Investigation of molecular changes in wine during storage in refrigerated cabinets

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Eidesstattliche Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit eigenständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet, sowie Literaturzitate kenntlich gemacht habe. Die Arbeit liegt weder in gleicher noch in ähnlicher Form in einem anderen Prüfungsverfahren vor.

Kaiserslautern, den ____

(Hannah Renner)

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I Publications

Peer-reviewed publications

Renner, Hannah; Richling, Elke, and Durner, Dominik (2022): Influence of Vibration on the Consumption of Oxygen and Sulfur Dioxide in Wine Bottles Considering Bottle Position and Headspace Volume. *American Journal of Enology and Viticulture,* 73 (1), 48-55.

Renner, Hannah, Elke Richling, and Dominik Durner (2022): Influence of vibration on volatile compounds, color, SO_2 and CO_2 of Riesling sparkling wine and white wine. *American Journal of Enology and Viticulture* Accepted manuscript.

Renner, Hannah, Elke Richling, and Dominik Durner (2022): The impact of temperature fluctuations on the composition, colour and flavour properties of wine during two years storage. *Australian Journal of Grape and Wine Research*, Submitted manuscript.

Other publications

Renner, Hannah und Pour Nikfardjam, Martin (2016): Silberchlorid - Altbewährtes neu entdeckt. *Der Deutsche Weinbau*, 22, 18-21.

Renner, Hannah und Pour Nikfardjam, Martin (2017): Kupfer- und Silbersalze gegen Böckser – Hintergrundwissen und Empfehlungen. *Der Winzer*, 73, 34-38.

Conferences

Renner, Hannah; Bergmann, Felix and Durner, Dominik (2018): Influence of different storage conditions on the quality of a commercial Riesling Wine. *Wine Graduates' Forum*, Stuttgart, 6. November 2018

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II Abbreviations

^{1}D	First-dimension column
^{2}D	Second-dimension column
3MeBuAc	3-Methylbutyl acetate
ANOVA	Analysis of variance
CIE	Commission internationale de l´éclairage
CO_2	Carbon dioxide
CT_{Alt}	Storage at alternating storage temperature starting from constant 6°C and changing to constant 18°C in 6 months intervals was conducted
CT_{ISO}	Storage at constant temperature of 12°C
DA	Descriptive analysis
DI	Direct immersion
DMDS	Dimethyl disulphide
DO	Dissolved oxygen
EI	Electron impact ionization
f	Modulation frequency
FID	Flame ionization detector
FTIR	Fourier transform mid-infrared
FT_{Peak}	Storage at fluctuating temperature with regularly recurring temperature peaks which increased wine temperature from 12 to 13.5°C every 6 h
FT_{SinHA}	Storage at fluctuating temperature with a high amplitude of ± 1.5°C cycling around 12°C with a period length of 4h
FT_{SinLA}	Storage at fluctuating temperature with a low amplitude of ± 0.5°C cycling around 12°C with a period length of 2 h
GC	Gas chromatography
GC×GC	Comprehensive two-dimensional gas chromatography
H/C MDGC	Heart-cut multidimensional gas chromatography
HS	Headspace
HSO	Headspace oxygen
ISTD	Internal standards
k_{DO}	Consumption rate of dissolved oxygen
k_{HSO}	Consumption rate of headspace oxygen

k_{SO2}	Consumption rate of sulfur dioxide
LOD	Limit of detection
LOQ	Limit of quantification
LRI	Linear retention index
LSD	Least significant difference
LST	Light-struck taste
MDGC	Multidimensional gas chromatography
MeSH	Methanthiol
M_R	Modulation ratio
MS	Mass spectrometry
N_2	Nitrogen
NIST	National Institute of Standards and Technology
O_2	Oxygen
OIV	International organization of vine and wine
OTR	Oxygen transfer rate
PA	Polyacrylate
PC	Principal component
PCA	Principal component analysis
PDMS	Polydimethylsiloxane
PE	Polyethylene
P_M	Modulation period
PVDC	Polyvinyl chloride
qMS	Quadrupole mass spectroscopy
SDE	Simultaneous distillation-extraction
SIDA	Stable isotope dilution assay
SO_2	Sulfur dioxide
SPE	Solid phase extraction
SPME	Solid phase micro extraction
TA	Titratable acidity
TCA	2,4,6-Trichloroanisole
TDN	1,1,6-Trimethyl-1,2-dehydronaphthaline
TIC	Total ion current

ToF-MS	Time-of-flight mass spectrometry
UV	Ultraviolet light
VA	Volatile acidity
VIS	Visible light
Φ	Phase shift
τ	lifetime

1. Abstract

Wine is a complex chemical mixture that is bound to change over time. Most wines are produced for consumption within months. Some premium wines are meant to be maturated for several years or even decades after bottling. The post-bottling evolution and the longevity of a wine depends on its initial chemical composition and the storage conditions. Temperature, exposure to light and the closure type are often mentioned as the most important storage influences. Especially elevated temperature is known to cause accelerated aging reactions in wine. Refrigerated wine storage cabinets promise to be the best storage option without the need of a wine cellar. They are available in different sizes and fit in every household. However, the influence of vibrations and low-interval temperature fluctuations caused by compressors are parameters that have been neglected in literature. The aim of this thesis was to investigate if vibrations and low-interval temperature fluctuations, which occur in refrigerated wine storage cabinets, have an influence on the post-bottling evolution of a wine. The influence of both parameters was studied separately from each other.

The impact of vibration on oxidation and gas uptake from the headspace of a wine bottle into the wine was investigated using a model wine with saturated O_2 and different headspace volumes. The study revealed that vibration promotes the dissolution of O_2 from the headspace of bottle into the wine resulting in a faster SO_2 consumption. Furthermore, it was shown that horizontal bottle position accelerated the O_2 uptake significantly. It was concluded that the increased surface size between headspace and wine accelerates the O_2 dissolution in wine. Also, bigger headspace volumes caused an accelerated O_2 uptake into the wine. An experiment without any headspace volume revealed that the factors vibration and bottle position did not accelerate the O_2 consumption in wine. This proves that vibration and bottle position accelerate only the dissolution of O_2 in wine, but not the chemical reaction of O_2 with wine constituents.

The influence of vibration on the volatile profile of wine was investigated using Riesling sparkling and still wines sealed with different closures that were subjected to vibration for six months. Vibration caused no CO_2 losses, SO_2 and color changes in all wines indicating that vibration caused by compressors has no impact on the gas permeability of the used closures. However, vibration affected the volatile profile of sparkling wine and Riesling still wine sealed with a screw cap. Similar to the model wine study described earlier, it was shown that the equilibrium of volatile substances between the wine and the headspace in a bottle was influenced by vibration. The gas-liquid-equilibrium of some volatile compounds was shifted towards wine, while others were shifted towards headspace. As a result of this, the concentration of volatile compounds in wine is changed. Besides this indirect influence of vibration, the results of this study also suggested that specific degradation and formation reactions of volatile compounds are directly influenced by vibration. These multiple effects of

vibration most likely explain why increasing vibration intensities could not be proportionally related to the observed volatile changes. The investigation of different wine styles revealed that the impact of vibration depends strongly on the initial composition of wine, age, and packaging conditions. Especially, headspace volume, closure type and CO_2 pressure are likely to influence the equilibrium of volatile substances between the wine and the headspace in a bottle.

Another study investigated the impact of low-interval temperature fluctuations on the volatile profile of wine. For this purpose, a Riesling wine was stored for two years under different temperature fluctuation patterns caused by compressors. Additionally, a model wine with nine volatile substances with known concentrations was stored for eight months under the same fluctuation patterns. The low-interval temperature fluctuations were compared to the mean value of the temperature fluctuations. Chemical and sensory analysis revealed that that low-interval temperature fluctuations accelerate wine aging reactions like ester hydrolysis and monoterpene degradation. Even small temperature amplitudes showed a significant impact on wine aging. The observed effect was explained by the Arrhenius equation which states that reaction rates exponentially increase with rising temperatures. A pump effect of air through the closure was initially assumed but not observed in this study. Small deviations in wine temperature, such as those caused by door openings of a refrigerator were found to be negligible. It was concluded that low-interval temperature fluctuations can accelerate wine aging reactions. The amplitude of the temperature fluctuations should be as small as possible during bottle storage of wine.

This thesis showed that both parameters, vibration, and low-interval temperature fluctuations, have been proven to influence the evolution of wine during bottle storage. Regarding storage conditions in a refrigerated wine storage cabinet, those parameters should be monitored. Wine connoisseurs should therefore consider good wine cabinets, since some manufacturers emphasize on the importance to minimize vibrations and temperature fluctuations in their devices. The development of technology should be advanced to reduce both vibration and temperature fluctuations in refrigerated wine storage cabinets. Future research should focus on specific wine compounds in model systems and realistic vibration conditions to reveal the relationship between vibration intensities and reaction rates. The impact of low-interval temperature fluctuations on wine compositional changes should be investigated considering horizontal and vertical bottle positions. The calculated acceleration factors due to temperature fluctuations have to be verified by isotherm storage conditions at higher temperatures.

2. Zusammenfassung

Wein ist ein komplexes chemisches Gemisch, das sich im Laufe der Zeit verändert. Die meisten Weine werden produziert, um innerhalb weniger Monaten konsumiert zu werden. Einige Premiumweine können nach der Abfüllung mehrere Jahre oder sogar Jahrzehnte reifen. Die Reifung und Langlebigkeit eines Weins hängen von seiner anfänglichen Zusammensetzung und den Lagerbedingungen ab. Als wichtigste Lagereinflüsse werden meist Temperatur, Lichteinfall und Verschlussart genannt. Hohe Temperaturen verursachen bekanntermaßen beschleunigte Alterungsreaktionen im Wein. Weinkühlschränke versprechen ideale Lagerbedingungen ohne die Notwendigkeit eines Weinkellers. Sie sind in verschiedenen Größen erhältlich und passen in jeden Haushalt. Der Einfluss von Vibration und kurzwelligen Temperaturschwankungen, die durch Kompressoren verursacht werden, sind jedoch Parameter, die in der Literatur bisher vernachlässigt wurden. Das Ziel dieser Arbeit war es zu untersuchen, ob Vibration und kurzwellige Temperaturschwankungen, die in Weinkühlschränken auftreten, einen Einfluss auf die Entwicklung eines Weins nach der Abfüllung haben. Der Einfluss beider Parameter wurde getrennt voneinander untersucht. Der Einfluss von Vibration auf Oxidationsreaktionen und die Gasaufnahme aus dem Kopfraum einer Flasche in den Wein wurde an einem sauerstoffgesättigten Model mit unterschiedlichen Kopfraumvolumina untersucht. Die Studie ergab, dass Vibrationen den Übergang von O_2 aus dem Kopfraum in den Wein fördern, was zu einem schnelleren SO_2-Verbrauch führt. Weiterhin zeigte sich, dass die die O_2-Aufnahme in liegenden Flaschen signifikant beschleunigt war. Es wurde der Schluss gezogen, dass die vergrößerte Oberfläche zwischen Kopfraum und Wein den O_2-Übergang in den Wein beschleunigt. Außerdem beschleunigten große Kopfraumvolumina die O_2-Aufnahme in den Wein. Ein Experiment ohne Kopfraum zeigte, dass Vibration und Flaschenposition die O_2-Abnahme im Wein nicht beschleunigen. Dies zeigt, dass Vibration und Flaschenposition nur den Übergang von O_2 in den Wein beschleunigen, nicht aber die chemischen Reaktionen von O_2. Der Einfluss von Vibration auf flüchtige Verbindungen in Wein wurde anhand von Schaum- und Stillwein untersucht. Diese waren mit unterschiedlichen Verschlüssen verschlossen und wurden sechs Monate lang Vibrationen ausgesetzt. Vibration verursachte bei allen Weinen weder CO_2-Verluste noch SO_2 und Farbveränderungen, was darauf hindeutet, dass Vibration, die durch Kompressoren verursacht wird, keinen Einfluss auf die Gasdurchlässigkeit der verwendeten Verschlüsse hat. Vibration beeinflusste jedoch flüchtige Verbindungen in Wein. Ähnlich wie bei der zuvor beschriebenen Modellweinstudie wurde gezeigt, dass das Gleichgewicht flüchtiger Substanzen zwischen dem Wein und dem Kopfraum in einer Flasche durch Vibration beeinflusst wird. Das Gas-Flüssigkeits-Gleichgewicht einiger flüchtiger Verbindungen wurde in Richtung Wein verschoben, während andere verstärkt in den Kopfraum übergingen. Dadurch veränderte sich die Konzentration flüchtiger Verbindungen. Neben diesem indirekten

Einfluss der Vibration legen die Ergebnisse dieser Studie nahe, dass spezifische Abbau- und Bildungsreaktionen flüchtiger Verbindungen direkt durch Vibration beeinflusst werden. Diese multiplen Effekte erklären höchstwahrscheinlich, warum die zunehmende Vibrationsintensitäten nicht proportional zu den beobachteten Veränderungen waren. Die Untersuchung verschiedener Weinstile ergab, dass die Auswirkung von Vibrationen stark von der ursprünglichen Zusammensetzung des Weins, dem Alter und den Verpackungsbedingungen abhängt. Insbesondere das Kopfraumvolumen, der Verschlusstyp und der CO_2-Gehalt beeinflussen das Gleichgewicht flüchtiger Substanzen zwischen dem Wein und dem Kopfraum der Flasche. Eine weitere Studie untersuchte die Auswirkungen von kurzwelligen Temperaturschwankungen auf flüchtige Substanzen in Wein. Dazu wurde ein Riesling-Wein zwei Jahre lang unter verschiedenen Temperaturschwankungen gelagert. Zusätzlich wurde ein Modellwein mit neun flüchtigen Substanzen bekannter Konzentration acht Monate lang unter den gleichen Schwankungsmustern gelagert. Eine Kontrollgruppe wurde bei dem Mittelwert der Temperaturschwankungen gelagert. Chemische und sensorische Analysen ergaben, dass kurzwellige Temperaturschwankungen Reaktionen wie Esterhydrolyse und Monoterpenabbau beschleunigen. Selbst kleine Temperaturamplituden zeigten einen signifikanten Einfluss auf die Weinalterung. Der beobachtete Effekt wurde durch die Arrhenius-Gleichung erklärt, die besagt, dass die Reaktionsgeschwindigkeit mit steigender Temperatur exponentiell zunimmt. Ein Pumpeffekt von Luft durch den Verschluss wurde zunächst angenommen, aber in dieser Studie nicht beobachtet. Kleine Zunahmen der Weintemperatur, wie sie beispielsweise durch Türöffnungen eines Kühlschranks verursacht werden, erwiesen sich als vernachlässigbar. Es wurde der Schluss gezogen, dass kurzwellige Temperaturschwankungen die Weinalterung beschleunigen können. Die Amplitude der Temperaturschwankungen sollte bei der Flaschenlagerung von Wein möglichst gering sein. Diese Arbeit zeigte, dass beide Parameter, Vibrationen und kurzwellige Temperaturschwankungen, nachweislich die Entwicklung von Wein während der Flaschenlagerung beeinflussen. Hinsichtlich der Lagerung in einem Weinkühlschrank sollten diese Parameter überwacht werden. Weinkenner sollten daher gute Weinkühlschränke in Betracht ziehen, da einige Hersteller Wert darauf legen Vibrationen und Temperaturschwankungen in ihren Geräten zu minimieren. Die Entwicklung von Technologien sollte vorangetrieben werden, die sowohl Vibrationen als auch Temperaturschwankungen in Weinkühlschränken reduziert. Zukünftige Forschung sollte sich auf spezifische Verbindungen und realistische Vibrationsstärken konzentrieren, um die Beziehung zwischen Vibrationsstärke und Reaktionsgeschwindigkeit aufzudecken. Die Auswirkung von kurzwelligen Temperaturschwankungen auf Veränderungen der Weinzusammensetzung sollte unter Berücksichtigung liegender und stehender Flaschenlagerung untersucht werden. Die berechneten Beschleunigungsfaktoren der Temperaturschwankungen müssen durch isotherme Lagerbedingungen bei höheren Temperaturen verifiziert werden.

3. Introduction

3.1. Wine storage

During storage wine composition is subject to continuous changes. Especially for premium wines time can be beneficial if they are stored under proper conditions. One of the main challenges of the oenologist is to preserve a high wine quality for as long as possible. The maturation of all wines goes through three stages; the first is maturation, when the taste and the aroma of a wine are improving, in the second period the wine reaches the peak of its quality, while in the third period quality decreases (Arapitsas et al. 2014). The duration of these periods is dependent on the initial composition of the wine and on storage conditions like temperature, light exposure and relative humidity (Echave et al. 2021). The most published studies, reviewed by Martin and Canas (2006), on this subject recommend a storage temperature between 10 and 15°C and a relative humidity between 50 and 80%. Underground wine cellars are still considered as the most suitable storage location for high quality wines (Echave et al. 2021). However, suitable cellars with all required features are rare. For this reason, more and more wineries, restaurants, but also private households are investing in wine storage cabinets, considering them as ideal storage location. Furthermore, wine storage cabinets come in a variety of configurations, from a whole wine cellar to small refrigeration units. But also, during storage in a wine cabinet, wines are exposed to vibrations and temperature fluctuations due to compressor cycling. Chung et al. (2008) already showed that vibration has an impact on propanol and isoamyl alcohol concentrations in wine. This shows the relevance of vibrations and underlines the importance of further research on this topic. In addition, there have been several studies which proved that fluctuating temperature have a similar effect on wine than elevated temperature (Robinson et al. 2010, Crandles et al. 2016, Walther et al. 2018). Hirlam et al. (2019) even suggests that fluctuating temperature causes a pump effect through the closure and therefore accelerates wine oxidation reactions. However, the so far published studies on temperature fluctuations regarded exclusively diurnal temperature fluctuations in simulated transport conditions. To our knowledge, there has been no study so far investigating low-interval temperature fluctuations which occur in a wine storage cabinet due to compressor cycling.

The following chapters review the literature that has been published on the most important influencing factors during wine storage and those in a wine storage cabinet.

3.2. Aroma chemical changes during bottle storage

The volatile profile of a wine consists of hundreds of different compounds. However, many of them are almost irrelevant for the wine aroma. In general, all grape varieties have the same odor-active compounds or precursors, but in different concentrations (Wüst 2003). The concentration of the volatile compounds in wine changes constantly over time. Especially in young wines acetate and ethyl esters are very important contributors to the sensory profile of a wine. Acetate and ethyl esters are formed in excess during fermentation. During storage they decrease due to hydrolysis until they reach equilibrium with their corresponding acids and alcohols (Figure 1). Ethyl esters of saturated straight chain fatty acids hydrolyze slower than acetate esters. This is due to the high concentrations of ethanol, which is a hydrolysis product of these esters. In contrast, the concentrations of ethyl esters of diprotic acids, like succinic acid, show a constant increase over time (Rapp and Mandery 1986).

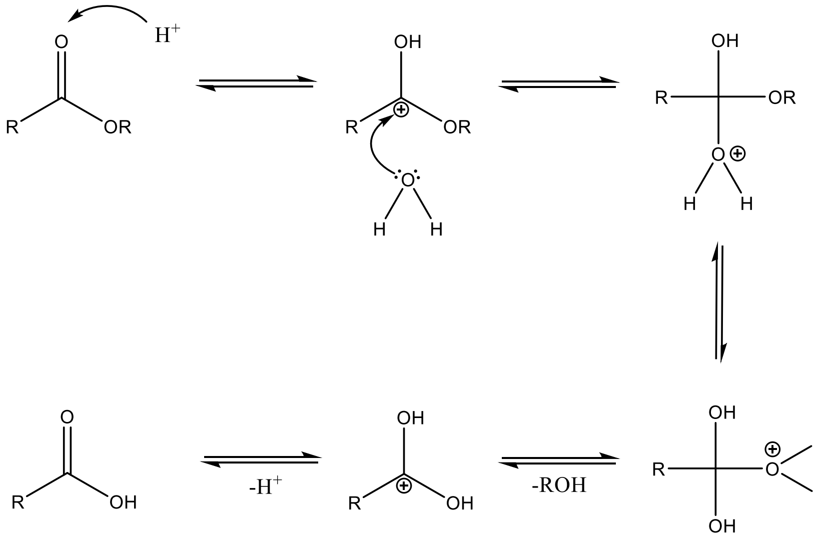

Figure 1:Acid catalyzed ester hydrolysis in wine (modified according to Ramey and Ough (1980)).

Monoterpenes characterize the aroma of many white wines like Muscat, Gewürztraminer and Scheurebe. They are also important contributors to the Riesling aroma, although to a lesser extent than the aforementioned varieties. Monoterpene alcohols like linalool, geraniol and citronellol decrease during bottle storage due to oxidation reactions and acid catalyzed rearrangement. Figure 2 shows the acid catalyzed rearrangement of linalool in wine. This rearrangement leads to an increase in the concentration of α-terpineol (Marais 1983). The carotene derived compounds vitispirane and TDN are known to increase during bottle storage and are associated with a kerosene like odor in Riesling wine (Rapp et al. 1985, Winterhalter and Gök). Another important compound originating from carotene metabolism is β-damascenone. In contrast to vitispirane and TDN, the β-damascenone concentration decreases during bottle storage (Daniel et al. 2004). The furane derivates furfural and 5-hydroxymethyl furfural, which are both sugar degradation products, are formed during bottle storage and important wine aging markers.

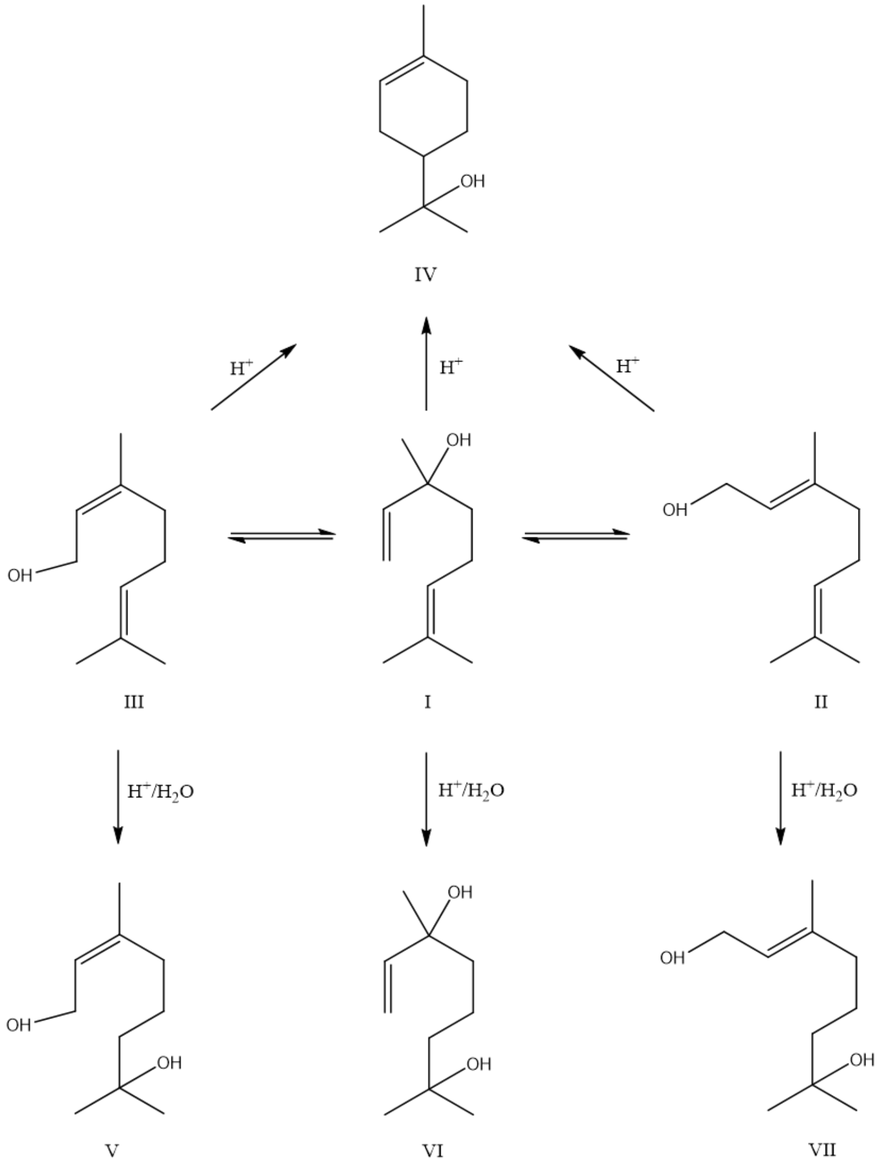

Figure 2: Acid catalyzed rearrangement of linalool (I) into other monoterpene alcohols like geraniol (II), nerol (III), α-terpineol (IV), hydroxynerol (V), hydroxylinalool (VI) and hydroxygeraniol (VII) during bottle aging of wine (modified according to Rapp and Mandery (1986)).

External factors like temperature, light, and closure type have a major influence on the development of a wine during bottle aging (Dias et al. 2013, Giuffrida de Esteban et al. 2019). These and other influencing factors will be discussed in detail in the chapters 3.4-3.5.

3.3. Riesling aroma

Riesling is with over 24,000 hectares the most planted grape variety in Germany (Statistisches Bundesamt 2021). Approximately 40% of the worldwide Riesling production originates from Germany. Riesling is a slow ripening variety that is "*terroir*-expressive", meaning that the aroma of Riesling wines is influenced by climate and the mineral content of the soil (Rapp and Hastrich 1978, Fischer et al. 1999). The aroma of Riesling wines is characterized through monoterpenes, C13-norisoprenoids, ethyl and acetate esters (Rapp et al. 1985). Riesling was chosen for this thesis due to its well-studied aroma changes during bottle ageing to describe the impact of vibrations and temperature fluctuation on the chemical and sensory characteristics of wine.

The most important substance classes contributing to Riesling aroma are higher alcohols, esters, terpenes and C13-norisoprenoids. Figure 3 shows some aroma compounds of Riesling wine.

Esters are primary formed during alcoholic fermentation and are one of the most important substance classes contributing to wine aroma. Especially the aroma of young withe wines is characterized by acetate esters and fatty acid ethyl esters (Rapp and Mandery 1986). Important esters in Riesling wine are isoamyl acetate, hexyl acetate, ethyl octanoate, ethyl decanoate and diethyl succinate (Komes et al. 2006).

Monoterpenes are found in grape juice and in wine. During fermentation there are only small changes in the concentration of monoterpene alcohols and ethers (Rapp and Mandery 1986). Terpenes are responsible for the characteristic aroma of muscat and aroma related cultivars. Terpene compounds may also contribute to the aromas of other cultivars, like Gewürztraminer, Scheurebe and Riesling. Nearly 50 terpene compounds in grapes and wine are known at this stage (Marais 1983). Quantitatively relevant terpene compounds identified in Riesling cultivars are linalool, geraniol, nerol, hotrienol and α-terpineol (Marais 1983, Rapp et al. 1985, Komes et al. 2006, Dziadas and Jeleń 2010).

The C13-norisoprenoids result from carotenoid degradation and belong therefore structurally to the group of terpenes. They are an important source of grape-derived flavors in wines. These compounds are completely glycosylated in the grape and, in contrast to terpenes, they are found in the same quantities in all the grape varieties. Because of their low sensory threshold C13-norisoprenoids have a high potential to contribute to wine aroma. Especially The characteristic aromatic features of Riesling and Chardonnay are connected to C13-norisoprenoids. Important C13-norisoprenoids in white wines are β-damascenone, β-ionone, Riesling acetal, vitispirane and 1,1,6-trimethyl-1,2-dehydronaphthaline (TDN) (Wüst 2003). Vitispirane and TDN contribute to the characteristic bottle-aged aroma of Riesling wine (Simpson and Miller 1983, Skouroumounis et al. 2005a).

