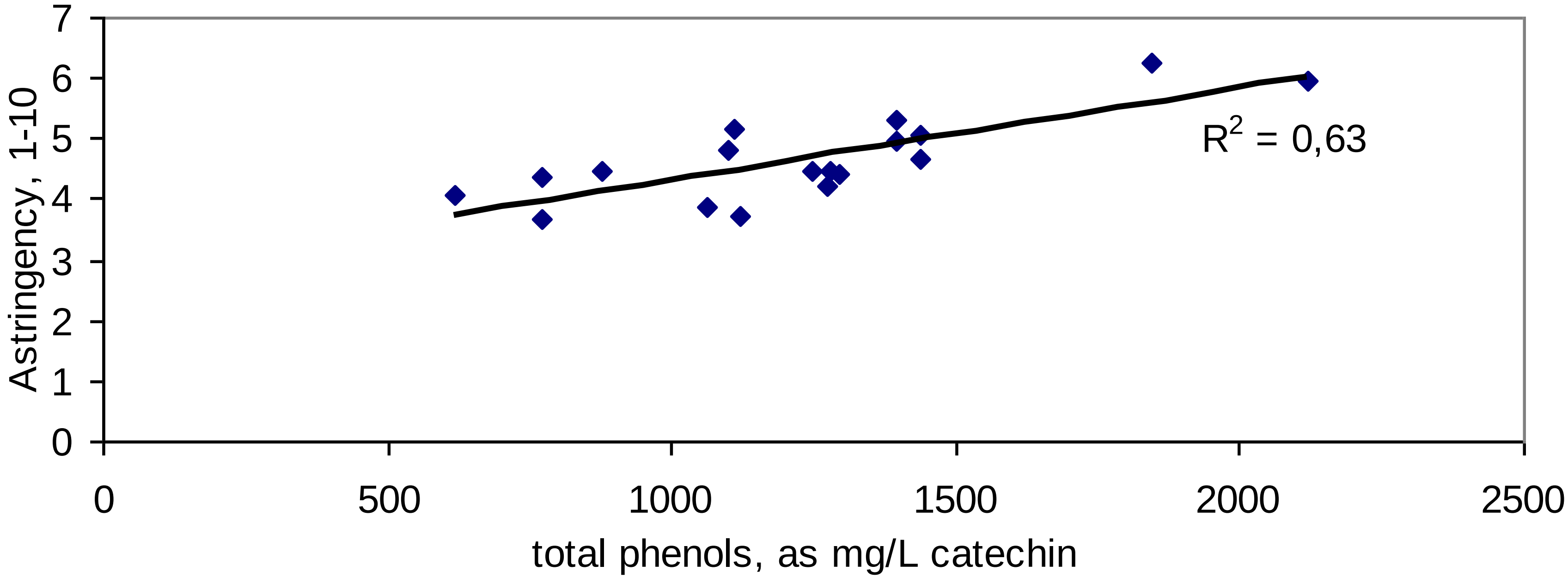
(only r > 0.7) (German red wines, 1999)

	astringency	bitterness	volume
total phenols	0,77	0,70	
anthocyanins			0,83
total flavonoid phenols	0,77	0,73	
monomeric flavonoid phenols	0,82	0,72	
astringent flavonoid phenols	0,77	0,72	

Total phenols, total flavonoid phenols, monomeric flavonoid phenols, and astringent flavonoid phenols characterize perceived astringency with comparable precision.

Correlation between astringency and total phenol content in 18 cool climate red wines.

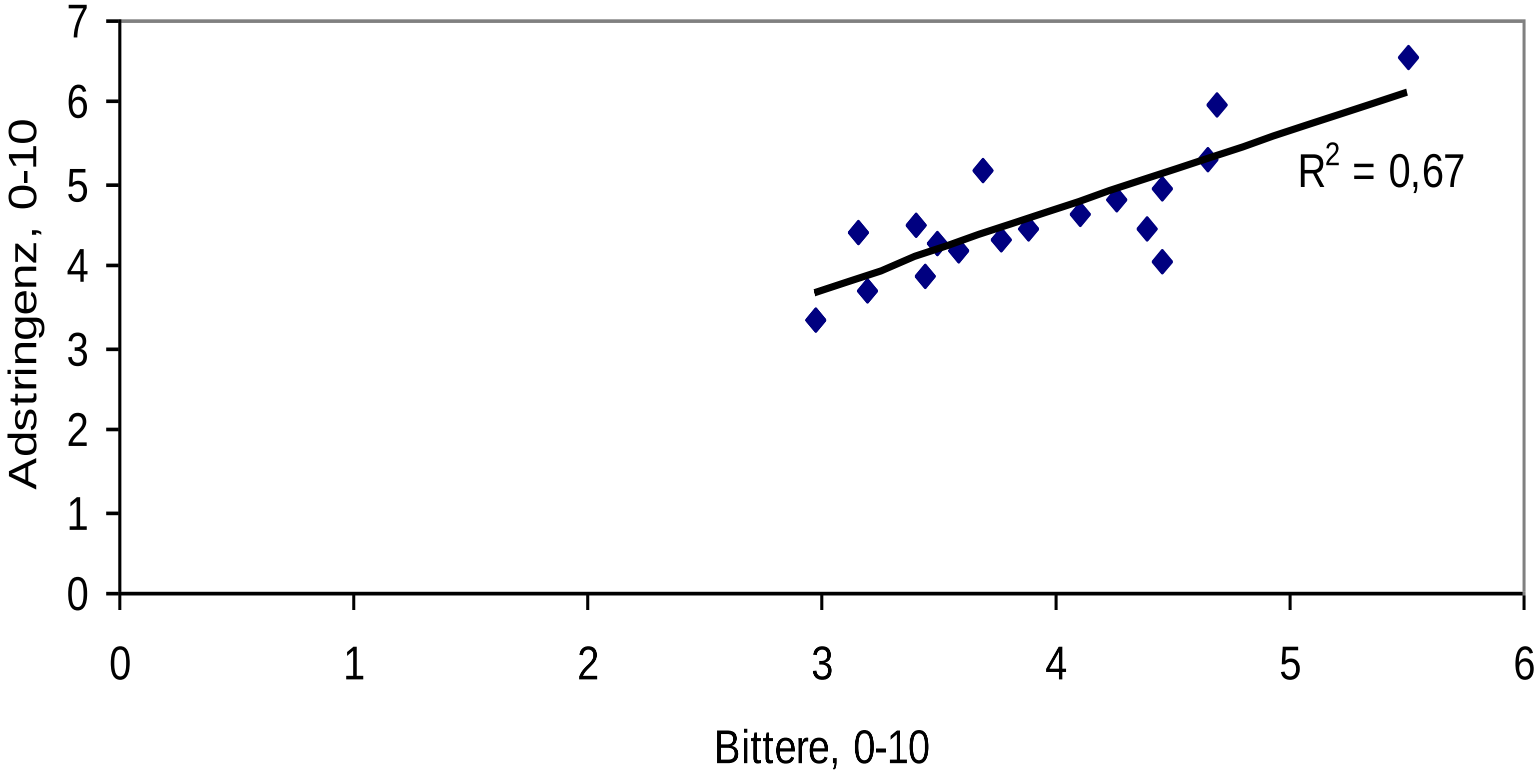
(Germany, 21 judges)



The total phenol content of red wines provides an information about the intensity of astringency (63 %) – similarly to that the total acidity gives about the intensity of the sour taste.

Correlation between astringency and bitterness in 18 cool climate red wines of various cultivars

(Germany, 21 judges)



In this set of red wines, perceived bitterness correlated to 67 % with perceived astringency. The terms of bitterness and astringency are frequently mistaken in descriptive sensory analysis.

For sensory training, bitterness is represented by quinine chloride and astringency by aluminium potassium sulfate solutions.

Currently used methods to measure total phenols in routine quality control

1. By spectrophotometry using Folin-Ciocalteu's-reagent at 720 nm
   Also suitable for quantification of various phenolic fractions after fractionation steps.

2. By spectrophotometry measuring A 280 nm
   Less specific and less reproducible than 1. since absorption maximum is slightly variable, usually around 285 nm in cool climate red wines.

3. By FTIR (Fourier transformation infrared spectroscopy)
   Calibration based on methods 1. und 2.

Results are expressed as mg/L gallic acid or mg/L catechin (calibration!).

1 mg gallic acid ≈ 1,4 mg catechin.

Bear in mind the reference used !

Currently used methods to measure anthocyanins in routine quality control

1. By spectrophotometry at 520 nm before and after addition of SO_2 in excess.

2. By spectrophotometry at 520 nm before and after acidification to pH 0,6 using HCl.

Results use to be expressed as mg/L malvidinglucoside.

Summary:
Analytical assessment of tannin and anthocyanin content

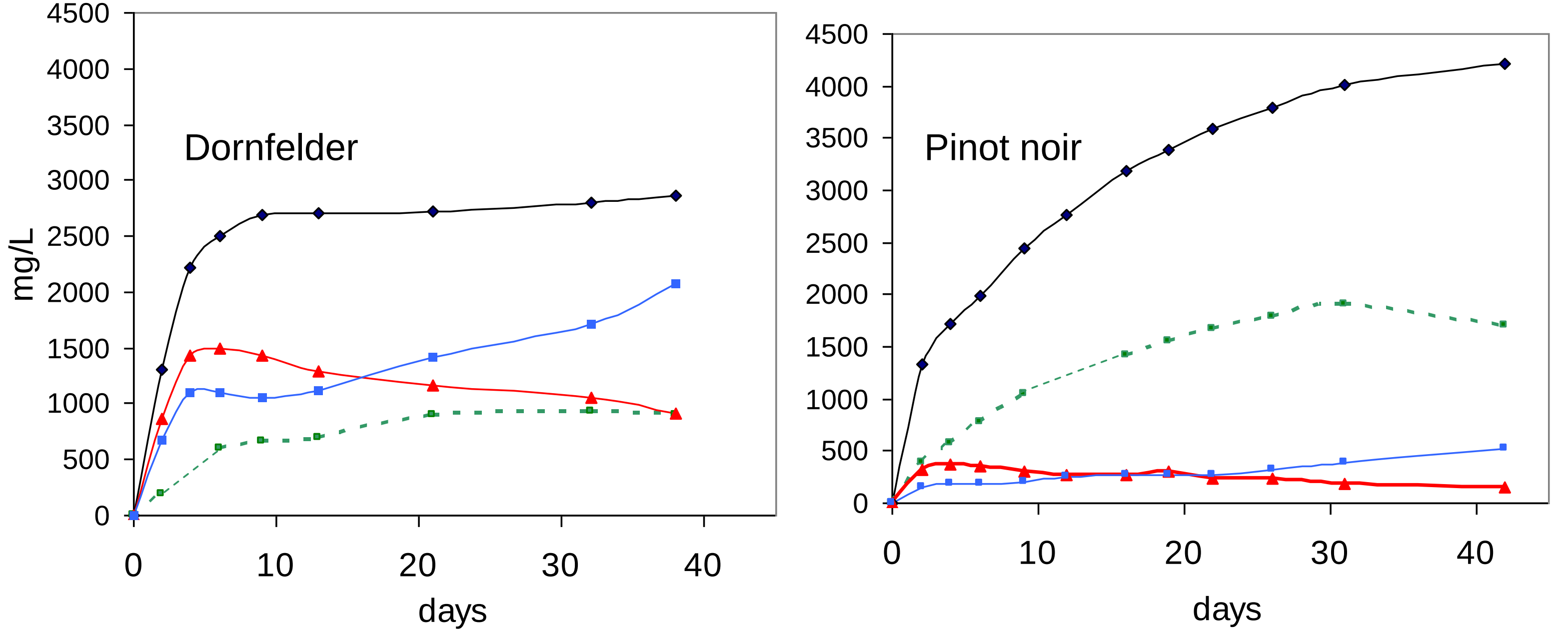
- **The content of total phenols represents the sum of both tannins and anthocyanins.**
- **It is a simple analytical approach to describe the intensity of the typical red wine characteristics on the palate. However, it is not capable of describing the sensory quality of tannin.**
- **Its meaningfulness is limited without information about the anthocyanin content.**
- **The ratio 'total phenols : anthocyains‘ provides an index of the tannin-anthocyanin-ratio.**
- **Light red wines display 1000 to 1500 mg/L total phenols (as catechin), heavy red wines more than 3000 mg/L.**
- **Slightly colored young red wines (Pinot noir) display 150 to 250 mg/L anthocyanins when they are young, strongly colored red wines (Norton, Regent, Dornfelder etc.) may exceed 1000 mg/L.**
- **Anthocyanins decrease during aging due to polymerization with tannins.**

Analytical tools support sensory evaluation.

The measurement of the total phenol content of red wines has the same importance as measuring alcohol, sugar, pH, total acidity etc.

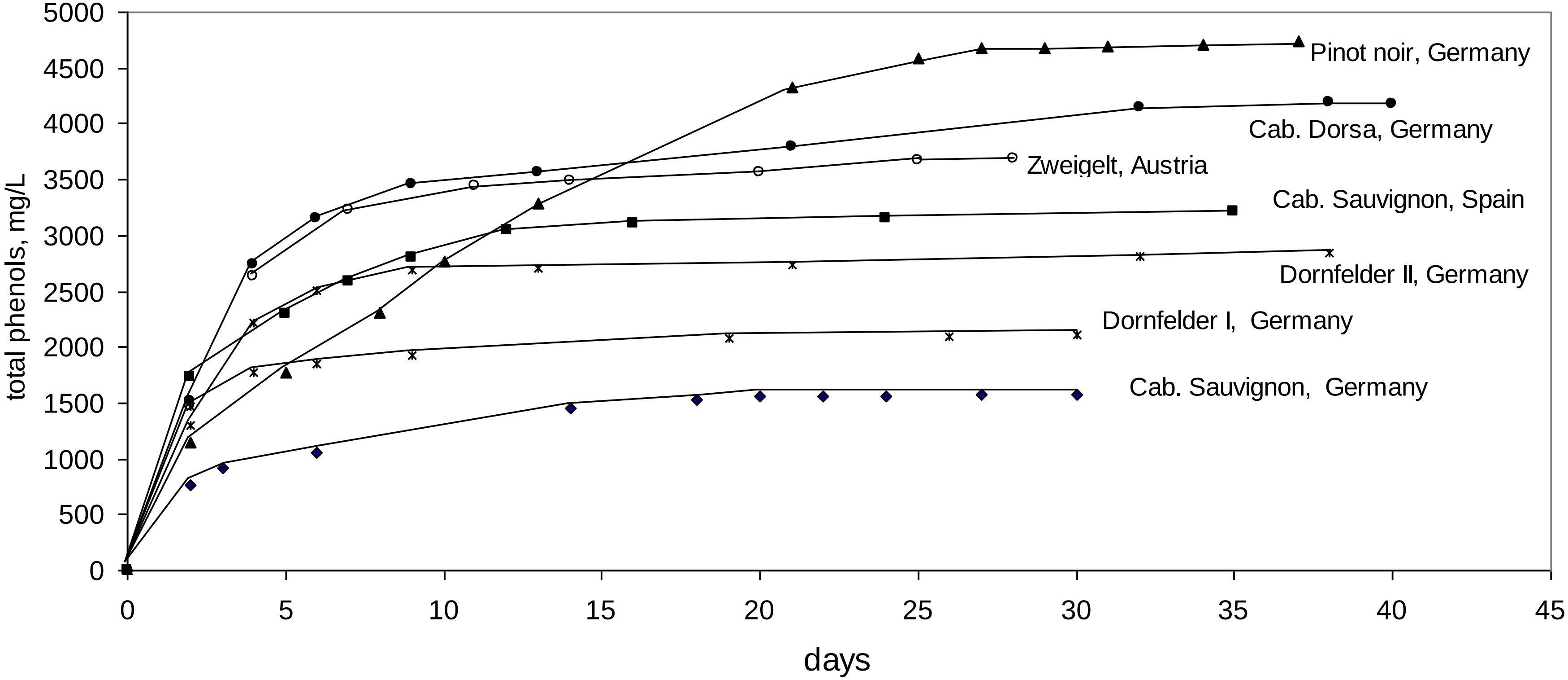
Kinetics of tannin and anthocyanin extraction during skin contact time of two different cultivars at 25° C.

----- = total phenols; ---- = anthocyanins; ----- = monomeric flavonoids; ----- = polymeric pigments



The extraction of anthocyanins comes to an end after 5 to 7 days of skin contact (at 25° C), while the exhaustive extraction of tannins may require, in some varieties, more than 6 weeks.

Extraction of total phenols during skin contact of different cultivars from various origins at 25° C.



-The amount of extractable, total phenols depends on the physiological ripeness (not Brix!) of the fruit.

- Its extraction during skin contact proceeds, under comparable conditions, with different rates and is not related to fermentation kinetics. The end of alcoholic fermentation does not coincide with the end of phenol extraction.

-Measuring total phenol content during skin contact is a useful tool to optimize vatting time and the moment of pressing, as well as to create different wine styles.

Summary:
Extraction of tannins and anthocyanins during skin contact

- **Tannin content of the fruit and its extractability depends on the physiological ripeness of the grapes and displays no direct relationship with alcoholic ripeness (Brix).**

- **The extractability of primary color (anthocyanins) during skin contact is completed after 5 to 7 days (25° C). After that period of time, only tannins are extracted.**

- **Skin contact time does not allow to predict the amount of extracted tannins.**

- **However, in most varieties, 85 % of total phenols (~ tannins) are extracted after 10 days of skin contact (25° C, 3 punchings per day).**

- **Post mazeration skin contact (after alcoholic fermentation completed) may extract supplementary amounts of tannins, but must not do so.**

- **Post mazeration skin contact tends to extract considerable amounts of seed tannins which might be too harsh and astringent. Use it only on very ripe fruit (brown seeds) !**

The purpose of oxygen management in red wines

- **Oxygen supply to red wines serves to increase sensory maturity on the palate and aromatic complexity by smell.**
- **The primary oxygen acceptor (after filtration) is tannin whose quality is aimed to be enhanced by polymerization.**

- **Passive oxygen supply during storage in wood, PVC, flex tanks, bottles closed with corks, through wine surface, during cellar operations….**
- **Active oxygen supply by pumping over (splashing), micro-oxygenation….**

The ultimate aim is to manage O_2 uptake as perfectly as SO_2 additions.

Reactions of polymerization in red wine during aging as affected by the tannin-anthocyanin ratio.

Type	Kind of red wine	Sensory outcome
Tannin – Tannin	Red wines with low color and high tannin, e.g. Pinot noir	Oxidative aging (“dry herbs”), increase of astringency during aging, browning in extreme cases.
Anthocyanin – Anthocyanin	Red wine with strong color and low tannin, e.g. Dornfelder, Regent, Alicante Bouschet	Decrease of volume in mouth through loss of anthocyanins, precipitation of colored pigments in severe cases.
Tannin – Anthocyanin	Red wines with balanced tannin-anthocyan ratio (TP **:** A = 3**:**1 – 5**:**1), e.g.. Cabernet Sauvignon, Portugieser, Zweigelt	Fairly stable in smell and taste during storage, good ageability and long term stability.

The tannin-anthocyan ratio is of outstandig importance during red wine storage and aging. It governs the sensory effects of oxygen supply and aging. – Anthocyanins turn tannins softer on the palate and more soluble.