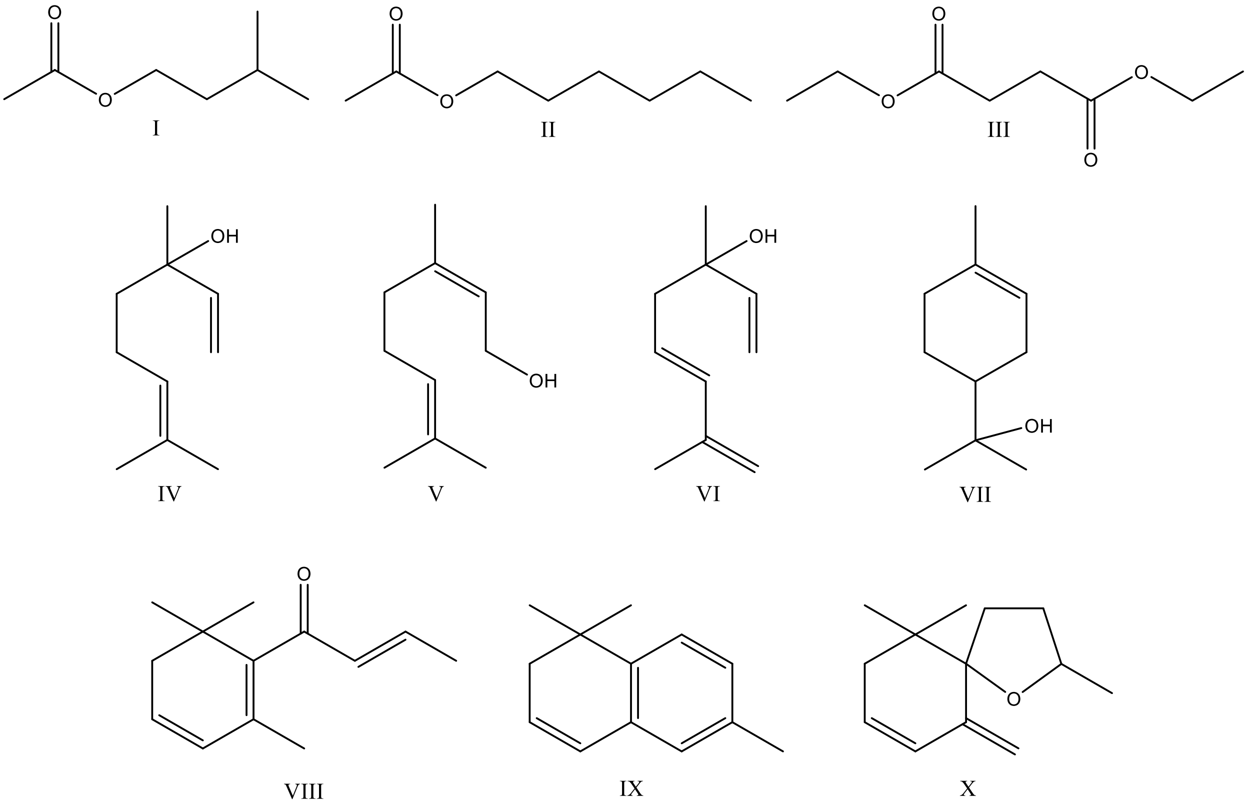

Figure 3: Some important aroma compounds in Riesling wine: **I** Isoamyl acetate; **II** Hexyl acetate; **III** Diethyl succinate; **IV** Linalool; **V** Nerol; **VI** Hotrienol; **VII** α-Terpineol; **VIII** β-Damascenone; **IX** TDN; **X** Vitispirane.

3.4. Influencing factors during wine storage

3.4.1. Temperature

Temperature plays an important role in the production and storage of wine. Elevated temperature is a significant risk to the sensory attributes of wine and its shelf-life. It has been well described in literature that a temperature over 20°C leads to significant changes in wine composition and sensory profile (Dallas and Laureano 1994, Sivertsen et al. 2001, Pérez-Coello et al. 2003, Robinson et al. 2010, Hopfer et al. 2013, Cejudo-Bastante et al. 2013, Scrimgeour et al. 2015, Giuffrida de Esteban et al. 2019). The temperature dependence of those reactions can be described with the Arrhenius equation (Equation 1).

$$k\,(T) = Ae^{\frac{-E_A}{RT}} \qquad (1)$$

Where k is the temperature dependent rate constant, E_A is the Arrhenius activation energy and A is a pre-exponential factor. E_A and k_0 are both usually treated as independent from the temperature. The Arrhenius equation can be rearranged to calculate a relative reaction rate between two temperatures (Equation 2).

$$\frac{k_{A,T_2}}{k_{A,T_1}} = e^{\frac{-E_A}{R}(\frac{1}{T_2}-\frac{1}{T_1})} \qquad (2)$$

This calculation assumes an equal initial concentration at T_1 and T_2. Figure 4 shows the relative change of the reaction rate with rising temperature for different activation energies (Atkins et al. 2020). This shows that the relative change in the reaction rate depends not only on the temperature, but also on the reactions activation energy. A common rule of thumb is that the rate of reaction doubles with a 10°C increase in temperature. However, the dependence of the relative reaction rate on the activation energy shown in Figure 4 shows that this rule should be used with caution.

The aging of wine is a consequence of many complex chemical reactions. To evaluate the oxidative state or shelf-life of a wine sulfur dioxide (SO_2) is often used a marker substance (Scrimgeour et al. 2015). Since SO_2 is the most common antioxidant added to wine, its degradation is directly related to oxidative reactions that took place during storage. Temperature has a strong influence on the reaction mechanism of free SO_2 with oxygen (O_2), as already shown by several studies (Ough 1985, Ribéreau-Gayon 2006, Boulton et al. 2013). During storage, also the volatile composition of wine changes because of different reactions taking place. Changes in ester concentrations will occur during storage and the reaction rate is influenced by the storage temperature. Acetates are hydrolyzed faster than the ethyl esters of short chain fatty acids (Ramey and Ough 1980). The degradation of esters and other volatile compounds, which appears to be accelerated with increasing temperature, may lead to the loss of fruitiness in a young white wine (Makhotkina and Kilmartin 2012). Conversely, elevated temperatures promote the formation of aging associated volatile compound in wine, like TDN and β-damascenone (Ramey and Ough 1980, Hopfer et al. 2012, Cejudo-Bastante et al. 2013, Tarasov et al. 2021).

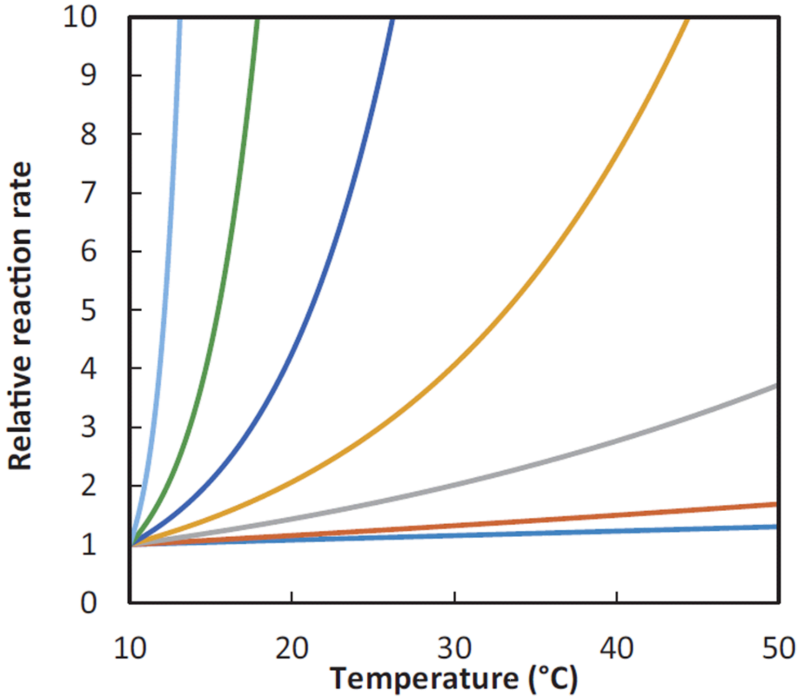

Figure 4: Arrhenius plot for different activation energies. Reaction rates relative to those at 10°C for the Arrhenius activation energy 5 kJ (—), 10 kJ (—), 25 kJ (—), 50 kJ (—), 100 kJ (—), 200 kJ (—) and 500 kJ (—) (Scrimgeour et al. (2015)).

Besides volatile compounds, which are important for the aroma perception of a wine, non-volatile compounds play an important role for the mouthfeel and the visual characteristics. Some important classes of non-volatile compounds in wine are organic acids, polysaccharides, sugars, proteins, and polyphenols. The latter is the most sensitive group to temperature-related changes. Important phenolic compounds in white wine are catechin, gallic acid, caftaric acid and caffeic acid. Those substances react readily with oxygen to form brown pigments (Harbertson 2007). Figure 5 shows the reaction of catechin with glyoxylic acid to a yellow colored xanthylium cation. Elevated temperatures promote reactions which lead to browning in white wine (Fulcrand et al. 2006, Scrimgeour et al. 2015, Ricci et al. 2017). This shows that elevated storage temperature accelerates the aging processes in wine.

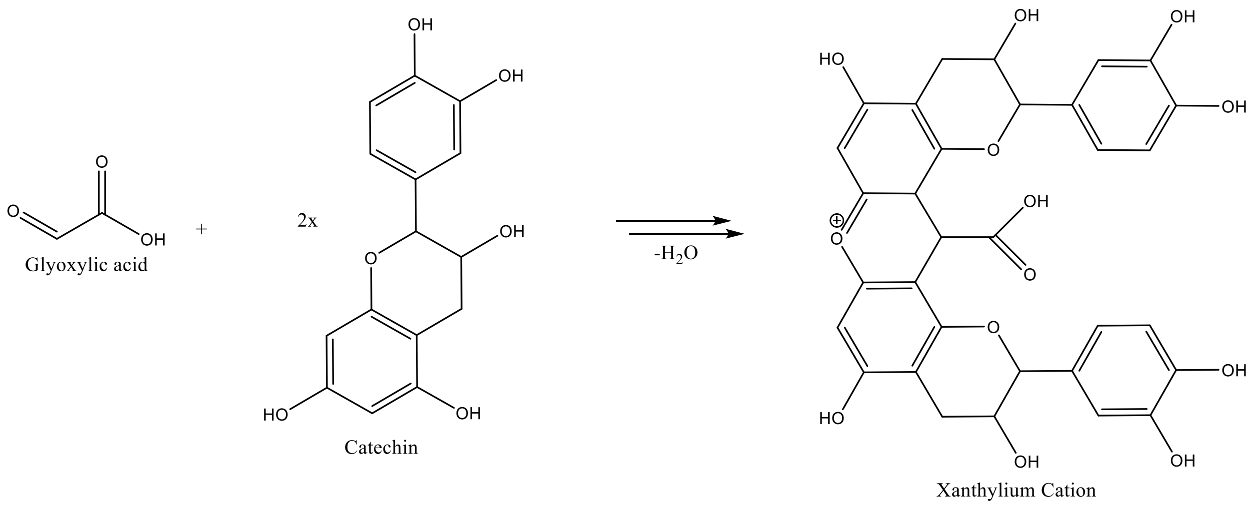

Figure 5: The simplified reaction mechanism of catechin with glyoxylic acid to a yellow colored xanthylium cation (modified according to Fulcrand et al. 2006).

3.4.2. Light

Light exposure during bottle storage can cause significant changes in wine and induce off-flavors that are associated to the light-struck taste (LST). This fault is mainly due to photochemical oxidation processes induced by the photosensitizer Riboflavin. Methanethiol (MeSH) and dimethyl disulphide (DMDS) are generated from sulfur-containing amino acids. Figure 6 shows the formation of methional due to light exposure. Volatile sulfur compounds possess unpleasant cabbage- and onion-like odors (Fracassetti et al. 2021).

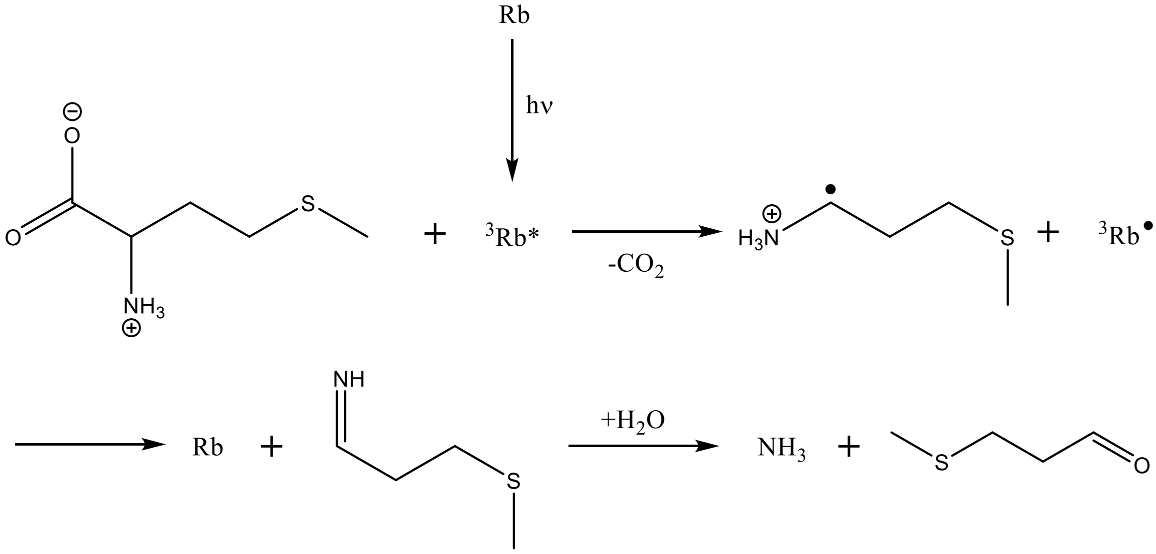

Figure 6: Reaction scheme of methional formation out of methionine and riboflavin (Rb) (modified according to Fracassetti et al. (2021).

Wine is often bottled in clear glass, since consumers prefer to see the color of the wine. However, the protection from ultraviolet (UV)/visible (Vis) light offered by clear glass is significantly lower compared to other commonly used bottle colors, such as amber or green. Flint glass allows to pass about 90% of the harmful light (under 500 nm), whereas green and amber bottles allow to pass 50% and 10% of light (Clark et al. 2015). There are several studies that already showed that light exposure leads not only to sensory changes, but also accelerated browning of wine (Dias et al. 2012, Hopfer et al. 2012, Benucci 2020). A recent study from Arapitsas et al. (2020) simulated the light conditions in a supermarket for several weeks. Sensory analysis revealed that the wines stored in clear glass bottles developed LST. On the other side, the wines stored in green glass bottles did not develop LST within this experiment. This shows that dark bottles protect wine better from light induced faults than clear glass bottles. Nonetheless, even though dark bottles can shield the light and prevent the appearance of LST, the light exposure may still affect the wine quality during storage. Maury et al. (2010) showed that wines stored in dark bottles showed high levels of xanthylium ions as a consequence of higher temperatures in the dark bottles. This shows that not only photochemical reactions This shows that light can not only cause photochemical, but also temperature-induced changes in wine.

3.4.3. Bottle position

Wine bottles sealed with natural cork closure are traditionally stored horizontally. In the 1930s Ribéreau-Gayon found that the O_2 transfer is lower during horizontal bottle storage than under vertical bottle storage. He stated that horizontal storage prevents air from entering the bottle. Furthermore, the liquid prevents the cork from drying out. Experimental data published on the influence of horizontal and vertical bottle position on changes in wine composition is nowadays contradictory. Several studies found that vertical storage promotes wine oxidation during bottle storage (Mas et al. 2002, Hernanz et al. 2009, Venturi et al. 2017). Other research groups found no effect of the bottle position on wine development during storage (Skouroumounis et al. 2005a, Lopes et al. 2006).

3.4.4. Relative humidity

The opinion that wine bottles should be stored at a relative humidity between 50 and 70 % is considered common sense in the wine industry (Silva et al. 2011, Boulton et al. 2013, Ocón et al. 2014, Arapitsas et al. 2014). A humidity of less than 40 % is associated with a drying out of natural cork closures and thus a loss of their impermeability to O_2 (Barker 2004, Karbowiak et al. 2009, Faria et al. 2011). On the other hand, high humidity levels above 80 % promote the growth of molds (Ocón et al. 2014). There are several studies that investigated the fungal methylation of halogenated phenols, leading to haloanisoles which are responsible for the cork-taint in wine (Pereira et al. 2000, Sefton and Simpson 2005, Prak et al. 2007). However, there are no studies so far that examined the influence of storage under different humidity condition on wine development.

3.4.5. Bottle closures

The development of a wine after bottling is directly related with its composition at bottling. The exposure of a wine to O_2 is the most studied parameter during bottle storage. The exposure to O_2 of bottled wines mainly depends on O_2 levels in the HS at bottling, O_2 ingress into the bottle through the closure, O_2 ingress into the bottle through the closure/bottle interface, and from the closure into the bottle (Lopes et al. 2006, Kontoudakis et al. 2008, Silva et al. 2011). Therefore, the choice of closure is the most important factor influencing wine maturation after bottling.

Natural cork closures are the traditional choice for wine bottling since their introduction by Dom Pérignon in the 17th century. Cork has been reported to be the ideal closure for sealing wine bottles due to its unique physical properties: high elasticity, compressibility, chemical inertness, and impermeability to liquids and gases (Prat et al. 2011). Additionally, natural cork closures are generally preferred by consumers and associated with a higher wine quality (Reynolds et al. 2018). However, 2,4,6-trichloroanisole (TCA) contamination, characterized by a musty and moldy odor usually referred as “cork taint”, has brought up alternative sealing systems into the closures market (Pereira et al. 2000, Sefton and Simpson 2005, Hopfer et al. 2013).

Agglomerated cork closures are manufactured from natural cork granules through extrusion or single moulding. Agglomerated cork closures are a low-cost option, generally used for wine that should be consumed within 12 months. Champagne/sparkling wine cork closures are a special type of agglomerated cork closures. They consist of an agglomerated cork body with a natural cork disk facing the inside of the bottle. These corks have a larger diameter than for normal wine corks to retain the high internal pressures generated by CO_2 in sparkling wine.

Agglomerated cork closures have lower O_2 transfer rates (OTR) than natural cork closures (Lopes et al. 2005, Lopes et al. 2006). Wines sealed with agglomerated cork closures retain fruity-associated volatile compounds in a similar manner as screw cap closures during bottle storage (Liu et al. 2015, Oliveira et al. 2020). However, wines sealed with agglomerated cork closures are more susceptible to moldy off-odors than natural one-piece cork closures (Mas et al. 2002). Furthermore, Oliveira et al. (2020) detected 2,4-di-tert-butylphenol and trans-4-tert-butylcyclohexanol in wines sealed with agglomerated cork closures. Those substances are commonly used plastic materials.

Synthetic cork closures are produced from polymers by injection moulding or extrusion. They were developed to offer an alternative to natural cork closures with standardized product properties. The first synthetic cork closures were used in the early 1990s. Due to the increased occurrence of sensory defects in wines, their high O_2 permeability, and poor extractability from the bottle, they met with widespread rejection (Silva et al. 2011). However, recent studies show the quality improvement of synthetic cork closures. They showed good performance in maintaining oxidative and sensory stability up to 2 years of storage after bottling (Hopfer et al.

2013, Vidal et al. 2017). Nowadays, producers of synthetic cork closures guarantee chemical and microbiological inertia, standardized and individually adaptable OTRs.

The screw cap closure creates an airtight seal around the rim of the bottle. The inner liner of the screw cap typically consists of a 19 µm polyvinyl chloride (PVDC) film in contact with the wine, a 20 µm layer of tin foil as a gas barrier, and a 2 mm polyethylene (PE) disc to maintain compression. Screw cap closures are mainly associated with a low OTR. Wines sealed with screw cap closures tend to have more fruity and fresh sensory attributes than wines sealed with cork closures (Godden et al. 2001, Brajkovich et al. 2005). However, long-term storage under low O_2 exposure may lead to a reductive off-flavor induced by low molecular weight sulfur compounds (Skouroumounis et al. 2005b, He et al. 2013). In Australia and New Zealand nowadays the majority of all wines are bottled with screw caps (The Australian Wine Research Institute (AWRI) 2020).

3.4.6. Oxygen in bottled wine

Oxygen (O_2) in bottled wine derives from the filling process or enters through the closure. In white wine, a moderate O_2 exposure is regarded as favorable to avoid reductive off-odors, while excessive O_2 exposure can result in loss of fresh and fruity aromas as well as oxidative browning. Furthermore, elevated O_2 levels in wine result in a loss of sulfur dioxide (SO_2), the main wine antioxidant (Skouroumounis et al. 2005a, Lopes et al. 2006), as shown in Figure 7. During the first months of bottle storage, SO_2 loss is closely dependent on headspace (HS) O_2. The O_2 dissolves from the HS into the wine and reacts with phenolic compounds and metal ions, the primary compounds responsible for wine oxidation. Once all HS O_2 is consumed, O_2 entering through the closure becomes the main factor affecting SO_2 decline (Lopes et al. 2009, Dimkou et al. 2011, Dimkou et al. 2013). A reduction in HS volume and a proper inertization of the HS at bottling can reduce the overall SO_2 consumption during storage significantly (Kontoudakis et al. 2008, Dimkou et al. 2011).

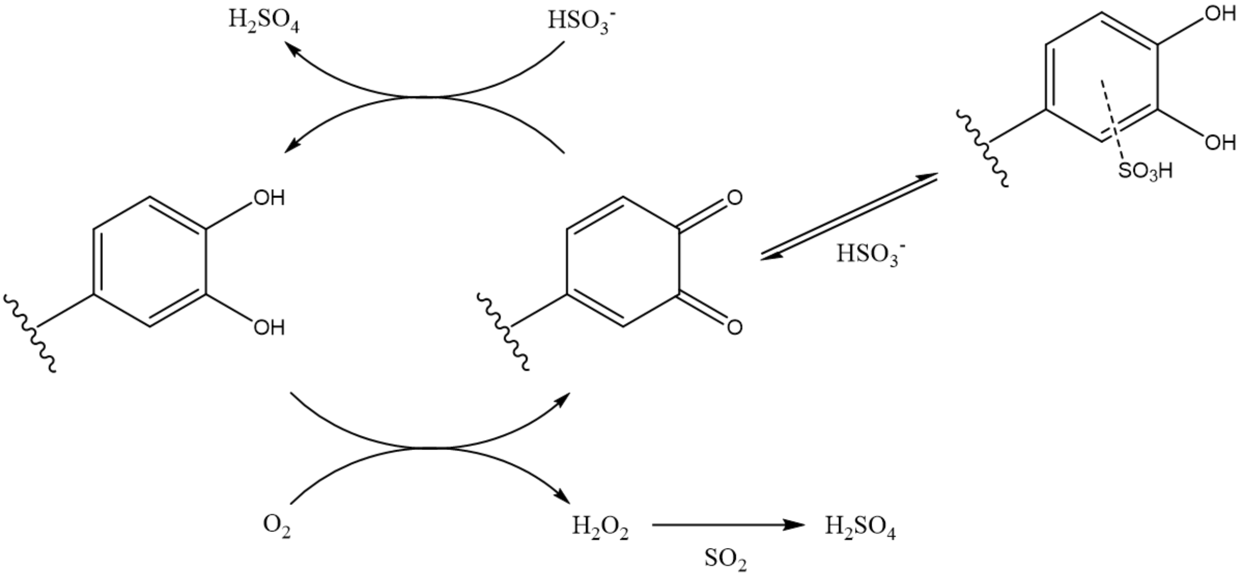

Figure 7: Antioxidative effect of sulfur dioxide in wine (modified according to Bradshaw et al. (2011)).

3.5. Influencing factors in a wine storage cabinet

3.5.1. Vibration

Vibration caused by engines and road irregularities during transportation and by compressors during storage in a refrigerated wine storage cabinets are unavoidable. However, vibration is a so far largely neglected parameter in literature on wine development during storage. So far, there have been several studies which suggest that vibrations influence the quality of beverages. Janssen et al. (2014) even suggest real-time measurements of temperature, humidity and acceleration (for vibration and shock event monitoring) during the transport of beverages in order to calculate transport-related shelf life models. However, there are only two publications so far, which investigated the influence of vibrations on wine (Chung et al. 2008, Zhao et al. 2018). Chung et al. (2008) showed that vibration leads to significant changes in the content of higher alcohols and organic acids in red wine during a storage period of 18 months. Zhao et al. (2018) investigated the effect of elevated temperatures and movement over a period of 15 days. They concluded that the influence of short time vibration on volatile substances in wine is negligible compared to the influence of high temperatures during storage. Recent studies on beer revealed that vibration in combination with elevated temperatures can cause significant chemical changes in the volatile composition and accelerated turbidity formation (Paternoster et al. 2018, Jaskula-Goiris et al. 2019, Paternoster et al. 2019). Though the reviewed studies suggest that vibration have an impact on wine composition the magnitude of this impact stays unclear, since they analyzed only few compounds and parameters. Furthermore, they investigated mostly combined vibration-temperature effects, did often not contain complete specifications of vibration conditions.

3.5.2. Fluctuating temperature

In addition to constantly high temperatures fluctuating temperatures, can have an impact on compositional changes during bottle storage. During transport wine is often suspected to temperature differences up to 20°C, due to night and day temperature fluctuations (Butzke et al. 2012, Mac Cawley).

Robinson et al. (2010) examined the effect of temperature fluctuations on the volatile profile of red and white wine by subjecting them to simulated transport conditions. They stored the wines over a period of 21 days using constant 20°C to reflect room temperature, constant 40°C to reflect a hot environment, and a diurnal temperature cycle (20°C/40°C alternating every 12 hours) to simulate transcontinental shipping conditions. The study showed that constant 40°C had a higher impact on the sensory and volatile profile of the wines compared to the 20°C/40°C cycled treatment and constant 20°C. The cycled treatment had a higher impact on the wines than storage under constant 20°C. Wines which were subjected to higher temperature had significantly higher concentration of TDN and vitispirane and a lower concentration of isoamyl acetate, hexyl acetate and 2-phenyl acetate. It is evident from this study that storage at fluctuating temperature results in the loss of fruit-associated esters and the increase in aging-associated compounds.

Crandles et al. (2016) investigated the impact of linear increasing temperatures and diurnal fluctuating temperatures on Scheurebe and Müller-Thurgau wines. The linear increasing temperature from 15°C to 45°C for six days simulated an oversea transport. The diurnal fluctuations between 15°C and 40 °C for twelve hours for 8 days simulated a stay at the port. The results of the study showed that fluctuating temperatures affect the pressure inside a wine bottle and could therefore induce a pump effect of air inside the bottle. However, the authors observed no increased oxygen levels in the bottles due fluctuating temperature, but an increased risk of pushed out cork closures. One month after the experiment a trained sensory panel was able to distinguish between Scheurebe wines submitted to simulated transport conditions and a control group, stored at 12°C. Eight months after the experiment no significant differences were found for Scheurebe wines. No sensory differences were found for Müller-Thurgau wines one month after the experiment. However, eight months after the experiment significant differences between Müller-Thurgau wines stored under diurnal temperature fluctuations and wines stored at constant 12°C were revealed. The authors concluded that their simulated transport conditions were too short to impact the sensory profile of the two white wines. These results show that the impact of temperature on wine is dependent on its composition.

Walther et al. (2018) monitored temperatures during bulk shipping of wine from Australia to Germany and investigated the impact on chemical and sensory characteristics of Chardonnay wine. The study revealed temperature fluctuations of over 40°C in ship containers. Wines which were exposed to temperature above 25°C during shipment showed a significant decrease in sulfur dioxide (SO_2) and increase in yellow color. Esters associated with young wine decreased significantly under high temperatures. Descriptive sensory analysis revealed that wines which were subjected to shipping temperatures are less fresh and fruity.

Hirlam et al. (2019) investigated the impact of diurnal temperature fluctuations on the O_2 permeability of different closure types, considering the bottle position. They found that changing temperature three times a week between 17°C and 28°C caused a pump effect of air through natural and synthetic cork closures. This effect was more pronounced in vertically stored bottles. The permeability of screw caps and technical cork stoppers were not influenced by fluctuation temperatures. The authors concluded that fluctuating temperature increase the risk of oxidative spoilage during transport. They suggest better packaging solutions during shipment to minimize wine spoilage from premature oxidation (Hirlam et al. 2019).

The reviewed studies show that diurnal temperature fluctuation accelerate wine aging reactions and have the potential to cause a pump effect through cork closures. However, to our knowledge, none of those studies compared the applied temperature fluctuations to the mean storage temperature, as calculated from the fluctuation pattern. Furthermore, the influence of low-interval temperature fluctuations occurring in refrigerated wine storage cabinets due to compressor cycling have not been regarded before.

3.6. Oxygen measurement in wine

The fluorescence based O_2 measurement was a central analysis in the first publication of this thesis (Chapter 4). For this reason, this method is described in detail in the next chapter.

Fluorescence based Oxygen measurement

O_2 management during wine bottling is a very important aspect for winemakers. Wine development during bottle storage is highly dependent on the initial O_2 content at bottling (Dimkou et al. 2011, Dimkou et al. 2013) and the O_2 permeation through the closure system during storage (Godden et al. 2001, Lopes et al. 2009). Therefore, a user-friendly and reliable method is required to monitor O_2 contents in the HS and dissolved in wine at bottling and during storage.

There are different methods to determine dissolved O_2 in wine, including colorimetric (Ribéreau-Gayon 1933, Lopes et al. 2005), electrochemical (Nevares and del Álamo 2008) and optical methods (Lopes et al. 2005, Dieval et al. 2009, Dimkou et al. 2013). Optical methods for the determination of O_2 have proven themselves advantageous over colorimetric or electrochemical methods. Most optical sensors are based on luminescent probes. The measurements are non-invasive, fully reversible and have a good precision and accuracy (Wang and Wolfbeis 2014).

Luminescence quenching can be measured either based on the luminescence intensities or on the luminescence lifetimes. Either the intensity or the lifetime will decrease upon quenching. This process is usually described by modified Stern–Volmer kinetics. Optical O_2 sensors which are based on intensity quenching of the fluorescence have certain disadvantages. These include susceptibility to light source and detector drift, to changes in optical path, and drift due to degradation or leaching of the dye. These effects can be minimized by operating the sensor in the time domain instead of the intensity domain (McDonagh et al. 2001).