Basic chemical mechanisms of polymerization

1. **Condensation of "Tannin + Anthocyanin" or "Tannin + Tannin"; without oxygen.**

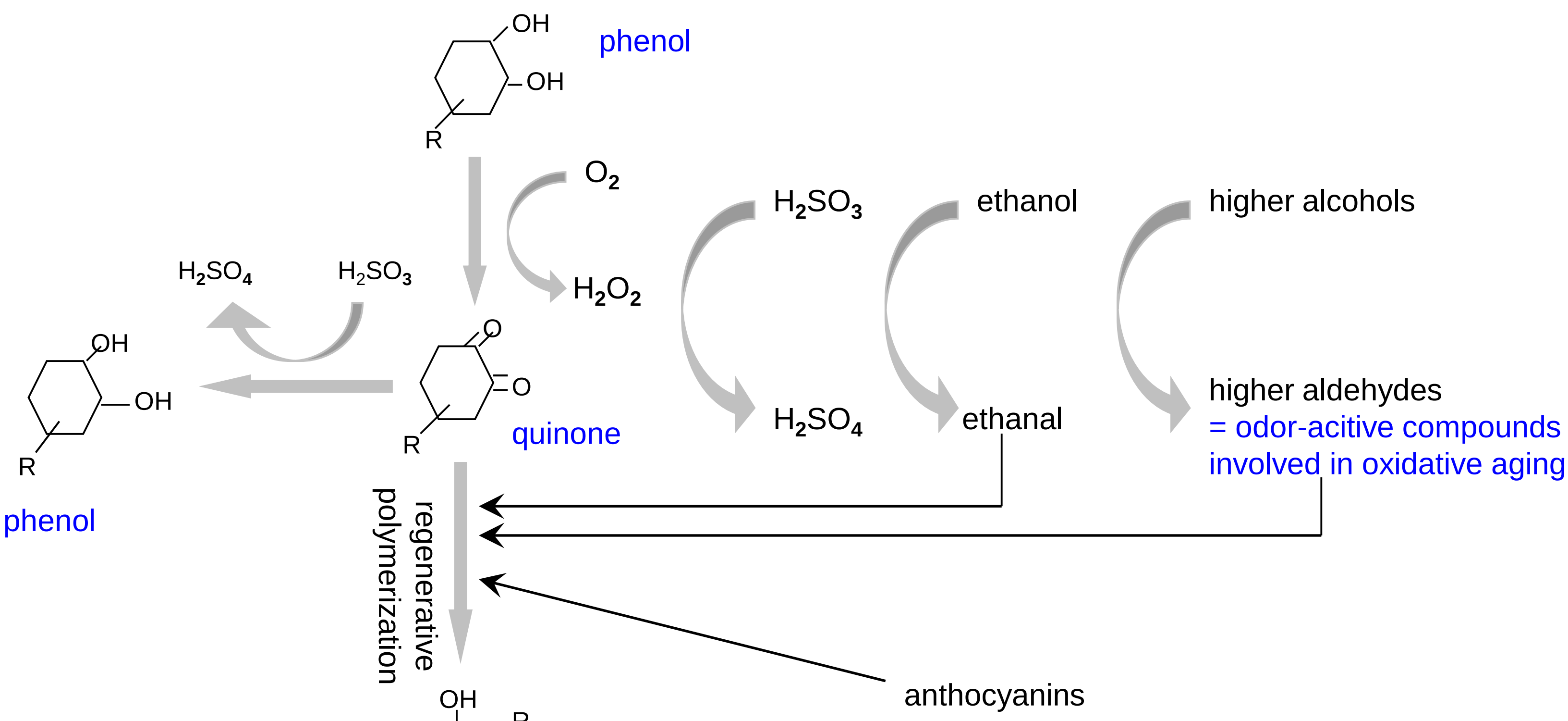
2. **Direct addition of "Tannin + Anthocyanin"; requires oxygen, very slow.**

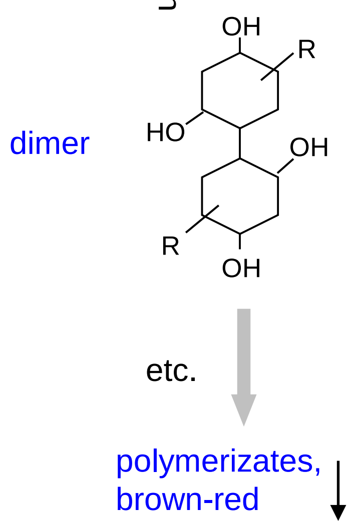
3. **Addition of ethanal and pyruvate to C4 of anthocyanins > very stable adducts.**

4. **Ethyl bridge form of "Phenol-Ethyl-Phenol";**
   - requires oxygen to generate ethanal by coupled oxidation of ethanol and phenols.
   - fivefold faster than polymerizations of type 1 and 2.
   - Bonding of an anthocyanin at the end of the chain impedes further polymerization → lower degree of polymerization in wines with high anthocyanin contents.

1. **Providing DO by oxygenation accelerates polymerization of the type "Phenol-Ethyl-Phenol", e.g. "Tannin – Ethyl – Tannin - Ethyl – Tannin - Ethyl – Anthocyan".**
2. **Oxygen is not indispensable for red wine aging, but accelerates it.**

Oxidation and regenerative polymerization of phenols

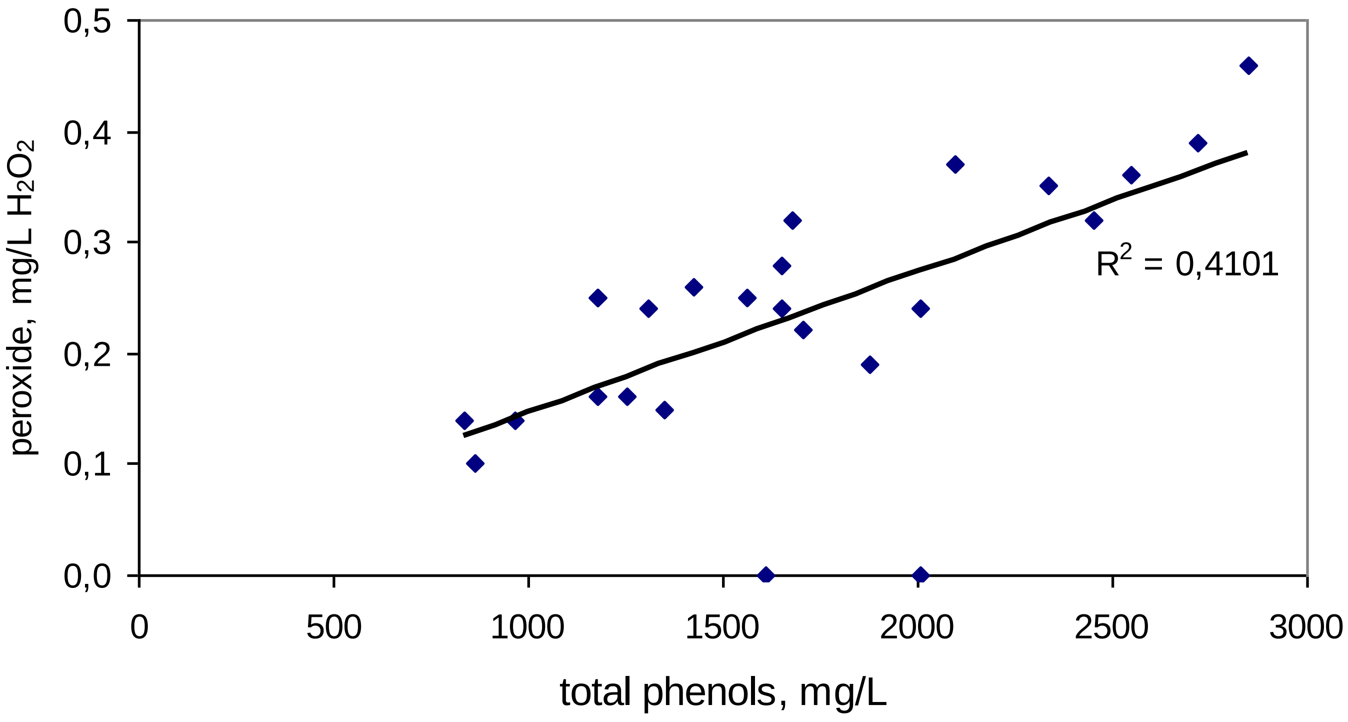




1. Chemical oxidation of phenols producing the respective quinones.
2. Peroxides produced hereby undergo reduction by SO_2 , ethanol, higher alcohols, aromatics, other phenols…..
3. Higher aldehydes (oxidative aging!) generated can be involved in polymerization likewise ethanal. In white wines, they would remain unbound and odor-active. Therefore, red wine aroma is more resistant to oxidation by smell.
4. Reduction of quinones by SO_2 or by regenerative polymerization.
5. Regenerative polymerization means that the original phenolic OH-groups are regenerated.

Instantaneous concentration of peroxides (as H_2O_2) during the oxygenation of red wines (without free SO_2) as affected by total phenol content.

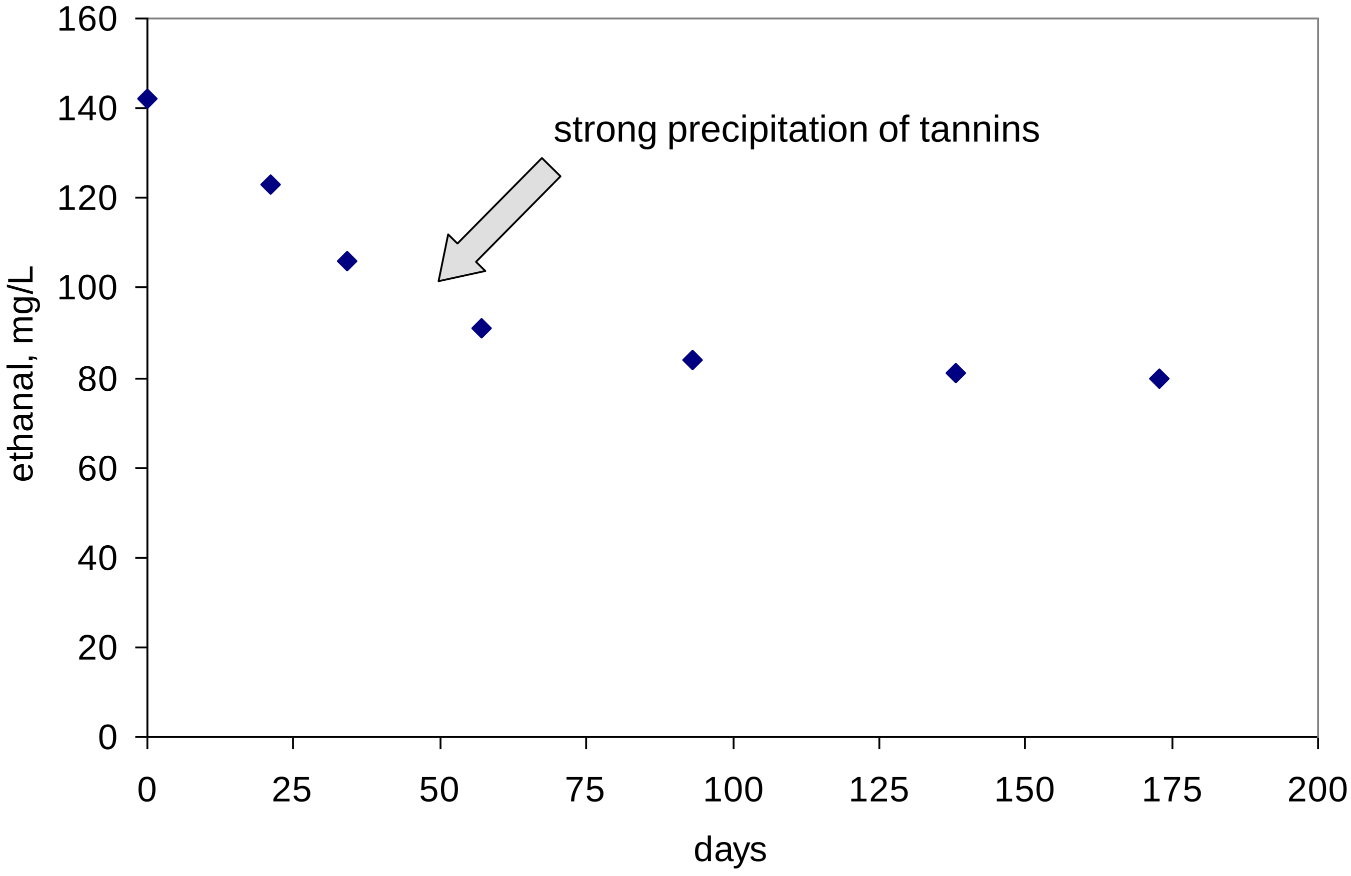
Data obtained enzymatically using NADP-peroxidase.



The oxidation of phenols generates peroxides. In the absence of free SO_2, peroxides can build up to measurable amounts during oxygen uptake by red wines. Under comparable conditions, their concentration correlates positively with total phenol content.

Binding of ethanal in red wine during airtight storage

(total phenols = 3200 mg/L, free SO_2 = 0 mg/L)



In red wine, free ethanal is gradually tied up by tannins and tends to disappear. Strong accumulation of free ethanal under oxidative conditions (no free SO_2) brings about a precipitation of tannins as soon as a certain degree of polymerization is reached.

Recap:
Oxidation and regenerative polymerization of phenols

- **In the course of regenerative polymerization, phenolic OH-groups lost by oxidation are regenerated.**

- **Regenerated phenols are again available for oxidation. Therefore, red wine tannin is able to bind much more oxygen than one could expect from stoichiometric data.**

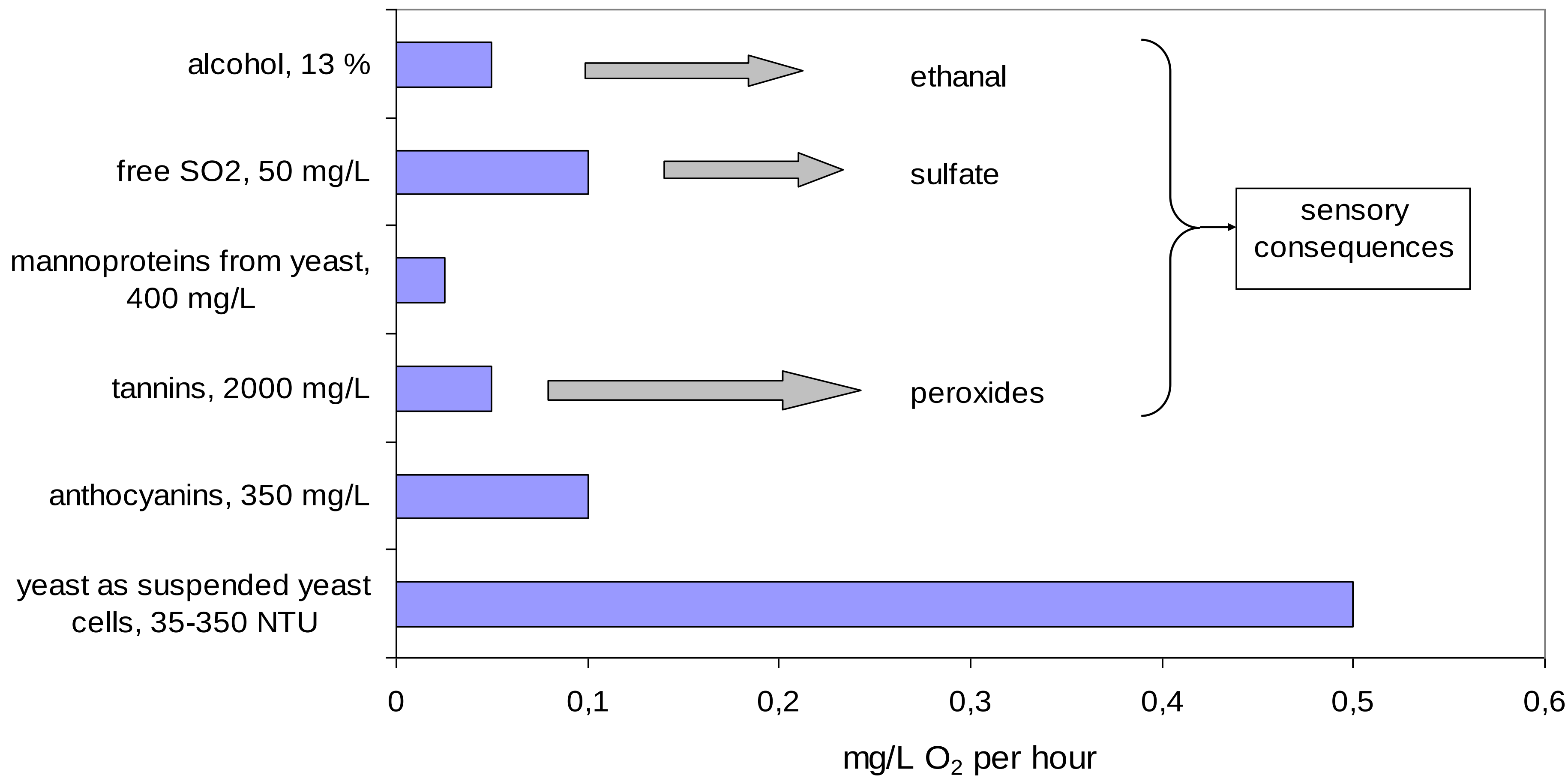
- **As a consequence, the capability of red wines to consume oxygen is unlimited and has no defined endpoint.**

- **Under practical winemaking conditions however, the capability of red wines to consume oxygen is limited**
  - by their total phenol content (risk of tannin precipitation, oxidative degradation of colored anthocyanins)
  - by the oxidative degradation of aromatics thru intermediate peroxides.

- **The oxidation of phenols generates peroxides which are reduced by SO_2, ethanol (→ ethanal), aromatics, and other phenols.**

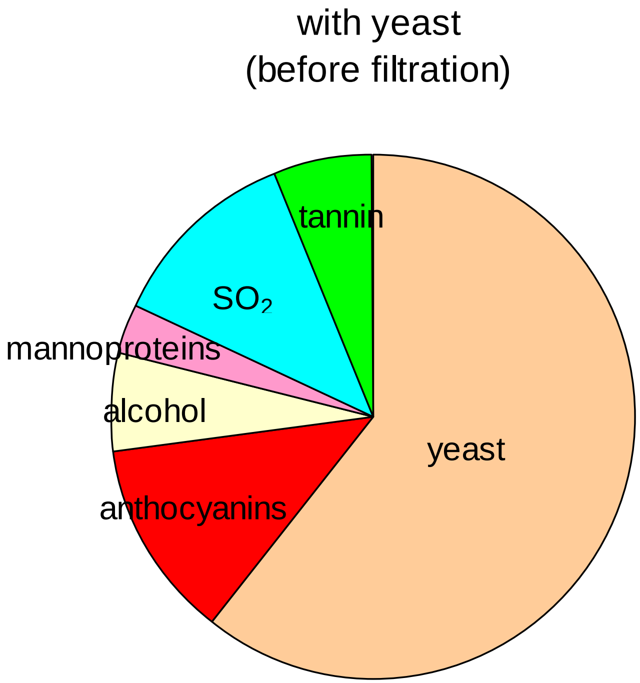
- **Ethanal generated is bound to tannins (ethyl-bridge!)**

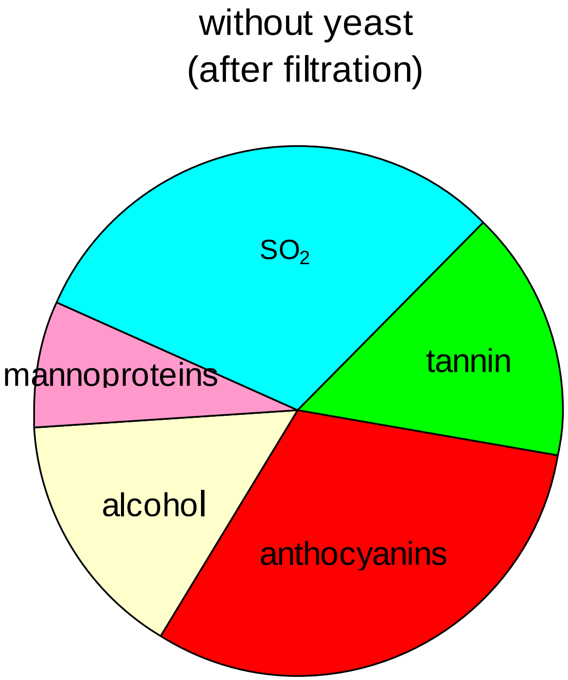
Oxygen consumption by major red wine constituents before filtration. Example of a typical red wine.



Phenols are the most important, but not exclusive oxygen acceptors in red wines. In red wines with low total phenol content, the role of non-phenolic oxygen acceptors like SO_2 is increasingly important.

Impact of filtration and residual yeast on the reaction of dissolved oxygen with majors red wine constituents.