Figure 8 shows a schematic illustration of a typical luminescent sensor for O_2. The sensor consists of an optically transparent “solid support”, an O_2-permeable “sensing layer”, containing a fluorescent dye and an “optical isolation”.

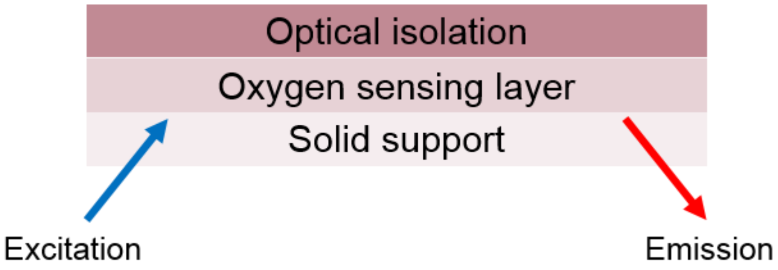

Figure 8: Schematic cross-section of a typical planar luminescent sensor layer. Modified according to Wang and Wolfbeis (2014).

Common fluorescent dyes, used for this application, are Ruthenium-ligand complexes. In the presence of molecular O_2, the decay time is reduced. In case of a sinusoidally modulated excitation signal, the fluorescence signal is a phase shifted sinus function (Figure 9). This phase shift Φ is related to the modulation frequency f and to the lifetime τ as shown in Equation 3.

$$\tau = \frac{\tan \Phi}{2\pi f} \tag{3}$$

The relationship between the lifetime τ and the O_2 concentration is described by the Stern-Volmer equation (Equation 4).

$$\frac{\tau_0}{\tau} = 1 + K_{SV} * pO_2 \tag{4}$$

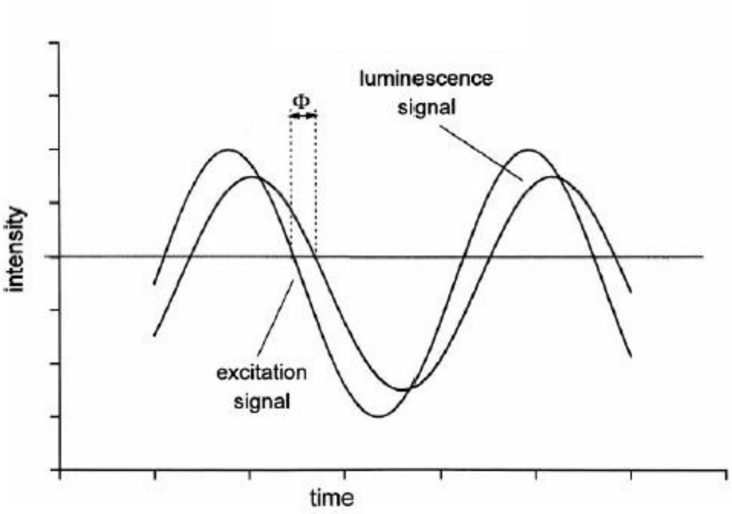

Figure 9: Principle of phase fluorometric technique (McDonagh et al. 2001).

This study used a NOMASense O_2 P6000 O_2 meter (Vinventions Deutschland GmbH, Fußgönheim, Germany). The O_2 sensors were attached with transparent silicone on the inside of the bottles glass. The used sensors were PSt3 sensors (0 – 100% O_2) for the HS, and PSt6 sensors (0 – 2 mg/l) for dissolves O_2 (Presens Precision Sensing GmbH, Regensburg, Germany).

Figure 10 shows a bottle equipped with O_2 sensors for HS O_2 (1) and dissolved O_2 (2). The measurement is conducted with probe consisting of optical fiber which transmits blue light. The sensor dot (marked with arrows in Figure 10) responds by emitting a red light, which indicates the presence of O_2. The measured signal is translated by an analyzer to a specific O_2 concentration.

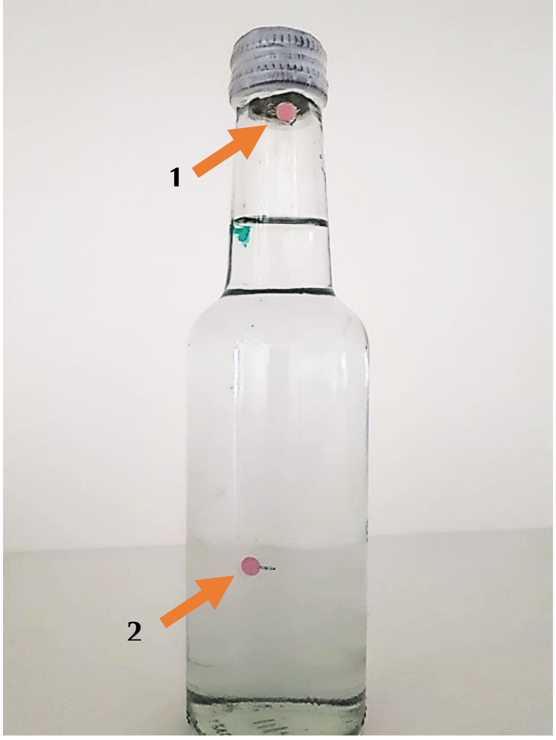

Figure 10: Bottle equipped with oxygen sensors, filled with model wine solution and sealed with a screw cap.

3.7. Analysis of volatile substances in wine

The approach of comprehensive two-dimensional gas chromatography (GC×GC) in combination with solid phase microextraction (SPME) was the main method in this thesis to evaluate changes in the volatile profile of wine during the storage experiments. The next chapters describe SPME, GC×GC, and the chemometrics used in this thesis.

3.7.1. Solid Phase Micro Extraction

The analysis of volatile compounds, such as aromatic substances, usually requires an extraction and concentration of analytes prior to gas chromatographic separation. The first SPME method was developed in the early 1990s by Arthur and Pawliszyn (1990) to minimize the time and effort required for sample preparation. The method combines several sample preparation steps, as sampling, purification, concentration and transfer to the instrumental analysis system in s single process (Arthur and Pawliszyn 1990).

In contrast to other extraction and concentration methods like liquid-liquid extraction, solid phase extraction (SPE) or simultaneous distillation-extraction (SDE) the SPME needs no organic solvents. There are two basic application practices: The solid sorption phase can be placed directly in the sample (direct immersion, DI), or in the HS above the sample, which is especially useful for the investigation of volatile substances (Yang and Peppard 1994, Sides et al. 2000, Bosch-Fusté et al. 2007). In the HS mode the extraction material has no direct sample contact. This minimizes the risk of interference by matrix components such as high-boiling non-polar substances, proteins, salts, or acids. Consequently, the sample matrix can be modified by adjusting the pH value or increasing the ionic strength for higher volatility without damaging the extraction material (Souza-Silva et al. 2015). The SPME is characterized by its quick and easy implementation, relatively low costs and good sensitivity (Sides et al. 2000). Extraction from the gas phase offers additional advantages, especially with regard to the discrimination of non-volatile compounds and the minimization of solvent effects (Vas and Vekey 2004).

The SPME technique uses short, fused silica fibers (1-2 cm) coated with an adsorbent. Materials of different polarities are used. Common materials are polydimethylsiloxane (PDMS, apolar) and polyacrylate (PA, polar) (Pawliszyn 1997). The selection of an appropriate fiber material depends on the polarity of the analyte. Mixed phase coatings are most appropriate for the analysis of volatile compounds (Sides et al. 2000).

The extraction of analytes using HS-SPME is very sensitive to experimental conditions. There are numerous of variables during the extraction process, which must be controlled to optimize the adsorption. These include sample pH, HS volume, sampling time, temperature and agitation or stirring speed. Agitating the SPME fiber, stirring and heating reduce the extraction time for less volatile compounds. The addition of salt usually enhances the adoption (Sides et al. 2000). In the quantitative analysis of substance mixtures, matrix effects such as different ethanol contents, pH or composition of the sample, have a major influence on the HS-SPME. A major disadvantage of HS-SPME technique is its susceptibility to fluctuations in the extraction process. In addition, the HS-SPME is susceptible to fluctuations in the extraction. When analyzing complex mixtures of substances and in the presence of solvents such as ethanol, displacement effects can occur (Górecki et al. 1999, Contini and Esti 2006, Spietelun et al. 2013, Gionfriddo et al. 2015). It is therefore important to use suitable internal standards (ISTD) to ensure the collection of valid quantitative data. Stable isotope-labeled - deuterated or ^{13}C-labeled - standard substances are best suited here (Ganss et al. 2011). For screening methods usually only one ISTD is used to compensate fluctuations in the extraction. Substance-specific losses are only compensated to a limited extent due to the lack of structural similarity with all analytes and shifting retention times. When measuring samples with a comparable matrix - pH value and ethanol content - a semiquantitative determination of data is possible.

3.7.2. Comprehensive two-dimensional gas chromatography

GC×GC is a multidimensional gas chromatography (MDGC) method. MDGC is characterized by two or more dimensions connected in series, with the aim to improve separation (Marriott 2001, Marriott et al. 2012). In contrast to the so-called heart-cut (H/C) MDGC, which focuses on a limited number of sampled ^{1}D regions, the GC×GC uses fast, continuous heart-cutting (modulation) for non-discriminative analysis. This is realized by a rapid separation in the second dimension using a short column with a smaller internal diameter and a sampling period less than the width of a ^{1}D peak (Phillips and Beens 1999). GC×GC has proved advantageous over H/C MDGC due to its complete or comprehensive application of multidimensional separation to the entire sample in a single analytical run. A significantly faster separation on the ^{2}D column enables generation of a complete ^{2}D chromatogram within the time for a single H/C event of the sampled zone of ^{1}D eluate (Marriott et al. 2012).

The achievement of maximum orthogonality of the two columns is an often-stated aim for GC×GC, implying that the separation mechanisms in ^{1}D and ^{2}D are independent of one another. This is realized by using different stationary phases in both dimensions (Marriott et al. 2012). An apolar phase in ^{1}D and a polar phase in ^{2}D are often used. To investigate volatile compounds in wine, a reverse order was chosen in this study. In ^{1}D a polar ZB-WAX column (30 m × 0.25 mm i.d. fused silica column coated with 0.5 µm polyethylene glycol phase (ZB-Wax, Phenomenex, Aschaffenburg, Germany) was used, in ^{2}D an apolar BPX-5 phase (2 m × 0.15 mm i.d. capillary, coated with 0.25 µm of a 5% phenyl containing polydimethylsiloxane phase (BPX-5, SGE, Griesheim, Germany).

The modulator is considered as the key component of GC×GC. Its main functions are to trap, refocus and release narrow fractions in a continuous cycle after separation in ^{1}D for separation in ^{2}D. The time intervals in which focusing, and re-injection take place are called modulation periods (P_M) and are usually between 1 s and 8 s. The modulation ratio (M_R) describes the number of modulations per peak. This ratio should be at least 3 for quantification; a value of 1.5 is also acceptable for screening methods (Marriott et al. 2004, Marriott et al. 2012).

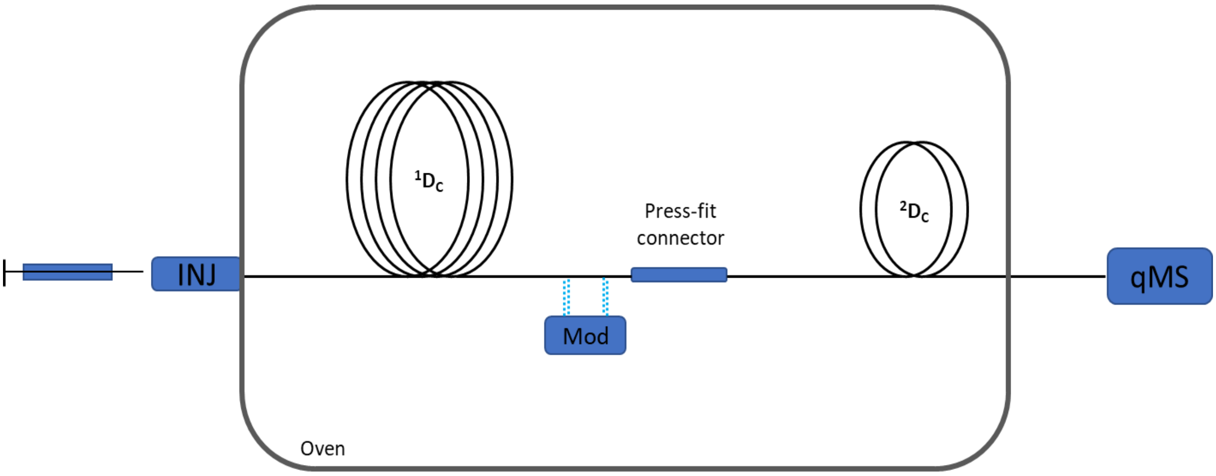

Figure 11: Schematic illustration of a GC×GC-qMS system (INJ: Injector; 1DC: first dimension column; 2DC: second dimension column; Mod: Modulator; qMS: Quadrupole mass spectrometer).

There are valve-based and thermal modulators (Tranchida et al. 2011). Thermal modulation is the most applied technique. The most effective thermal modulators are based on cryogenic focus with liquid nitrogen (N_2) or CO_2 (Bahaghighat et al. 2019). The dual-stage cryo-jet used in this work consists of two nozzles through which liquid CO_2 is alternately sprayed against the outer wall of the separation column. The expansion of the CO_2 freezes the column, and the analytes are focused; the remobilization takes place after the CO_2 flow is interrupted due to the temperature of the column oven. The double focusing causes a significant reduction in the peak base width (100 ms to 200 ms in ^{2}D) (Beens et al. 2001).

A proper monitoring of these narrow peaks requires a data acquisition rate of greater than 100 Hz. A flame ionization detector (FID) with its high acquisition rate of 50 Hz to 300 Hz is often used coupled with GC× GC. However, it does not provide structural information. The use of mass spectrometric detection provides additional information on the identity of the analytes (Adahchour et al. 2005, Schmarr and Bernhardt 2010). Due to high acquisition rates, Time-of-flight (ToF)-MS is often used for quantitative analyzes (≥ 100 scans/s) (Phillips and Beens 1999, Mühlen et al. 2008). Figure 11 shows the schematic illustration of a GC×GC system coupled with a quadrupole mass spectrometer (qMS) that was used in this thesis. The exact quantification using GC×GC-qMS is limited due to the acquisition rate of the detector (~ 20 Hz). Therefore, a screening method, which provides additional information about the identity of the analytes based on the recorded fragment spectra was applied on the data.

3.7.3. Data processing for comprehensive two-dimensional gas chromatography

Chemometric tools are useful for GC×GC applications in targeted and untargeted screening. However, they are most used to handle untargeted investigations. The process of untargeted research is more complex, since the analyst does not have a priori knowledge about the sample composition or the relevant compounds to monitor. Advanced chemometrics generally relies on a multi-step workflow of mathematical and statistical operations, which allows to robustly and reliably extract the relevant information (Stefanuto et al. 2021). For this purpose, many software applications have been developed recently (Schmarr and Bernhardt 2010, Bankó and Abonyi 2012, Bean et al. 2015, Freye et al. 2018, Wilde et al. 2020, Gawlitta et al. 2021).

This study uses an image processing technique known from 2D gel electrophoresis, which was introduced in 2010 by Schmarr and Bernhardt. The software used by Schmarr and Bernhardt (2010) was further developed for GC×GC applications and released under the name GasPedal (Decodon, Greifswald, Germany) in 2017.

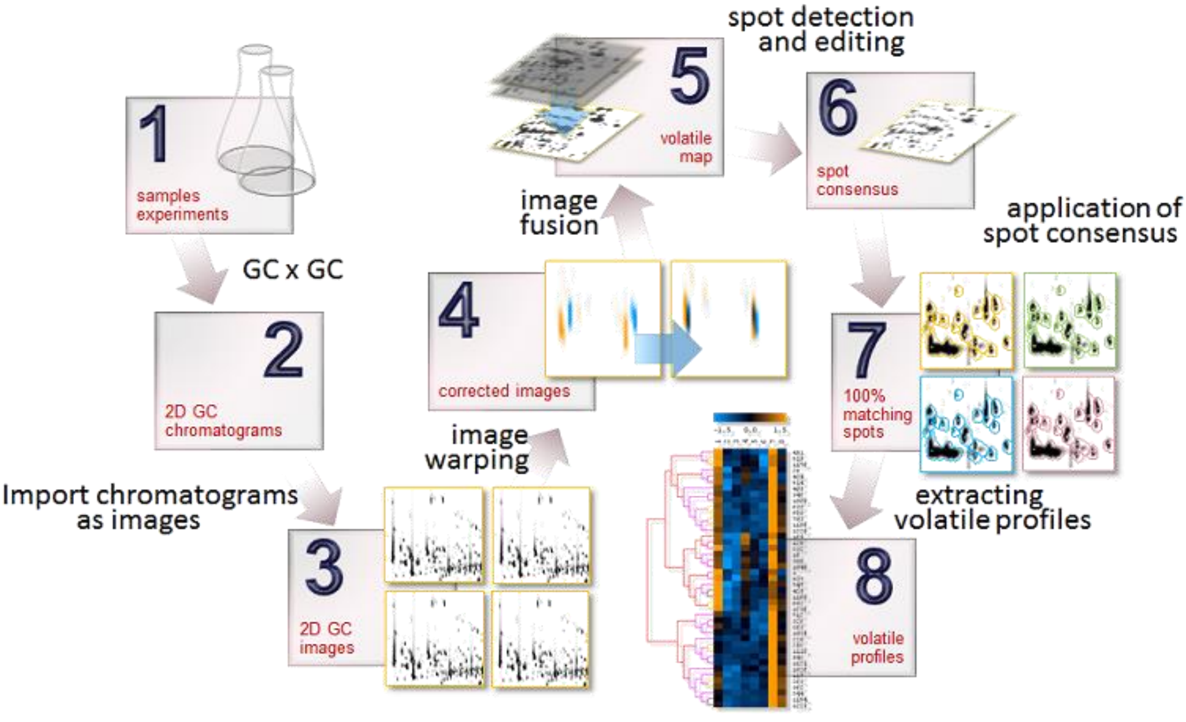

Figure 12: Workflow off the GC x GC data processing. Modified according to Schmarr and Bernhardt (2010). (1) Sample preparation. (2) Analysis by HS-SPME-GC x GC-qMS (3) 2D GC chromatograms were imported to GasPedal. (4) Image correction (warping) to compensate shifts in retention time (dual channel overlay color code: blue = image1, orange = image2 and black = overlap. (5) Volatile map resulting of project-wide 2D GC image fusion (6) Detected spot consensus (7) Spot consensus boundaries were applied to all 2D GC images for gray level integration. (8) Gray level integration results in quantitative data which can be summarized in volatile profiles.

Figure 12 shows the image processing workflow of 2D-GC chromatograms in the software GasPedal. For data alignment, the chromatograms are imported as .cdf (common data format)-

Export into GasPedal software. Additionally, the P_M and an “initial time offset” has to be provided. The imported data sets are further processed similar to the established workflow (Schmarr and Bernhardt 2010). Besides the chromatographic profile, GasPedal also uses the corresponding mass spectral information for the alignment, so called ‘warping’, of the two-dimensional data (Figure 12, section 3). Subsequently to the warping, the chromatographic images are fused to one artificial image (Figure 12, section 4). On this artificial image (fused image), peaks (also called ‘spots’) are detected (Figure 12, section 5-6) and the matching information is extracted and summarized in a quantitation table. GasPedal provides finally several statistical applications like Analysis of Variance (ANOVA), Principal Component analysis (PCA) and hierarchical cluster analysis (HCA) (Figure 12, section 8). For this study the quantitation table was exported, and the data was analyzed with XLSTAT software (Addinsoft, Paris, France).

Volatile compounds were identified by comparing the MS spectra with the MS spectra from the NIST 11 database and by comparing the linear retention indices (LRIs), based on n-alkanes, with an in-house database or with literature data. Some compounds were also identified with reference substances. Table 5 in the appendix (Chapter 8) shows all identified compounds in the examined wines.

3.8. Scope and aim

There have been numerous studies which investigated the compositional changes in wine during bottle storage. Those studies have been extensively reviewed by Scrimgeour et al. 2015, Agriopoulou and Stamatelopoulou 2017 and Echave et al. 2021. Temperature, bottle closure, bottle position, relative humidity and vibration are mentioned as factors influencing the shelf-life of bottled wine. Temperature is always mentioned as the main influencing factor during bottle storage of wine. Most studies which investigated the influence of temperature on compositional changes of wine during storage focused on constantly high temperatures (Dallas and Laureano 1994, La Presa-Owens and Noble 1997, Czibulya et al. 2012, Hopfer et al. 2012, Hopfer et al. 2013, Cejudo-Bastante et al. 2013, Giuffrida de Esteban et al. 2019). Fewer studies examined on diurnal fluctuating temperatures using simulated transport conditions (Robinson et al. 2010, Butzke et al. 2012, Crandles et al. 2016, Walther et al. 2018, Hirlam et al. 2019). Those studies compared the change in wine composition due to fluctuating temperatures with an ideal storage temperature at cellar conditions (12 – 15°C). But no study investigated so far, the influence of temperature fluctuations compared to the arithmetic mean of the storage temperature.

Vibration is a so far largely neglected parameter during the storage of wine, though there have been numerous studies which suggest an impact of vibrations during transportation on the quality of food and beverages (Geyer et al. 2009, Robinson et al. 2010, Aba et al. 2012, Tabatabaekoloor et al. 2013, Janssen et al. 2014, Crandles et al. 2016, Paternoster et al. 2018, Zhao et al. 2018, Jaskula-Goiris et al. 2019, Paternoster et al. 2019, Walkowiak-Tomczak et al. 2021). Paternoster et al. (2019) showed that vibration have the ability to accelerate the oxygen consumption in beer. There has been no study so far, which investigated the influence of vibration on oxygen consumption in wine. Overall, only few studies investigated the impact of movement or vibration on wine (Chung et al. 2008, Robinson et al. 2010, Crandles et al. 2016, Zhao et al. 2018). Those studies examined mostly combined vibration-temperature effects and are all lacking complete specifications of the vibration conditions. A study from 2008 already claims that vibrations affect the volatile profile of wine (Chung et al. 2008). However, they analyzed only the content of two higher alcohols during the vibration experiment of 18 months. Although higher alcohols are quantitatively important representatives of the volatile compounds in wine, they only make a small contribution to sensory perception. Since then, there has been no further study that focused on the effect of vibration on the volatile profile of wine. There is no sufficient prove so far that vibrations have an impact on the evolution of wine during storage.

The current market trends indicate that customers spend more money on premium wine, implying a growing market for refrigerated wine storage cabinets (Anderson et al. 2017). Since wine storage cabinets are considered as ideal storage location and not every household possess an appropriate cellar for wine storage, wine storage cabinets become more and more important. To guarantee the best possible storage in a wine refrigerator, there are various technical requirements. These technical requirements include low temperature fluctuation and as little vibration as possible. Both temperature fluctuations and vibration occur in a wine storage cabinet due to compressor cycling. The effect of both parameters was investigated separately from each other in two independent experiments. Low interval temperature fluctuations were regarded to examine the influence of temperature fluctuations due to cooling devices, such as compressors in refrigerators. The temperature fluctuated continuous for two years around the ideal storage temperature of 12°C. This should provide further information as to whether the arithmetic mean of the storage temperature provides sufficient information about the storage conditions of the wine. Additionally, it should be examined whether low interval temperature fluctuation cause a pump effect through the bottle closure and thus have the potential accelerate wine oxidation processes. Furthermore, it was important to investigate the sole influence of vibration on wine, using a simulation experiment with a detailed set of specifications for a reproducible and standardized experiment. The vibrations simulated devices such as cooling units in warehouses, compressors in refrigerators and motors of transport vehicles. With this experiment it should be clarified if vibration promotes the oxygen uptake into wine and if vibration induced changes in the volatile profile of wine. Other parameters such as SO_2, color and CO_2 were studied to investigate the influence of vibration on the gas permeability of screw caps, natural and agglomerated cork closures.

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4. Influence of Vibration on the Consumption of Oxygen and Sulfur Dioxide in Wine Bottles considering Bottle Position, and Headspace Volume

Oxygen is one of the most important factors influencing wine evolution during bottle storage. Propper oxygen management at bottling though closure choice, inert gas covering and minimizing the headspace volume are therefore important tools to adjust an appropriate oxygen content in the wine bottle. The influence of vibration on oxygen consumption has already been shown for other beverages like beer and milk. No research group investigated the influence of vibration on the oxygen consumption in wine so far. The fact that wine is subjected to vibrations during transportation and storage is unavoidable. Vibrations are emitted by engines of all types of vehicles, ships, cooling units in warehouses, and from compressors in wine refrigerators. Therefore, it is crucial to investigate if these vibrations have an impact on the oxygen consumption in wine. Vibration promoted the dissolution of oxygen from the headspace of the bottle into the wine causing accelerated sulfur dioxide degradation. The effect of vibration was larger in horizontally stored bottles indicating that a larger surface promotes oxygen uptake into the wine. In absence of headspace oxygen, vibration showed no influence on sulfur dioxide-related oxygen degradation. Furthermore, it was shown that the dissolution of oxygen was faster under cork closure than under screw cap due to the overpressure by corking process. It was concluded that vibration has a major impact on the dissolution of headspace oxygen from the headspace of the bottle into the wine but not on the chemical reaction of the dissolved oxygen with sulfur dioxide. The larger surface between the headspace and wine in horizontally stored bottles and the overpressure created by corking process accelerates the oxygen uptake from the bottle's headspace into the wine.

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4.1. Abstract

In this study, the influence of vibration, bottle position, and initial headspace volume on the oxygen distribution inside a wine bottle were investigated. For this purpose, a model wine was filled in 0.75 L wine bottles and stored horizontally and vertically under different vibration intensities (500 mm/s^2 and 1000 mm/s^2) at a constant frequency of 50 Hz. The bottles were sealed with screw cap and cork closure and two different headspace volumes for each closure type. Our results indicated, that vibration and horizontal bottle position promoted the dissolution of oxygen from the headspace of the bottle into the wine causing accelerated sulfur dioxide degradation. The effect of vibration was larger in horizontally stored bottles indicating that a larger surface promotes oxygen uptake into the wine. In absence of headspace oxygen, vibration and bottle position showed no influence on sulfur dioxide-related oxygen degradation. Furthermore, it was shown that the dissolution of oxygen was faster under cork closure than under screw cap due to the overpressure by corking process. It was concluded that vibration and horizontal bottle position have a major impact on the dissolution of headspace oxygen from the headspace of the bottle into the wine but not on the chemical reaction of the dissolved oxygen with sulfur dioxide. The larger surface between the headspace and wine in horizontally stored bottles and the overpressure created by corking process accelerates the oxygen uptake from the bottle's headspace into the wine.

4.2. Introduction

Most of the negatively associated quality changes during shipment and bottle storage of wine are induced by oxidative reactions (Marais 1998, Silva Ferreira et al. 2003, Du Toit et al. 2006). Therefore, it is important to identify all factors affecting these reactions. Two so far largely neglected parameters during storage are vibration and bottle position. Vibration caused by engines are unavoidable. There have been several studies which suggest that vibrations influence the quality of beverages. Chung et al. (2008) showed that the storage of wine in presence of vibration led to significant changes in the intensities of higher alcohols and organic acids. Janssen et al. (2014) outlined that vibration induced turbidity in beer. Other studies revealed that the combined effect of temperature and vibration accelerated the decreases in oxygen (O_2) concentrations, increased colloidal instability and caused significant changes in the chemical composition of beer (Paternoster et al. 2019, Jaskula-Goiris et al. 2019).

Experimental data published on the influence of horizontal and vertical bottle position on changes in wine composition is nowadays contradictory. Mas et al. (2002) investigated the influence of vertical and horizontal bottle position on the development of red and white wine with six different closures. Vertical bottle position increased intensities of acetaldehyde in bottles sealed with agglomerated cork closures, plastic stoppers, and screw cap for red and white wine. Oxidative browning was promoted in bottles sealed with plastic stopper and screw cap in white wine and for all closure types in red wine. Hernanz et al. (2009) observed a decrease in the content of some phenolic compounds in vertically stored bottles without providing information about the used closure type. Skouroumounis et al. (2005) showed that the bottle position had no significant influence after three years of storage on the sensory profile of a Riesling and a Chardonnay with cork closure. Lopes et al. (2006) found that the O_2 ingress rates through natural cork closures and screw caps were not influenced by the bottle position over 12 months of storage. Venturi et al. (2017) monitored the total sulfur dioxide (SO_2) content in wine over 12 month in horizontal and vertical stored bottles sealed with cork closure. They observed that the total amount of SO_2 decreased significantly faster in vertically stored bottles. The authors did not discuss possible explanations for this observation.

The initial O_2 content in the headspace (HS) of bottles depends on the HS volume, and the use of inert gas cover at bottling process. Moreover, Kontoudakis et al. (2008) showed that the use of cylindrical closures generate an overpressure in the HS of bottles after the corking process elevating the initial O_2 content using cylindrical closures for an unknown time. There have been several studies indicating excessive oxidative spoilage of wine was caused by elevated initial O_2 concentration in HS of bottles (Brajkovich et al. 2005, He et al. 2013, Morozova et al. 2015). Dimkou et al. (2011) observed an accelerated O_2 uptake from HS to wine under cylindrical closures compared with screw cap suggesting the effect of overpressure under cylindrical closures.