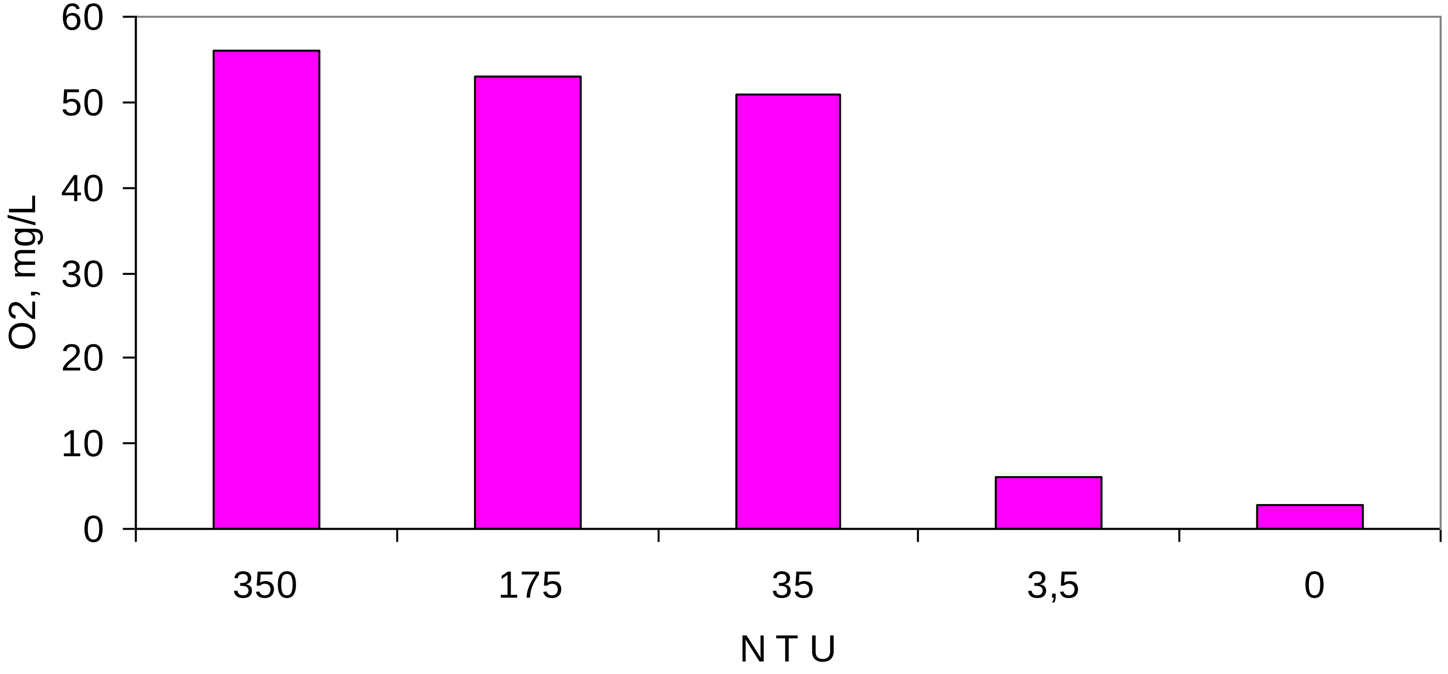




The percentage of dissolved oxygen reacting with tannins depends significantly on the amount and the biochemical status of suspended yeast cells post fermentation.

Consumption of oxygen (mg/L O_2 in 100 h) by yeast

in a young, unfiltered white wine as affected by turbidity, resp. suspended yeasts, under conditions of unlimited oxygen supply.



Very few amounts of suspended yeasts cells (~35 NTU, opalescence !) suffice to maintain their oxygen consumption capacity.

Properties of suspended yeast (fine lees) post fermentation

1. **Protection against oxidation** √
   (only by suspended yeast cells (not lees), slightly dependant on the amount of yeast)

2. **Adsorption of heavy metal ions (Cu for treatment of reduction flavor!)**
   (only by suspended yeast cells, strongly dependant on the amount of yeast)

3. **Adsorption of anthocyanins and tannins until saturation**
   (only by suspended yeast cells, strongly dependant on the amount of yeast)

4. **Release of mannoproteins (→ volume by mouth, protection colloids)**
   (by suspended **and** settled yeast, strongly dependant on the amount of yeast)

5. **Release of amino acids, including reducing amino acids**
   (by suspended **and** settled yeast, strongly dependant on the amount of yeast)

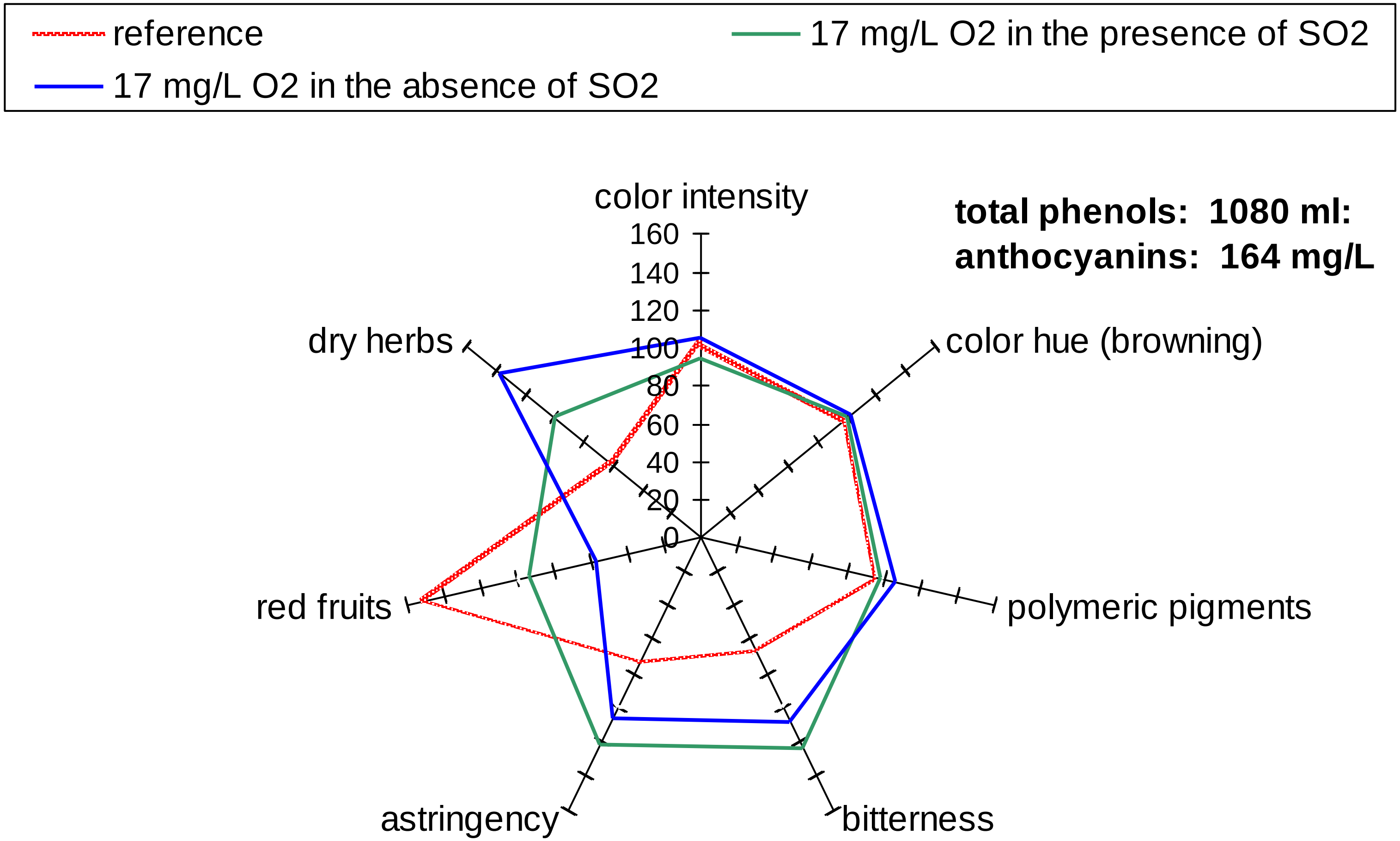
In the presence of suspended yeast cells (fine lees), oxidative polymerization of tannin slows down.

Any “sur lie” effects on the palate derived from the release of mannoproteins require high amounts of yeast.

Mannoproteins combine with tannins, thus lowering their astringency.

Sensory impact of oxygenation (2 x 8.5 mg/L O_2) as affected by SO_2 in a low-phenol red wine (Portugieser) after filtration.

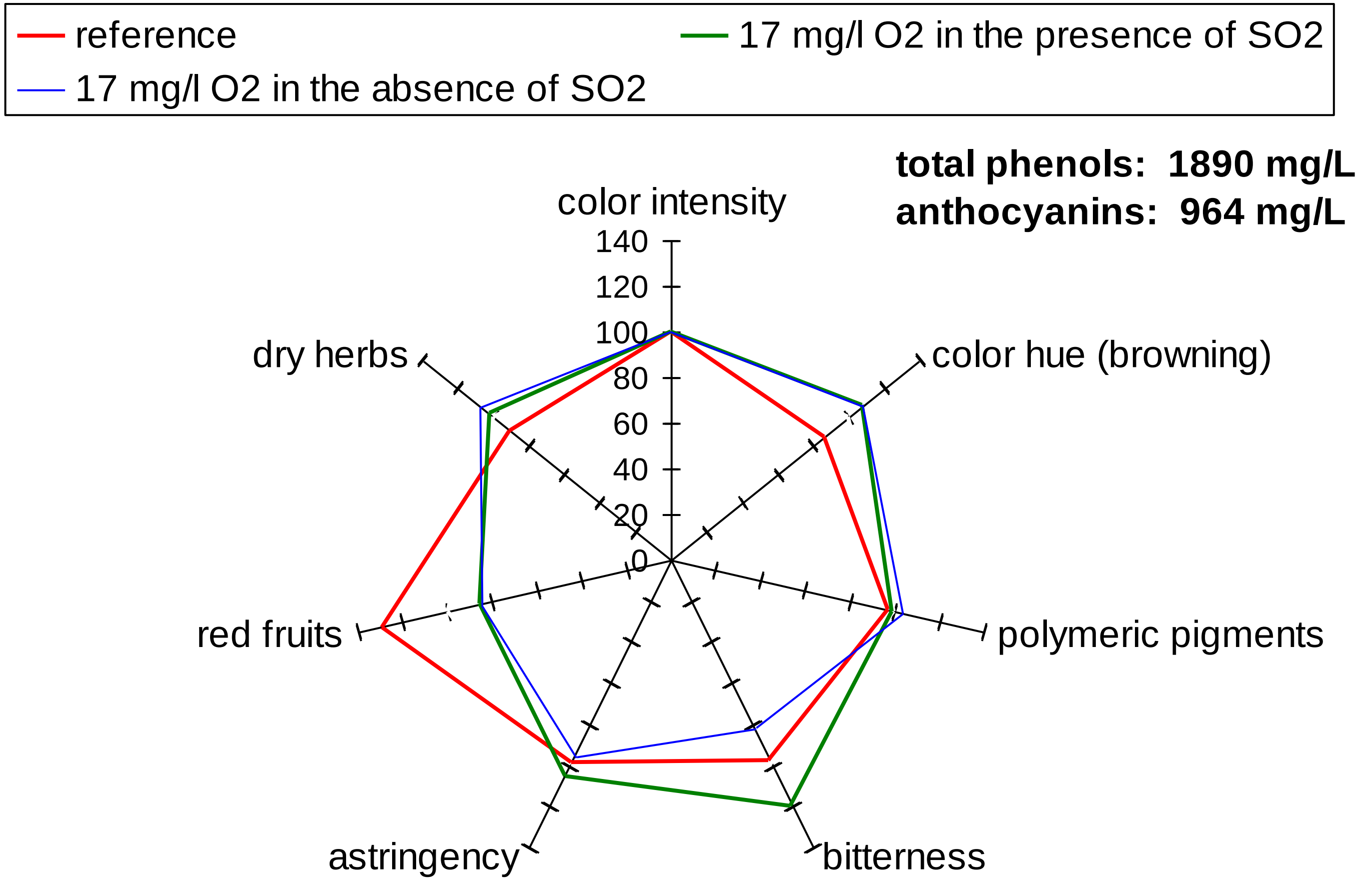
Data in % as compared to the mean = 100 %.



In low-phenol red wines, consumption of oxygen leads to heavy aroma damage (over-oxidation) if no free SO_2 is present. In such wines, SO_2 is an important oxygen acceptor endorsing the reducing effect of phenols.

Sensory impact of oxygenation (2 x 8.5 mg/L O_2) as affected by SO_2 in a high-phenol red wine (Dornfelder) after filtration.

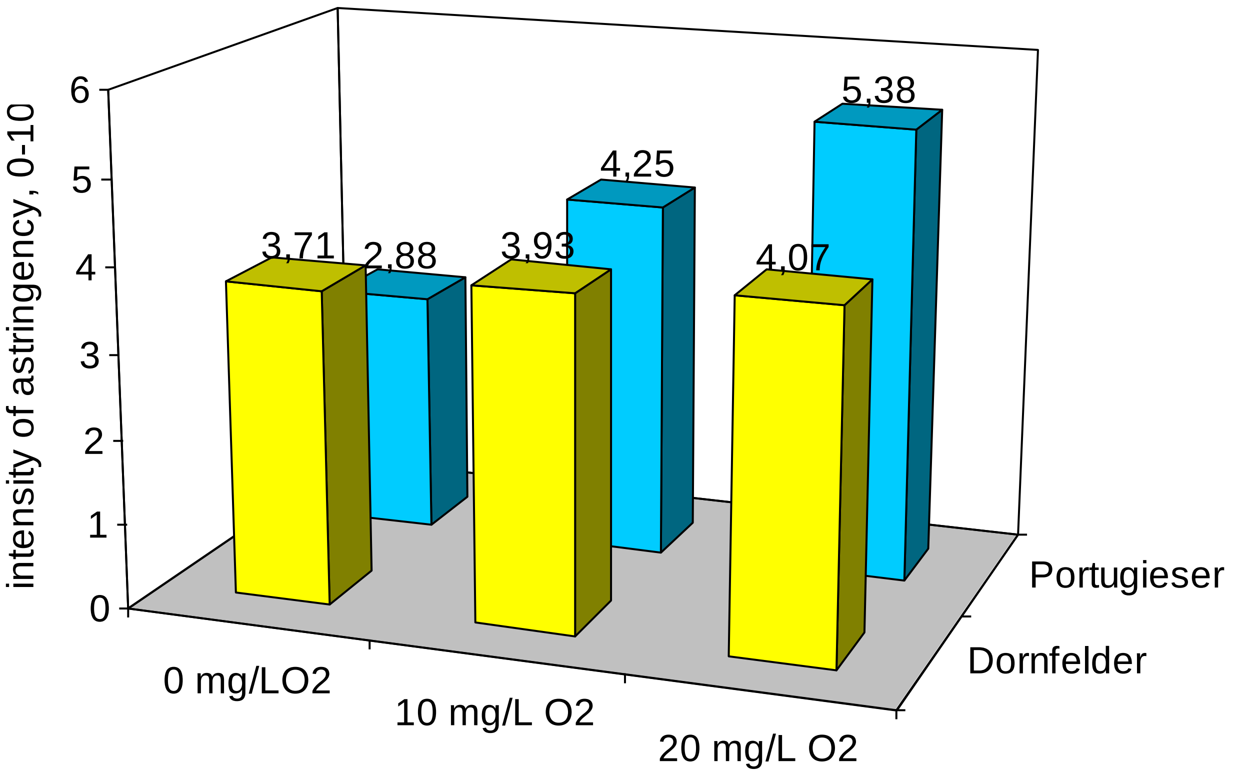
Data in % as compared to the mean = 100 %.



Under comparable conditions, SO_2 is less important as an oxygen acceptor when the wine is higher in tannins and anthocyanins; the consumption of oxygen causes less losses of fruity primary aromas.

Impact of the ‘total phenol-anthocyanin’ ratio on perceived astringency after consumption of oxygen.

Portugieser: total phenols (TP) = 1080 mg/L, anthocyanins (A) = 165 mg/l, TP:A = 6,6.
Dornfelder: total phenols (TP) = 1890 mg/L, anthocyanins (A) = 964 mg/l, TP:A = 2,0.

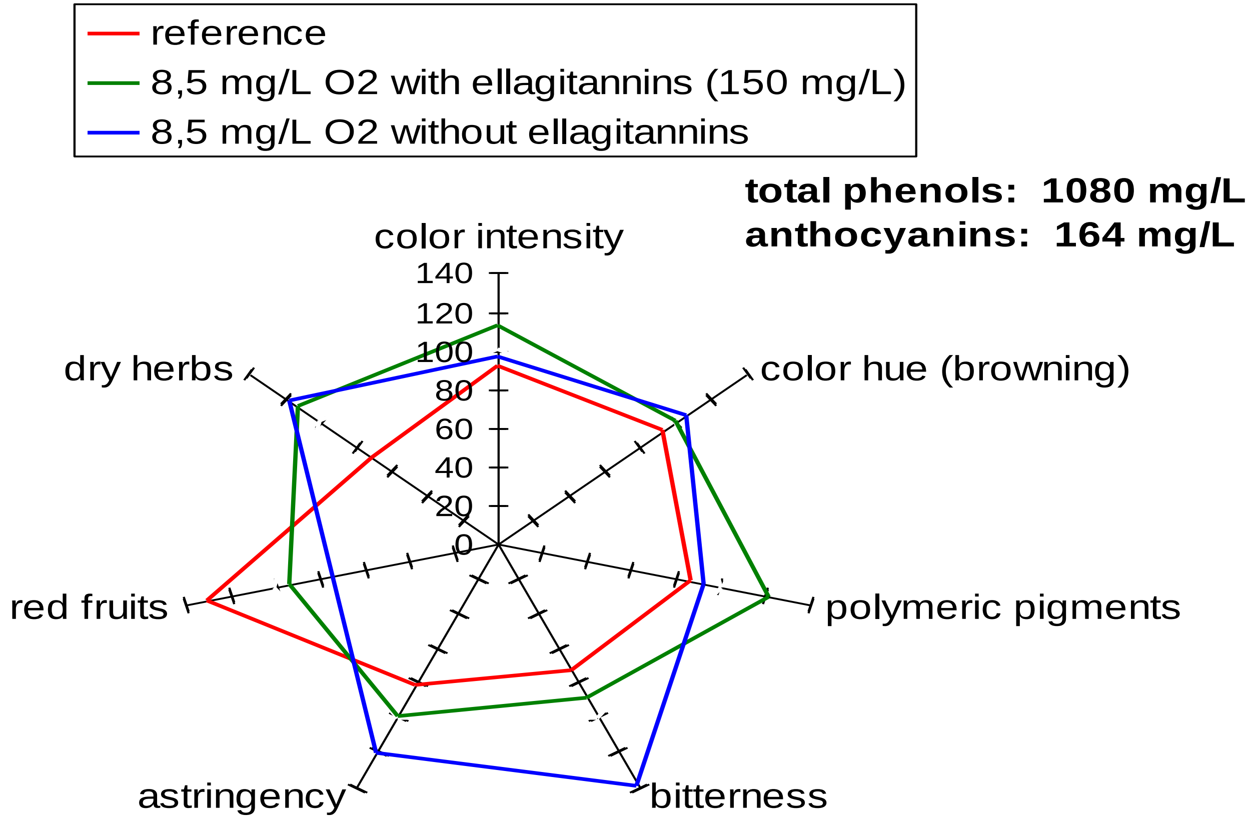


Red wines with a high proportion of anthocyanins in their total phenol content (low 'tannin : anthocyanin‘ ratio) hardly show any sensory response (astringency) after oxygen is consumed.

Oxygen consumption did not decrease astringency in any of these wines !

Impact of ellagitannin addition on the oxygenation (1 x 8.5 mg/l O_2) in a low-phenol red wine (Portugieser) after filtration and SO_2 addition.

Data in % as compared to the mean.

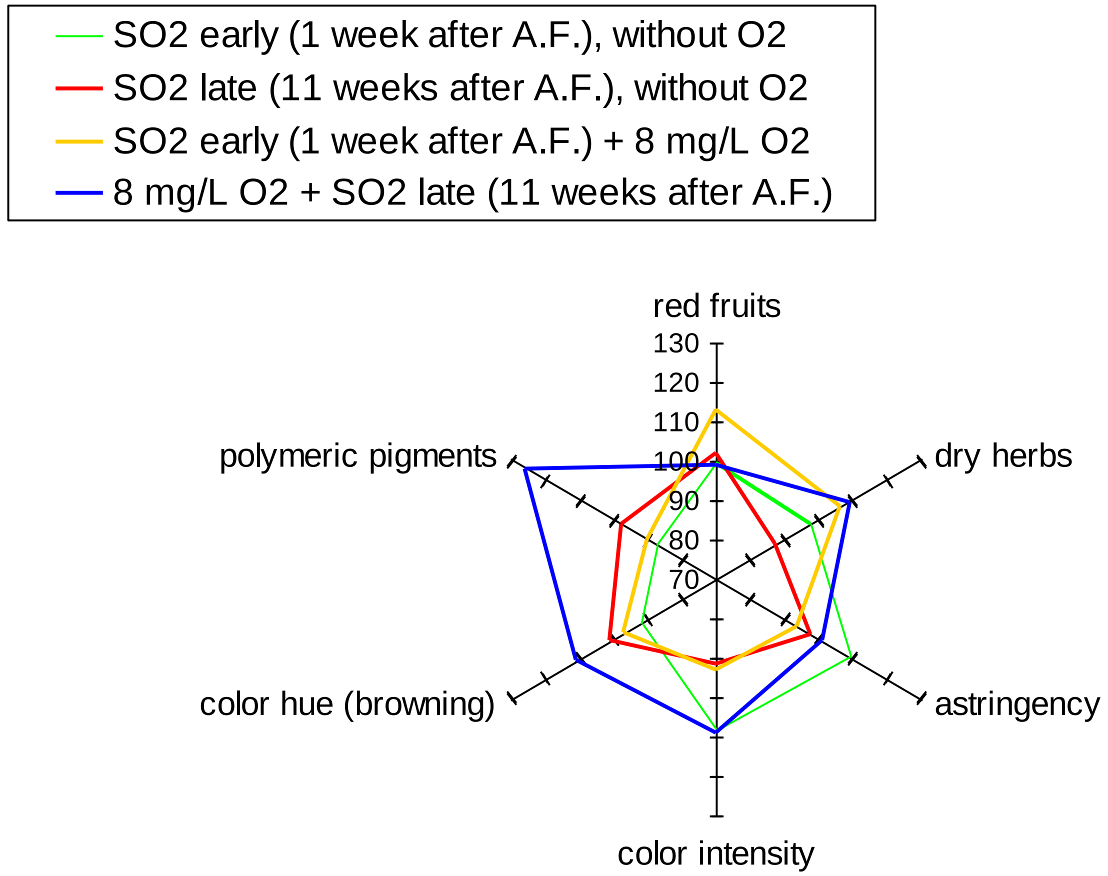


In low-phenol red wines, ellagitannins mitigate the detrimental effects (aroma degradation, enhanced astringency) of excessive oxidation.