This study investigates the impact of vibration and bottle position (horizontal or vertical) on the O_2 distribution between HS oxygen (HSO) and dissolved oxygen (DO) inside a bottle. Recent studies showed the technical relevance for low frequency vibrations (< 100 Hz) (Paternoster et al. 2018). The presented work considered different HS volumes regarding the effect of the initial O_2 concentration. In combination with different HS volumes wine bottles were sealed with either cork stoppers or screw caps as the most common closure types in wine industry. The objective was to provide evidence if vibration has an influence on the dissolution of HSO from the HS of the bottle into the wine. Furthermore, the impact of horizontal and vertical bottle position on O_2 distribution inside the bottle was investigated. Different closure types were used to investigate if vibration possibly affects the initial O_2 content in the HS of the bottle.

4.3. Materials and Methods

Experimental setup

The model wine was an aqueous solution with 12 % vol. ethanol, 5 g/L potassium hydrogen tartrate, 1 mg/L Fe^{2+}, 1 mg/L Fe^{3+}, 100 mg/L catechin, 100 mg/L potassium metabisulfite, pH 3.5 and O_2 (saturated). Catechin was used as a compound which occurs naturally in wine and is prone to oxidation. The chosen concertation of catechin aimed to simulate the total phenol content in wine. Fe^{2+} and Fe^{3+} were used to catalyze oxidation reactions. This highly efficient experimental setup was created to observe the oxidative pathways in a short period directly after the bottling process. The model wine was filled in 750 mL Alsace-style wine bottles (450 g). The wine was filled under atmospheric pressure without inert gas cover to allow for a maximum but still realistic amount of O_2 in the HS of the bottles. The bottles were sealed with screw caps and cork closures (both Vinventions Deutschland GmbH, Fußgönnheim, Germany). For each closure type, two different HS volumes were investigated. HS volumes of 5 and 10 mL were chosen for the bottles sealed with cork closures. HS volumes of 15 and 10 mL were chosen for bottles with screw cap. These HS volumes were chosen because they meet common industry standards. An additional experiment without HS volume was conducted in bottles sealed with screw cap.

Two vibration intensities with 500 and 1000 mm/s² at a constant frequency of 50 Hz were chosen to simulate uniform vibration conditions of electrical devices such as a cooling units in warehouses. The vibration experiments were conducted on an experimental vibration plate. The vibration plate was built on a linear guide rail, which was connected to a magnetic vibratory motor. The motor initiated an oscillation movement of the plate in one direction only. The vibration strength was infinitely adjustable by acceleration. The different vibrations intensities were obtained by changing the acceleration amplitude. All bottles were placed and fixed inside a wire mesh container which was screwed down to the vibration plate. Horizontally stored bottles were stacked in the wire mesh container with no gaps between the bottles to avoid resonance vibration of the bottles. Vertically stored bottles were fixed with cable ties at the sides of the wire mesh container. The experiment was conducted at a controlled and constant temperature of 23°C in the dark over a period of 17 or 18 days, respectively, which represents typical shipping times across Europe. The treatments included a control group stored at the same temperature conditions without vibration. The ambient vibration in the room was tested and recorded (< 50 mm/s²). All 24 treatments (three vibration levels, two bottle positions and four closure type/headspace volume combinations) and the four treatments of the experiment without headspace volume were conducted in duplicate.

Vibration measurement ("proof of concept")

The vibration measurement was carried out with a PCB-356A15 three-axis acceleration sensor (PCB Synotech GmbH, Hückelhoven, Germany). Prior to the experiment the vibration was measured at nine different locations in the wire mesh container. The sensor was attached with an adhesive glue to a bottle filled with water and connected to a computer. The sensor-equipped bottle was further used to survey the vibration intensity prior and during the experiment. DasyLab (2016) software (National Instruments, Austin TX, USA) was used for data acquisition. These continuous measurements were carried out for one month to control a uniform distribution and constant conditions of vibration during the experiment.

Oxygen measurement

A non-invasive chemoluminescence based method for O_2 measurement was chosen to enable the observation of a closed system. The bottles of all treatments and duplicates were equipped with O_2 sensor spots to measure HSO and DO. O_2 measurements were carried out with a NOMASense O_2 P6000 O_2 meter (Vinventions France SAS, Rivesaltes, France). The O_2 sensors were attached with transparent silicone on the inside of the bottles glass. The used sensors were PSt3 sensors for the HS, and for dissolved O_2 (Presens Precision Sensing GmbH, Regensburg, Germany). The sensors for DO measurement were placed 10 cm above the bottle bottom with permanent wine contact. The sensors for HSO measurement were placed in the bottleneck without liquid contact for vertically stored bottles. For horizontally stored bottles, the sensors for HSO measurement were placed in the gas bubble.

Sulfur dioxide measurement

Free SO_2 was determined with iodometric titration by Ripper method using the Titrator T50 (Mettler Toledo, Gießen, Germany). Sampling for each treatment was conducted in duplicate. Bottles used for SO_2 measurement were not returned to the experiment.

Statistical evaluation

All statistical analyses were performed using XLSTAT (Version 19.02, Addinsoft, France). Regression analyses on SO_2 and O_2 over time were performed using the model of pseudo-first order kinetics $y= c_0 \times e^{-kt}$. The consumption rate k was taken from this equation. DO data was analyzed using a one-way analysis of variance (ANOVA), followed by a Least significant difference (LSD) test ($p = 0.05$). The SO_2 data and the DO model without HS was analyzed using a two-way ANOVA model and LSD test ($p = 0.05$). A three-way ANOVA was performed on the HSO data and on the O_2 ratios between HSO and DO. Least significant difference test was used to determine statistically different values at a significance value of ($p = 0.05$).

4.4. Results and Discussion

Influence of vibration on dissolved oxygen (DO)

DO decreases during storage of wine as a result of oxidation. Chung et al. (2008) investigated the influence of vibration on higher alcohols and organic acids in bottled wines. However, the influence of vibration on DO was not reported in the study of Chung et al. (2008). Figure 1 displays the influence of vibration on the decrease of DO over 17 days in horizontally (Figure 1A) and vertically (Figure 1B) stored bottles with 15 mL HS volume and screw cap. The initial DO was between 7 and 8 mg/L and set to 100 % for illustration. DO decreased over time in all experiments. The coefficients of variation were below 10 %. The regression analyses yielded the consumption rates k_{DO} for each treatment. Depending on the vibration level and the bottle position, the consumption rates k_{DO} were between 0.10 and 0.15 1/d. These values are in accordance with those calculated by Danilewicz (2011). According to one-way ANOVA on the consumption rate k_{DO}, the DO decreased faster in samples which were vibrated with 1000 mm/s² for the vertical and the horizontal bottle position. In horizontally stored bottles, a vibration intensity of 500 mm/s² had no significant influence on the consumption rate k_{DO}. In vertically stored bottles, a vibration intensity of 500 mm/s² caused a significant higher DO decrease than in non-vibrated bottles. Overall, the results indicate that vibration increases the consumption rate k_{DO}. Previous literature reports similar observations for beer. The combined effect of elevated temperatures and vibration led to higher decrease of DO in beer (Paternoster et al. 2019, Jaskula-Goiris et al. 2019). Danilewicz (2007) showed that the reaction of catechin with O_2 is slower than of other phenolic compounds. In addition Danilewicz (2007) showed that the reaction is influenced by the initial phenol concentration. Since wine is a complex mixture and contains more than one phenolic compound, it is likely that the influence of vibration will be different for each wine. Nevertheless, the results in the present study indicate an influence of the bottle position in context with vibration. It is assumed that the increased surface between the HS and the wine, when bottles are stored horizontally, influence the O_2 uptake from HS to the wine**.** The larger surface possibly promotes a faster O_2 uptake from HS to wine stimulated by vibration and increases the consumption of O_2.

Influence of vibration and bottle position on SO_2

Figure 2 shows the influence of vibration and bottle position on free SO_2. The initial free SO_2 content was between 40 and 45 mg/L. The bottles had a HS volume of 15 mL and were sealed with screw cap. The free SO_2 decreased in all experiments over time. The coefficients of variation were below 10 %. The consumption rate k_{SO2} was significantly accelerated by vibration. The consumption rate k_{SO2} was higher in bottles vibrated at 1000 mm/s² compared to those at 500 and 0 mm/s² ($p = 0.05$). SO_2 was also more quickly degraded in horizontally stored bottle than in vertically stored bottles. According to the two-way ANOVA, the impact of bottle position (F-value = 39.6) was even higher than the impact of vibration (F-value = 21.6). Table 1 shows the regression parameters for the SO_2 consumption curves in Figure 2. The consumption rate k_{SO2} reveals that the impact of bottle position decreased with an increasing vibration intensity. The difference between the consumption rates $\Delta\ k_{SO2}$ of horizontally and vertically stored bottles was least for 1000 mm/s² (0.7×10^{-2} 1/d), followed by 500 mm/s² (3.0×10^{-2} 1/d) and highest for non-vibrated bottles (4.6×10^{-2} 1/d). These findings support the earlier observation that the bottle position influences the consumption rate k_{DO} in context with vibration (Figure 1). The larger surface facilitates the O_2 uptake from the HS into the wine.

Under screw caps the HS volume is generally larger than under cylindrical closures. A larger HS volume results in a larger surface for a horizontal bottle position. Additionally, the bottleneck diameter and the filling height are two other factors, which influence the surface size for vertical bottle position. The effect of vibration and bottle position on the accelerating oxygen consumption is therefore connected to HS volume and closure type.

Influence of vibration and bottle position on headspace oxygen (HSO)

Figure 3 shows the influence of vibration and bottle position on HSO in bottles filled with 15 mL HS volume and sealed with screw cap. The initial HSO content was between 5 and 6 mg/L and set to 100 % for illustration. The coefficients of variation were below 20%. The decrease of HSO content was affected by vibration. For both, vibrated and non-vibrated bottles, the HSO content of horizontally stored bottles decreased faster than in vertically stored bottles. The evaluation of the HSO decrease over time requires the additional consideration of the initial HS volume and closure type.

Influence of vibration, bottle position, headspace volume and closure type on headspace oxygen (HSO)

Closure type and HS volume affect quality parameters like free SO_2, color, and sensory profile of the wine during storage (Brajkovich et al. 2005, He et al. 2013). In practice, the closure type and the HS volume in a bottle are connected to each other. Screw caps usually require larger

HS volumes under the closure than cylindrical closures. Screw caps are not able to absorb gas when wine is expanding/contracting in a bottle as a result of temperature changes. Closure type and HS volume were regarded as a combined factor in this study. Larger HS volumes resulted in higher initial O_2 content inside the bottle. Hence, it is likely that oxidation processes are more promoted for larger HS volumes (Vidal and Moutounet 2006, Morozova et al. 2015).

The influence of vibration and bottle position on HSO was investigated by also considering the influence of the initial HSO content by using a screw cap with 10 and 15 mL HS volume and a cork closure with 5 and 10 mL HS volume (Table 2). The coefficients of variation were up to 40 % for the cork closure and below 20 % for the screw cap. Depending on the initially HS volume of 5 or 10 mL, the initial HSO contents in bottles with cork closure were between 3.3 and 6.7 mg/L. The initial HSO contents in bottles with the screw cap were between 4.2 and 5.5 mg/L for 10 and 15 mL HS volume, respectively. Overall, the HSO values are realistic for commercial wine bottles which were not treated with an inert gas cover (Kontoudakis et al. 2008, Vidal et al. 2006). Table 2 shows that the initial HSO content was highest in bottles sealed with cork closure and HS volume of 10 mL. A reduction in volume of 50 % under the cork closure from 10 to 5 mL resulted in half as much initial HSO content. A HS volume of 10 mL was considered for both, cork closure and screw cap. Although equal in volume, the resulting initial HSO content was significantly higher under the cork closure. This observation can be explained by the sealing process displacing approx. 15 mL of the HS volume by the cork closure and eventually producing a temporary overpressure inside the bottle (Kontoudakis et al. 2008).

Table 3 shows the influence of vibration, bottle position, HS volume, and closure type on consumption rates k_{HS}. The decrease of HSO was significantly faster when a vibration intensity of 1000 mm/s² was applied. A vibration intensity of 500/mm/s² showed no significant differences to non-vibrated bottles. Over all factors, the bottle position showed no significant difference on the O_2 uptake from HS to model wine (Table 3).

The results from three-way ANOVA (Table 3) revealed that vibration was the strongest factor (F = 21.7), the bottle position had the lowest influence on the O_2 uptake from HS to wine (F = 3.6). The factor HS volume and closure type could be also identified as a strong impact factor (F = 4.5) on the consumption rate k_{HS}. Bottles sealed with cork closure showed significantly faster O_2 uptake from HS to wine than screw caps. The overpressure produced during sealing process with cork, not only yielded higher initial O_2 contents in the HS, but also accelerated the O_2 uptake from HS into wine. These findings are in accordance with the Henry's law, which states that the solubility of gases increase under high pressure. The findings are also in accordance with an earlier study which assumed that an overpressure after sealing with a cork accelerates the O_2 uptake from HS into the wine (Dimkou et al. 2011).

Influence of vibration and bottle position on dissolved oxygen in bottles without headspace volume

The previous results revealed that vibration at an intensity of 1000 mm/s² had a significant impact on HSO and DO decrease (Figure 1, Figure 3 and Table 3). Moreover, vibration and bottle position had a significant impact on SO_2 decrease (Figure 2). The overpressure created by cylindrical closures increased the solubility of O_2 in wine and hence promoted the O_2 uptake from HS to wine (Table 3). These results provide evidence that vibration and bottle position accelerate the dissolution of O_2 from the HS of the bottle into the wine and thus accelerate the consumption rates k_{DO} and k_{SO2}. However, the dissolution of O_2 in wine is a physical process and not a chemical reaction. Therefore, the influence of vibration and bottle position on the reaction of O_2 in wine needs to be clarified. To investigate the effect of vibration on the reaction rate k_{DO} an additional experiment without any HS volume was conducted. A vibration intensity of 1000 mm/s² was chosen for this experiment, since it showed a significant influence on the consumption rates k_{DO} in the previous experiment.

Figure 4 shows the influence of vibration on the DO content in horizontally and vertically stored bottles without HS and sealed with screw cap. The coefficients of variation were below 5 %. The ANOVA on the consumption rate k_{DO} revealed no significant differences between consumption rates k_{DO}. As a consequence, it was concluded that neither vibration nor bottle position had an influence on the consumption rate k_{DO}. These findings confirm that vibration and bottle position accelerate only the dissolution of O_2 into the wine and provide insight in the kinetics of SO_2 loss right after bottling. Vibration and horizontal bottle storage possibly lead to faster SO_2 consumption in the early stage of bottle storage. Therefore, vibration and horizontal bottle position should be considered as important influences on the consumption of initial HSO in wine bottles. This underlines the importance of inert gas cover to reduce initial O_2 intensities at bottling. Several studies already stated that O_2 management at bottling is crucial for the development of wine aroma during storage. Large HS volumes with high initial O_2 are related to a premature oxidative spoilage of wine (Brajkovich et al. 2005, Dimkou et al. 2011, He et al. 2013, Morozova et al. 2015).

The fact that vibration promotes O_2 uptake from HS to wine, makes it also likely that the O_2 transfer rate (OTR) of the closure is affected. Hence, vibration could lead to higher OTR. In terms of the bottle position, it should be considered that a horizontal bottle position possibly reduces the O_2 transfer through the closure despite of vibration. Further research is required to observe the long-term effects of vibration on O_2 transfer through the closure.

Distribution of oxygen inside the bottle

So far the results of this study indicate that vibration and bottle position have an influence on O_2 distribution in a wine bottle, considering the initial O_2 content in the HS. Figure 5 displays the changes in O_2 ratios between HSO and DO in bottles sealed with screw cap and 15 mL HS volume over the time of the experiment. The initial O_2 ratio was set to zero. The coefficients of variation were below 10 %. The O_2 ratio in vertically stored non-vibrated bottles and bottles vibrated at 500 mm/s^2 shifted towards HS. Vertically stored vibrated bottles at 1000 mm/s^2 did not show this shift towards HS until the last days of the experiment. Horizontally stored bottles kept the initial O_2 ratio unless they were vibrated at 1000 mm/s^2. In this case, the O_2 ratio showed a shift towards DO. Again, a shift towards HS was observed until the last days of the experiment. These results confirm the earlier observations that the influence of vibration is dominant in vertically stored bottles. The differences in O_2 ratio between non-vibrated and vibrated bottles stored horizontal position are rather small compared to those between vertically stored bottles. The increased surface between HS and wine in horizontally stored bottles obviously affects the O_2 distribution inside a wine bottle and promotes a shift towards DO. The fact that the O_2 ratio in bottles vibrated at 1000 mm/s^2 shifts from day 12 towards HS could be due to the constant change in O_2 concentration during the experiment. Due to the constant decrease of DO, an O_2 gradient was created from HS into the wine. The DO in bottles vibrated at 1000 mm/s^2 decreased faster and DO is nearly consumed at day 12. The O_2 concentration is barely affected afterwards and then a new distribution of O_2 between HS and wine was observed.

Table 4 shows the results of three-way ANOVA over the time of the experiment. The O_2 ratio in bottles stored without vibration was on the side of the HSO. In contrast, the O_2 ratios of vibrated bottles were on the side of the DO. The influence of vibration was significantly different over the whole time of the experiment. However, the probability value increased towards the end of the experiment suggesting a decreasing influence. Although still significantly different, the LSD analysis showed no significant differences between vibration intensities after day ten. This implies that this factor was influenced by other parameters. Interactions between vibration and position confirm that especially vertically stored bottles that were not vibrated showed the highest O_2 ratio over the whole experiment (Table 4). The interactions 500 mm/s^2×vertical and 500 mm/s^2×horizontal differ significantly from each other up to day four. Bottles vibrated at 1000 mm/s^2 showed no significant interaction between vibration and bottle position. Therefore, it was concluded that the higher the vibration intensity the smaller the influence of bottle position.

Vertically stored bottles had a significantly higher O_2 ratio between HSO and DO than horizontally stored bottles for the first eight days. Bottles closed with screw cap and 15 mL HS volume showed significantly higher O_2 ratios than bottles sealed with cork closure and 10 mL HS volume. These observations support the assumption that an overpressure, caused by corking processes, promotes the O_2 solution into the wine. Vibration and horizontal bottle position showed a significant influence on O_2 distribution inside a wine bottle. If that is the case for O_2, it is likely that other gases, such as CO_2, behave similar. Furthermore, the distribution of volatile compounds between the HS and the liquid, which is an important factor for the perceived wine aroma, could also be affected. This could be helpful to explain the “bottle shock” or “bottle sickness”. This phenomenon describes the muted aroma perception of wines that have recently been bottled. So far, there is no scientific evidence for the existence or reasonable cause of this condition.

4.5. Conclusion

It was shown that vibration promotes the dissolution of O_2 from the HS of bottle into the wine. As a result, SO_2 consumption in wine might be accelerated due to vibration. In contrast to vertical storage, horizontal bottle position accelerates the consumption of SO_2 suggesting that the larger wine surface facilitates the O_2 uptake from the HS of the bottle into the wine. The effect of vibration is less pronounced in horizontally than in vertically stored bottles. The influence of bottle position is less pronounced with increasing vibration intensity. Both, vibration and bottle position have a major impact on the dissolution of O_2 in wine, but not on the chemical reaction rate of O_2. Bottles sealed with cork closure are significantly higher in the initial O_2 content than bottles sealed with screw cap with the same HS volume. Due to the overpressure by the corking process, the O_2 uptake from HS into wine is faster under the cork closure than under the screw cap. It can be concluded that the O_2 distribution inside a wine bottle is influenced by external factors like vibration, bottle position and bottle closure. Further research is required to investigate the effect of vibration on real wines for several months of bottle storage. Different wines that are more or less avid to oxygen and have different initial O_2 at bottling should be considered in future research as well as closure types with different closure OTRs.

4.6. Tables

Table 1. Regression parameters (regression function, consumption rate k_{SO2} and coefficient of determination) for SO_2 consumption curves shown in Figure 2.

Vibration [mm/s^2]	**Bottle position**	**Regression function**	**k_{SO2} [1/d]**	**R^2**
0	vertical	$y = 43.7 \times e^{-0.1102 \times t}$	11.0×10^{-2}	0.992
	horizontal	$y = 45.6 \times e^{-0.1561 \times t}$	15.6×10^{-2}	0.991
500	vertical	$y = 46.2 \times e^{-0.1255 \times t}$	12.6×10^{-2}	0.997
	horizontal	$y = 47.6 \times e^{-0.1552 \times t}$	15.5×10^{-2}	0.995
1000	vertical	$y = 43.5 \times e^{-0.1636 \times t}$	16.4×10^{-2}	0.986
	horizontal	$y = 43.6 \times e^{-0.1709 \times t}$	17.1×10^{-2}	0.987

Table 2. Influence of headspace volume and closure type on initial headspace oxygen (HSO) content. The probability value is provided in the one-way ANOVA. Mean values are provided with different letters indicating significant differences at $p \leq 0.05$.

	Initial HS oxygen content [mg/L]
HS volume/closure type	$p < 0.0001$
5 mL cork	3.3 c
10 mL cork	6.7 a
10 mL screw cap	4.2 c
15 mL screw cap	5.5 b

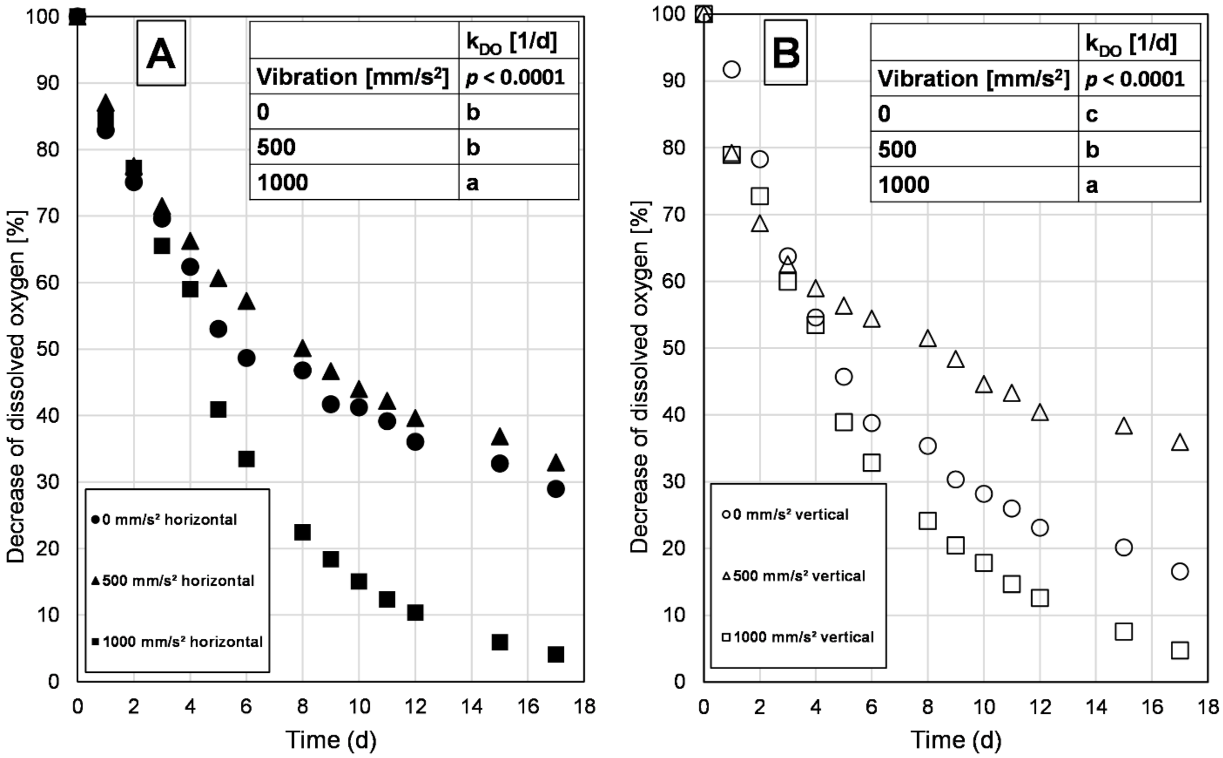
Table 3. Influence of vibration, bottle position, headspace volume and closure type on consumption rate of headspace oxygen k_{HS} Probability values are provided for each factor regarded in the three-way ANOVA. Mean values are provided with different letters indicating significant differences at $p \leq 0.05$.

	k_{HS} [1/d]
Vibration	$p < 0.0001$
0 mm/s^2	16.2×10^{-2} b
500 mm/s^2	12.8×10^{-2} b
1000 mm/s^2	26.1×10^{-2} a
Bottle position	$p = 0.065$
vertical	16.7×10^{-2} a
horizontal	20.0×10^{-2} a
HS volume/closure type	$p = 0.008$
5 mL cork	21.6×10^{-2} a
10 mL cork	21.4×10^{-2} a
10 mL screw cap	16.1×10^{-2} b
15 mL screw cap	14.3×10^{-2} b

Table 4. Influence of vibration and bottle position on changes of oxygen ratio between headspace and dissolved oxygen (n=2 for 1000 and 500 mm/s^2; n=4 for 0 mm/s^2) over 17 days. Probability values are provided for each factor regarded in the three-way ANOVA. Mean values are provided with different letters indicating significant differences at $p \leq 0.05$.

Day	**1**	**2**	**3**	**4**	**5**	**6**	**8**	**9**	**10**	**11**	**12**	**15**	**17**
Vibration	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p = 0.001$	$p = 0.005$	$p = 0.020$	$p = 0.018$	$p = 0.016$	$p = 0.016$
0 mm/s^2	a	a	a	a	a	a	a	a	a	a	a	a	a
500 mm/s^2	b	b	b	b	b	b	b	ab	ab	a	a	a	a
1000 mm/s^2	b	c	c	c	b	b	b	b	b	a	a	a	a
Position	$p = 0.45$	$p = 0.007$	$p = 0.000$	$p = 0.000$	$p = 0.001$	$p = 0.003$	$p = 0.005$	$p = 0.098$	$p = 0.097$	$p = 0.115$	$p = 0.092$	$p = 0.107$	$p = 0.279$
vertical	a	a	a	a	a	a	a	a	a	a	a	a	a
horizontal	a	b	b	b	b	b	b	a	a	a	a	a	a
HS volume/ closure type	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p = 0.000$	$p = 0.008$	$p = 0.007$	$p = 0.017$	$p = 0.011$	$p = 0.015$	$p = 0.008$
5 mL cork	c	c	c	c	c	c	c	b	b	b	b	b	b
10 mL cork	b	b	b	b	b	b	b	ab	ab	ab	ab	ab	ab
10 mL screw cap	a	a	b	b	b	b	ab	a	a	a	a	a	a
15 mL screw cap	a	a	a	a	a	a	a	a	a	a	a	a	a
Vibration× bottle position	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$
0 mm/s^2× vertical	a	a	a	a	a	a	a	a	a	a	a	a	a
0 mm/s^2× horizontal	b	c	c	c	b	b	b	b	b	b	b	b	b
500 mm/s^2× vertical	b	b	b	b	b	b	b	b	b	b	b	b	b
500 mm/s^2× horizontal	c	cd	c	c	b	b	b	b	b	b	b	b	b
1000 mm/s^2× vertical	bc	cd	c	c	b	b	b	b	b	b	b	b	b
1000 mm/s^2× horizontal	c	d	c	c	b	b	b	b	b	b	b	b	b

4.7. Figures



	k_{DO} [1/d]
Vibration [mm/s^2]	$p < 0.0001$
0	b
500	b
1000	a

	k_{DO} [1/d]
Vibration [mm/s^2]	$p < 0.0001$
0	c
500	b
1000	a

Figure 1. Influence of vibrations (n=2 for 1000 and 500 mm/s²; n=4 for 0 mm/s²) on the decrease of dissolved oxygen (DO) (initial oxygen = 100 %) over 17 days in horizontally (A) and vertically (B) stored bottles with 15 mL headspace volume and screw cap. Different letters indicate significant differences for the calculated degradation rates k_{DO} at $p \leq 0.05$.

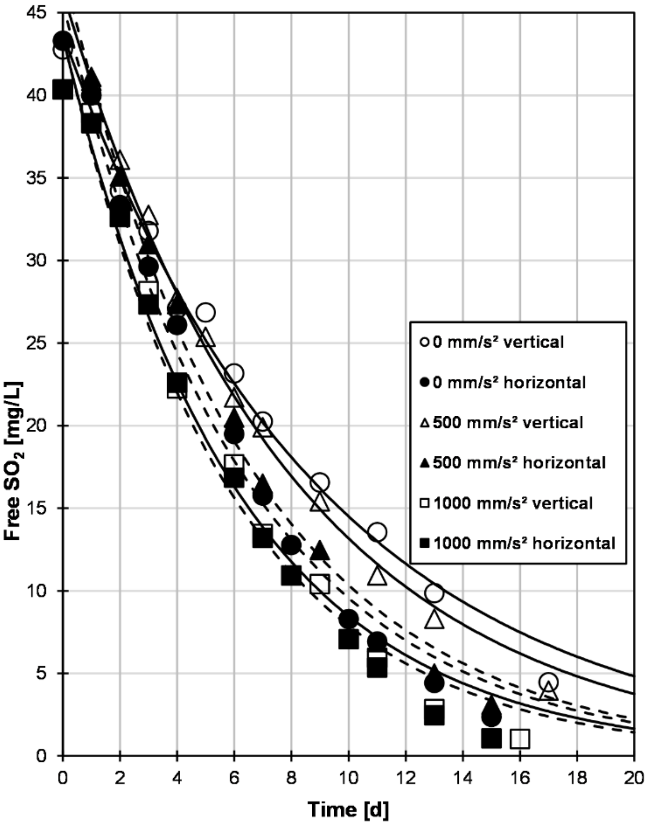


Figure 2. Influence of vibration (n=2 for 1000 and 500 mm/s²; n=4 for 0 mm/s²) and bottle positions (horizontal and vertical) on free SO_2 over 17 days in bottles with 15 mL headspace volume and screw cap. Different letters indicate significant differences for the calculated reaction rates k_{SO2} at $p \leq 0.05$.

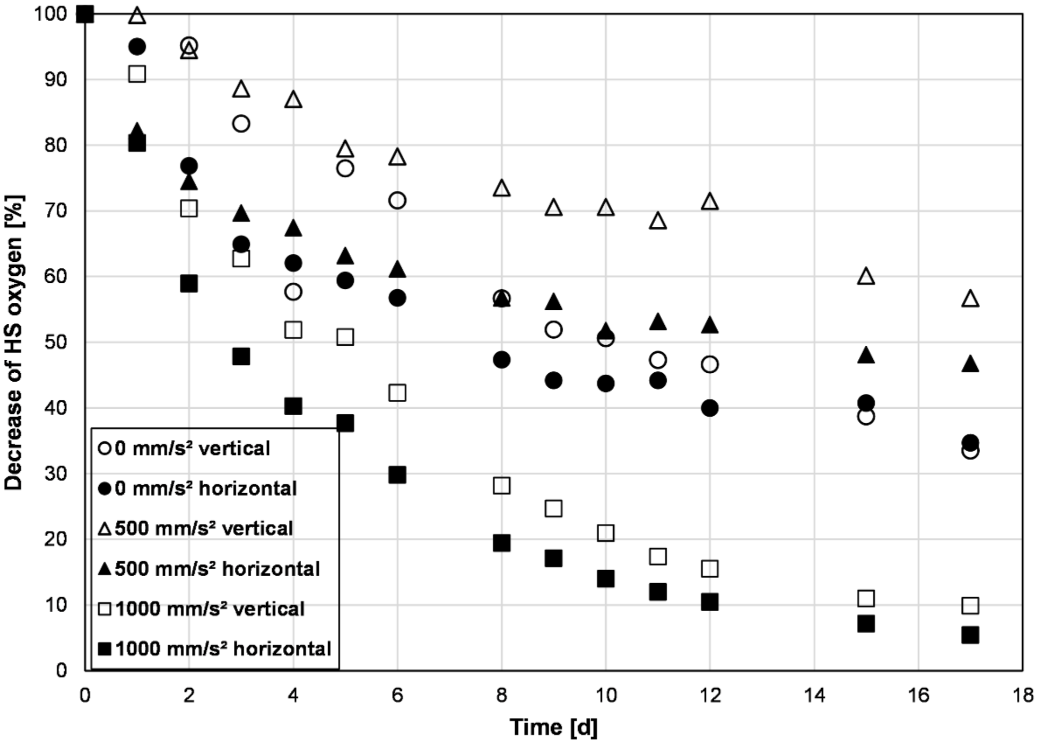


Figure 3. Influence of vibrations (n=2 for 1000 and 500 mm/s²; n=4 for 0 mm/s²) and bottle positions (horizontal and vertical) on the decrease of headspace oxygen (initial oxygen = 100 %) over 17 days in bottles with 15 mL headspace volume and screw cap.

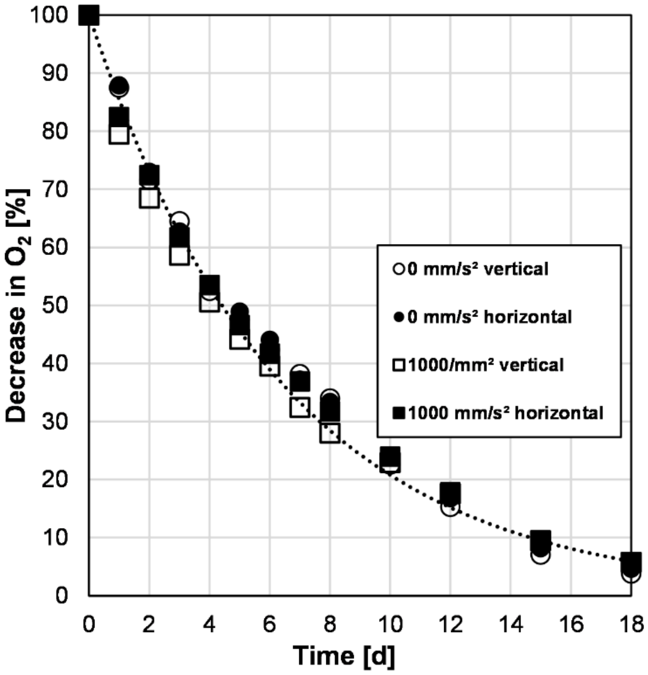


Figure 4. Influence of vibrations on the dissolved oxygen content in horizontally and vertically stored bottles without HS over 18 days sealed with screw cap (n=8). Different letters indicating significant differences for the calculated reaction rates k_{DO} at $p \leq 0.05$.

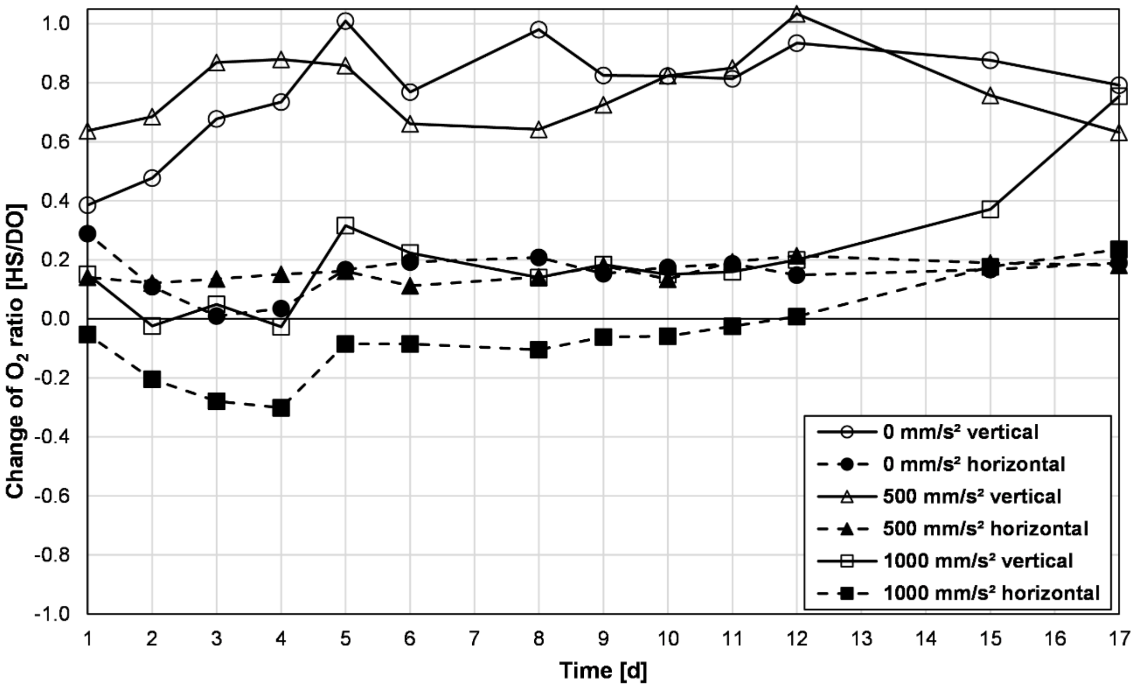


Figure 5. Influence of vibrations on changes in oxygen ratios between headspace and dissolved oxygen (n=2 for 1000 and 500 mm/s²; n=4 for 0 mm/s²) in bottles with 15 mL headspace volume over 17 days sealed with screw cap.

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5. Influence of vibration on volatile compounds, color, SO_2 and CO_2 of Riesling sparkling wine and white wine

The effect of vibration on wine composition is a topic which has been widely neglected. Wine bottles are exposed to vibrations during shipment through engines and road transportation. The objective of this study was to investigate continuous vibration conditions occurring during bottle storage in warehouses and road transportation emitted by cooling units, refrigerators, or motors in a simulation experiment. The aim was to investigate vibration-induced changes of the aroma profile, color, SO_2 and CO_2 of three commercial wines. The sparkling wine was from 2017 vintage and sealed with an agglomerated cork closure. White wines were from 2018 vintage with screw cap closure and from 2017 vintage with a natural cork closure. Wines were stored at different vibration intensities for six months. The results showed that vibration did not affect the barrier properties of the closures. However, vibration could have an impact on total SO_2 and the volatile profile of wine. Young wines, which are still developing, are more likely to be affected by vibration than older wines. Not all aroma compounds were affected equally by vibration. The observed changes could not be proportionally related to the investigated vibration intensities indicating interferences of chemical and physical effects. It was assumed, that vibration shifts the equilibrium of volatiles and gases between the headspace and dissolution in wine. Therefore, especially wines which are bottled with large headspace volumes could be sensitive to vibration-induced changes. It is also assumed that vibration influences formation and/or degradation reactions of volatiles in wine.

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5.1. Abstract

The effect of vibration on wine composition is a topic which has been widely neglected. The motivation of this study was to examine continuous vibration, as emitted by cooling units, refrigerators, or motors during bottle storage in warehouses and road transportation, in a simulation experiment. The objective was to investigate vibration-induced changes of the volatile profile, color, SO_2 and CO_2 of sparkling wine and white wine. A Riesling sparkling wine and two Riesling still wines from different vintages and with different closures were chosen and stored at vibration intensities of 500 mm/s^2 and 1000 mm/s^2 with a constant frequency of 50 Hz for six months and constant temperature. The results showed that vibration did not affect the gas permeability of the closures. However, total SO_2 and the volatile profile of the wines were affected by vibration. Vibration seems to accelerate the formation and/or degradation reactions of some volatiles in wine. At the same time, vibration seems to shift the equilibrium of volatiles inside a wine bottle between the wine and the headspace. Accordingly, wine bottles with a large headspace volume are more sensitive to vibration-induced changes. The magnitude of the observed changes were not proportional to the vibration intensities suggesting an interference of chemical and physical effects.

5.2. Introduction

As a result of growing export markets for wine, there have been numerous studies that investigated wine composition changes during transportation and bottle storage (Du Toit and Piquet 2014, Crandles et al. 2016, Walther et al. 2018). It is well known that elevated temperatures and exposure to light can result in a decrease in wine quality (Ough 1985, Hopfer et al. 2012, Makhotkina et al. 2012, Cejudo-Bastante et al. 2013), though during overseas shipment and road transportation wine bottles are also subjected to vibrations and shock events. Direct economic loss through mechanical damage caused by vibration and shock events is a well-known problem (Geyer et al. 2009, Aba et al. 2012, Tabatabaekoloor et al. 2013). Walkowiak-Tomczak et al. (2021) showed that vibration during the transportation of apples causes changes in the chemical composition of some cultivars and accelerates ripening. Chung et al. (2008) showed that vibration leads to significant changes in the content of higher alcohols and organic acids in red wine during a storage period of 18 months. Jung et al. (2014) simulated the transport of wine during summer and winter conditions over 50 - 69 days. Wines exposed to elevated temperatures in combination with vibration were rated less fresh and less fruity. Crandles et al. (2016) investigated the effects of simulated transportation conditions on Müller-Thurgau and Scheurebe. A sensory panel was able to distinguish between control wines stored for one month at constant 15 °C without movement and wines subjected to fluctuating temperatures with movement using an orbital shaker. However, after 8 months those differences were no longer observed, leading the authors to conclude that young white wine is able to recover from transportation stress. Zhao et al. (2018) investigated the effects of elevated temperatures and movement over a period of 15 days, and concluded that the influence of short-time vibration on volatile substances in wine is negligible compared to the influence of high temperatures during storage.

Janssen et al. (2014) suggest real-time measurements of temperature, humidity, and acceleration (for vibration and shock event monitoring) during the transport of beverages in order to calculate transport-related shelf life models. Recent studies revealed that vibration in combination with elevated temperatures can cause significant chemical changes in beer aroma composition and accelerated turbidity formation (Paternoster et al. 2019, Jaskula-Goiris et al. 2019).

The reviewed studies investigated mostly combined vibration-temperature effects, did often not contain complete specifications of vibration conditions and/or analyzed only few compounds and parameters. The aim of this study was to explore the sole effect of vibration (without temperature influence). The study is based on a simulation experiment with a detailed set of specifications for realistic vibration conditions. An extensive analysis of volatiles by comprehensive two-dimensional gas chromatography (GC×GC) with mass spectrometry (MS) and the analysis of other relevant wine parameters is an important part of this study in order to understand the influence of vibration in still and sparkling wine. The study investigates the influence of continuous vibration at constant temperature on the volatile profile, color, SO_2 and CO_2 of sparkling wine and white wine. The chosen vibration intensities of 500 and 1000 mm/s² and the constant frequency of 50 Hz are comparable to those of previous studies simulating transport conditions of beverages (Paternoster et al. 2018, Jaskula-Goiris et al. 2019, Paternoster et al. 2019).

5.3. Materials and Methods

Wine

Three wines were produced from grapes from *Vitis vinifera* var. Riesling of the same origin. Riesling was chosen due to the well examined changes during wine ageing. The same grape variety and same origin should allow for a comparable volatile profile over all three products. One grape variety but three different wines should allow differential vibration-induced changes. A description of the three wines and packaging specifications are given in Table 1.

Experimental set up

Two vibration intensities of 500 and 1000 mm/s² at a constant frequency of 50 Hz were chosen to simulate uniform vibration conditions of devices such as cooling units in warehouses, compressors in refrigerators and motors. The vibration experiments were conducted on an experimental vibration plate. The vibration plate was built on a linear guide rail, which was connected to a magnetic vibratory motor. The motor initiated an oscillation movement of the plate in one direction. The vibration intensity of the equipment was adjustable by acceleration. The different vibrations intensities were obtained by changing the acceleration amplitude. All bottles were fixed inside a wire mesh container, which was screwed down to the vibration plate. The bottles were stored horizontally under several layers of water-filled bottles to avoid resonance vibration of the bottles. The experiment was conducted at a controlled and constant temperature of 23°C in the dark. The treatments included a control group stored at the same temperature conditions without vibration. The ambient vibration in the room was measured and recorded (< 50 mm/s^2). Monthly sampling was carried out to monitor the changes in wine aroma over time, obtaining time-intensity relationships. Two bottles per wine, per treatment (experimental replicate) and per monthly sampling date were analyzed.

Vibration measurement

A sensor-equipped bottle was used to survey the vibration intensity during the experiment. The sensor was attached with an adhesive glue to a bottle filled with water and connected to a computer. The vibration measurement was carried out with a PCB-356A15 three-axis acceleration sensor (PCB Synotech GmbH, Hückelhoven, Germany). DasyLab (2016) software (National Instruments, Austin, USA) was used for data acquisition. These measurements were carried out to control a uniform distribution and constant conditions of vibration during the experiment.

Standard chemical analysis

Ethanol, residual sugar, titratable total acidity (TA), volatile acidity (VA) and pH were determined by Fourier transform mid-infrared (FTIR) Foss WineScan FT120 Basic (Hillerød, Denmark). Free and total SO_2 were determined with iodometric titration by Ripper method using the Titrator T50 (Mettler Toledo, Gießen, Germany). Measurement of the CO_2 content in wine was performed using the multiple expansion method (CarboQC, Anton Paar GmbH, Graz, Austria). The calibration was provided by Anton Paar.

Color analysis

Prior to analyses, wines were filtered through a 0.45 µm membrane filter (DIA-Nielsen, Düren, Germany). Absorbance spectra were recorded in undiluted samples between 360 and 830 nm with a Cary 100 double-beam spectrophotometer (Varian, Palo Alto, California, USA) using a semi-micro cuvette (pathlength 1.0 cm) (Brand, Wertheim, Germany). A resolution of 1 nm and a slit width of 2.0 nm were applied for all measurements. The b*-value (yellow color; positive values on the blue-yellow axis according to the CIEL*a*b* method) was calculated with the Cary WIN UV Color 2.00 software (Startek, Boronie, Australia) using the CIE method (Commission Internationale de l'Eclairage 2004) with the 10° standard observer and the illuminant D65, according to the OIV recommendations (OIV 1990).

Headspace solid-phase microextraction with two-dimensional gas chromatography-quadrupole mass spectroscopy (HS-SPME-GC×GC-qMS)

The automated headspace-solid phase microextraction (HS-SPME) was performed with a CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) equipped with a single magnet mixer and a fiber conditioning station (Thermo Fisher Scientific, Dreieich, Germany). The GC system consisted of a Trace GC×GC Ultra, equipped with a dual-jet CO_2 modulator coupled to a DSQ quadrupole mass spectrometer (Thermo Fisher Scientific, Dreieich, Germany). The first-dimension (^{1}D) column was a 30 m x 0.25 mm i.d. fused silica column coated with 0.5 µm polyethylene glycol phase (ZB-Wax, Phenomenex, Aschaffenburg, Germany). The second-dimension column (^{2}D) was a 2 m x 0.15 mm i.d. capillary, coated with 0.25 µm of a 5% phenyl containing polydimethylsiloxan phase (BPX-5, SGE, Griesheim, Germany). The columns were connected with a press-fit connector.

Wine samples were prepared in a 20 mL headspace vial with 1 g sodium chloride and 5 mL wine. The sodium chloride was conditioned over night at 260 °C. For quantification, an internal standard (2-heptanol) was added at a concentration of 163 µg/L. Volatile extraction was performed with an 85 µm polyacrylate fiber (CTC Analytics, Zwingen, Germany). Prior to use, the fiber was conditioned according to manufacturer instructions. After the vials were closed with a silicon-coated rubber septum, they were incubated for 2.5 min at 45 °C. At the same temperature, volatiles were extracted for 10 min and subsequently desorbed from the SPME fiber at 270 °C in the vaporizing injector, which was equipped with a dedicated small bore SPME liner (BGB Analytik, Böckten, Switzerland). After 2 min the split valve was opened with the flow rate set to 16 mL/min. Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. After an initial time of 5 min at 50 °C, the oven temperature was raised to 230 °C at 4.5 °C/min. The cryo-modulation with liquid CO_2 (food grade, Tyczka, Lampertheim, Germany) took place at the end of the first column. A modulation period of 6 s was used with a time delay of 5 min. Electron impact (EI) ionization was used with an electron energy of 70 eV, and mass spectra were recorded in positive ion mode. The ion source and transfer line were set to 240 °C. The total ion current (TIC) chromatograms were recorded in two segments. The early-eluting compounds were recorded over 5 – 25 min with the mass range set to m/z 40 – 210 and a scan frequency of 18 Hz. For later-eluting compounds the mass range was m/z 40 – 250 and the scan frequency was 16 Hz. The identification of volatile compounds was achieved by comparing mass spectra against those from the NIST 11 library (National Institute of Standards and Technology, Gaithersburg, Maryland, USA). Linear retention indices (LRIs) were obtained by injecting a homologous series of n-alkanes (C_{10} - C_{25}) and compared with retention indices reported in the literature for 1D-GC.

For system control and data acquisition XCalibur (version 1.4) software was used. The 2D chromatograms were processed following a modified workflow described by Schmarr et al. (2010) using GasPedal software (version 1.0, Decodon, Greifswald, Germany). Signal intensities of all detected volatile compounds were normalized to the internal standard (2-Heptanol). The obtained normalized intensity values were used for further statistical analysis.

Statistical evaluation

Standard deviation was calculated for standard analytical parameters, free SO_2, total SO_2 and CO_2 content as well as the b*-value by using the individual values of experimental replicates. Other statistical analyses were performed using XLSTAT (Version 19.02, Addinsoft, Paris, France). One-way ANOVA was used to reduce the data of HS-SPME-GC×GC-qMS analyses and to evaluate whether the normalized intensities of volatile compounds were significantly different between vibration intensities and storage times. Principle component analysis (PCA), using a Pearson correlation, was applied on the mean of the normalized intensities of volatile compounds which were significantly different ($p \leq 0.05$). Two-way ANOVA and Fisher (LSD) test were used to evaluate color, SO_2 and CO_2 data as well as the relative changes in TDN, linalool and 3-methyl butyl acetate.

5.4. Results

Chemical composition of wine samples after the vibration experiment

Neither vibration nor time had a significant impact on ethanol, titratable acidity (TA), volatile acidity (VA), pH, and reducing sugars (Table 2).

Carbon dioxide

The concentration of CO_2 in wine is known to affect the mouthfeel and other sensory characteristics (Chandrashekar et al. 2009, McMahon et al. 2017). A loss of CO_2 during bottle storage is not desired. CO_2 concentrations before and after the vibration experiment are shown in Table 3. The CO_2 content in wine 1 decreased significantly over time. The vibration×time interaction showed significant differences. The CO_2 concentration in wine 2 and wine 3 was not affected by storage time and vibration.

Sulfur Dioxide

The concentration of SO_2 typically decreases during bottle storage of wine. The rate at which SO_2 decreases in the first few months depends on the initial O_2 content in the bottle (Dimkou et al. 2011). Over a longer period of time, the oxygen transfer rate (OTR) through different closure types during bottle storage affects the rate of SO_2 loss (Skouroumounis et al. 2005). Table 3 shows free and total SO_2 concentrations before and after the vibration experiment in all three wines. Storage time significantly affected the total SO_2 concentration in wine 3 but not in wine 1 and 2. Vibration had no significant impact on free and total SO_2 levels in any of the three wines.

Color

The color of all the wines became browner during the six months of storage as indicated by increasing b*-values (Table 3). However, no significant color changes due to vibration were observed.

Volatile Profile

In order to monitor the changes in the volatile profile of the three wines due to vibration during six months storage, the wines were analyzed by HS-SPME-GC×GC-qMS on monthly basis. The evaluation of two-dimensional chromatograms yielded 138, 120 and 118 volatile compounds for wines 1, 2, and 3, respectively. Statistical data reduction yielded 26 compounds for wine 1, 32 compounds for wine 2, and three compounds for wine 3.

The PCA plots for wine 1 are shown in Figure 1 and the volatile compounds are summarized in Table 4. The volatile compounds and wine samples are projected on PC 1 and PC 2, which explain 43 % and 29 % of the variance of the data, respectively. PC 1 separates the wines based on the applied vibration intensity. The vibration intensity of 500 mm/s^2 shifted the wines positively on PC 1 and the vibration intensity of 1000 mm/s^2 shifted the wines negatively on PC 1. Higher alcohols, such as hexanol and phenyl ethanol, are loaded positively on PC 1, suggesting therefore that a vibration intensity of 500 mm/s^2 increases higher alcohols while a vibration intensity of 1000 mm/s^2 decreases higher alcohols. Storage time shifted the wines negatively on PC 2. Volatile esters, like hexyl acetate and ethyl dodecanoate, are loaded positively on PC 2. Therefore a decrease of these volatile compounds is suggested over time.

The PCA plots for wine 2 are shown in Figure 2. Table 5 summarizes the volatile compounds used for the PCA. The volatile compounds and wine samples are projected on PC 1 and PC 2 which explain 52 % and 20 % of the variance of the data, respectively. Similar to wine 1, PC 1 separated the wines on the basis of vibration and PC 2 on the basis of storage time. The vibration intensity of 500 mm/s^2 shifted the wines positively on PC 1 and the vibration intensity of 1000 mm/s^2 shifted the wines negatively on PC 1. Storage time caused a positive shift on

PC 2, which was more pronounced for the vibration intensity of 1000 mm/s^2 than for the vibration intensity of 500 mm/s^2. Decanoic acid, dodecanol and ethyl butanoate are loaded positively on PC 1, indicating an increase of these compounds with the vibration intensity of 500 mm/s^2 and a decrease with the vibration intensity of 1000 mm/s^2. The volatile components linalool and hexyl acetate, which contribute to a fruity wine aroma, were negatively loaded on PC 2 and indicate therefore a decrease over storage time. Compounds associated with wine aging like TDN, vitispirane and nerole oxide are loaded positively on PC 2, corresponding to an increased storage time of the wine. Overall, a decrease of fruit-associated compounds and an increase of age-associated compounds during the experiment over time was observed.

No PCA was calculated for wine 3 because the ANOVA on GC×GC-MS data of wine 3 yielded only three volatile compounds which showed significant differences: ethyl hexadecanoate, phenethyl acetate and 2-methylbutanol.

Changes in TDN, linalool and 3-methyl butyl acetate.

TDN, linalool and 3-methylbutyl acetate (3MeBeAc), which are characteristic for Riesling (Rapp et al. 1985), were chosen to represent three important classes of volatile compounds: C13-norisoprenoids, monoterpenes, and esters. The initial normalized intensities of TDN, linalool and 3-metylbutyl acetate were all assigned a value of 1, such that subsequent monitoring of these compounds to compare wines and vibration effects gives changes over the duration of the experiment relative to their initial concentration (Figure 3). The results from the two-way ANOVA are displayed in Table 6.

Vibration significantly affected the TDN concentration in the three wines. The TDN content increased up to 7-fold of the initial concentration in wine 2 due to vibration at 1000 mm/s^2. This effect was also visible for wine 3, but less pronounced. The TDN content in wine 1 was least affected by vibration and time. Linalool decreased significantly in wines 1 and 2 over six months, but did not change significantly in wine 3. Vibration had no significant influence on linalool concentration in any of the three wines. 3MeBuAc did not change significantly during the experiment in wines 1 and 3, but did decrease significantly over time in wine 2. Vibration caused a significant decrease in 3MeBuAc in wine 2.

5.5. Discussion

Ethanol, TA, VA, pH, and reducing sugars were not influenced by vibration during the 6-month experiment, suggesting that vibration intensities of 500 and 1000 mm/s^2 do not initiate chemical reactions causing changes to the abovementioned parameters. In contrast, Chung et al. (2008) found effects of vibration on standard chemical parameters in wine, though vibration intensities and experimental duration were different from those used here, making a comparison of findings untenable.

The decrease of CO_2 concentration in sparkling wine (wine 1) over time is a result of pressure equalization and a normal process during bottle storage. The CO_2 losses in sparkling wine through the closure over time observed in our study (Table 3) agree with previous reports (Liger-Belair and Villaume 2011). Vibration as a single factor had no significant influence on the CO_2 concentration in sparkling wine (wine 1), suggesting that the applied vibration intensities did not change the CO_2 transfer through the bottle closure. However, the vibration×time interaction showed significant differences (Table 3), suggesting that vibration intensifies the time effect of CO_2 loss.

No time- and vibration-induced changes in CO_2 concentration were observed in still wine with screw cap (wine 2) and with cork closure (wine 3). Compared to sparkling wine, the concentration of dissolved CO_2 in still wine is low. Consequently, the partial pressure difference between the inside and outside of the bottle is low for still wines. Brazinha et al. (2013) showed that the force that regulates gas transport through cork is the gradient of partial pressure. Therefore, it is not surprising that vibration did not affect the diffusion of CO_2 through the screw cap or the natural cork closure of the still wines (wine 2 and 3) during the 6 months observation period (Table 3).

Several milligram free and total SO2 were lost over the time of the experiment, significant losses were observed in wine 3. However, the results from this study show that vibration had no significant effect on free and total SO_2 in the three wines over six months of storage (Table 3). Among the three closure types investigated, natural cork closures have the highest OTR relative to microagglomerated cork and screw caps (Pons et al. 2021). Since no vibration effect on SO_2 was observed, it is proposed that the O_2 permeability of screw caps, microagglomerated cork, and natural cork were not influenced by vibration.

Other than time, which was a significant browning factor in the experiment, vibration did not accelerate the browning of the wines, again indicating that vibration does not influence O_2 ingress through the three investigated closure types (Table 1). Similar findings were reported by Paternoster et al. (2019), who detected no significant changes in beer color after a vibration experiment.

The volatile profiles of the 2017 sparkling wine (wine 1) and the 2018 still wine (wine 2) were significantly affected by vibration, while the 2017 still wine (wine 3) showed only minor changes. An explanation for this could be the vintage difference between the wines. Wine 3 was from the 2017 vintage and aged one year longer than wine 2, which was produced in 2018. Wines that have already gone through a certain maturation period could be less susceptible to external factors like vibration. This is in agreement with Crandles et al. (2016), who observed that the volatile profile of younger white wines were more sensitive to simulated transportation conditions than the volatile profile of older vintages.