<u>But:</u> Addition of ellagitannins to meager wines <u>may</u> also distort their balance by badly integrated astringency (not in this wine).

Impact of the time point of SO_2 (70 mg/L) and O_2 (8 mg/L) addition on a low-phenol Pinot noir red wine after filtration.

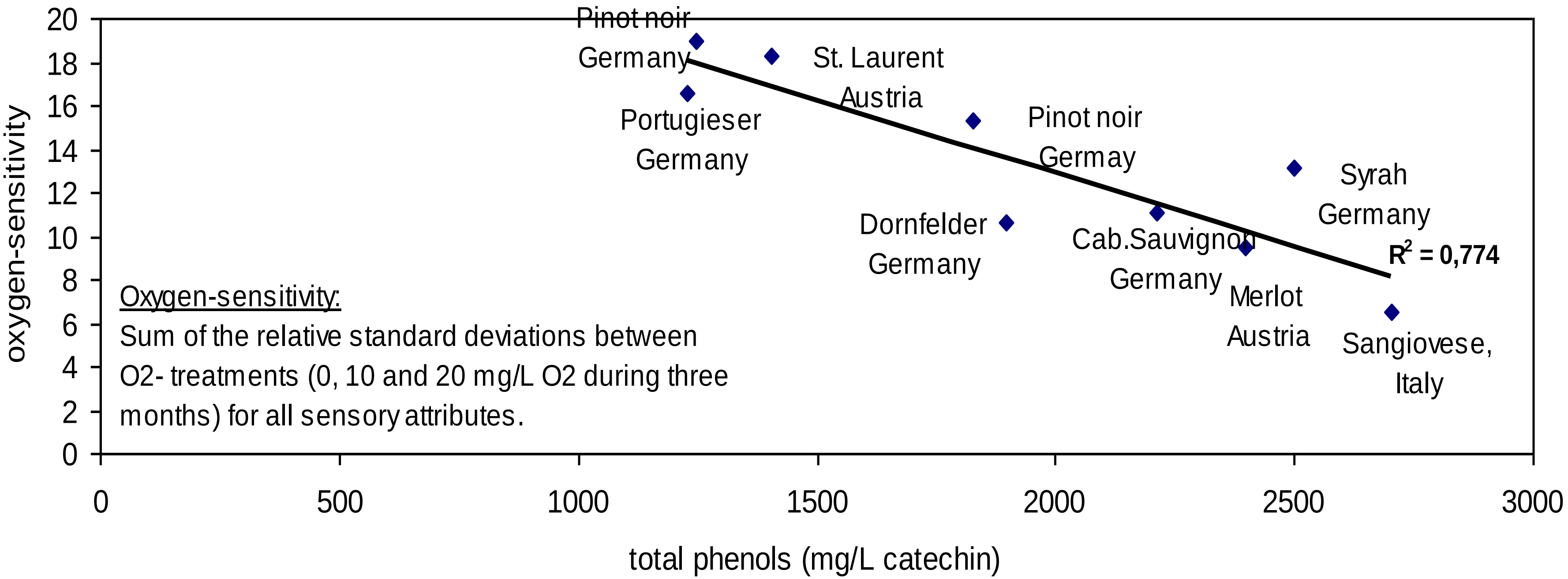
Data in % as compared to the mean.



- SO_2 early, without O_2 > lowest scores for primary aromas and color intensity, highest astringency.
- O_2 before SO_2 late > lowest scoring of primary aromas, highest color intensity and oxidation by smell.
- SO_2 early and O_2 afterwards > strongest primary aromas, lowest scorings for color intensity and astringency.

Timing and sequence of O_2 and SO_2 additions are of primary importance in low phenol red wines. Impacts decrease as total phenols and suspended yeasts increase.

Microoxygenation of red wines: Correlation between total phenols and oxygen sensitivity.



The higher the total phenol content, the less a wine responds sensorially to oxygen and the more oxygen it needs to age. Early information about total phenols provides information about how to handle the wine post fermentation regarding oxygen uptake.

Recap: Sensory consequences of oxygen consumption and the polymerization of polyphenols

- **The oxidation at the beginning of skin contact is an enzymatical one (by-product = H_2O), but it is a chemical one in the wine (by-product = H_2O_2).**
- **Tannins, anthocyanins, and SO_2 are the primary oxygen acceptors in filtered red wines.**
- **In turbid red wines before filtration, suspended yeast cells consume a significant part of the oxygen taken up without sensory effects.**
- **The oxidation of tannin accelerates its polymerization.**
- **Tannin polymerization changes the sensory characteristics of the wine (maturation, aging), <u>but does not necessarily decrease astringency.</u> The impact of mannoproteins on the perception of astringency and volume is important.**
- **The requirements of O_2 of red wines and their resistance to oxidation depend to a large extent on their total phenol content.**
- **This guideline is subject to further differentiation by the amount of anthocyanins in the total phenol content or the 'tannin-anthocyanin' ratio, respectively.**
- **Ellagitannins, yeast, and SO_2 act as complementary and variable oxygen acceptors competing with tannin for oxygen and mitigating the sensory effects of oxygen consumption.**
- **Overoxidation leads to a temporary emergence of free peroxides causing irreversible degradation of fruit aroma.**

Average passive O_2-uptake occuring during standard cellar operations in small and middle sized wineries

operation	**O_2 , mg/L**
Transfer by filling from the bottom	0,5 – 1,0
Transfer using a leaking sucking hose	5 - 8
Transfer by filling from the top	2 - 4
Centrifugation	3 - 4
Pad filtration	2 - 4
Cross-Flow-Filtration	1 - 4
Mixing	1 - 4
Cold stabilization	3 - 8
Transport in tanks with air-headspace	5 - 8
Bottling	1-2
Storage in big wooden casks, per year	10
Storage in barrels (225-300 L) per year, new barrels	20-40
Storage in barrels (225-300 L) per year, old barrels	≈ 10

The larger the lot, the less oxygen (in mg/L) is taken up. Small lots get easily overoxidized while aging in big tanks is delayed.

Any CO_2 in reds disturbs on the palate. By the time it is totally driven out by splashings etc., the wine has already picked up an amount of oxygen wich may suffice for low-phenol red wines.!

Means of active oxygen supply

Advantages and drawbacks

Operation	Effects
racking by splashing	- High O_2-uptake at rackings and transfers as long as the containers are filled from the top. - **But:** Low O_2-uptake at the first racking post A.F. when container is filled from the top due to CO_2-escaping from the young wine.
Sucking air through the leaking sucking nozzle of the pump	Variable, rather high O_2-uptake, difficult to adjust. Sensory effect hardly predictable.
Sucking air through a porous suction tube (sintered stainless steel)	Variable, rather high O_2-uptake. Sensory effect hardly predictable.
Micro-oxygenation	Oxygen supply (mg / L / month) easy to adjust over a large range. Easy to monitore by sensory means.
Storage under air-headspace	For microbiological security, only until 10° C (50 F). May need mixing. Easy to monitore by sensory means.
Wooden casks, barriques	Slow O_2-uptake from headspace and through wood. Easy to monitore by sensory means.
Flex- (PVC)-Tanks	Fast O_2-uptake through semi-permeable material, depending on the tank volume. Easy to monitore by sensory means.

Uptake und combination of oxygen in wine:

Or: What happens to the oxygen in wine ?

2 Steps :

1. **Absorption of atmospheric oxygen by the liquid:**
   No sensory consequences; oxygen is dissolved as gas and can be measured as DO.

2. **Binding of the dissolved oxygen to wine constituents = oxidation:**
   When oxygen binds, it disappears and cannot be measured any more; sensory effects can be observed.

2 reaction models :

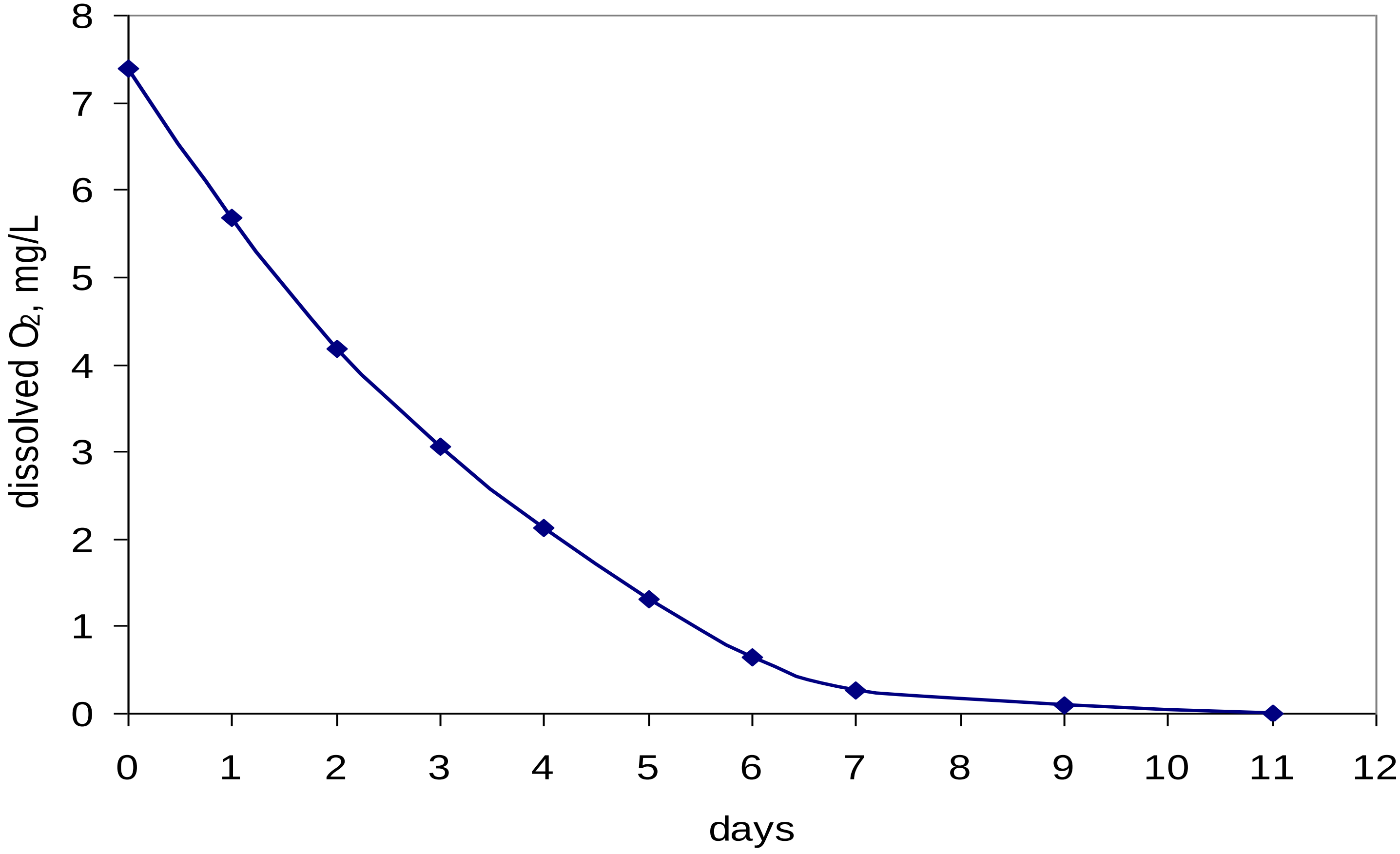
- The absorption of oxygen by wine is faster than its binding
  → increase of dissolved oxygen (DO).

- The absorption of oxygen by wine is slower than its binding
  → no DO can be measured.

The dissolved oxygen (DO) content which is measured is the instantaneous net difference between absorption and binding.

Typical course of dissolved oxygen binding in red wine

(airtight storage, no headspace)



DO binds at a rate of approximately 1 mg/L per day during the first week. It disappears to 90 % within one week as long as no further oxygen can be taken up through the liquid surface.

Micro- vs. Macro-Oxygenation

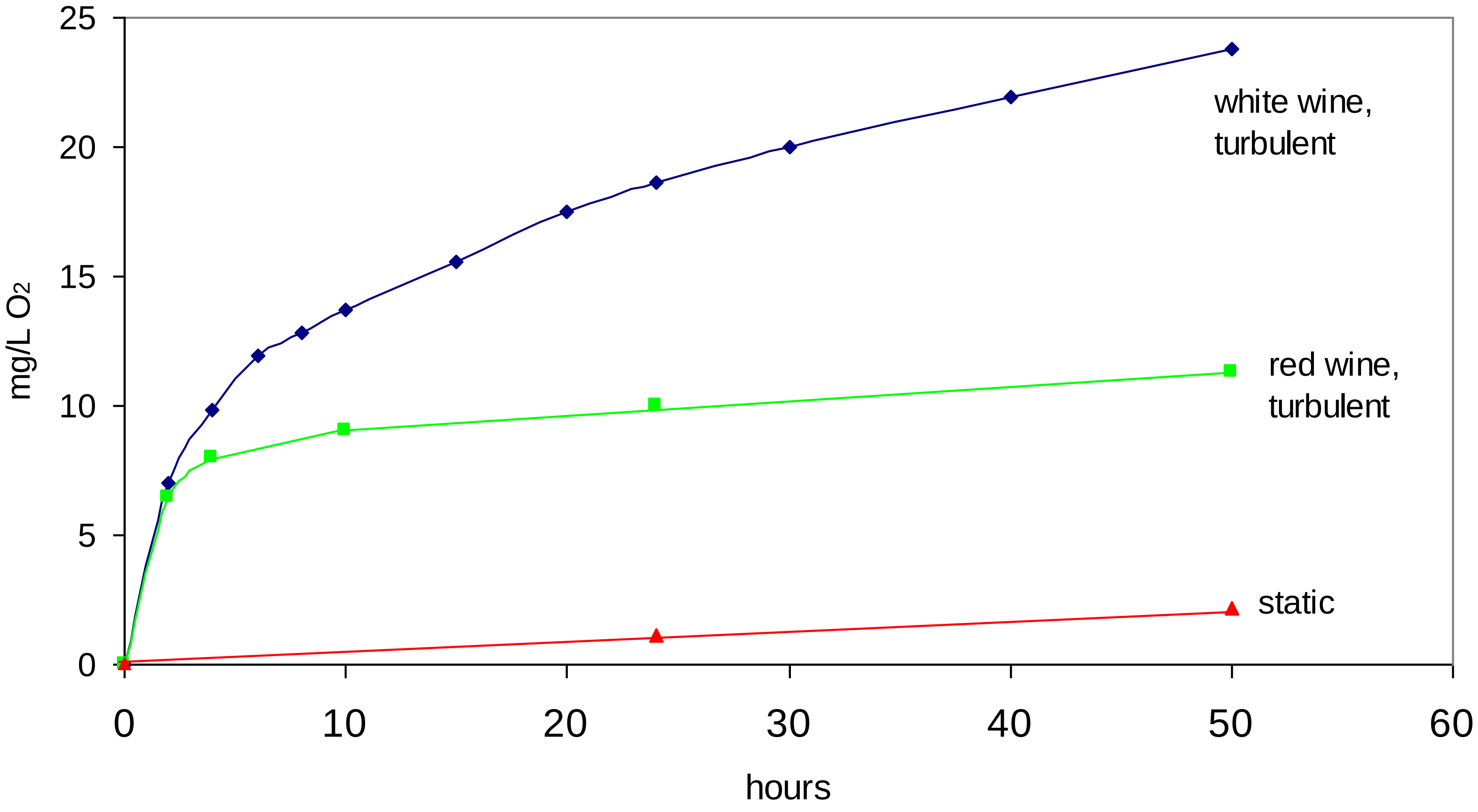
Macro-Oxygenation:	**Micro-Oxygenation:**
Fast one-time oxygenation in a range around 5 mg / L / day.	Slow, continuous oxygenation in a range of around 5 mg / L / month.
→ regenerative polymerization is slower than oxidation	→ O_2-binding faster than O_2-supply
→ accumulation of dissolved O_2	→ no dissolved O_2 measurable
→ oxidizable phenols are rapidly consumed	→ polymerization undoes the effect of oxidation
→ anthocyanins and aromatic compounds can be easily destroyed	

Oxygen uptake during current cellar operations and wine treatments equates to macro-oxygenation.

Micro-oxygenation requires hands-on experience to adjust O_2-supply (1-10 mg/L ▪ month) to the amount and diversity of the oxygen acceptors involved.

Purpose: O_2-supply < O_2-binding → no dissolved O_2.

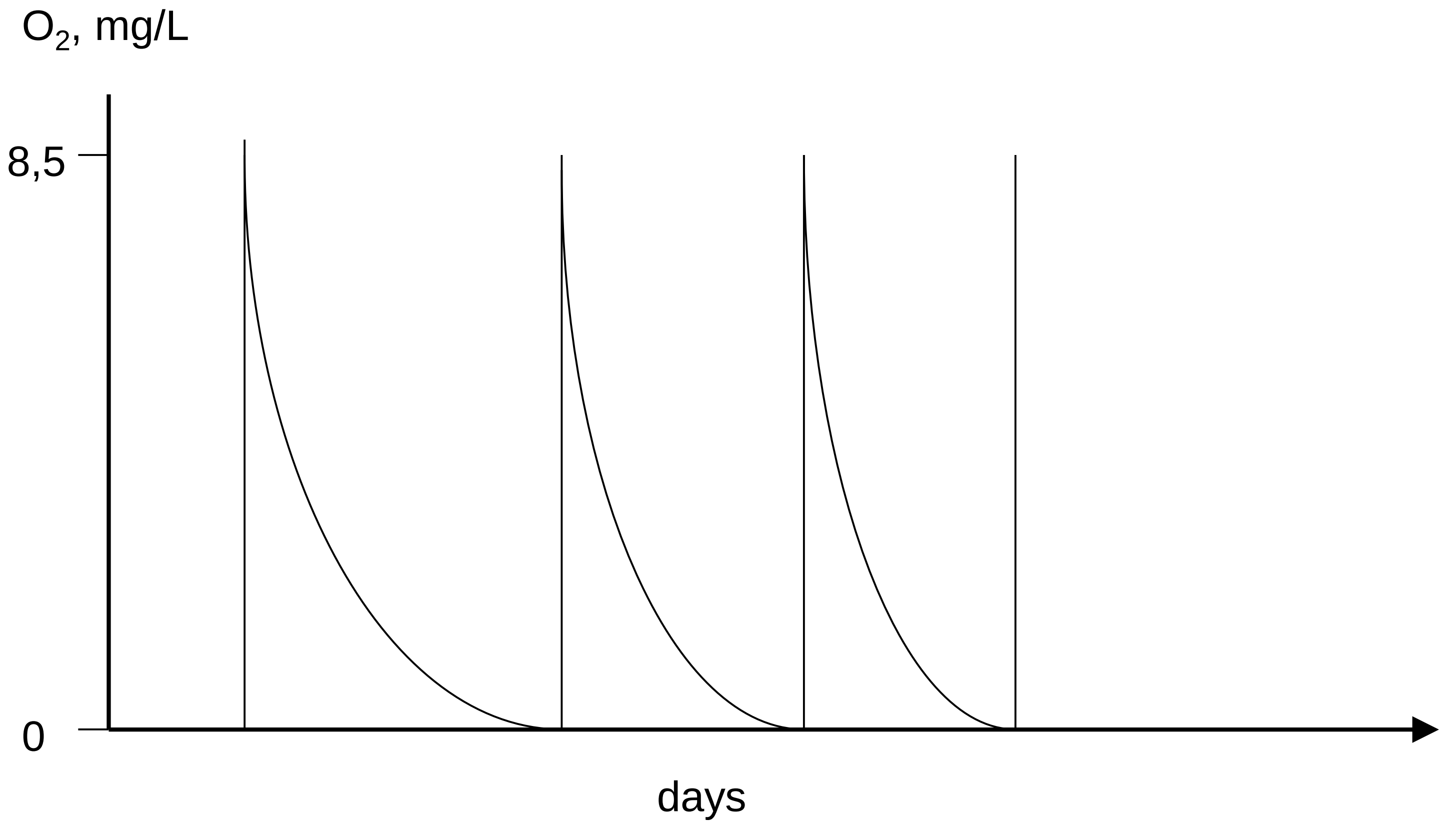
Typical oxygen binding rates in filtered wines stored under a turbulent surface (100 cm^2/L) at 20° C in contact with air, atmospheric pressure.