The vibration intensity of 500 mm/s^2 caused an increase of higher alcohols and fatty acids indicating that ester hydrolysis was accelerated due to vibration of sparkling wine (wine 1). The vibration intensity of 1000 mm/s^2 caused an overall decrease of volatile compounds suggesting that a high vibration intensity promotes a loss of volatile compounds. Non-polar volatile compounds like esters are known to interact with CO_2 (Mouret et al. 2014). Since the CO_2 concentration of the sparkling wine was affected during the experiment (Table 3), a higher loss of volatiles along with CO_2 is feasible. However, the comparison of the two intensities suggest that vibration must exceed a certain threshold to shift the equilibrium from dissolved CO_2 towards headspace CO_2 and consequently induce the loss of volatiles.

Similar to the sparkling wine (wine 1), the vibration intensity of 500 mm/s^2 caused an increase of higher alcohols and fatty acids in the still wine with screw cap (wine 2). Again, this suggests an accelerated ester hydrolysis due to vibration. The vibration intensity of 1000 mm/s^2 caused a decrease of some fermentation-associated esters over time, but also caused some age-associated compounds to increase. This observation is in contrast to wine 1. The vibration intensity of 1000 mm/s^2 seems to accelerate the aging process of wine 2 in particular. This could be due to the lower pH of wine 2 than wine 1, which promotes ester hydrolysis and rearrangement reactions of monoterpenes (Rapp and Mandery 1986).

Vibration affected the volatile profile of wine 1 and 2 in different ways. A vibration induced loss of volatiles along with CO_2 was observed in wine 1. This is explained by the high CO_2 content. The vibration induced change of volatiles, as observed in wine 2, may be explained by the low pH value. Other than low pH value and high CO_2 content, a large headspace volume might contribute to a loss of volatile substances. The loss of volatile substances is thought to be due to a shift of volatiles from the wine towards gaseous headspace. Overall, two different vibration induced effects seem to occur at the same time. Chemical effects such as accelerated ester hydrolysis and terpene rearrangement might take place with an equilibrium shift of volatile substances between the wine and the headspace.

TDN is an important aging marker for Riesling wine. The formation and relevance of TDN, which depends on several factors, has been studied extensively (Gerdes et al. 2001, Kwasniewski et al. 2010, Friedel et al. 2016, Ziegler et al. 2020). In the present study, TDN increased significantly in the 2018 still wine (wine 2) (Figure 3). This effect was also visible but less pronounced for the 2017 sparkling wine (wine 1) and the 2017 still wine (wine 3). This supports the theory discussed earlier, that the volatile profile of a younger wine is more prone to changes than of an older wine.

TDN was least affected in sparkling wine with an microagglomerated cork closure (wine 1) (Figure 3). This could be due to an adsorption effect of the bottle closure. Tarasov et al. (2019) showed a high adsorption potential for TDN in agglomerated cork closures. After six months, over 90% of the TDN contained in the sample was adsorbed by the microagglomerated cork stoppers. In contrast, natural one-piece cork closures showed a fast but limited adsorption effect for TDN, removing 40% of the TDN in wine in three months, while screw caps exhibited no significant TDN adsorption.

In both still wines (wine 2 and wine 3), the vibration intensity of 1000 mm/s^2 accelerated the increase of TDN relative to the non-vibrated control (Figure 3). The vibration intensity of 500 mm/s^2 decelerated the increase of TDN relative to the non-vibrated control. It is thought that vibration shifts the equilibrium from dissolved TDN to the gaseous headspace explaining the deceleration observed for 500 mm/s^2. A higher vibration intensity of 1000 mm/s^2 could have promoted TDN formation from precursors due to hydrolysis or rearrangement reactions. This is in agreement with Chung et al. (2008), who showed disproportional responses of volatile substances to vibration treatments at different intensities.

Linalool is one of the most important terpenes in grapes and wine, particularly in Riesling. The linalool content in wine decreases during aging due to acid-catalyzed rearrangement (Rapp and Mandery 1986). The decrease in linalool was not affected by vibration.

3MeBuAc is produced during alcoholic fermentation by yeast and is a key contributor to the young wine character in Riesling wine (Marais et al. 1992, Schwinn et al. 2019). Acetate esters decrease during storage due to hydrolysis until chemical equilibrium is reached (Ramey and Ough 1980, Pérez-Coello et al. 2003). 3MeBuAc was significantly affected by vibration in 2018 still wine (wine 2), though no significant effects on 3MeBuAc were observed in the 2017 sparkling wine (wine 1) and the 2017 still wine (wine 3). Wine 2 is the youngest of the three wines and therefore more prone to changes of the volatile profile due to external factors like vibration. The biggest change in ester concentration of a wine happens in the first year of storage (Pérez-Prieto et al. 2003).

Vibration at 1000 mm/s^2 decelerated the decrease in 3MeBuAc, while vibration at 500 mm/s^2 resulted in an accelerated decrease in 3MeBuAc similar to that observed in the non-vibrated bottles. This is unexpected but similar to the observations made for TDN above and for propanol (Chung et al. 2008). The effect of vibration on wine volatiles is evidently not proportional. Two different effects, physical and chemical, could occur at the same time and thereby interfere with each other. On one hand, vibration may induce the formation or degradation of volatiles, while on the other, vibration may influence partitioning between the liquid and gaseous phases. Results indicate the differential effects of vibration on different volatile substances.

5.6. Conclusion

The results of this study show that vibration, which is emitted by electrical devices, machinery and motors, has the potential to change the composition of wine. Though vibration had no impact on standard analytical parameters of wines, including SO_2 and CO_2 concentrations, and on the oxygen permeability of different bottle closures, the volatile profile of bottled sparkling and still wine was altered. Vibration could accelerate the formation and/or degradation reactions of some volatiles in wine, particularly in young wines which are still developing. In particular, it is assumed that vibration shifts the equilibrium of volatile substances from the wine toward the headspace in a bottle, an effect that is more apparent with larger headspace volumes. As a result, the kinetics of wine ageing reactions might be altered.

The observed changes in the volatile profile are disproportionate to the applied vibration intensities and inconsistent between the wines. Different volatiles are affected differently, suggesting mutual interferences between the chemical and physical effects of vibration. The overall impact of vibration on a wine therefore strongly depends on its composition. Additional research is required to better understand the relationship between vibration intensity and aroma-related chemical changes, with attention to the actual concentration of impact volatile compounds. The influence of wine age, closure type and headspace volume should be regarded in investigations considering vibration. Further studies could investigate vibration-induced changes together with other ageing-related factors such as the impact of temperature. Further research should study the long-term effects of vibration on the volatile profile and the sensory relevance of vibration-induced changes. Additionally, the impact of vibration on the adsorption kinetics of volatile substances on different closure types has yet to be clarified. With regard to storage in cooled warehouses and wine refrigerators, future research should also consider lower vibration intensities. To assess the vibration stress on wine during transportation and during storage in warehouses, acceleration sensors should be used.

5.7. Tables

Table 1: Information about the Riesling wines originating from Neustadt an der Weinstraße (Pfalz, Germany).

	Wine 1	**Wine 2**	**Wine 3**
Wine style	Sparkling	Still	Still
Vintage	2017	2018	2017
Closure type	Microagglomerated cork	Screw cap (Saran Tin)	Natural one-piece cork
Headspace volume	8 mL	10 mL	6 mL

Table 2: Changes in standard analytical parameters during the three vibration experiments over a period of six months. (n=2; Value ± Std Dev).

			Ethanol [g/L]	**Total acidity (TA) [g/L]**	**Volatile acidity (VA) [g/L]**	**pH**	**Reducing sugar [g/L]**
Wine 1	**Before experiment**		105 ± 0	7.9 ± 0.0	0.3 ± 0.0	3.0 ± 0.0	6.9 ± 0.3
	After 6 months	**0 mm/s^2**	105 ± 1	7.9 ± 0.1	0.3 ± 0.1	3.0 ± 0.1	6.5 ± 0.1
		500 mm/s^2	106 ± 1	8.0 ± 0.0	0.3 ± 0.1	3.0 ± 0.0	6.7 ± 0.1
		1000 mm/s^2	105 ± 1	8.0 ± 0.0	0.3 ± 0.0	2.9 ± 0.0	6.9 ± 0.2
	R^2 (model)		0.250	0.733	0.333	0.733	0.733
	***p* (model)**		0.734	0.121	0.615	0.121	0.121
Wine 2	**Before experiment**		101 ± 1	7.9 ± 0.0	0.5 ± 0.0	2.8 ± 0.0	1.7 ± 0.0
	After 6 months	**0 mm/s^2**	100 ± 2	8.0 ± 0.1	0.5 ± 0.0	2.8 ± 0.0	1.9 ± 0.2
		500 mm/s^2	101 ± 0	8.1 ± 0.0	0.5 ± 0.0	2.8 ± 0.0	1.8 ± 0.1
		1000 mm/s^2	100 ± 0	8.0 ± 0.0	0.5 ± 0.0	2.7 ± 0.0	1.9 ± 0.1
	R^2 (model)		0.375	0.667	1.000	1.000	0.380
	***p* (model)**		0.555	0.184	1.000	1.000	0.547
Wine 3	**Before experiment**		102 ± 1	7.3 ± 0.0	0.5 ± 0.0	3.1 ± 0.0	5.7 ± 0.0
	After 6 months	**0 mm/s^2**	102 ± 1	7.3 ± 0.0	0.5 ± 0.0	3.1 ± 0.0	5.6 ± 0.3
		500 mm/s^2	102 ± 0	7.3 ± 0.0	0.5 ± 0.0	3.1 ± 0.0	5.8 ± 0.1
		1000 mm/s^2	101 ± 0	7.3 ± 0.0	0.5 ± 0.0	3.1 ± 0.0	5.8 ± 0.0
	R^2 (model)		0.500	1.000	1.000	1.000	0.496
	***p* (model)**		0.381	1.000	1.000	1.000	0.386

Table 3: Changes in free SO_2, total SO_2 and CO_2 content and the b*-value in CIELab color space during the three vibration experiments over a period of six months. (n=2; Value ± Std Dev).

	Time	Vibration	CO_2 [g/L]	Free SO_2 [mg/L]	Total SO_2 [mg/L]	b*-value
Wine 1	Before experiment	-	**9.21 ± 0.3 a**	26 ± 1.3	115 ± 0.9	**8.4 ± 0.3 b**
	After 6 months	0 mm/s^2	**8.44 ± 0.5 b**	23 ± 2.7	106 ± 5.1	**9.1 ± 0.1 a**
		500 mm/s^2	**8.96 ± 0.0 b**	23 ± 0.7	112 ± 0.5	**8.7 ± 0.1 a**
		1000 mm/s^2	**9.01 ± 0.2 b**	23 ± 1.5	105 ± 3.1	**9.0 ± 0.2 a**
	R^2 (model)		0.676	0.312	0.420	0.795
	p (model)		**0.023**	0.368	0.204	**0.004**
	p (time)		**0.007**	0.322	0.175	**0.001**
	p (vibration)		0.203	0.336	0.229	0.156
	p (time × vibration)		**0.027**	0.596	0.532	0.653
Wine 2	Before experiment	-	2.08 ± 0.0	37 ± 0.7	91 ± 0.7	**5.3 ± 0.5 b**
	After 6 months	0 mm/s^2	2.14 ± 0.1	39 ± 0.3	87 ± 8.7	**7.2 ± 0.8 a**
		500 mm/s^2	2.07 ± 0.0	39 ± 0.1	86 ± 0.1	**7.4 ± 0.1 a**
		1000 mm/s^2	2.04 ± 0.0	36 ± 3.8	83 ± 0.4	**6.7 ± 0.0 a**
	R^2 (model)		0.254	0.108	0.535	0.804
	p (model)		0.478	0.808	0.091	**0.003**
	p (time)		0.681	0.550	0.019	**0.000**
	p (vibration)		0.331	0.755	0.748	0.863
	p (time × vibration)		0.256	0.745	0.877	0.457
Wine 3	Before experiment	-	1.81 ± 0.1	27 ± 0.5	**80 ± 1.4 a**	**6.1 ± 0.3 b**
	After 6 months	0 mm/s^2	1.83 ± 0.0	27 ± 1.8	**78 ± 4.2 b**	**7.0 ± 0.2 a**
		500 mm/s^2	1.91 ± 0.1	24 ± 2.4	**75 ± 2.8 b**	**7.3 ± 0.8 a**
		1000 mm/s^2	1.78 ± 0.0	22 ± 1.3	**72 ± 3.2 b**	**7.2 ± 0.2 a**
	R^2 (model)		0.372	0.581	0.669	0.863
	p (model)		0.269	0.062	**0.005**	**0.001**
	p (time)		0.286	0.038	**0.005**	**0.000**
	p (vibration)		0.240	0.145	0.558	0.685
	p (time × vibration)		0.159	0.051	0.378	0.867

Table 4: Identified volatile compounds in wine 1, which were used for the PCA in Figure 1.

Nr.	Compound	CAS-Nr.	$\mathrm{LRI}_{\mathrm{PEG}}$[1]	Identification[2]	*p*
1	3-Methyl butanol	123-51-3	1216	MS, LRI	0.023
2	Ethyl hexanoate	123-66-0	1233	MS, LRI	0.012
3	Hexyl acetate	142-92-7	1272	MS, LRI, Std	0.000
4	Ethyl lactate	687-47-8	1352	MS, LRI	0.007
5	Hexanol	11-27-3	1358	MS, LRI, Std	0.002
6	2-Nonanone	821-55-6	1390	MS, LRI	0.017
7	Methyl octanoate	111-11-5	1390	MS, LRI	0.003
8	Ethyl octanoate	106-32-1	1434	MS, LRI	0.017
9	Linalyl propionate	144-39-8	1448	MS, LRI	0.030
10	Acetic acid	64-19-7	1478	MS, LRI, Std	0.019
11	Vitispirane	65416-59-3	1535	MS, LRI, Std	0.021
12	Linalool	78-70-6	1549	MS, LRI, Std	0.031
13	Ethyl decanoate	110-38-3	1638	MS, LRI	0.000
14	3-Methylbutyl octanoate	2035-99-6	1656	MS, LRI	0.000
15	Hotrienol	29957-43-5	1615	MS, LRI, Std	0.009
16	4-Butoxybutanol	4161-24-4	1698	MS, LRI	0.008
17	α-Terpineol	98-55-5	1702	MS, LRI, Std	0.001
18	3-Dodecanone	1534-27-6	1750	MS, LRI	0.012
19	TDN	30364-38-6	1758	MS, LRI, Std	0.001
20	Phenethyl acetate	101-97-3	1798	MS, LRI, Std	0.002
21	Ethyl dodecanoate	106-33-2	1840	MS, LRI	0.007
22	Hexanoic acid	142-62-1	1865	MS, LRI	0.020
23	Phenethyl alcohol	60-12-8	1929	MS, LRI	0.005
24	Octanoic acid	124-07-2	2077	MS, LRI	0.022
25	Decanoic acid	334-48-5	2290	MS, LRI	0.000

[1] LRI = Linear retention indices on 1D-column based on n-alkanes (PEG, polyethylene glycol stationary phase)

[2] Identification based on: MS: Comparison of mass spectra with NIST 11; LRI:

Comparison of linear retention indices based on *n*-alkanes with in-house data base or with published data; Std: Measurement of the standard

Table 5: Identified volatile compounds in wine 2, which were used for the PCA in Figure 2.

	Compound	**CAS-Nr.**	**LRI$_{PEG}$**[1]	**Identification**[2]	**p-value**
1	3-Methyl butyl acetate	123-92-2	1120	MS, LRI, Std	0.016
2	Butanol	71-36-3	1153	MS, LRI	0.009
3	3-Methyl butanol	123-51-3	1214	MS, LRI	0.030
4	Hexyl acetate	142-92-7	1272	MS, LRI, Std	0.000
5	Ethyl heptanoate	106-30-9	1335	MS, LRI	0.009
6	Hexanol	11-27-3	1358	MS, LRI	0.024
7	Methyl octanoate	111-11-5	1390	MS, LRI	0.016
8	Ethyl octanoate	106-32-1	1434	MS, LRI	0.039
9	Linalyl propionate	144-39-8	1448	MS, LRI	0.003
10	Isopentyl hexanoate	2198-61-0	1458	MS, LRI	0.002
11	Nerol oxide	1786-08-9	1475	MS, LRI, Std	0.023
12	Acetic acid	64-19-7	1478	MS, LRI	0.008
13	Geranyl ethyl ether	40267-72-9	1509	MS, LRI	0.001
14	Vitispirane	65416-59-3	1535	MS, LRI, Std	0.000
15	Ethyl-2-hydroxy-4-methyl-pentanoate	10348-47-7	1549	MS, LRI	0.016
16	Linalool	78-70-6	1549	MS, LRI, Std	0.000
17	Octanol	111-87-5	1560	MS, LRI	0.017
18	Ethyl decanoate	110-38-3	1638	MS, LRI	0.030
19	Riesling acetale	129601-94-1	1641	MS, LRI	0.013
20	Ethyl-9-decenoate	67233-91-4	1691	MS	0.014
21	α-Terpineol	98-55-5	1702	MS, LRI	0.041
22	3-Tridecanone	1534-27-6	1738	MS, LRI	0.009
23	TDN	30364-38-6	1758	MS, LRI, Std	0.003
24	Phenethyl acetate	101-97-3	1798	MS, LRI, Std	0.000
25	Ethyl dodecanoate	106-33-2	1840	MS, LRI	0.032
26	Phenethyl alcohol	60-12-8	1929	MS, LRI	0.038
27	Dodecanol	112-53-8	1968	MS, LRI	0.000
28	Ethyl tetradecanoate	110-27-0	2045	MS, LRI	0.029
29	Octanoic acid	124-07-2	2077	MS, LRI	0.036
30	Pentadecanol	629-76-5	2275	MS, LRI	0.009
31	Decanoic acid	334-48-5	2290	MS, LRI	0.013

[1] LRI = Linear retention indices on 1D-column based on n-alkanes (PEG, polyethylene glycol stationary phase)

[2] Identification based on: MS: Comparison of mass spectra with NIST 11; LRI:

Comparison of linear retention indices based on *n*-alkanes with in-house data base or with published data; Std: Measurement of the standard

Table 6: ANOVA table for relative change in TDN, linalool and 3-methyl butyl acetate; vibrated at 500 mm/s^2, 1000 mm/s^2 and non-vibrated stored over a period of 6 months (n=2).

		TDN	**Linalool**	**3-Methyl butyl acetate**
Wine 1	R² (model)	0.706	0.679	0.613
	p (model)	**0.029**	**0.049**	0.144
	p (time)	0.647	**0.022**	0.069
	p (vibration)	**0.000**	0.445	0.015
	p (time × vibration)	0.442	0.115	0.847
Wine 2	R² (model)	0.785	0.901	0.732
	p (model)	**0.003**	**0.000**	**0.016**
	p (time)	**0.002**	**0.000**	**0.011**
	p (vibration)	**0.001**	0.767	**0.000**
	p (time × vibration)	0.325	0.952	0.989
Wine 3	R² (model)	0.748	0.488	0.509
	p (model)	**0.010**	0.491	0.422
	p (time)	0.556	0.143	0.135
	p (vibration)	**0.000**	0.157	0.206
	p (time × vibration)	0.148	0.953	0.838

5.8. Figures

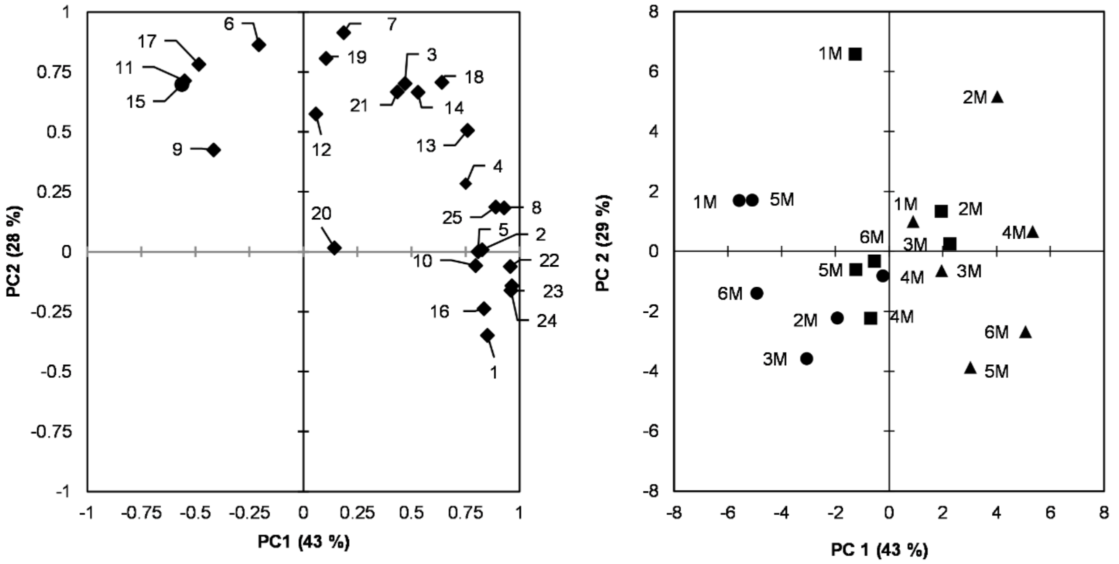

Figure 1. Projection of volatile compounds as loadings (♦) and wine 1 non-vibrated (■), vibrated at 500 mm/s^2 (▲) and vibrated at 1000 mm/s^2 (●) stored over a period of 6 months (labeled as 1M-6M) as scores on the principal component 1 and 2 (n=2).

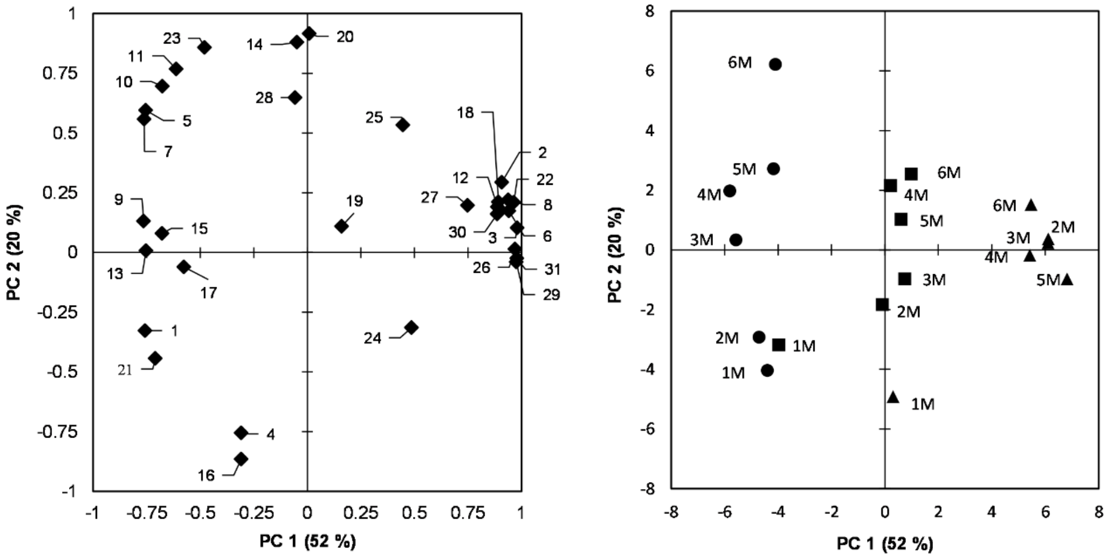

Figure 2. Projection of volatile compounds as loadings (♦) and wine 2 non-vibrated (■), vibrated at 500 mm/s^2 (▲) and vibrated at 1000 mm/s^2 (●) stored over a period of 6 months (labeled as 1M-6M) as scores on the principal component 1 and 2 (n=2).

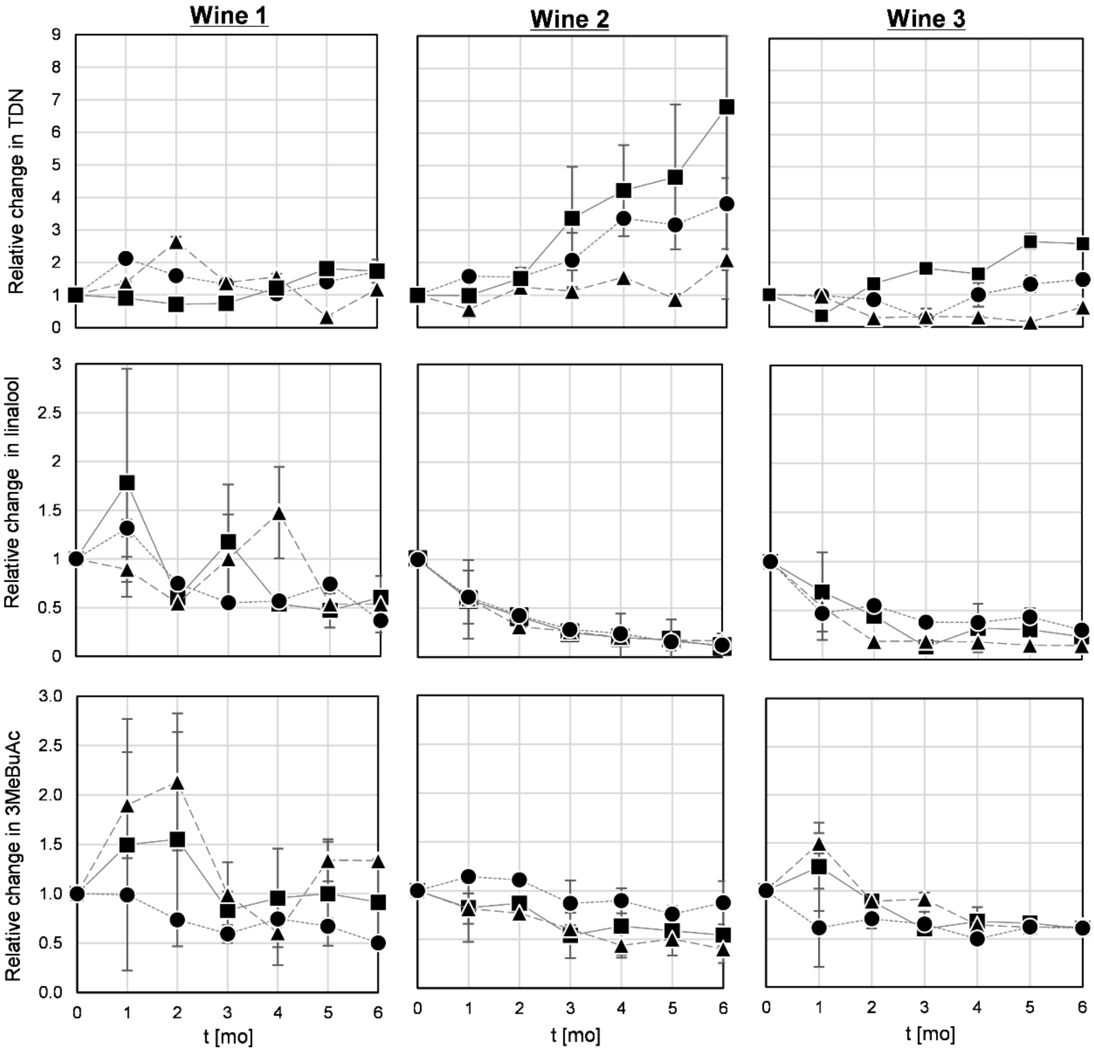

Figure 3. Relative change in TDN, linalool and 3-methyl butyl acetate (±SD) for Wine 1, Wine 2, and Wine 3; non-vibrated (■), vibrated at 500 mm/s^2 (▲) and vibrated at 1000 mm/s^2(●) stored over a period of 6 months (n=2). Initial value was set to 1.

5.9. Literature Cited

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6. The impact of temperature fluctuations on the volatile composition, colour and sensory properties of Riesling wine during two years storage

This study investigated if fluctuating temperatures, as they occur in refrigerated wine cabinets, can accelerate wine ageing reactions. Storage under low-interval temperature fluctuations is compared to the mean storage temperature of these fluctuations. A Riesling wine was stored at constant temperature, two sinusoidal temperature fluctuation with different amplitudes, a non-sinusoidal temperature fluctuation with regularly recurring temperature peaks which increased wine temperature by 1.5°C and an alternating storage temperature treatment changing 6 months intervals. Additionally, a model wine experiment with volatile compounds typical for Riesling was conducted to calculate the degradation rates of individual volatile compounds in relation to the temperature amplitudes. The aim of the study was to examine if the applied temperature fluctuations have an impact on wine aging reactions during bottle storage of wine. Sensory, and chemical analysis revealed that low-interval temperature fluctuations have the potential to accelerate wine aging reactions. This effect was more pronounced for higher temperature amplitudes. However, no pump effect of air through the bottle´s closure was observed due to fluctuating temperature. The model wine experiment proved that the hydrolysis of esters and monoterpene degradation is accelerated by temperature fluctuations. The degradation rate of those compounds increased with rising temperature amplitude. This confirms that the mean storage temperature does not provide sufficient information about whether a wine has been stored appropriately. Concluding that temperature fluctuations should be held as small as possible during bottle storage of wine.

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6.1. Abstract

Background and Aims: This study investigates the influence of low-interval temperature fluctuations caused by compressor cycling in refrigerated wine storage cabinets.