Continuous mixing of half-filled containers results in a macro-oxygenation. A turbulent surface increases the oxygen uptake ~10-fold as compared to a static surface.

Pattern of several consecutive saturations with oxygen.

Saturation concentration = 8.5 mg/L O_2 at 20° C.

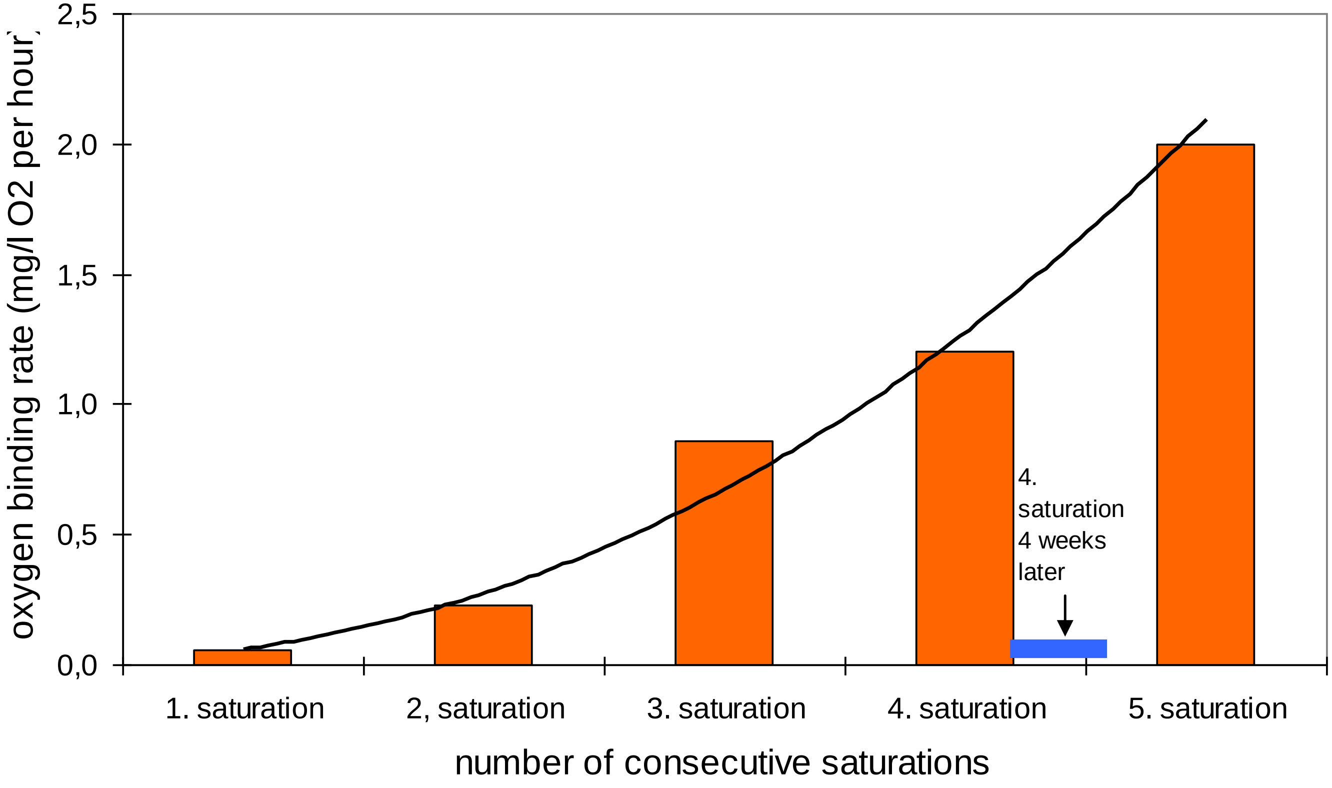


A wine at cellar temperature can take up as much as 8,5 g/L O_2 (saturation). Only after this amount has decreased or disappeared by binding, more oxygen can be taken up.

Overoxidation, Scenario I:

Oxygen binding rate (mg/L O_2 / h) in the course of several consecutive saturations (8.5 mg/L O_2) in a Pinot noir red wine.

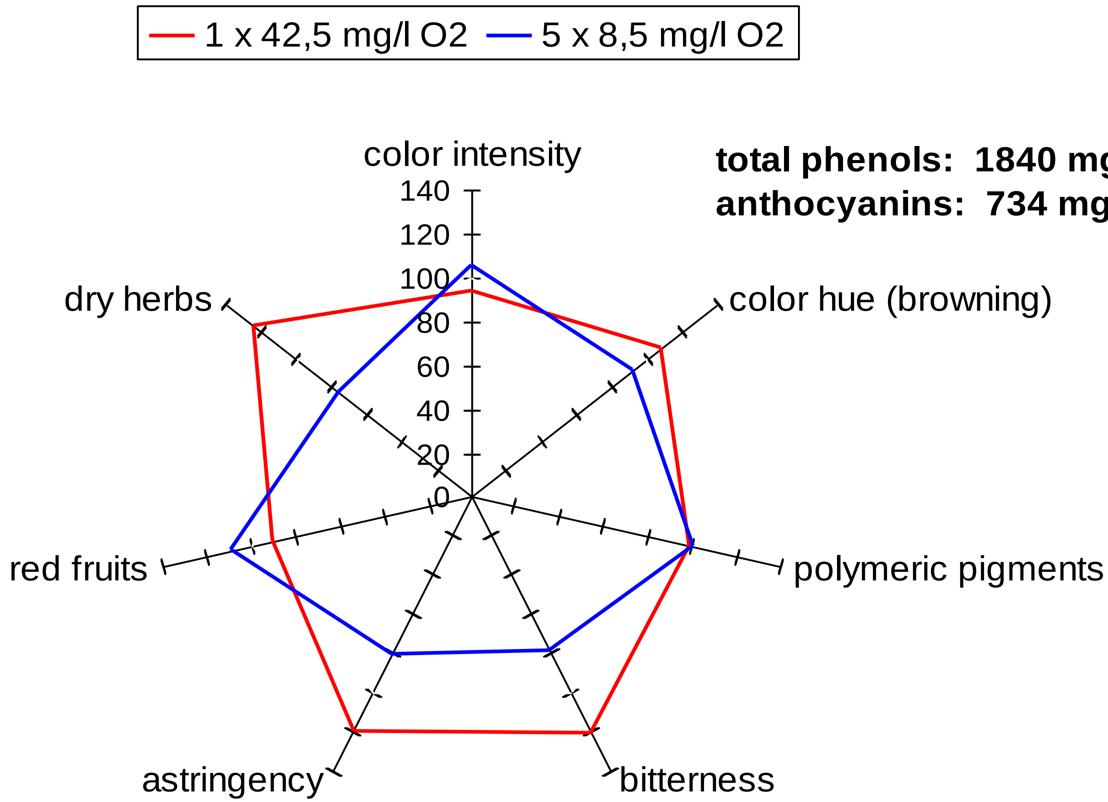
Each saturation takes place immediately after the DO of the previous saturation has been bound.



Overoxidation under conditions of unlimited oxygen supply is auto-catalytic, i.e., its speed increases exponentially. Cause: Polymers being formed are more ionized (lower pKa) and bind oxygen faster than their precursors of lower molecular weight.

Overoxidation, Scenario II:

Fast vs. slow oxygen supply rate: Effect of the oxygenation intensity on a Dornfelder red wine.



total phenols: 1840 mg/L
anthocyanins: 734 mg/L

For the same total amount (mg/L) of oxygen, its supply in form of consecutive smaller fractions produces better sensory results than the one-time supply of the whole amount.

Cause: At a high oxygen supply rate, regenerative polymerization of phenols lags behind their oxidation → accumulation of peroxides etc.

Solution: Micro-oxygenation – if the wine really requires more oxygen.

Experimental determination of oxygen requirements

1. **Fill two bottles of 0.75 L (total volume = 785 mL) to the brim with a hose stuck to the bottom of the bottles and submerged into the wine.**
   Purpose: No O_2-uptake at filling.

2. **Close one bottle immediately with a screwcap → reference.**

3. **From the second bottle, remove 20 mL with a pipette and screwcap it. The oxygen available in the headspace equals 7,7 mg/L O_2.**
   Calculation basis: Air contains 20,8 %-vol. oxygen, 1 mL O_2 = 1,4 mg O_2.

4. **Shake daily without opening the bottles.**

5. **Taste the treated samples and the reference after 1-2 weeks. Add some SO_2 if there is a strong smell of free ethanal.**

Short-term effect of oxygenation (decanting, 1-2 hours)

- **Red wine tannin occurs in a concentration range of mg/L or g/L. Its chemical modification requires the binding of several mg/L oxygen which takes several days.**
  → Decanting the day of consumption does not change tannin quality..

- **Aroma compounds occur in a concentration range of µg/L or mg/L. Their chemical modification requires the binding of less than 0,1 mg/L oxygen which takes less than one hour.**
  → Decanting before consumption changes the aroma profile in the short term.

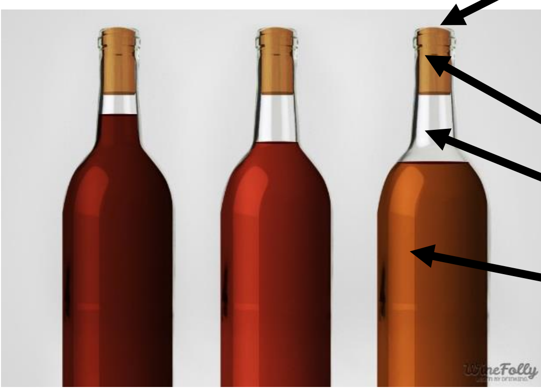
- **Decanting removes CO_2 disturbing on the palate; the change by taste is mistaken as a modification of tannin quality.**

The difficulty of SO_2-adjustment before bottling

- When wines are prepared for bottling, they are fined, pumped, mixed, filtered, blended.... and tortured frequently.
- At the same time, they pick up oxygen from the headspace in tanks, hoses, filters and wherever the wine has a surface in contact with air.
- Amounts of 3-5 mg/L with peaks of up to 7 mg/L O_2 occur frequently under practical winery conditions.... and without any control. They equal a macro-oxygenation just before bottling.
- In these situations, dissolved oxygen oxidizes SO_2 almost according to stoichiometry: 1 mg/L O_2 = 4 mg/L SO_2.
- Cause: Accumulation of intermediate quinones oxidizing SO_2 before they are reduced back to phenols by regenerative polymerization; they act as oxygen transmitters.
- Consequence: Variable und heavy losses of free SO_2 shortly after bottling, occurence of free ethanal (smell!) in the worst case.

Conclusion: The knowledge of the level of free SO_2 is only useful as far as one knows how much oxygen is dissolved in the wine at the precise moment.

The oxygen in the bottle.
The meaning of "total package oxygen“



After bottling, wine is subject to the effect of oxygen resulting from 4 different sources.:

- Oxygen diffusing through the bottle closure (genereally, high diffusion rates for synthetic corks, very variable diffusion for natural corks, and a consistently low diffusion for screwcaps).

- Oxygen contained in the cork tissue.

- Oxygen contained in the bottle headspace.

- Oxygen dissolved in the wine before bottling.

∑ = total package oxygen (TPO), in mg
. = total amount of O_2 contained in the bottle, in mg.

The TPO allows to predict SO_2 losses after bottling. When free SO_2 has totally disappeared by oxidation, a smell reminding sherry (free ethanal) appears.

Device for non-invasive measurement of gaseous (in the headspace) and dissolved (in the liquid) oxygen using luminescence.

Recap:
Active und passive oxygen supply

- **Passive O_2-uptake during wine storage and treatments up to the point CO_2 is completely removed frequently suffices for low-phenol red wines; further active O_2 supply as occuring in barrels may be detrimental to quality.**

- **Passive O_2-uptake during cellar operations depends strongly on lot size and on CO_2 which can escape from the wine.**

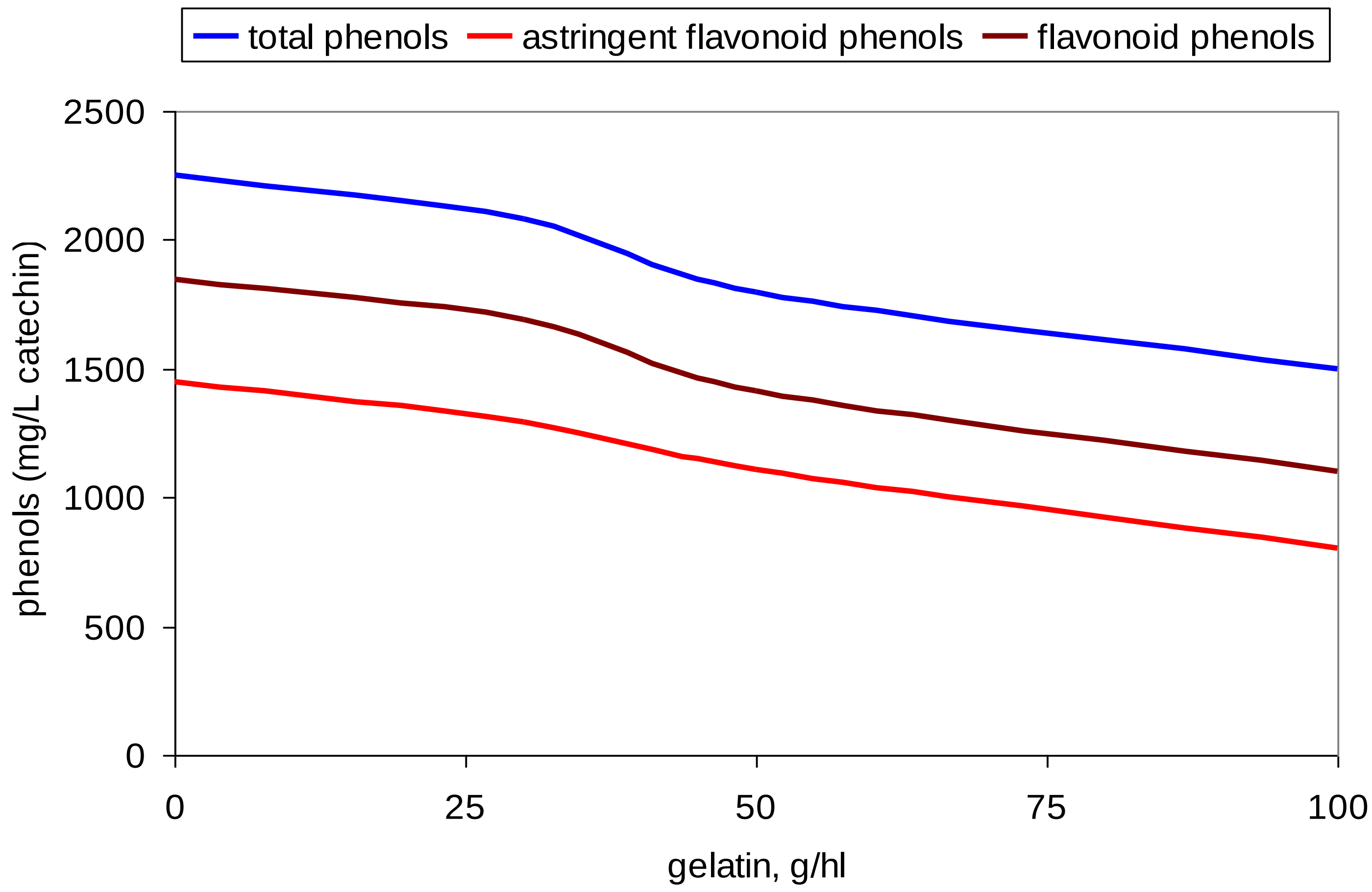
- **Passive O_2-uptake at the first racking can be minimal due to escape of CO_2.**

- **Micro-oxygenation is beneficial only to wines with a high tannin content and a balanced 'tannin : anthocyanin‘ ratio (total phenols : anthocyanins = 5:1 to 3:1).**

- **For stabilizing free SO_2, oxygen uptake must be prevented the last week before bottling in order to make sure that dissolved oxygen has bound and that there is time left to add more SO_2 if necessary.**

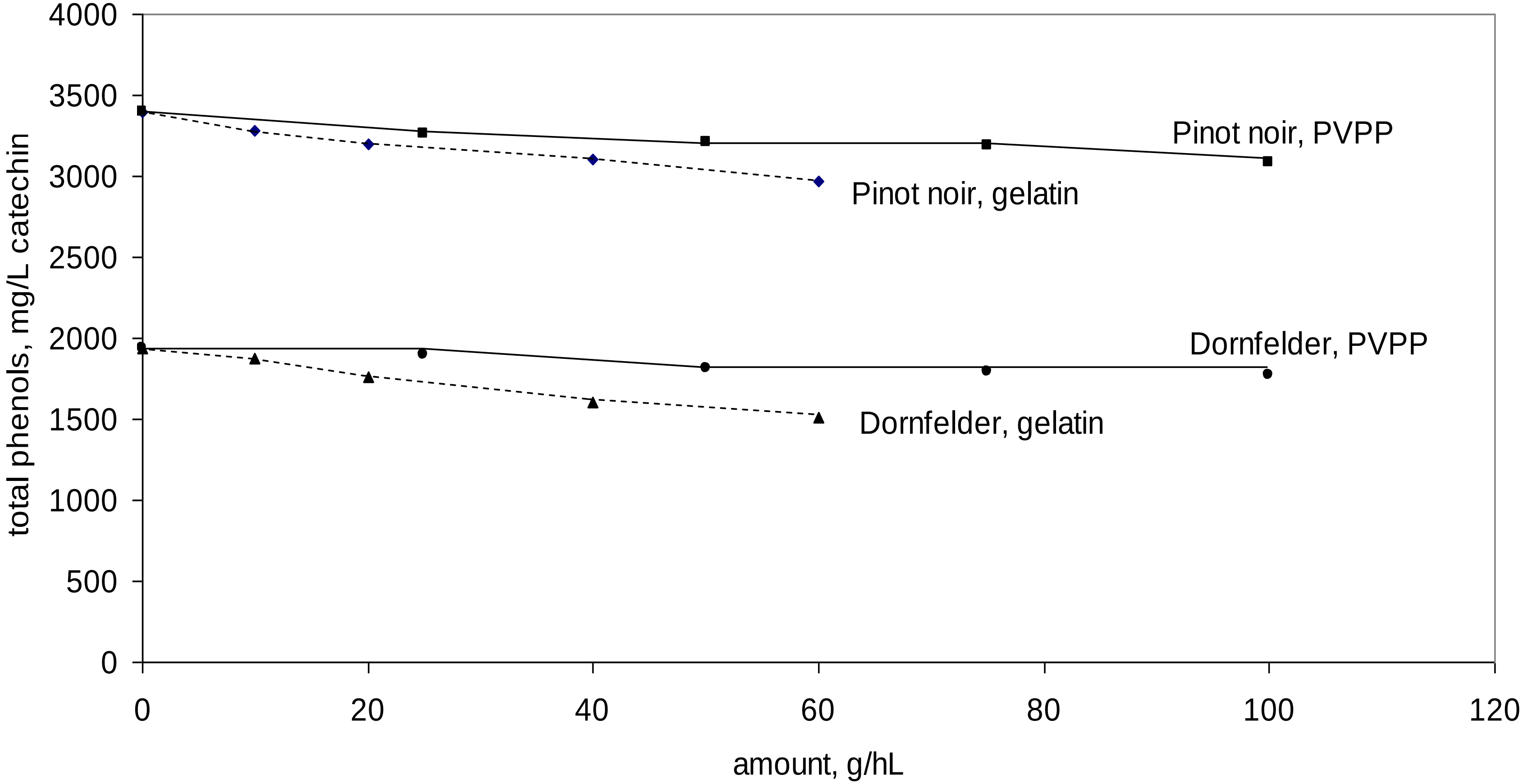
- **Choosing the bottle closure with is specific OTR has a significant impact on the post bottling development.**

Fining a red wine with gelatin: Decrease of total, flavonoid, and astringent flavonoid phenols.



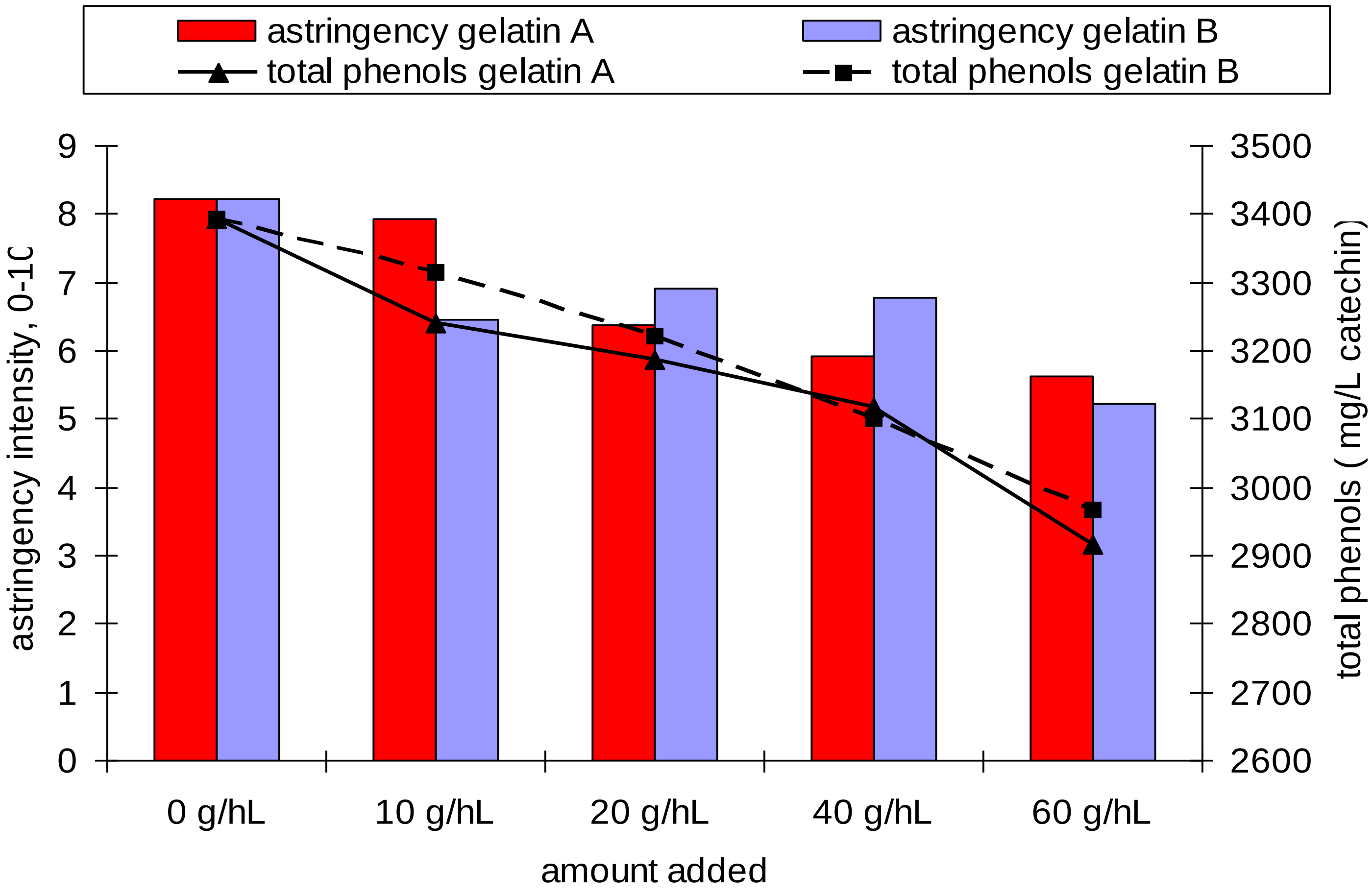
When red wines are fined with gelatin, the decrease of flavonoid phenols and astringent flavonoid phenols correlates with the decrease of total phenols. Measuring total phenols is a suitable quality control instrument for red wine astringency.

Removing total phenols from red wines using gelatin (average of three gelatins) and PVPP.



The removal of a given amount of total phenols requires a corresponding amount of proteins (or PVPP) whose most concentrated and less expensive form is available as gelatin. PVPP is less effective than gelatin. Egg white acts only slightly on a g/hl basis.

Effect of two gelatins (A and B) on total phenol content and astringency in a Pinot noir red wine.

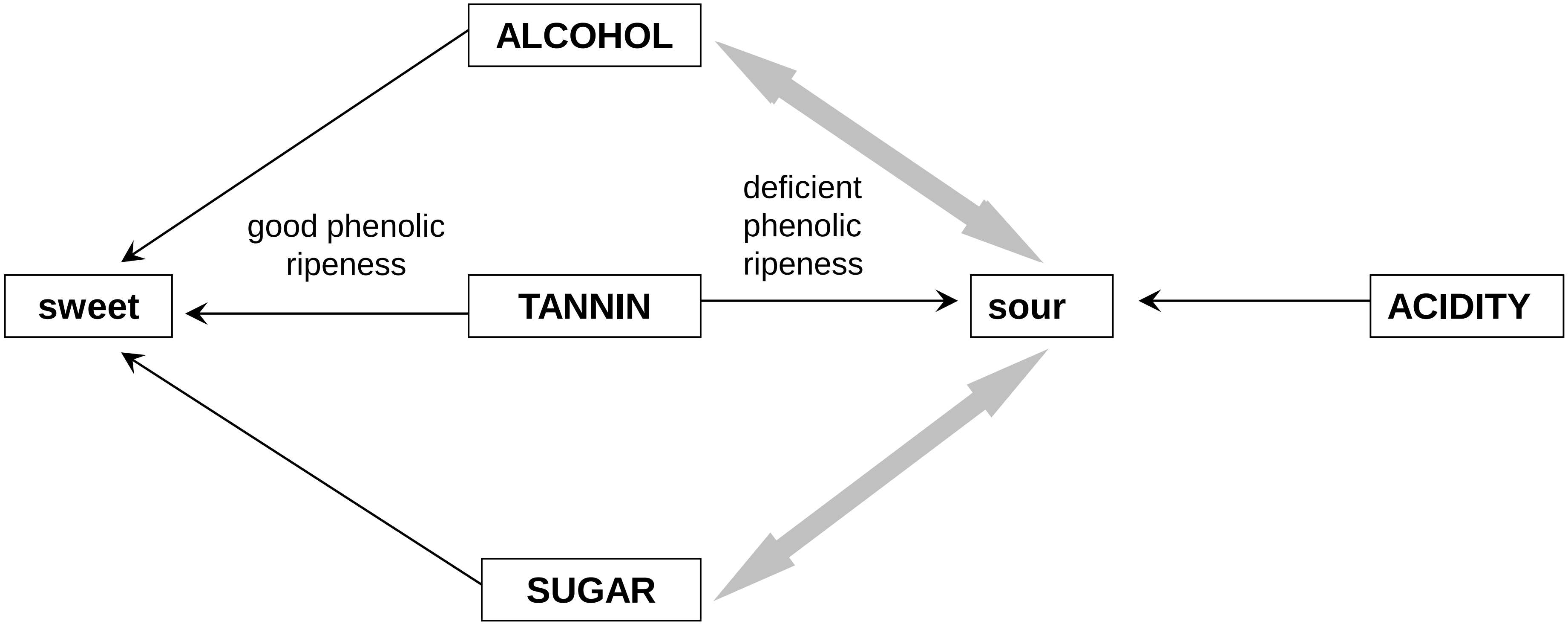


When excessive astringency of red wine is reduced by fining with an albuminous fining agent likewise gelatin, there is a strong correlation between the amount of fining agent, the decrease of total phenols, and the decrease of perceived astringency.

Measuring total phenols can help decide about fining when red wines are considered too harsh on the palate, and monitore the fining effect.

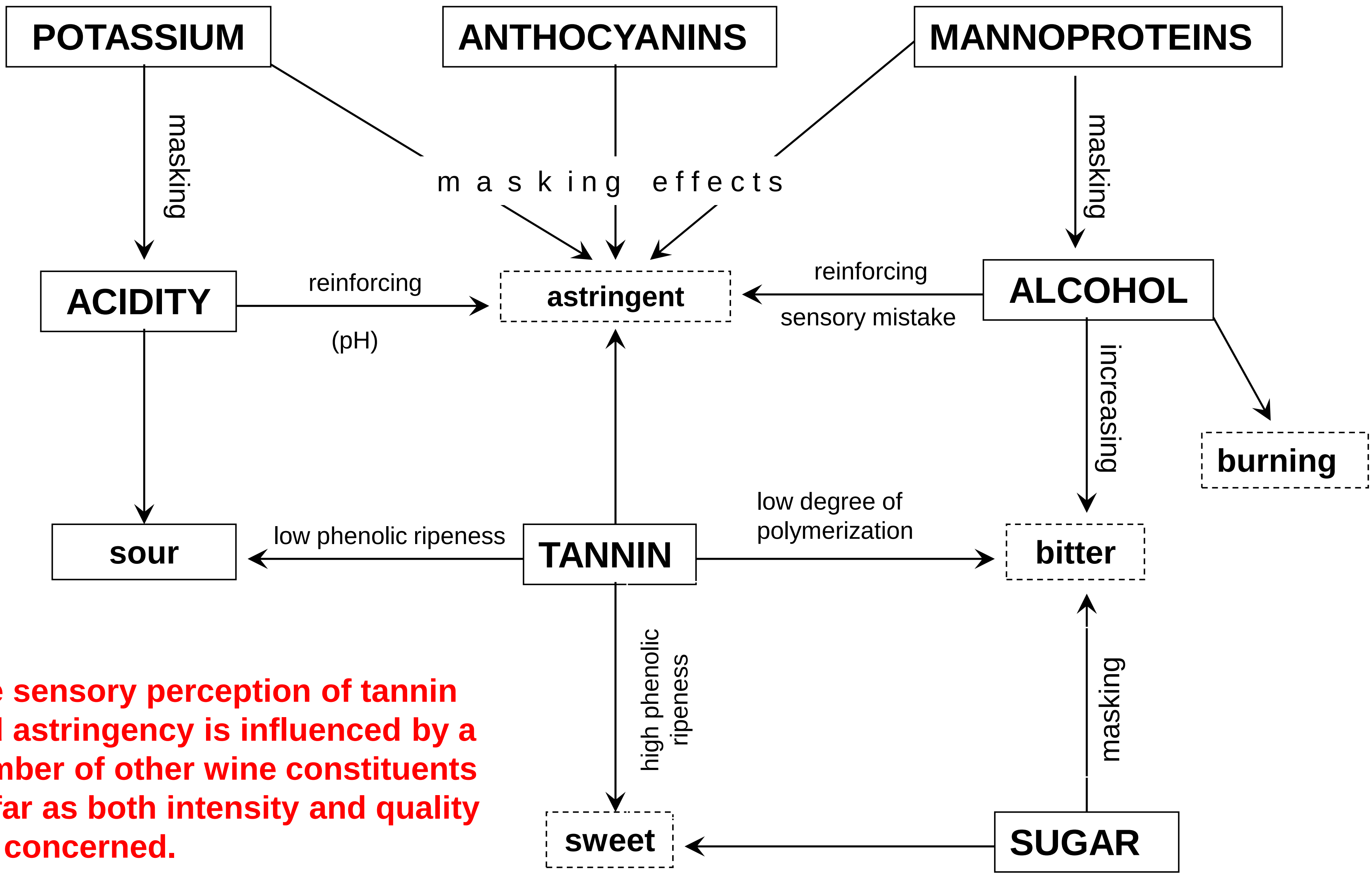
Interaction between tannin and sourness:

Effect of tannin and other constituents on perceived sourness in red wine.



Tannins from ripe fruit display a sweet subquality on the palate, tannins from unripe grapes a sour one. The sensory evaluation of tannin quality is only possible after excessive sourness has been removed (deacidification trials with $KHCO_3$).

Sensory expressions of tannins; interaction with other wine constituents



The sensory perception of tannin and astringency is influenced by a number of other wine constituents as far as both intensity and quality are concerned.

Recap:
Reducing astringency by finings

- **An excessively high astringency can be caused by too much tannin or by tannin of bad quality.**
- **Gelatin is the most efficient fining agent for reducing too much tannin; other fining agents require far higher application rates to achieve to same effect.**
- **Gelatin amounts of 10 g/hl or more result in sensorially significant differences; amounts around 20 g/hl are often useful to balance red wines considered too harsh.**
- **Before any such fining, first try to reduce acidity since high acidity enhances the perception of astringency and reduces volume / weight.**
- **In some individual cases, a reduction of astringency and a better integration of tannin can be achieved by increasing the mannoprotein content (yeast, commercial products).**
- **Oxygen supply is not a useful means to reduce astringency in the short-term, i.e. shortly before bottling.**

Tannin management in cool climate red wines consists to a large extent in acidity management.

Acidity management in cool climate red wines

Starting point :

- MLF is indispensable for red wines
- Under cool climate conditions, MLF is often not sufficient to balance sourness
- Excessive TA increases adstringency and decreases perceived volume (weight) on the palate
- Additional deacidification by chemical means may turn necessary after MLF completed.

Specific conditions in red wines :

- High pH is increased further (3.7 to 4.0) → microbiological risks when T > 10° C and wine not filtered.
- Tannins enhance K^+-solubility
- Tannins delay cold stabilization.

Solutions :

- Deacidification after MLF, SO_2 addition and filtration (tight or sterile)
- Choose the deacidification agent according to the chemical make-up of the individual wine. There are no general rules!

Under cool climate conditions, great red wines have TA ≤ 5.0 g/L, depending on tannin quality and quantity. Higher TA requires hot climate tannin !

Difference: Calcium *vs.* Potassium
- Chemistry -

Calcium carbonate ($CaCO_3$) :

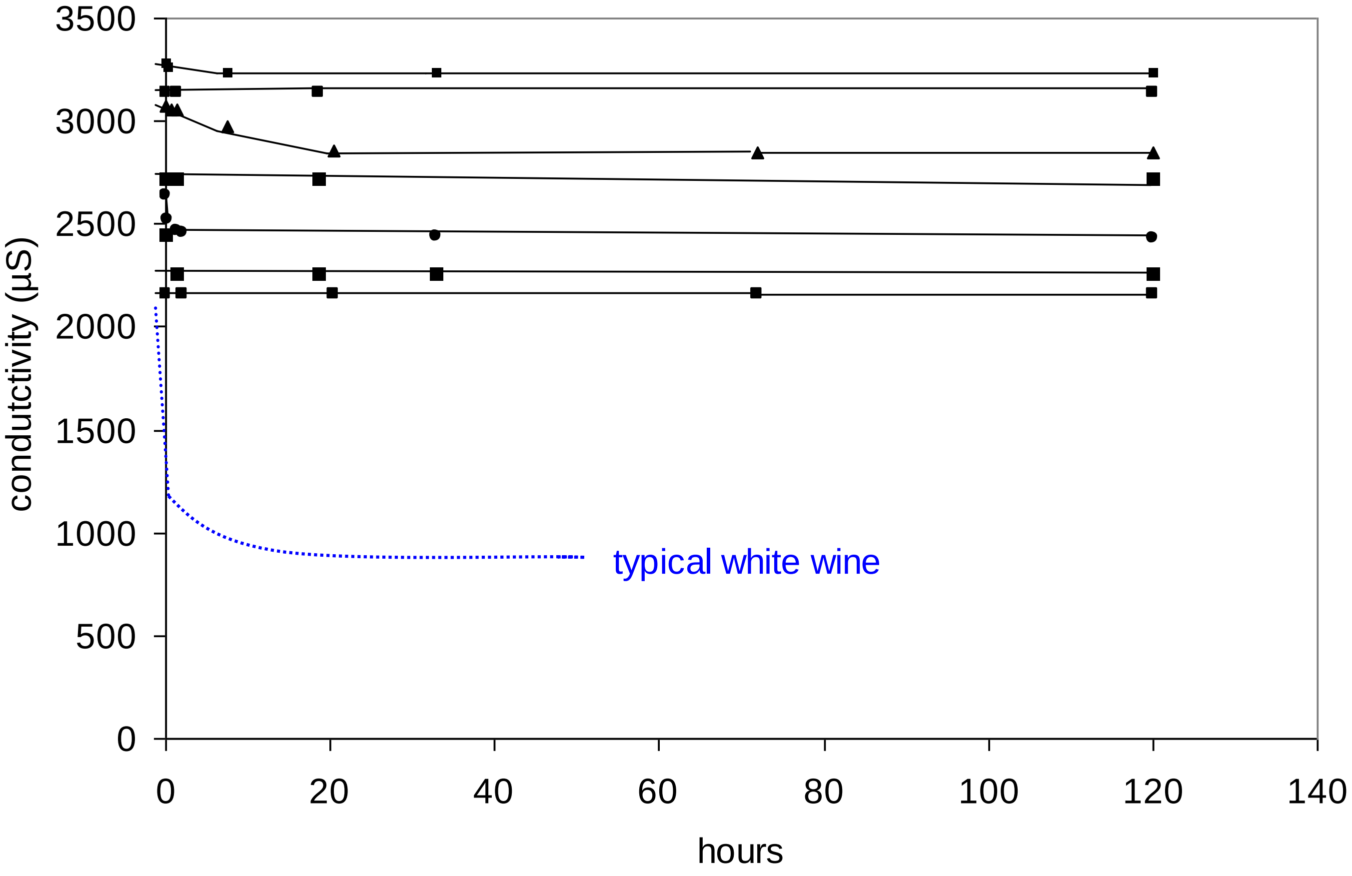
- Precipitates only tartaric acid which is more than 1 g/L
- 0.7 g/L $CaCO_3$ removes 1.0 g/L tartaric acid = 1.0 g/L T.A.
- Acidity reduction is immediate
- Precipitation of Ca (as Ca-tartrate) is delayed (1 to 3 months in reds)
- Ca-tartrate crystal instability cannot be remedied by cold stabilization

Potassium bicarbonate ($KHCO_3$) :

- Expected to precipitate tartaric acid as KH-tartrate, but precipitation is largely impeded by red wine tannins (acting likewise metatartaric acid)
- 0.7 g/L $KHCO_3$ removes 1.0 g/L T.A. if K^+ added precipitates completely
- 0.7 g/L $KHCO_3$ removes 0.5 g/L T.A. if K^+ added remains in solution.
- The actual T.A. reduction depends on the extent to which K^+ drops out.
- Under practical conditions, removal of 1.0 g/L T.A. in red wine requires 1.2 g/L $KHCO_3$ approximately.

The deacidification effect of $KHCO_3$ on T.A. figures is not exactly predictable in red wines.

Precipitation of KHT in 7 filtered red wines at 5° C in the presence of seed crystals (5 g/L) after previsious dissolution of 1.5 g/L KHT.



Precipitation of insoluble KHT as formed by deacidification with $KHCO_3$ is strongly impeded by red wine tannins; potassium remains in solution.

Difference: Calcium *vs.* Potassium
- Sensory -

<u>Starting point :</u>

Residues of the cations (calcium *vs*. potassium) used for deacidification explain different sensory outcomes for the same final T.A. level achieved.