Methods and Results: A Riesling wine was stored for two years under the influence of two sinusoidal temperature fluctuations with amplitudes of ± 0.5°C and ± 1.5°C cycling around 12°C and a non-sinusoidal fluctuation with regularly recurring temperature peaks which increased wine temperature from 12 to 13.5°C. These temperature fluctuations were compared to constant 12°C storage and an alternating storage temperature changing treatment starting from constant 6°C and changing to constant 18°C in six months intervals. Sensory and chemical analysis revealed that temperature fluctuations accelerated ester hydrolysis and monoterpene degradation. This effect became more pronounced for higher temperature amplitudes. A model experiment showed that the hydrolysis of 2,3-methylbutyl acetate was 3.6 times faster when the temperature cycled ± 1.5°C around 12°C for eight months.

Conclusion: The study revealed that wine ageing reactions are not decelerated during the cooling phases in wine storage cabinets in the same manner as they are accelerated during elevated temperature phases when the compressor is turned off. Temperature fluctuations in refrigerated wine storage cabinets should be held as small as possible, especially when a wine is stored for months or even years.

Significance of the study: This study shows that temperature fluctuations in refrigerated wine storage cabinets have to be known and evaluated, since they have the potential to accelerate wine ageing reactions.

Keywords: fluctuating temperature, wine ageing reactions, volatile profile, ester hydrolysis, GC×GC-MS

6.2. Introduction

Elevated temperatures are the main risk during wine transportation and bottle storage. It has been well described in literature that high temperatures can cause unwanted changes in wine composition and sensory characteristics (Dallas and Laureano 1994; Sivertsen et al. 2001; Pérez-Coello et al. 2003; Robinson et al. 2010; Cejudo-Bastante et al. 2013; Hopfer et al. 2013; Scrimgeour et al. 2015; Giuffrida de Esteban et al. 2019). The decrease of fruit-associated volatile compounds (La Presa-Owens and Noble 1997), the increase in oxidized characters (Hopfer et al. 2012), and excessive browning (Hernanz et al. 2009) are the main consequences of the exposure of wine to elevated temperatures.

Some studies have been published investigating changing temperatures to simulate different shipping conditions. During transportation, wine can be exposed to temperature differences up to 20°C, e.g. due to night and day temperature changes (Butzke et al. 2012; Mac Cawley). Robinson et al. (2010) examined the effect of transport conditions on the volatile profile of red and white wine. They stored the wines over a period of 21 days using constant 20°C to simulate room temperature, constant 40°C to simulate a hot environment, and a diurnal temperature cycle (20°C/40°C alternating every 12 hours) to simulate transcontinental shipping conditions. The wines which were stored at constant 40°C showed a decrease of esters and an increase of ageing-associated compounds and were therefore perceived less fruity and more oxidized compared to the wines stored under the cycled treatment and the constant 20°C storage.

Walther et al. (2018) monitored the temperatures during bulk wine shipping from Australia to Germany and investigated the impact on chemical and sensory characteristics of Chardonnay wine. The study revealed temperatures ranging from 10 to 40°C in containers. Wines which were heated up to 25°C during the shipment showed a significant decrease in SO_2, volatile esters and an increase in yellow colour. A trained sensory panel rated those wines less fresh and fruity. Crandles et al. (2016) investigated the impact of fluctuating temperatures on two different white wines. Diurnal fluctuations between 15°C and 40°C every twelve hours for eight days should simulate transhipping at the port. A trained sensory panel was able to distinguish between the simulated transport conditions and the control group stored at 12°C immediately after the experiment. After an additional storage time of eight months, the panellists were no longer able to distinguish between the conditions applied. The authors concluded that the simulated conditions were applied too short to impact the sensory profile of the two white wines long-term. However, the same study showed that the diurnal fluctuating temperatures can affect the pressure inside a wine bottle and therefore could promote an increased oxygen uptake through the closure (Crandles et al. 2016). Hirlam et al. (2019) investigated the influence of diurnal temperature fluctuations on the closure performance of screw saps, agglomerated, synthetic and natural cork closures over a period of three months. They compared wine storage at constant 17°C with cycling the wine temperature two or three times per week between 17 and 28°C. They found that all closures, except for the screw cap, exhibited higher oxygen ingress. The pump effect due to wine volume contraction and expansion causes an air ingress through the bottle closure. This and the effect of diurnal fluctuating temperatures on the pressure inside wine bottles, as described by Crandles et al. (2016), indicate that temperature fluctuations might cause compositional changes in a wine during bottle storage.

The aim of the presented study was to investigate if fluctuating temperatures can accelerate wine ageing reactions. According to the Arrhenius equation, any increase in storage temperature leads to an exponentially acceleration of the wine ageing reactions. In regard to fluctuating temperatures, this means that a temperature excess over mean temperature has a higher impact on the reaction rate than an equal temperature drop below mean temperature. The impact of low-amplitude and low-interval temperature fluctuations around the storage temperature of 12°C was investigated. These fluctuations are regarded to simulate the conditions of storage in refrigerated wine storage cabinets due to compressor cycling. Different temperature fluctuation patterns were applied to clarify whether a pump effect occurs during wine storage in refrigerators and to what extent temperature fluctuation can accelerate wine ageing processes. The presented study regards 12°C as typical for wine storage. Two years of storage time were used in the presented study according to other long-term wine storage studies (Godden et al. 2001; He et al. 2013; Azevedo et al. 2014; Giuffrida de Esteban et al. 2019). To our knowledge, the approach of comparing temperature fluctuations to the mean storage temperature, as calculated from the fluctuation pattern, has not been done before.

6.3. Material and methods

Wine

A Riesling wine from 2017 vintage was provided from a commercial winery (Deidesheim, Rheinland-Pfalz, Germany). It was bottled in 750 mL Alsace-style wine bottles and sealed with natural cork closure. The initial chemical composition of the Riesling was 105.2 g/L Alc., 1.9 g/L residual sugar, 5.9 g/L total acidity, pH 3.1, 13 mg/L free SO_2 and 53 mg/L total SO_2.

Model wine

The model wine was an aqueous solution with 12.0 % vol. ethanol, 1.5 g/L potassium hydrogen tartrate, 1.5 g/l malic acid, 1.7 g/L lactic acid, 6 g/L glycerine, 2.5 g/L glucose, 2.5 g/L fructose, adjusted to pH 3.5 with NaOH. Ethyl butanoate, 2,3-methylbutyl acetate, ethyl hexanoate, hexyl acetate, linalool, 2-phenethyl alcohol, ethyl octanoate, 2-phenethyl acetate, β-damascenone were added in a concentration realistic for wine. Initial concentrations of these substances were 404 µg/L ethyl butanoate, 289 µg/L ethyl hexanoate, 2494 µg/L ethyl octanoate, 1254 µg/L 2,3-methylbutyl acetate, 276 µg/L hexyl acetate, 446 2-phenethyl acetate, 233 µg/L linalool, 48 µg/L β-damascenone and 393 µg/L 2-phenethyl alcohol. The model wine was filled in 750 mL Alsace-style wine bottles and sealed with screw caps equipped with a saran-tin (Vinventions Deutschland GmbH, Fußgönnheim, Germany).

Experimental setup

Riesling was chosen for this study due to its well-studied aroma changes during bottle ageing to describe the impact of temperature fluctuation on the chemical and sensory characteristics of wine. A model wine experiment with volatile compounds typical for Riesling and known for their thermal instability was conducted to calculate the degradation rates of individual volatile compounds as a function of the temperature amplitudes. Riesling wine and model wine bottles were stored horizontally in programmable incubators (IPP PLUS 260, Memmert GmbH, Schwabach, Germany). The treatments included wine stored at constant 12°C (CT_{Iso}), a sinusoidal temperature fluctuation with a low amplitude of ± 0.5°C cycling around 12°C with a period length of 2 h (FT_{SinLA}) and a sinusoidal temperature fluctuation with a high amplitude of ± 1.5°C cycling around 12°C with a period length of 4 h (FT_{SinHA}). The amplitude of the applied temperature fluctuations is defined as the maximum absolute value of the deviation from the mean temperature. The treatments FT_{SinLA} and FT_{SinHA} simulate the reality in wine refrigerators and should provide information on the influence of moderate temperature fluctuations compared to the storage without temperature fluctuation (CT_{Iso}). A non-sinusoidal temperature fluctuation with regularly recurring temperature peaks which increased wine temperature from 12 to 13.5°C every 6 h (FT_{Peak}) was studied. The treatment FT_{Peak} simulates irregular, short-term increases in temperature during storage in a wine refrigerator caused, for example, by door openings or power failures. In addition, an alternating storage temperature changing treatment starting from constant 6°C and changing to constant 18°C (CT_{Alt}) in intervals of six months was conducted. The CT_{Alt} treatment was conducted to investigate whether storage at low temperatures can equalize storage at elevated temperatures. The storage was carried out for all treatments for two years. The model wine experiment was carried out for a reduced time of eight months. For each treatment, two bottles of Riesling wine and three bottles of model wine were sampled for chemical analysis. The sensory analysis of the Riesling wine was based on three replicates. The initial conditions are indicated with IN. Figure 1 shows the temperature curves for treatments FT_{SinLA}, FT_{SinHA} and FT_{Peak} recorded inside and outside wine bottles, accordingly, representing wine temperature and air temperature, respectively.

Sensory analysis

Descriptive analysis (DA) was performed three weeks after the storage experiment. The wines were stored at constant 12°C between the storage experiment and DA. The panel for evaluation consisted of 6 male and 10 female participants, with the age ranging from 24 to 60 years. The panellists were trained in three training sessions before sensory evaluation. Attributes were defined in bench tastings. Panellists agreed on the list of attributes. Recipes for reference standards, as defined in Table 1, were developed by repetitive bench tastings with reference to the experimental wines. This procedure was applied prior to formal evaluation. Wines were served with 30 mL at 12°C in transparent DIN 10960 wine tasting glasses (Schott, Mainz, Germany), covered with plastic lids. Three-digit coded samples were served to panellists in a fully randomized order. The wines were rated monadically using an unstructured line scale with anchor terms “not present” to “very intense”, except for body, where the wines were rated from “thin” to “full”, and except for mouthfeel, where the wines were rated from “smooth” to “harsh”. For panel calibration during evaluation sessions, reference standards for six of the nine attributes were provided to each judge (Table 1). For processing the sensory results, the ratings on the line scales were converted to numbers from 0 to 10 with one digit. Sensory evaluation sessions were administered and evaluated using FIZZ Network software (Version 2.50; Biosystèmes, Couternon, France).

Standard chemical analysis

Ethanol, residual sugar, titratable total acidity (TA), and pH were determined by Fourier transform mid-infrared (FTIR) Foss WineScan FT120 Basic (Hillerød, Denmark). Free and total SO_2 were determined with iodometric titration by Ripper method using the Titrator T50 (Mettler Toledo, Gießen, Germany).

Colour analysis

Prior to analyses, wines were filtered through a 0.45 µm membrane filter (DIA-Nielsen, Düren, Germany). Absorbance spectra were recorded in undiluted samples between 360 and 830 nm with a Cary 100 double-beam spectrophotometer (Varian, Palo Alto, California, USA) using a semi-micro cuvette (pathlength 1.0 cm) (Brand, Wertheim, Germany). A resolution of 1 nm and a slit width of 2.0 nm were applied for all measurements. The L*-, a*- and b*-value (according to the CIEL*a*b* method) were calculated with the Cary WIN UV Colour 2.00 software (Startek, Boronie, Australia) using the CIE method (Commission Internationale de l’Eclairage 2004) with the 10° standard observer and the illuminant D65, according to the OIV recommendations (OIV 2009).

HS-SPME-GC-qMS

The volatile compounds in the model wine solution were analysed by HS-SPME-GC-qMS. Analytical GC and MS was carried out on a Finnigan TRACE DSQ GC-MS (Thermo Fisher Scientific, Waltham, MA, USA) with a CombiPAL autosampler (CTCAnalytics, Zwingen, Switzerland). Wine samples (1 mL) were given into 20 mL glass vials and filled up with 9 mL of saturated sodium chloride solution. The analytical method started with a 10 min pre-incubation phase of the samples at 40°C. After exposing the polydimethylsiloxane (PDMS) fibre FIB-P100/10 (CTC Analytics) to the headspace in the vial, the vial was shaken for 20 min at 40°C to facilitate the maximum absorption of volatiles onto the SPME fibre. Finally, the fibre was desorbed at 240°C in the split/splitless-injector of the GC. The split valve was opened after 2 min and the split flow was set to 15 mL/min. The flow rate of the helium carrier gas was constant at 1.0 mL/min. The volatile compounds were separated on a 30 m × 0.25 mm fused silica column with a film thickness of 0.5 µm (Rxi-5Sil MS, Restek, Bad Homburg, Germany). After an initial period of 2 min at 40°C, the oven temperature was increased to 200°C with a rate of 3.5°C/min, followed by a further increase to 300°C with a rate of 25°C/min. The MS was operated with an electron energy of 70 eV and an ion source temperature of 240°C. Data was acquired in full-scan, positive ion mode (m/z 29–300). Identification and quantification were executed by stable isotope dilution analysis (SIDA), by adding a known amount of the stable isotopes, d5-ethyl hexanoate, d3-hexyl acetate, d5-linalool, d5-2-phenethyl alcohol, and d4-β-damascenone to samples before analysis. Ethyl butanoate and ethyl octanoate were quantified as ethyl hexanoate equivalents, while 3-methylbutyl acetate was quantified as hexyl acetate equivalents and 2-phenethyl acetate was quantified as 2-phenethyl alcohol equivalents. The software Xcalibur 2.2 (Thermo Fisher Scientific) was used for operating the HS-SPME-GC/MS and subsequently for processing data.

HS-SPME-GC×GC-qMS

The automated headspace-solid phase microextraction (HS-SPME) was performed with a CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) equipped with a single magnet mixer and a fibre conditioning station (Thermo Fisher Scientific, Dreieich, Germany). The GC system consisted of a Trace GC×GC Ultra, equipped with a dual-jet CO_2 modulator coupled to a DSQ quadrupole mass spectrometer (Thermo Fisher Scientific, Dreieich, Germany). The first dimension (^{1}D) column was a 30 m x 0.25 mm i.d. fused silica column coated with 0.5 µm polyethylene glycol phase (ZB-Wax, Phenomenex, Aschaffenburg, Germany). The second-dimension column (^{2}D) was a 2 m x 0.15 mm i.d. capillary, coated with 0.25 µm of a 5% phenyl containing polydimethylsiloxan phase (BPX-5, SGE, Griesheim, Germany). The columns were connected by a press-fit connector.

Wine samples were prepared in a 20 mL headspace vial with 1 g sodium chloride and 5 mL wine. The sodium chloride was conditioned over night at 260°C. For quantification, an internal standard (2-heptanol) was added at a concentration of 163 µg/L. Volatile extraction was performed with an 85 µm polyacrylate fibre (CTC Analytics, Zwingen, Germany). Prior to use, the fibre was conditioned according to manufacturer instructions. After the vials were closed with a silicon-coated rubber septum, they were incubated for 2.5 min at 45°C. At the same temperature, volatiles were extracted for 10 min and subsequently desorbed from the SPME fibre at 270°C in the vaporizing injector, which was equipped with a dedicated small bore SPME liner (BGB Analytik, Böckten, Switzerland). After 2 min the split valve was opened with the flow rate set to 16 mL/min. Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. After an initial time of 5 min at 50°C, the oven temperature was raised to 230°C at 4.5 °C/min. The cryo-modulation with liquid CO_2 (food grade, Tyczka, Lampertheim, Germany) took place at the end of the first column. A modulation period of 6 s was used with a time delay of 5 min. Electron impact (EI) ionization was used with an electron energy of 70 eV, and mass spectra were recorded in positive ion mode. The ion source and transfer line were set to 240°C. The total ion current (TIC) chromatograms were recorded in two segments. The early-eluting compounds were recorded over 5 – 25 min with the mass range set to m/z 40 – 210 and a scan frequency of 18 Hz. For later-eluting compounds the mass range was m/z 40 – 250 and the scan frequency was 16 Hz. The identification of volatile compounds was achieved by comparing mass spectra against those from the NIST 11 library (National Institute of Standards and Technology, Gaithersburg, Maryland, USA). Linear retention indices (LRIs) were obtained by injecting a homologous series of n-alkanes (C_{10} - C_{25}) and compared with retention indices reported in the literature for 1D-GC.

For system control and data acquisition XCalibur (version 1.4) software was used. The 2D chromatograms were processed following a modified workflow described by Schmarr et al. (2010) using GasPedal software (version 1.0, Decodon, Greifswald, Germany).

Statistical evaluation

All statistical analyses were performed using XLSTAT (Version 19.02, Addinsoft, Paris, France). Sensory data was analysed using a three-way mixed model ANOVA, treating the judges as a random factor and wines, sensory repetitions, and wines as fixed factors. One-way ANOVA was used to reduce the data of HS-SPME-GC×GC-qMS analyses and to evaluate whether volatile compounds were significantly different between the temperature treatments. Data from HS-SPME-GC-qMS, colour, SO_2 and standard chemical parameters were tested for normal distribution by a Shapiro–Wilk test, followed by ANOVA and least significant difference (LSD) post hoc test at a significance level of 5%. Principal component analysis (PCA) was performed on sensory data and on HS-SPME-GC×GC-qMS data using the Pearson correlation. The degradation rate was calculated from HS-SPME-GC-qMS data of the model wine experiment. The acceleration factor represents a relative degradation rate and was calculated in relation to the CT_{Iso} treatment.

6.4. Results and Discussion

After two years of storage, the Riesling wine was evaluated by means of DA to investigate the influence of temperature fluctuations on the sensory profile. Figure 2 shows the PCA of the sensory data. PC1 and PC2 explain 82.2 % of the total variance. The wine stored at constant temperature (CT_{Iso}) is loaded negatively on PC1, whereas high-amplitude temperature fluctuation (FT_{SinHA}) is shifted positively on PC1. This shift is explained by the significantly higher colour intensity and petrol character of the FT_{SinHA} treatment compared to the CT_{Iso} treatment. A similar observation was made for the alternating temperature storage (CT_{Alt}) which is also shifted positively on PC1. The CT_{Alt} treatment was rated significantly higher in colour intensity and petrol. On the contrary, the CT_{Iso} wine was perceived more sour and sweeter than FT_{SinHA} and CT_{Alt} wines. This shows that wine stored at constant temperature was perceived fresher and younger. Vice versa, temperature fluctuations and alternating temperature storage developed a more aged character. The low-amplitude temperature fluctuation (FT_{SinLA}) is located in between FT_{SinHA} and CT_{Iso} wines. This shows that low-amplitude temperature fluctuations also caused changes in aroma perception but to a lesser extent than high-amplitude temperature fluctuations (FT_{SinHA}). Irregular temperature fluctuations (FT_{Peak}) show a similar shift on PC1 like FT_{SinLA} towards aged attributes. This observation indicates that even small deviations from the average storage temperature have an impact on the aroma evolution of wine during storage.

It was shown by many publications that storage at elevated temperatures leads to higher colour intensity and a pronounced petrol character in Riesling (Simpson 1978; Marais et al. 1992; Blake et al. 2009; Tarasov et al. 2021). Literature also reports pigment enhancement in white wine at higher temperature (La Presa-Owens and Noble 1997; Hernanz et al. 2009; Dias et al. 2012; Hopfer et al. 2012; Mafata et al. 2019). Robinson et al. (2010) showed that diurnal temperatures fluctuations between 20 and 40°C have a similar but less pronounced effect on the Riesling aroma than constant storage at 40°C. Compared to wine stored at 20°C, the storage under fluctuating temperatures caused more pronounced aged characters. While the study compares the effects of temperature fluctuations with highest and lowest value of the fluctuations, no comparison to the mean of the temperature fluctuations was made.

Table 2 shows the results of standard chemical parameters, free and total SO_2, and colour parameters in the Riesling wine before and after two years of storage at different temperature treatments. The ANOVA revealed no significant impact of the temperature treatments on standard chemical parameters. Free SO_2 was significantly decreased over the two years of storage time but not influenced by fluctuating temperatures. Also, the b*-value significantly increased over time but was not affected by the different temperature treatments. However, the L*-value significantly decreased with an increasing temperature fluctuation indicating that the wine darkens. Also, the CT_{Alt} and FT_{Peak} treatments were significantly darker than the CT_{Iso}

wine. This is in good accordance with the sensory data shown earlier (Figure 2) revealing a higher colour intensity due to temperature fluctuations.

Crandles et al. (2016) observed that SO_2 and O_2 decreased significantly faster in wines that were stored under fluctuating temperatures. However, they concluded that this was due to high temperatures up to 40°C and not because of a pump effect through the closure. In contrast, Hirlam et al. (2019), who measured the oxygen transmission through different closure types, suggested a pump effect of air through natural cork closures as a result of temperature fluctuations.

In the present study, SO_2 did not decrease significantly due to fluctuating temperatures. Therefore, a pump effect caused by low-interval temperature fluctuations through the natural cork closure is unlikely. The observed intensification in colour by higher temperature fluctuation indicates that the mean temperature does not provide sufficient information about ageing reactions in wine. It is not possible to compensate a higher reaction rate at elevated temperatures by means of cooler temperatures. The Arrhenius equation describes that the rate of a chemical reaction rises exponentially with the temperature. Accordingly, the investigated temperature fluctuations result in a higher rate of ageing reactions as compared to constant 12°C.

Figure 3 shows the PCA biplot of volatile compounds obtained by HS-SPME-GC×GC-MS. The first two PCs of the PCA explain 87.2 % of the total variance. The initial wine (IN) is loaded positively on PC1, characterized by linalool and ethyl esters which is typical for a young Riesling wine. The storage period of two years caused a negative shift on PC1 for all temperature fluctuation treatments indicating a decrease in linalool and ethyl esters. Storage at constant 12°C (CT_{Iso}) caused the least negative shift on PC1 showing that the volatile profile of the Riesling wine changed least over the period of two years under storage at constant 12°C. In contrast, storage at alternating temperatures (CT_{Alt}) caused the most negative shift on PC1 indicating that CT_{Alt} was high in TDN and low in linalool and ethyl esters which is typical for aged Riesling wines. These results show that the storage at 6°C could not equalize the storage at 18°C. Storage at fluctuating temperatures also shifted the wine negatively on PC1, although the three treatments $FT_{SinLA,}$ FT_{SinHA} and FT_{Peak} were similar in their volatile profile and not able to distinguish by means of GC×GC analysis. All wines showed less linalool and ethyl esters compared to the CT_{Iso} treatment indicating that ageing reactions were accelerated by temperature fluctuations. These results underline the observation earlier that temperature fluctuations around a constant temperature result in increased degradation rates of volatile compounds as it is explained by an exponential temperature influence according to Arrhenius. Accordingly, it is not possible that storage at elevated temperatures to be equalized by storage at cooler temperatures.

Figure 4 shows the results from HS-SPME-GC-MS analysis of a model wine containing nine volatile compounds. All nine volatile compounds, except 2-phenethyl alcohol, showed a tendency to decrease over the storage period of eight months. These decreases were not significant for the storage at constant 12°C (CT_{Iso}), except for 2-phenethyl acetate, which decreased significantly over the storage period of eight months. Compared to CT_{Iso}, the high-amplitude temperature fluctuation (FT_{SinHA}) caused a significant decrease in the concentration of ethyl and acetate esters, except for 2-phenethyl acetate. The low-amplitude temperature fluctuation (FT_{SinLA}) had no significant impact on ethyl and acetate esters. Also, the irregular temperature fluctuations (FT_{Peak}) had no significant impact on ester concentrations. However, there is a clear trend for the decrease in esters with an increasing temperature amplitude. The observation that 2-phenethyl acetate decreased significantly over time but not due to temperature fluctuation indicates that the time and temperature influence on ester stability is different for the investigated wine esters. In this study, 2-phenethyl acetate was found to be more resistant to temperature fluctuations than the other esters. This is in contrast to the results of other studies that showed that 2-phenethyl acetate hydrolyses faster than other acetate esters (Ramey and Ough 1980; Makhotkina and Kilmartin 2012).

This study showed for the first time, that not only constantly high temperatures, but also fluctuating temperatures have the potential to accelerate ester hydrolysis. Other than esters, linalool and β-damascenone concentrations did not change significantly during the experiment. However, there is a tendency for those compounds to decrease with an increasing temperature amplitude. Regardless of the volatile compound investigated, recurring temperature peaks every six hours (FT_{Peak}) had no significant effect on linalool and β-damascenone concentrations.

Table 3 shows the degradation rates for CT_{Iso}, FT_{SinLA} and FT_{SinHA} and acceleration factors for 0.5 and 1.5°C temperature amplitudes of the nine volatile substances of the model wine. The acceleration factor refers to the degradation rate of the 0°C temperature amplitude (CT_{Iso}) set to 1.0.

The hydrolysis of ethyl esters was accelerated more than 1.5-fold when stored at fluctuating temperatures with 0.5°C amplitude (FT_{SinLA}). The temperature amplitude of 1.5°C (FT_{SinHA}) accelerated the hydrolysis of ethyl esters more than 3-fold. The hydrolysis of acetate esters was also accelerated at fluctuating temperatures with 0.5°C amplitude (FT_{SinLA}), except for 2-phenethyl acetate. Both 2,3-methylbutyl acetate and hexyl acetate hydrolysed 1.7 and 1.2 times faster under FT_{SinLA} treatment. The temperature amplitude of FT_{SinHA} treatment accelerated the hydrolysis of 2,3-methylbutyl acetate 3.6-fold. Hexyl acetate hydrolysed 2.2 times faster under FT_{SinHA} treatment compared to CT_{Iso} treatment. The hydrolysis of 2-phenethyl acetate was accelerated 1.3-fold through FT_{SinHA} treatment. Overall, wine storage under fluctuating temperatures accelerated the hydrolysis of ethyl and acetate esters in the model wine system. The hydrolysis was accelerated with increasing temperature amplitudes.

Linalool concentration decreased 1.7 times faster under storage at fluctuating temperature with 0.5°C amplitude (FT_{SinLA}) and 2.5 times faster under storage at fluctuating temperature with 1.5°C amplitude (FT_{SinHA}) compared to constant temperature storage (CT_{Iso}). β-Damascenone concentration did not decrease faster under storage at fluctuating temperature with 0.5°C amplitude (FT_{SinLA}) compared to constant temperature storage (CT_{Iso}). However, the degradation of β-damascenone was accelerated 1.9-fold under storage at fluctuating temperature with 1.5°C amplitude (FT_{SinHA}). The 2-phenethyl alcohol content did not decrease during the experiment. Due to hydrolysis of 2-phenethyl acetate, 2-phenethyl alcohol was formed in the model wine. The formation of 2-phenethyl alcohol was 1.4 times faster at fluctuating temperature with 0.5 and 1.5°C amplitude (Table 3).

The calculated degradation rates shown in Table 3 provide a good comparison of different volatile compounds to assess the influence of the temperature amplitude on their degradation. The ester 2,3-methylbutyl acetate is described a one of the most important volatile esters in wine (Plata et al. 2003). A significant decrease of this ester during wine storage correlates with the loss of fruity character (Rapp and Mandery 1986). After eight months, 27% of 2,3-methylbutyl acetate were hydrolysed at constant 12°C storage temperature. At a fluctuating temperature with 0.5°C amplitude (FT_{SinLA}), the concentration of 2,3-methylbutyl acetate was reduced by almost 50%. The 1.5°C temperature amplitude (FT_{SinHA}) even reduced the concentration by 96%. These results show that temperature fluctuations have the potential to accelerate wine ageing and should not be underestimated.

6.5. Conclusion

Low-interval temperature fluctuations due to compressor cycling accelerate wine ageing reactions. Recurring cooling phases, as those caused by refrigerator compressors or chillers in warehouses, do not decelerate ageing reactions in the same manner as analogously elevated temperature phases accelerate them. Even very small amplitudes, such as ±0.5°C, promoted wine ageing reactions such as ester hydrolysis and monoterpene degradation. Therefore, temperature fluctuations, caused by compressors and cooling devices, should be minimized, especially when a wine is stored for several months or even years. An allowance or a critical value for a maximum temperature amplitude cannot be specified, since even small temperature amplitudes accelerate wine ageing reactions.

By all means, the mean storage temperature is not sufficient to estimate whether a wine has been appropriately stored in long-term settings. Besides the mean storage temperature, also the temperature amplitude and the period lengths should be considered, respectively.

A pump effect of ambient air through the closure was not observed in this study. It is thought that the investigated temperature fluctuations were too small and/or horizontal bottle position prevented a pump effect of ambient air through the closure. Also recurring temperature peaks that appeared every six hours had minor impact on wine ageing reactions. This suggests that small deviations in wine temperature, such as those caused by refrigerator door openings, do not affect wine ageing reactions.

Future research in the field of temperature fluctuations should consider bottle shapes and weights with different thermal conductivity. Especially thicker glass bottles could shield the wine from temperature fluctuations of the ambient air. Vertical and horizontal bottle positions in combination with different closure types should be considered to investigate if air is pumped through the closure in vertically stored bottles. Also experiments with red wine and sparkling wine should be carried out in the future to examine if polyphenol changes and CO_2 losses occur due to temperature fluctuation.

6.6. Tables

Table 1: Aroma standards for the descriptive analysis of Riesling wine stored under different temperature treatments. All standards were prepared in Riesling base wine and replenished to 100 ml.