<u>Calcium :</u>

> Concentration range in untreated wines = 70 to 130 mg/L Ca^{++}

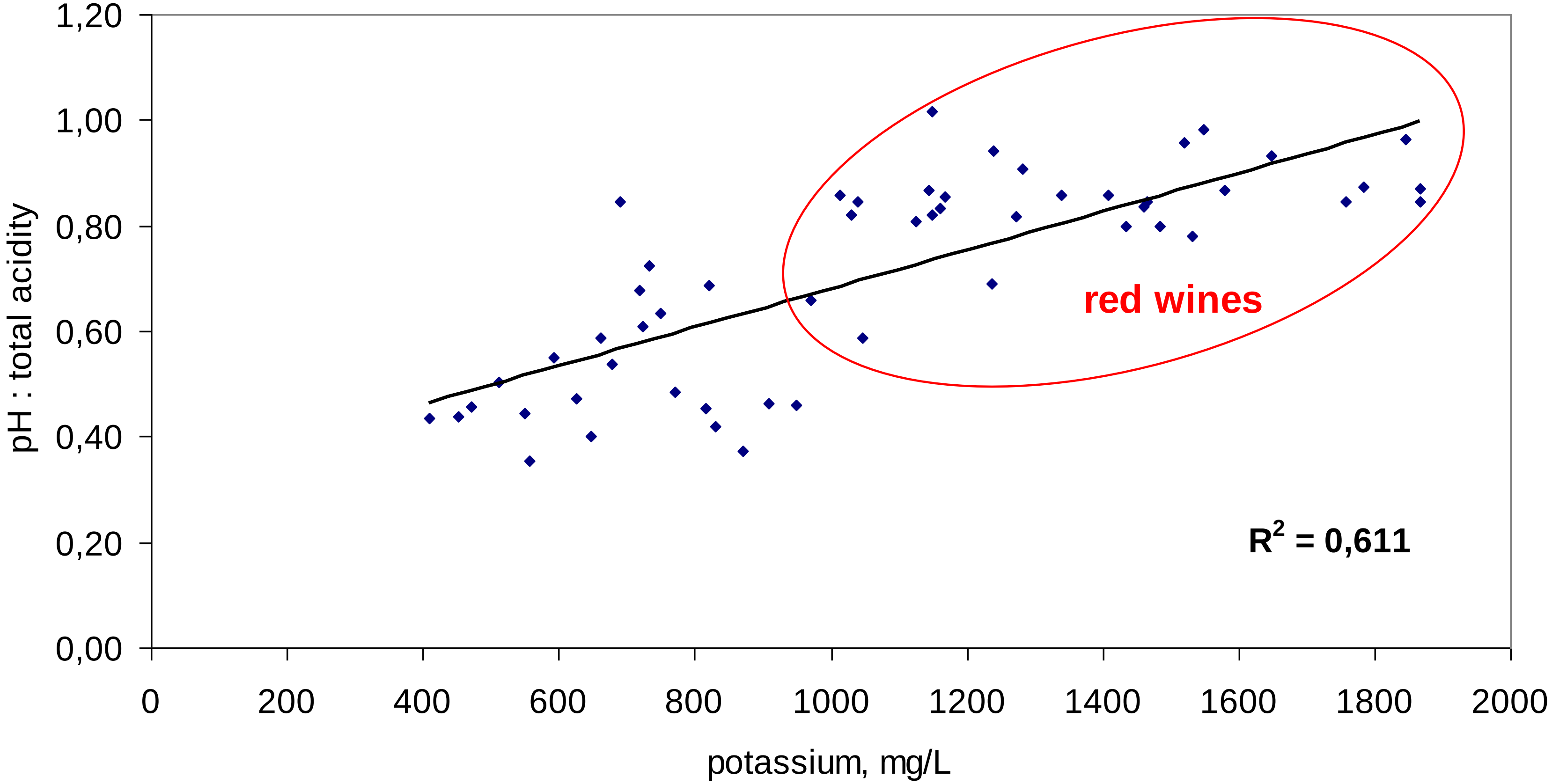
- Stability limit = 100 to 150 mg/L Ca^{++}, depending on pH, alcohol.....
- Detection threshold = 150 mg/L (white wine) to 200 mg/L (red wine)
- Concentration in red wines the first month after $CaCO_3$ treatment = 130 to 350 mg/L Ca^{++}
- Excessive calcium in red wine <u>does drop out</u> after 1-3 months

<u>Potassium :</u>

- Concentration range in untreated red wines = 1000 to 1700 mg/L K^{+}.
- Stability limit = 800 to 1500 mg/L K^+, depending on temperature, pH, alcohol, and tannin.
- Detection threshold (soapy) > 1800 mg/L K^+ in red wines
- Concentration in red wines after $KHCO_3$ treatment = 1200 to 1900 mg/L K^+, depending on the initial K^+-concentration
- Excessive potassium in red wine <u>does not drop out</u> to a large extent.

Potassium provides volume and weight by mouth. Under humid growing conditions as in the mid Atlantic area, untreated red wines display high potassium contents. Deacidification with $KHCO_3$ enhances them further up to amounts which can cause “soapiness” on the palate. Early deacidification with $CaCO_3$ is often preferable.

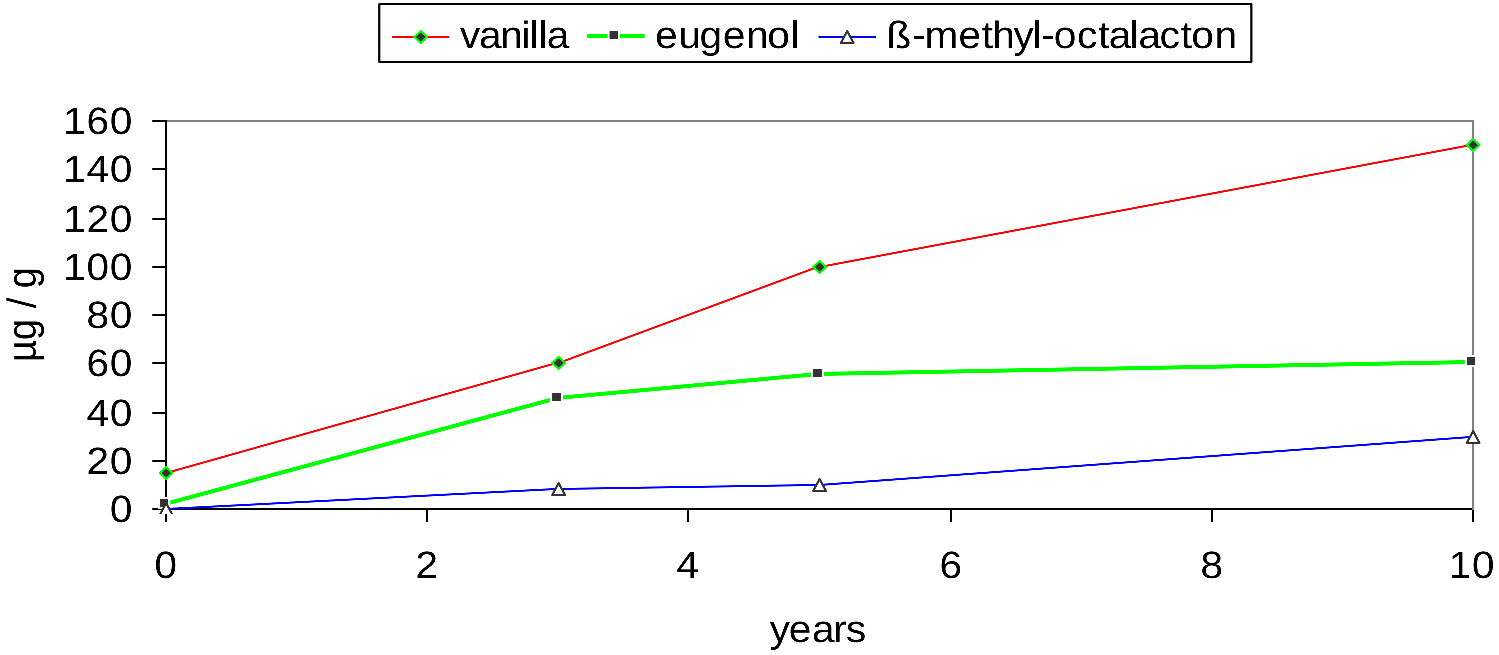
Correlation between potassium and the ‘pH : T.A.’ ratio



The ‘pH : T.A.’ ratio gives an idea about the potassium content to expect.

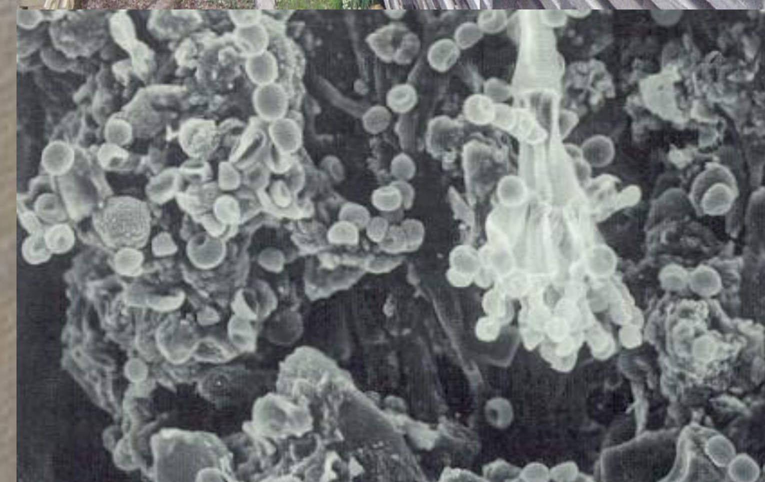
Experimental barrel aging in Old Europe

Impact of seasoning on important oak aroma compounds in 10 mm below wood surface



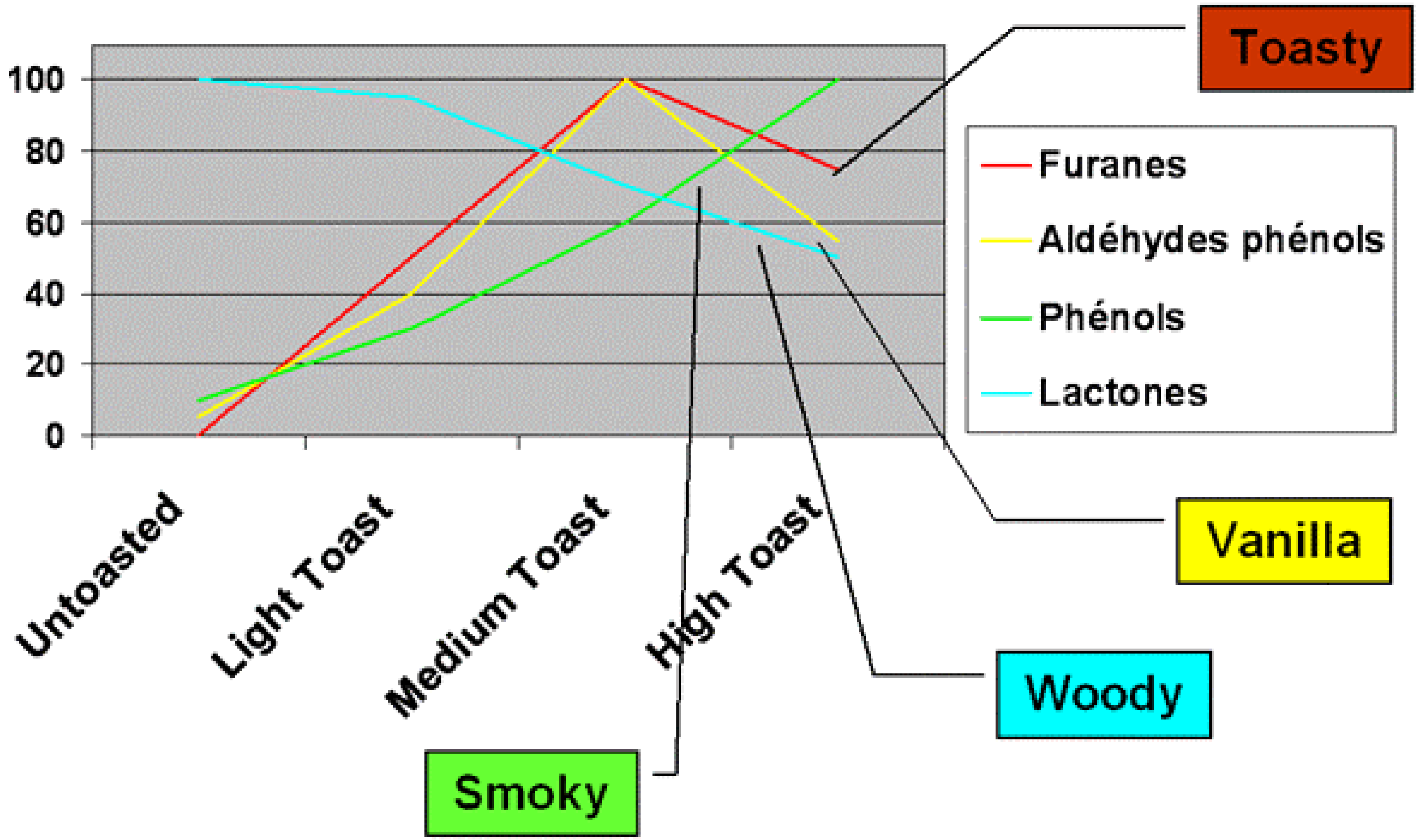
Most oak especia require 2 to 3 years of seasoning. Artificial drying does not provide satisfactory sensory results.

Seasoning outside (2-3 years)

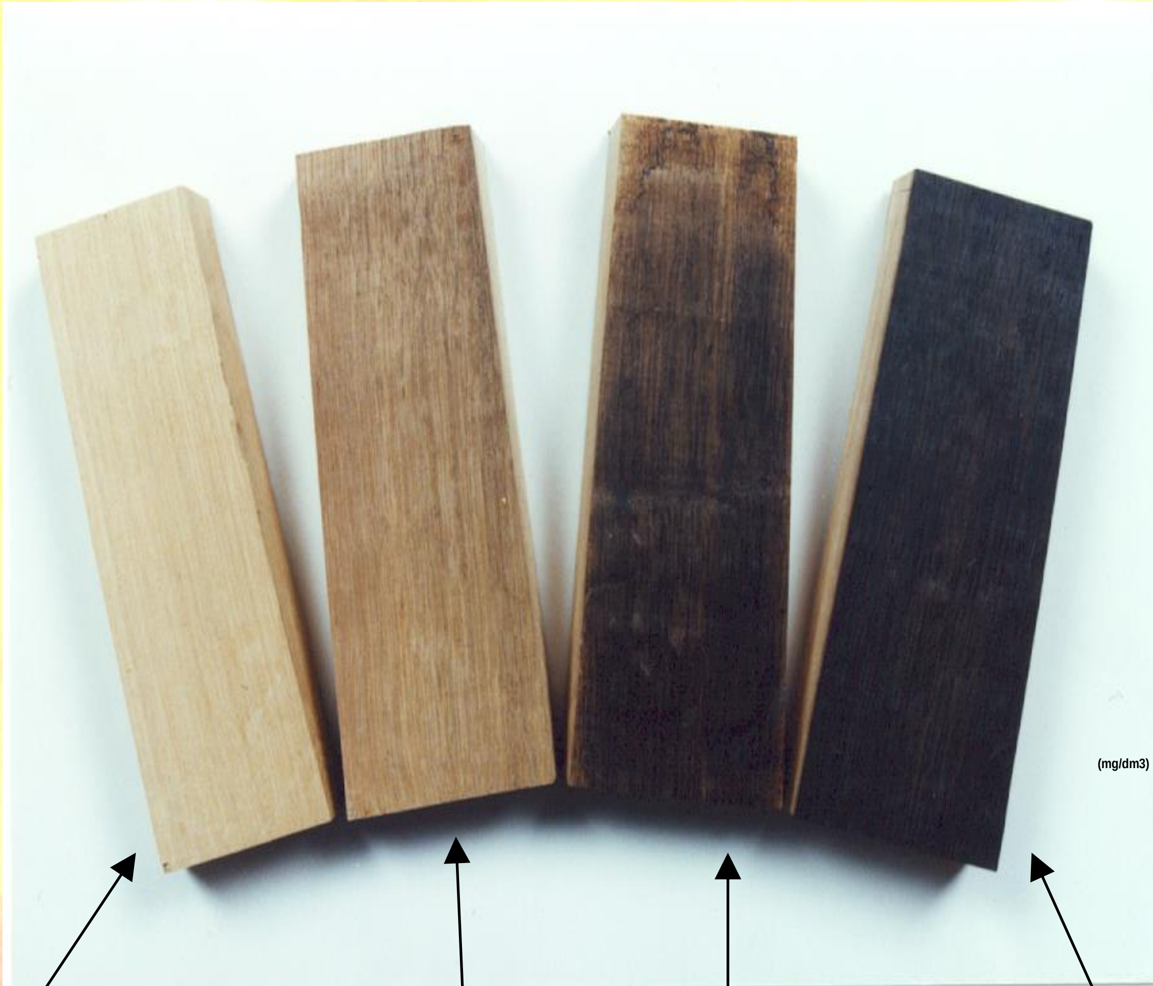


after 13 months

Impact of toasting degree on sensorially important oak compounds



The different toasting degrees

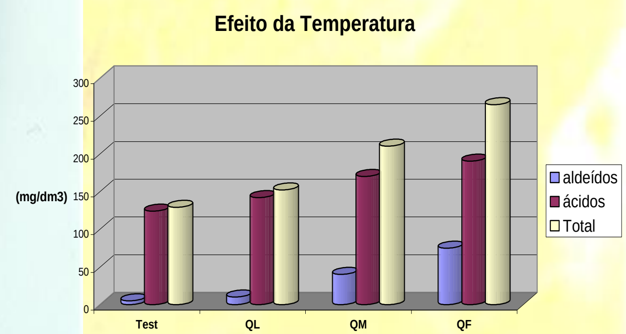


untoasted

light

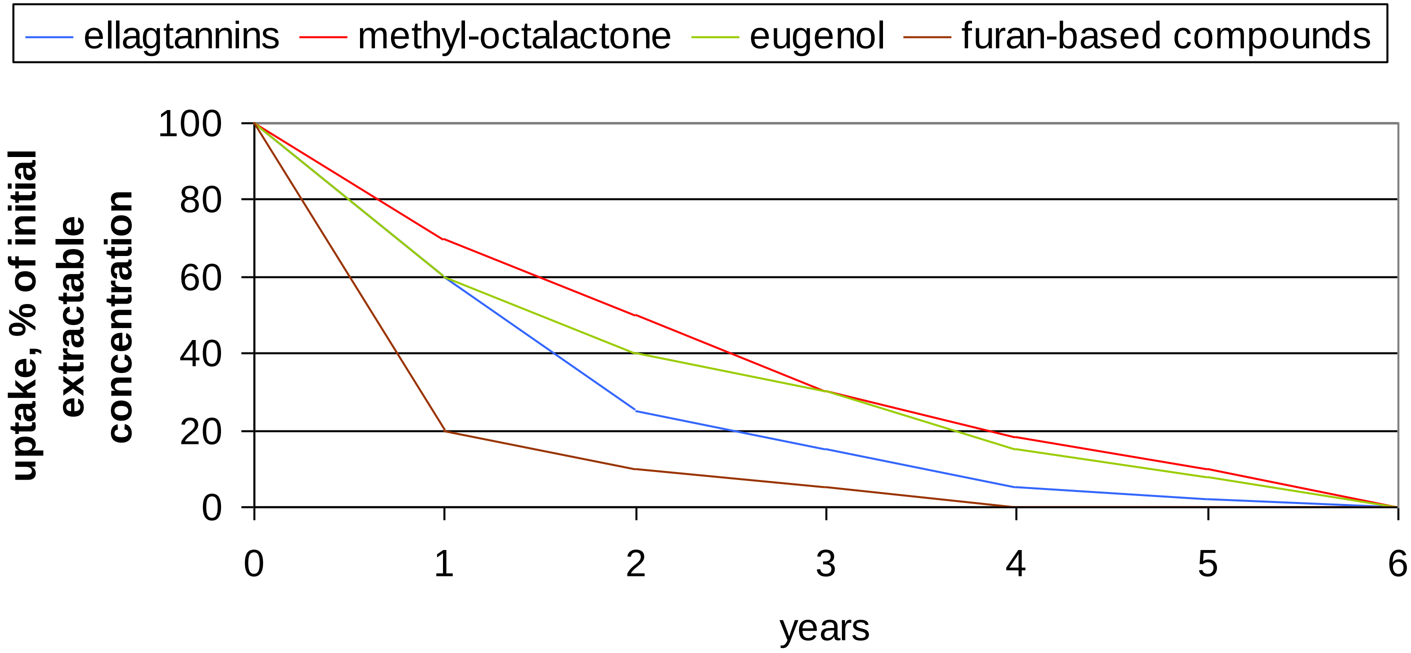
medium

heavy



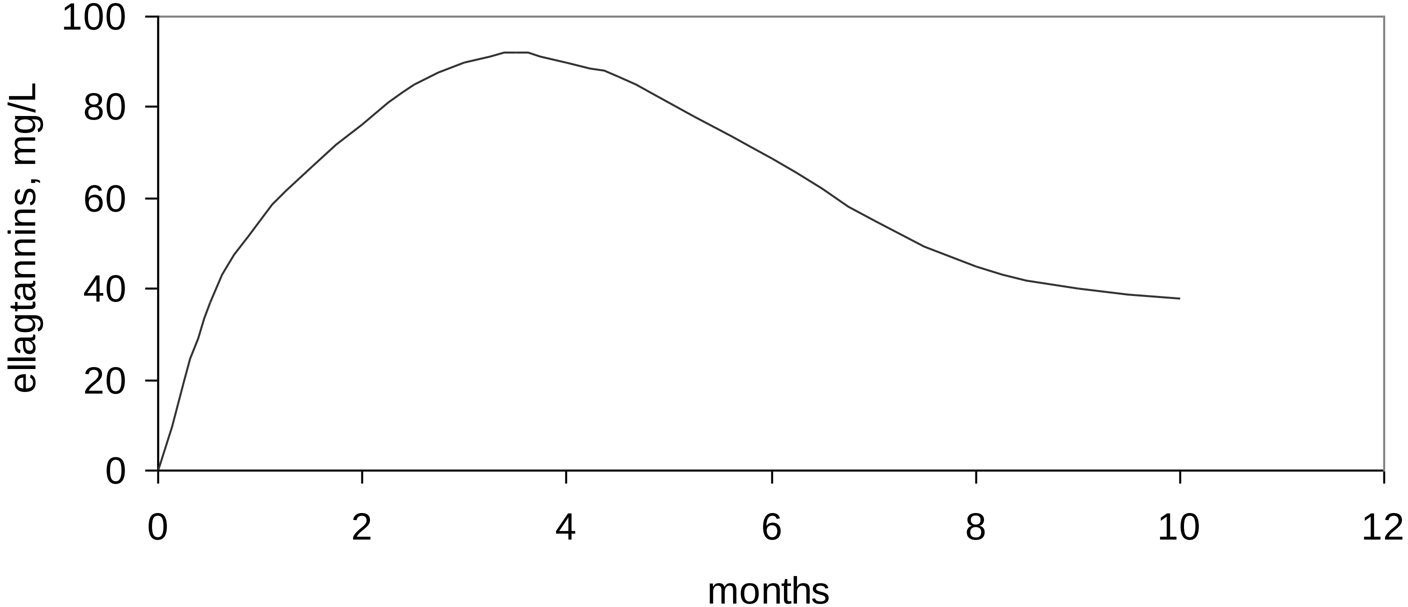
Traditional toasting using open fire

Effect of barrel age:
Time course of the extraction of oak compounds.



During the first year of barrel use, approximately half of the extractable oak compounds is extracted. After the third use of the barrels, they are largely depleted. Further barrel use only provides oxygen to the wine.

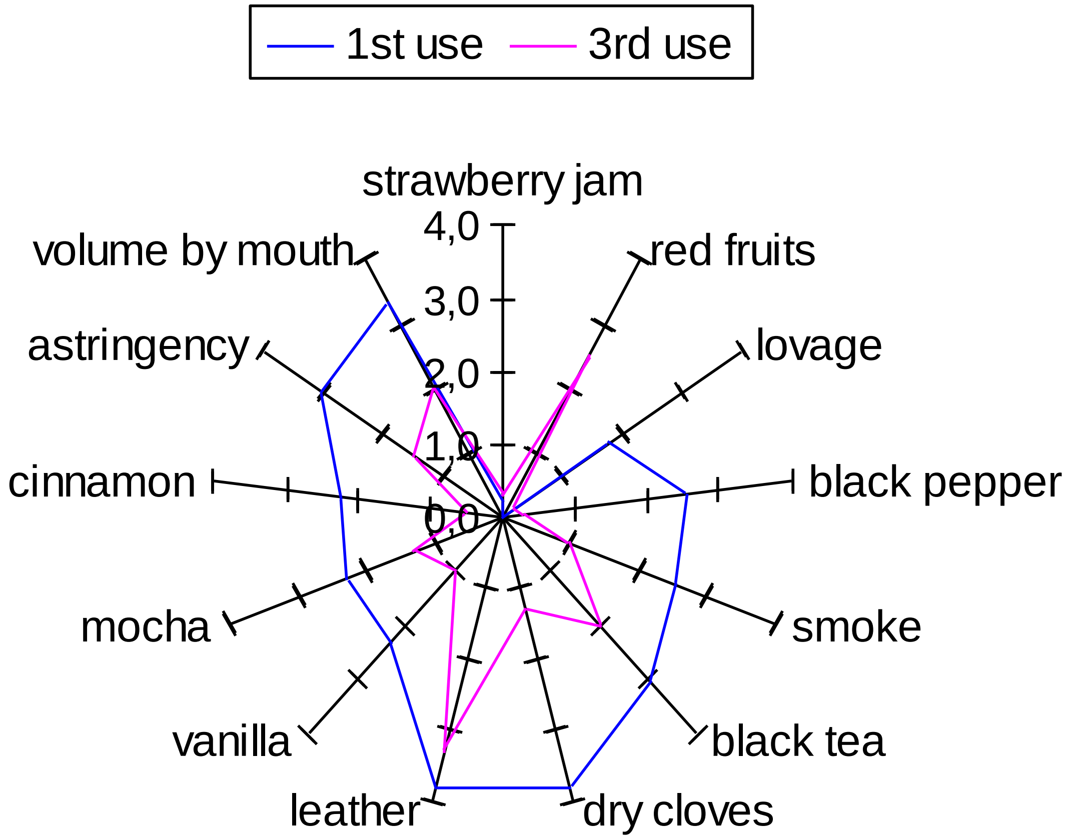
Time course of ellagitannin concentration in wine stored in new barrels without yeast.



In barrels of first use, ellagitannins and their astringency pass through a peak after four months of storage. Thereafter, their extraction from wood is slower than their degradation by oxidation and hydrolysis.

Effect of barrel age on the sensory intensity of “oak” for the same wine.

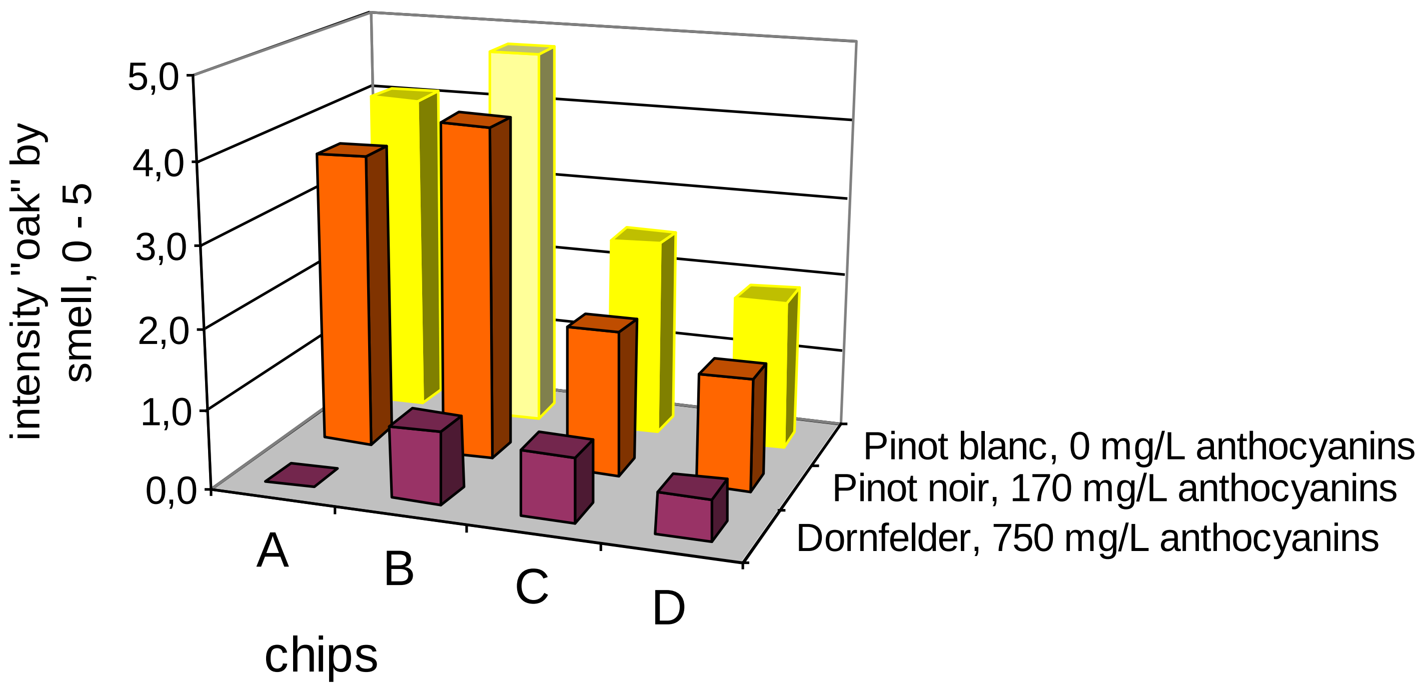
Cultivar = Touriga, Portuguese oak, storage = 1 year.



Purchasing used barrels is economically questionable, besides the risk of microbiological spoilage (Brett!).

Effect of wine (anthocyanin content and cultivar) on the intensity (0-5) of "oak" by smell of various kinds of oak chips (4 g/L).

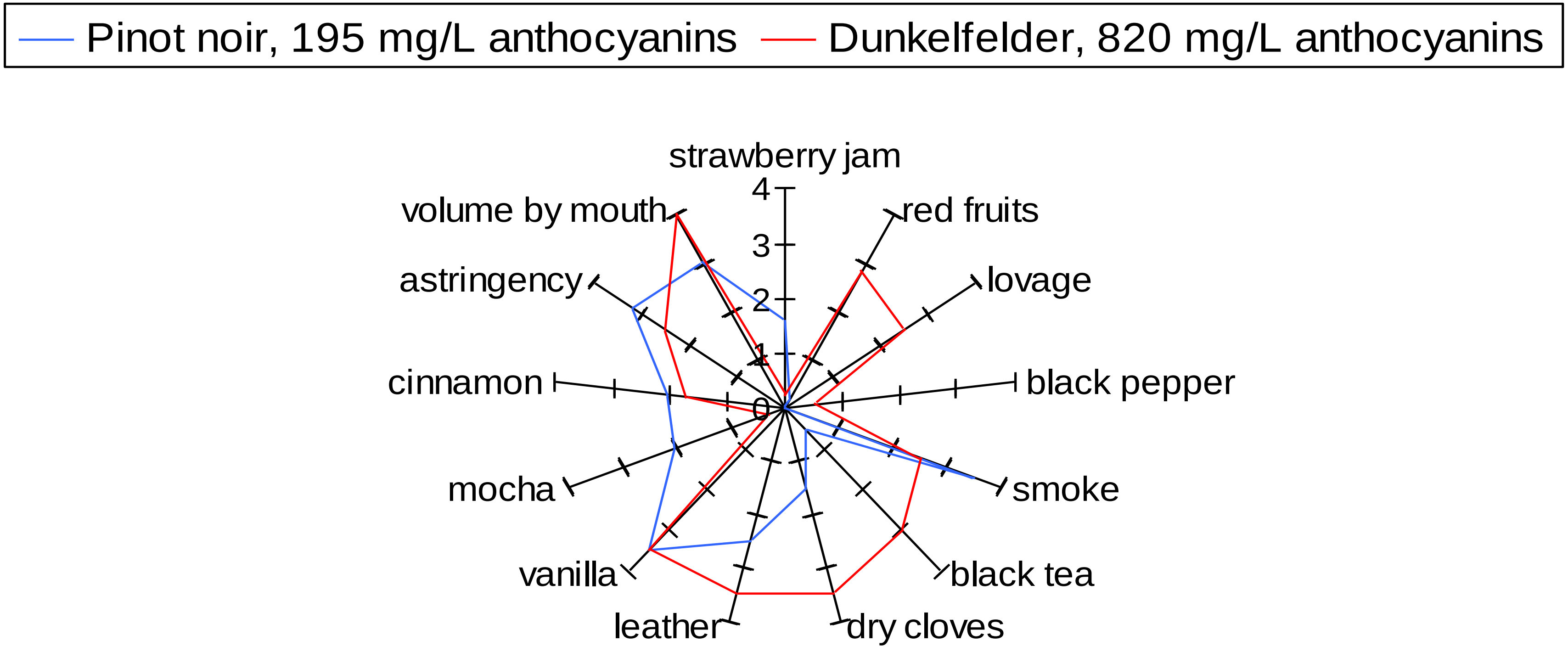
Extraction over four weeks, 20° C. Wines filtered, 30 mg/L free SO_2, 8 mg/L O_2.



Oak aroma compounds bind to anthocyanins. The higher the anthocyanin content of the wine, the less oak is expressed by smell. Slightly colored wines (Pinot noir) need less new oak than strongly colored varieties.

Effect of variety and anthocyanin content on the sensory expression of oak.

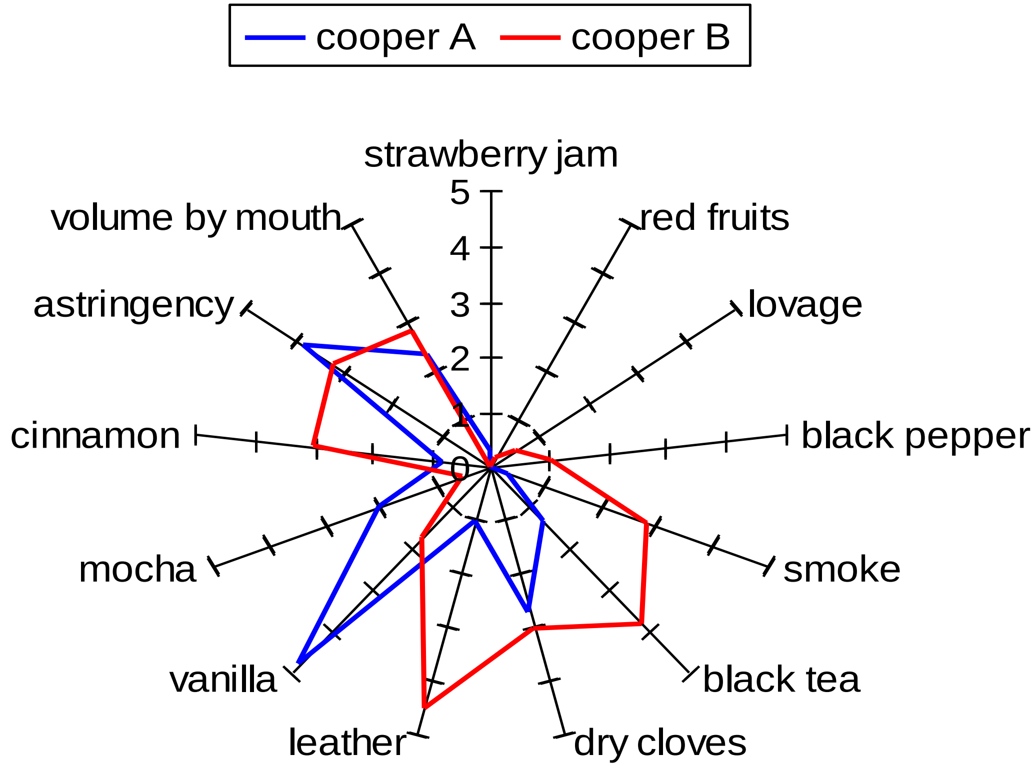
American oak, 1st wine, one year storage.



What is true for oak chips may not be true for barrels. The difference lies in the slow oxygen uptake during barrel aging.

Sensory differences between barrel makers for the same kind of oak.

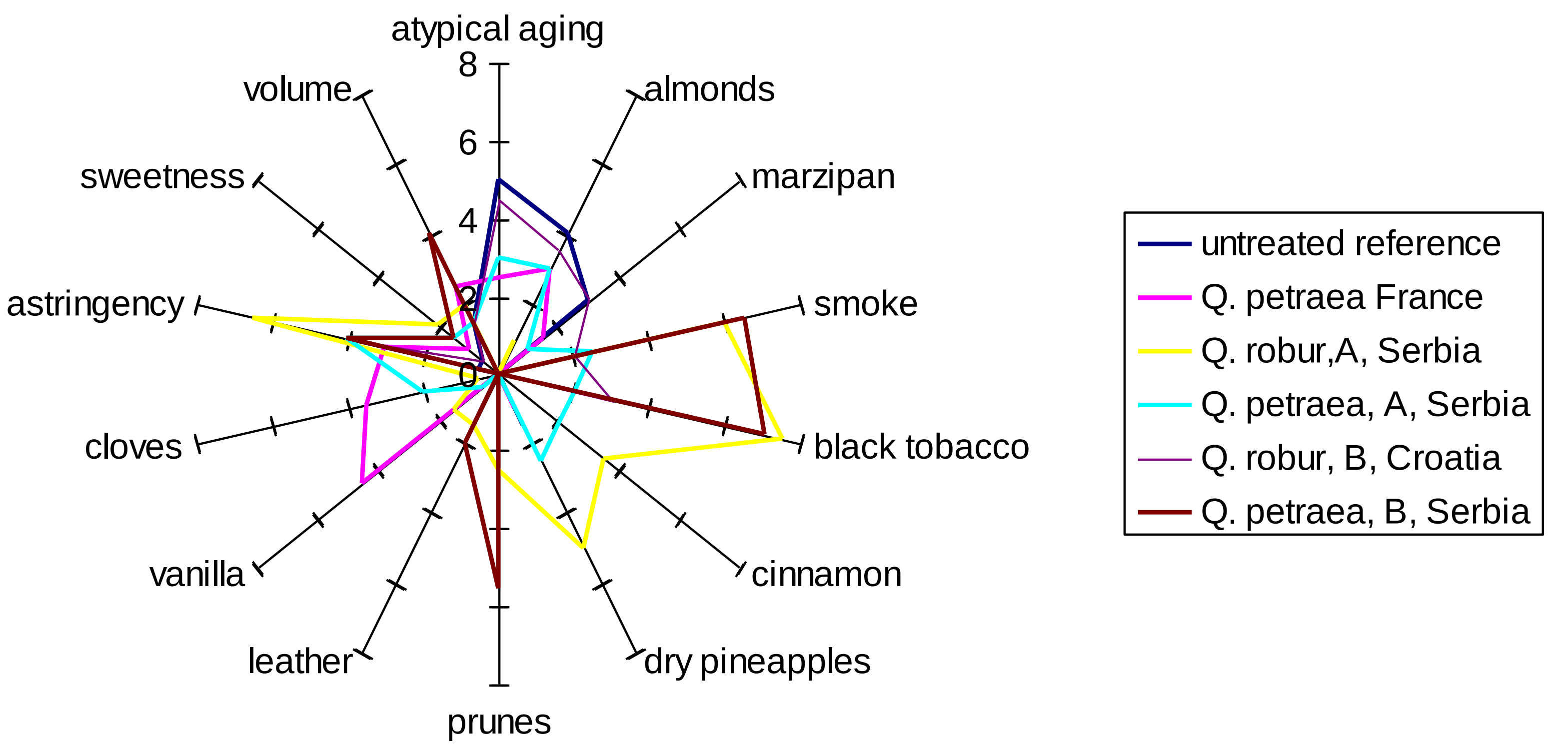
Pinot noir, American oak, new barrels, one year storage.



The barrel maker (selection of wood, aging, toasting) is more important than the origin of the oak.

Sensory evaluation of five different kinds oak chips from the same source.

Extraction of 4 g/L over 5 weeks in white wine.



Quality differences between oak chips are enormous and do not relate to the country of origine. Many commercial chip brands destroy the wine. Pilot trials are useful before technical use. Bad chips provide a strong, lingering astringency and a smell reminding pencil shave, green wood, coconuts, potatoes etc.

Enological tools for red wine barrel aging

Purpose :

- Creating volume on the palate by moderate oxydation and tannin polymerization.

- Enhancing complexity by extraction of oak aroma compounds

Treatment	**advantages**	**drawbacks**
filtration	• Fast development of oak aromatics by moderate oxidation • Less risk of microbial disorders (excepted V.A.)	• Less yeast mannoproteins, less volume / weight • Too much wood, lack of balance in new barrels • Risk of meager and astringent wines by overoxidation • More DO and risk of high V.A.
no free SO_2	• accelerated aging by oxidation / polymerization	• More micobiological risks, depending on pH and temperature (limit = 10° C).
addition of yeast from other wines, bâtonnage	• more volume / weight • softer tannins	• Yeast consumes oxygen, aroma development is slower.
active oxidation, rackings	• aroma development is faster • tannin polymerization is faster	• Risk of meager and thin wines by overoxidation.

Barrel aging – the most frequent mistakes

- **Trying to age red wines lacking tannin (min. 2000 mg/L as catechin) → thin wines become thinner**
- **Trying to age wines made from "green" fruit → green wines become greener**

Most cool climate red wines are not suitable for barrel aging.

- **Too much oxygen, not enough SO_2 → losses of fruit and tannin by overoxidation**
- **Not enough oxygen, too much SO_2 → oak aroma does not develop, tannins do not smoothen**

The right balance between oxidation and reduction is an important feature in barrel aging

- **Use of too much old wood → micro-oxygenation, but no oak aroma**
- **Use of too much new wood → more oak than wine, "carpentry flavor"**
- **Use of "green" oak → vegy-green aromatics, harsh tannins, the naked wine is preferred**

The knowledge of the barrel maker is more important than the origin of the wood.

- **Storing the wine in barrels and expecting a miracle → works out sometimes, but not always**
- **Barrel aging period too short → ellagitannins do not degrade, aroma lacking complexity**
- **Bottling with too much tannin → excessively high astringency**
- **Failures in balancing "sour" und "astringent → synergism between sourness and astringency**

Many barrel-aged wines may require corrections before bottling.

- **Failures in stabilizing free SO_2 before bottling → premature oxidation, free ethanal**

Recap:
Barrel aging of cool-climate red wines

- Barrel aging or oak chips are not an intrinsic feature of red wine making.

- Barrel aging alterates the wine, but does not necessarily improve it.

- Most cool-climate red wines are not suitable for barrel aging due to their lack of tannins.

- If tannin content is too low to consume the oxygen provided by barrel aging, oak chips might be the better solution for imparting oak flavor.