Descriptor	Composition
Aroma	
Honey	1 g of honey
Peach/Apricot	5 mL apple juice + 5 mL peach juice + 2 chopped dried apricots
Petrol	10 µg/L TDN
Taste	
Sweet	6 g/l fructose
Sour	2 g/l tartaric acid
Bitter	1 g/l caffeine

Table 2: Results from the analysis of colour and standard chemical parameters in Riesling wine after two years of storage under different temperature treatments (n = 2). Different letters indicate significant differences for $p \leq 0.05$.

	Alcohol [g/L]	**Residual Sugar [g/L]**	**Total acidity [g/L]**	**pH**	**Free SO_2 [mg/L]**	**Total SO_2 [mg/L]**	**L***	**a***	**b***
IN	105.2 a	1.9 a	5.9 a	3.1 a	13 a	53 a	97.9 a	- 1.2 a	7.7 a
$\mathrm{CT_{ISO}}$	105.2 a	1.9 a	5.9 a	3.1 a	11 b	60 a	97.9 a	- 1.3 a	9.5 b
$\mathrm{FT_{SinLA}}$	105.1 a	1.9 a	5.9 a	3.1 a	11 b	55 a	97.6 ab	- 1.3 a	9.8 b
$\mathrm{FT_{SinHA}}$	105.6 a	1.6 a	6.0 a	3.1 a	11 b	58 a	97.5 b	- 1.3 a	9.8 b
$\mathrm{FT_{Peak}}$	105.6 a	1.7 a	6.0 a	3.1 a	12 ab	57 a	97.0 c	- 1.3 a	9.8 b
$\mathrm{CT_{Alt}}$	105.5 a	1.8 a	6.0 a	3.1 a	12 ab	51 a	97.3 bc	- 1.3 a	9.9 b
p-value	*1.000*	*0.653*	*0.999*	*1.000*	*0.003*	*0.964*	*0.000*	*0.449*	*0.000*

Table 3: Effect of the amplitude of temperature fluctuations on the degradation rate (mean value ± SD) of several volatile compounds in a model wine (n=2). Acceleration factor for 0°C temperature amplitude (CT_{Iso}) was set to 1. Acceleration factors for the temperature amplitudes 0.5°C (FT_{SinLA}) and 1.5°C (FT_{SinHA}) were calculated in relation to the 0°C temperature amplitude.

Substance	**Temperature amplitude [°C]**	**Degradation rate [µg/d*L]**	**Acceleration factor**
Ethyl butanoate	0	0.6 ± 0.7	
	0.5	1.0 ± 0.5	1.7
	1.5	1.7 ± 0.2	2.9
Ethyl hexanoate	0	0.4 ± 0.4	
	0.5	0.6 ± 0.5	1.6
	1.5	1.2 ± 0.1	3.2
Ethyl octanoate	0	2.9 ± 1.9	
	0.5	5.6 ± 5.3	1.9
	1.5	9.8 ± 0.0	3.3
2,3-Methylbutyl acetate	0	1.4 ± 0.6	
	0.5	2.4 ± 2.7	1.7
	1.5	5.0 ± 0.1	3.6
Hexyl acetate	0	0.5 ± 0.3	
	0.5	0.6 ± 0.4	1.2
	1.5	1.1 ± 0.1	2.2
2-Phenethyl acetate	0	0.3 ± 0.2	
	0.5	0.3 ± 0.1	1.0
	1.5	0.4 ± 0.1	1.3
Linalool	0	0.1 ± 0.0	
	0.5	0.2 ± 0.1	1.7
	1.5	0.3 ± 0.3	2.5
ß-Damascenone	0	0.0 ± 0.0	
	0.5	0.0 ± 0.0	1.0
	1.5	0.1 ± 0.1	1.9
2-Phenethyl alcohol	0	-0.3 ± 0.1	
	0.5	-0.4 ± 0.2	1.4 (increase)
	1.5	-0.4 ± 0.1	1.4 (increase)

6.7. Figures

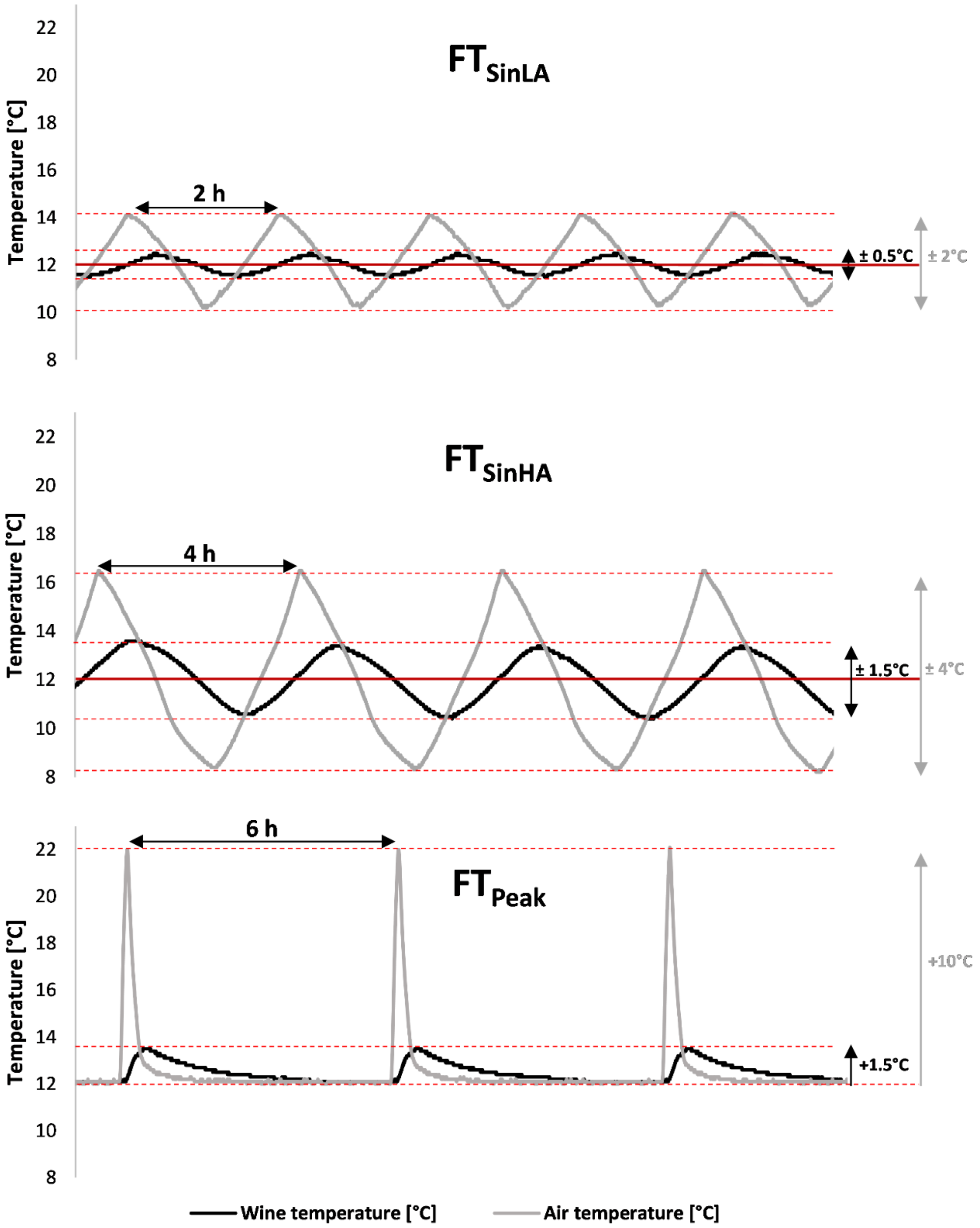

Figure 1. Recorded temperature during the treatments with fluctuating temperature FT$_{SinLA}$, FT$_{SinHA}$ and FT$_{Peak}$. Temperature was measured in (wine temperature) and outside (air temperature) the bottle. The solid red lines indicate the mean storage temperature; the dashed red lines indicate the temperature amplitudes of wine temperature and air temperature.

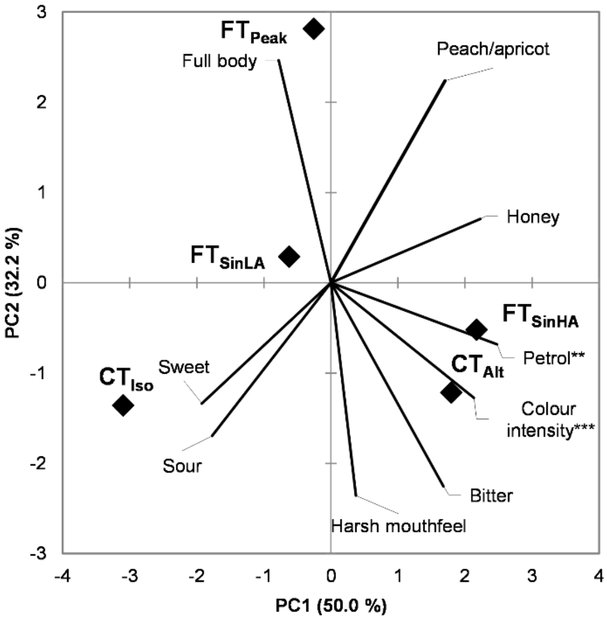

Figure 2. Principal component analysis (PCA) biplot of sensory attributes obtained by descriptive analysis (n = 16 × 3 judges) performed on Riesling wine which was stored for two years at constant 12°C (CT_{Iso}), uniform temperature fluctuation of 0.5°C around 12°C (FT_{SinLA}), uniform temperature fluctuation of 1.5°C around 12°C (FT_{SinHA}), alternating temperature which changed in six months intervals from constant 6°C to 18°C (CT_{Alt}) and irregular temperature fluctuation which increased the wine temperature every six hours from 12 to 14°C (FT_{Peak}). **= significant at $p \leq 0.01$; ***= significant at $p \leq 0.001$

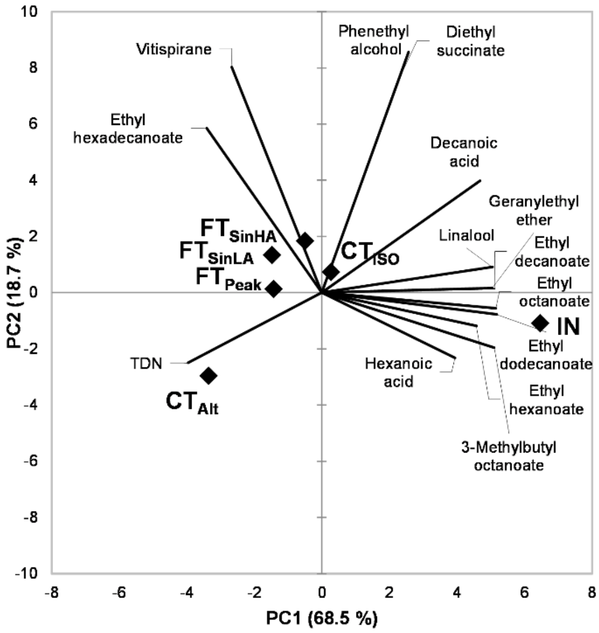

Figure 3. Principal component analysis (PCA) biplot of volatile compounds obtained by HS-SPME-GC×GC-MS performed on Riesling wine before the storage experiment (IN) and on Riesling wine which was stored for two years at constant 12°C (CT$_{\text{Iso}}$), uniform temperature fluctuation of 0.5°C around 12°C (FT$_{\text{SinLA}}$), uniform temperature fluctuation of 1.5°C around 12°C (FT$_{\text{SinHA}}$), alternating temperature which changed in six months intervals from constant 6°C to 18°C (CT$_{\text{Alt}}$) and irregular temperature fluctuation which increased the wine temperature every six hours to 14°C (FT$_{\text{Peak}}$).

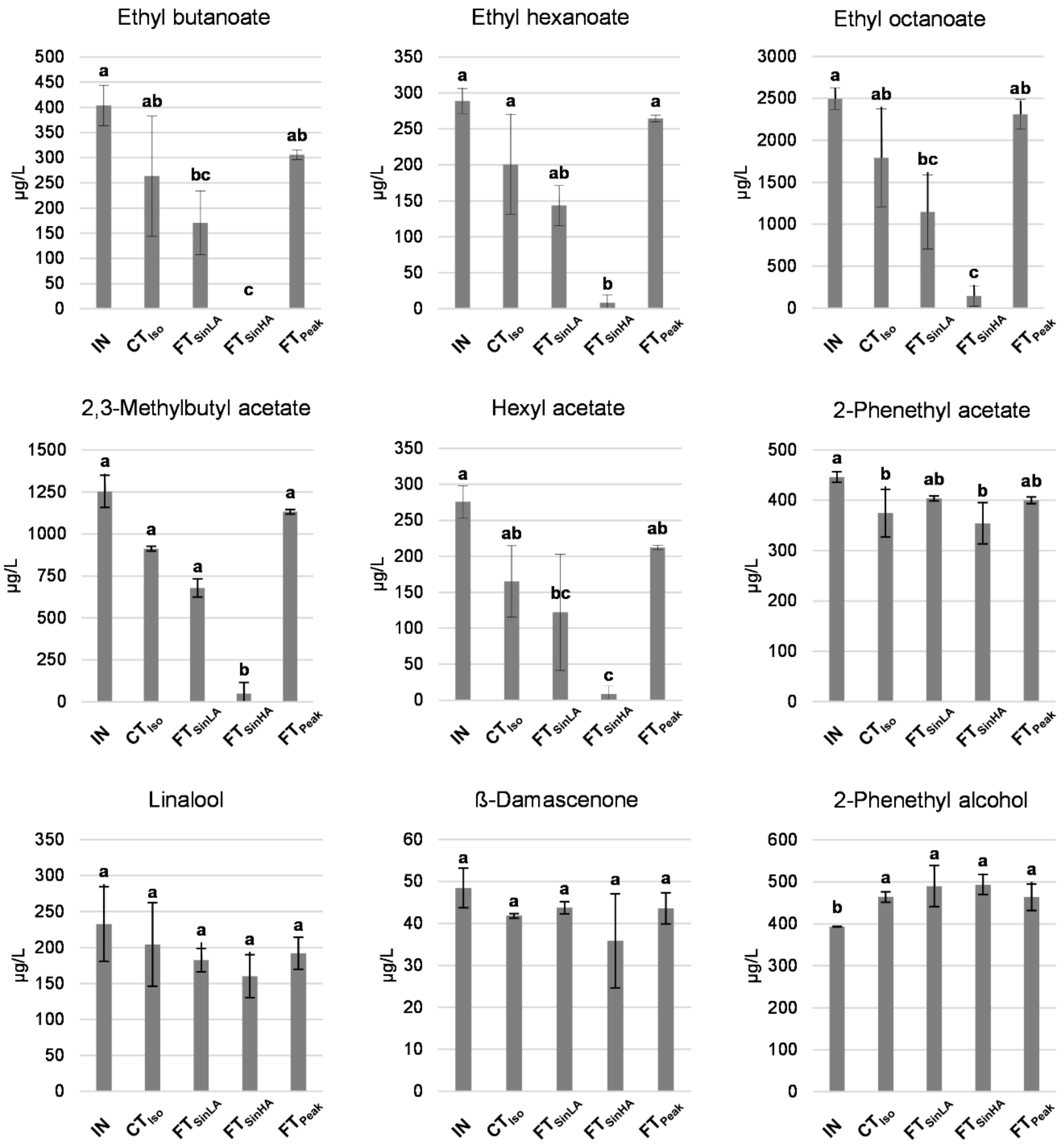

Figure 4. Mean values of volatile compounds analyzed by HS-SPME-GC-MS in model wine (n = 3) before the experiment (IN) and after eight months of storage at constant 12°C (CT_{Iso}), uniform temperature fluctuation of 0.5°C around 12°C (FT_{SinLA}), uniform temperature fluctuation of 1.5°C around 12°C (FT_{SinHA}) and irregular temperature fluctuation (FT_{Peak}) which increased the wine temperature every six hours from 12 to 14°C. The error bars show ±1SD. Different letters indicate significant differences for $p \leq 0.05$.

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7. Concluding remarks

This thesis investigated for the first time the influence of vibration on wine, using a detailed description of the vibration experiment. The constant frequency of 50 Hz and the vibration intensities of 500 and 1000 mm/s^2 were chosen to simulate uniform vibration conditions in a standardized and reproducible experiment. Those conditions are in accordance with previous studies focused on beer transport simulations (Paternoster et al. 2018, Jaskula-Goiris et al. 2019, Paternoster et al. 2019). The measured vibration intensities in a refrigerator by Schmoranzer et al. (2019) range from 10 to 250 mm/s^2 and are therefore lower than the investigated vibration intensities in this study. However, the long-term effects of vibration occurring in a refrigerator should not be underestimated. The results of this study showed that vibration accelerates O_2 uptake from the HS of a wine bottle into the wine. The same phenomenon has already been observed in beer (Paternoster et al. 2019). It is likely that vibrations caused by a compressor in a refrigerator accelerate also the O_2 uptake from the HS into the wine.

It was shown that vibration and horizontal bottle position accelerated only the dissolution of O_2 from the HS of the bottle into wine but not the chemical reaction of O_2 with other wine constituents. It was concluded that vibration has an influence on the equilibrium between the O_2 in the HS of the bottle and the O_2 in the wine. Therefore, it is assumed that the equilibrium of other gases like CO_2, which do not react with wine constituents, could also be affected by vibration. This is especially relevant for sparkling wines, which are bottled with a CO_2 overpressure. However, the vibration intensities in this study did not cause CO_2 losses through the closure in sparkling wine bottles. Furthermore, vibration also showed no influence on SO_2 and color in all wines indicating vibration has no impact on the O_2 permeability of the used closures. Furthermore, it was shown in this study that the bottle position has an impact on O_2 uptake from the HS into the wine and the O_2 distribution inside a wine bottle. The larger surface between liquid and HS promotes the O_2 uptake into the wine. The published studies so far focused on the OTR of the closure in horizontally and vertically stored bottles (Mas et al. 2002, Skouroumounis et al. 2005a, Lopes et al. 2006, Hernanz et al. 2009, Venturi et al. 2017). The fact that the surface area between HS and wine has an influence on the equilibrium in wine has not been described in literature before.

The phenolic composition of every wine is different, the sensitivity to O_2 is highly variable. Therefore, the O_2 uptake in real wines with different phenolic composition should be regarded. Danilewicz (2007) already showed that the reaction rate of O_2 with phenolic substances is influenced by their composition and initial concentrations. Moreover, the impact of vibration on the closure´s OTR has to be evaluated. For this purpose, a long-term study considering the bottle position and different closure types should be conducted. The increased O_2 solubility inside a wine bottle due to vibration could help to explain the “bottle shock” phenomenon. The so-called “bottle shock” describes a temporary condition of a wine, which occurs usually after filling or transportation of a wine. The equilibrium between HS and wine of volatile compounds could be temporary shifted toward solution by movement and vibration. This could cause the sensory description of those wines as “muted” and “flat”.

The fact that a horizontal bottle position influenced the equilibrium between HS O_2 and dissolved O_2 indicates that the equilibrium of volatile compounds could also be affected. Chung et al. (2008) showed that vibration leads to significant changes in the content of higher alcohols. Therefore, the influence of vibration on the volatile profile of real wine was investigated. The results revealed that vibration has an influence on the equilibrium of volatile substances between the HS of the bottle and the wine. Though the partitioning coefficient of volatile compounds in wine is mainly influenced by the wine’s composition (Robinson et al. 2009, Villamor et al. 2013), agitation and stirring have also been shown to promote the transfer of volatile compounds from the wine to the HS (Kataoka et al. 2000). It was concluded that vibration may influence partitioning between the liquid and gaseous phase. This possibly induces chemical changes in the volatile profile. The equilibrium of esters is shifted more towards solution, and they are more likely to be hydrolyzed. In contrast, the equilibrium of other less polar volatile compounds is shifted towards the headspace, hence being subjected to interaction with the closure material.

The influence of vibration on the partitioning coefficient of certain volatile compounds has to be investigated. Different HS volumes and the bottle position should be considered. The relevance of HS volume and the bottle position for the dissolution of O_2 and vibration influence has already been shown in this study. Furthermore, the impact of vibration on the adsorption kinetics of volatile substances on different closure types should be studied.

The earlier described results indicate that wine should be protected from extensive vibrations. Acceleration sensors should be used to assess the vibration stress in different storage locations and during shipment of wine. The advancement of technology which reduces vibration transmission on wine bottles in refrigerated wine storage cabinets and chilled warehouses could be helpful to protect wine from vibration induced changes. Moreover, the vibration profile in wine storage cabinets has to be analyzed. Further studies should also include detailed information about the vibration experiments, including not only the vibration amplitude but also the frequency. Long-term storage experiments with real wine and realistic vibration patterns could provide information about the sensory relevance of vibration induced changes in wine composition. Besides analysis of vibrations, all possible sources off vibration stress on wine must be revealed and reduction strategies have to be considered. In the case of wine storage cabinets wood shelves are already used due to their vibration absorbing abilities. However, the use of wood shelves also increases the risk of a TCA contamination.

The influence of low-interval temperature fluctuations on wine was investigated using a commercial Riesling wine and a model wine. The low-interval temperature fluctuations simulated realistic conditions of cooling devices such as compressors in refrigerators. Storage at low-interval temperature fluctuations was compared to storage at the mean storage temperature. It was shown that these fluctuations have a significant impact on the wine temperature inside the wine bottle. As a consequence, wine aging reactions were accelerated. The results of this study revealed that the degradation rate of several volatile compounds increased significantly due to fluctuating temperature. A temperature amplitude of 1.5°C increased the degradation rate of 2,3-methyl butyl acetate up to 3.6 times. Temperature fluctuations during bottle storage and transport should be logged for amplitude and frequency. Every increase in temperature will accelerate the aging reactions of the stored wine. However, a decrease in wine temperature will not decelerate wine aging reactions in the same manner. This is due to the exponential relationship between reaction rate and temperature as given in the Arrhenius equation. The van't Hoff rule says that the rate of chemical reactions is doubled for each 10°C rise in temperature. However, this is only a rule of thumb and should be used with caution. As shown in this study, even temperature amplitudes of 1.5°C accelerated ester hydrolysis by a factor of 3.6. The detailed kinetics of the formation and degradation of volatile wine compounds under fluctuating temperature have to be determined. Furthermore, not only a comparison of the temperature fluctuations with the mean storage temperature is required, but also with higher storage temperatures. This could provide a more detailed insight into how temperature fluctuations affect the reaction rates of different aging processes in wine. Although no pump effect of air through the closure was observed due to the applied temperature fluctuations, the possibility of such an effect should not be ruled out completely. Vertical and horizontal bottle position in combination with different closure types should be considered, regarding the influence of temperature fluctuations on the closure´s OTR. Hirlam et al. (2019) already showed that a vertical storage position promotes oxygen ingress due to temperature fluctuations during bottle storage. Furthermore, experiments in real wine storage cabinets have to be conducted, considering the temperature set point, temperature zones, the total loading of the cabinet and the ambient temperature inside the room. Different wines should be examined, since it has been shown that the influence of temperature on chemical changes in wine is highly independent on the wine´s composition (Skouroumounis et al. 2005b, Hernanz et al. 2009, Robinson et al. 2010, Mafata et al. 2019). In the case of sparkling wine CO_2 losses due to temperature fluctuation could be relevant. Benucci (2020) showed that storage at elevated temperature leads to a significant decrease of CO_2 during bottle storage. Moreover, the influence of temperature fluctuations on the wine temperature inside bottles with different shapes and weights should be investigated. In this study only one bottle type was used. Due to the increasing importance of sustainability in wine production, more and more wines are filled in thin-walled glass bottles. However, thin glass could be more prone to temperature fluctuations.

The air temperature inside a refrigerator fluctuates constantly due to the compressor cycling. This may cause temperature differences up to 6°C in a standard domestic refrigerator (Jofré et al. 2019). Future research should investigate technologies to minimize compressor induced temperature fluctuations in refrigerators. Afonso and Matos (2006) already showed that temperature fluctuation inside a domestic refrigerator can be reduced by insulation of the compressor.

Another so far completely neglected parameter during bottle storage of wine is the relative humidity. It is common sense in the wine industry to believe that humidity levels below 50% will cause natural cork closures to dry out and increase their oxygen permeability (Barker 2004, Karbowiak et al. 2009, Faria et al. 2011). Humidity levels of 70 % and higher are considered to avoid wine losses through evaporation (Negré et al. 1965). Closure types like screw caps and synthetic cork are considered insensitive to low humidity levels closures due to their hydrophobic material (Silva et al. 2011). However, there are no studies so far that examined the influence of storage under different humidity condition on material properties of wine closures and the development of wine during bottle storage. Furthermore, current literature does not report optimal values for air velocities in storage facilities or wine storage cabinets. Ocón et al. (2014) already observed that natural ventilation is an effective way to reduce mold formation in wine cellars. The evaluation of different air velocities could be also relevant for wine storage cabinets to maintain a uniform relative humidity. Future research should investigate the influence of relative humidity on different closure materials and resulting the consequences for the wine composition. This could help to provide well-founded storage recommendations for all closure types.

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8. Appendix

8.1. Supporting information on: Influence of Vibration on the Consumption of Oxygen and Sulphur Dioxide in Wine Bottles considering Bottle Position, and Headspace Volume:

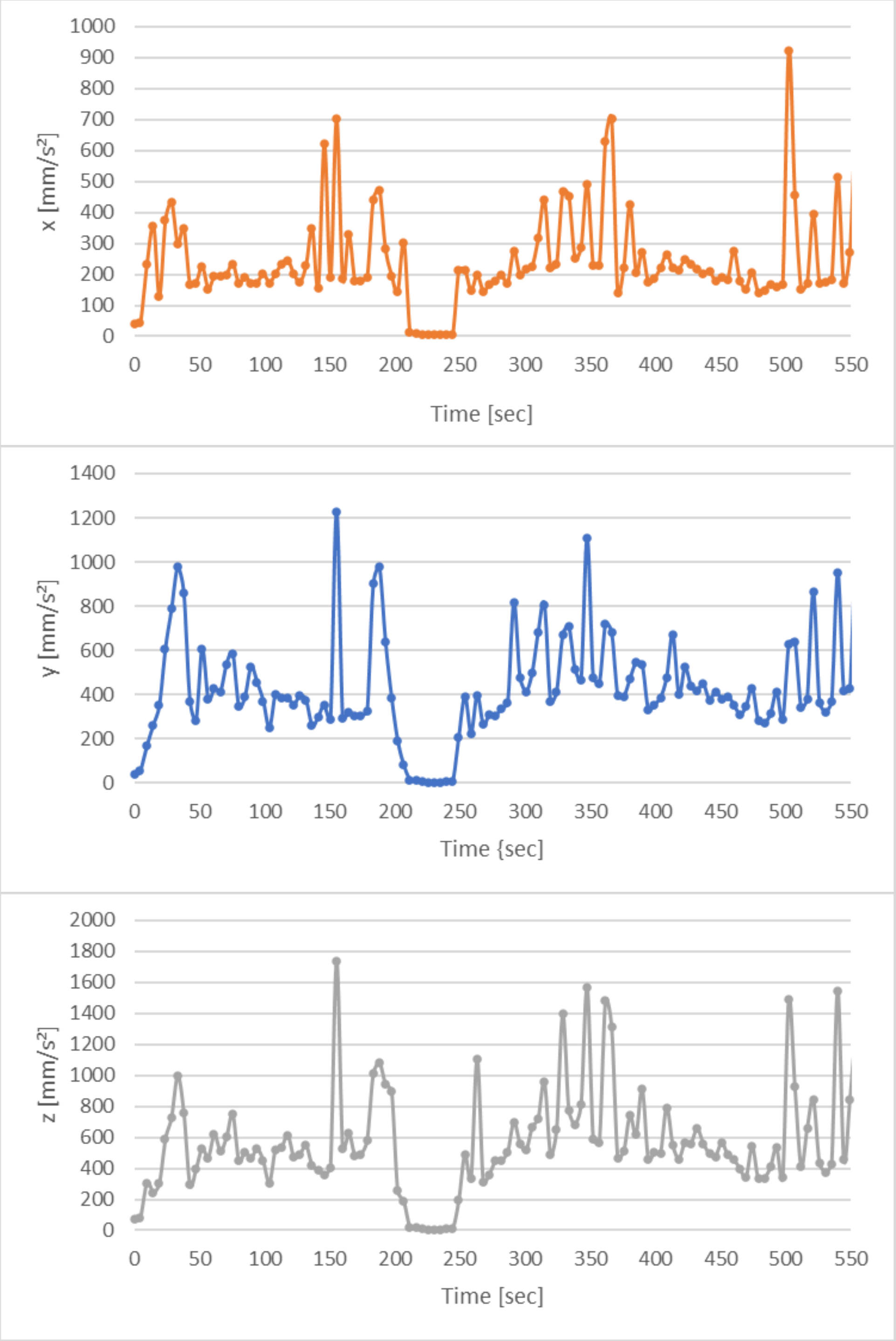

Figure 13: Three-dimensional (x, y, z) acceleration measurement during a car ride on a German "Landstraße".

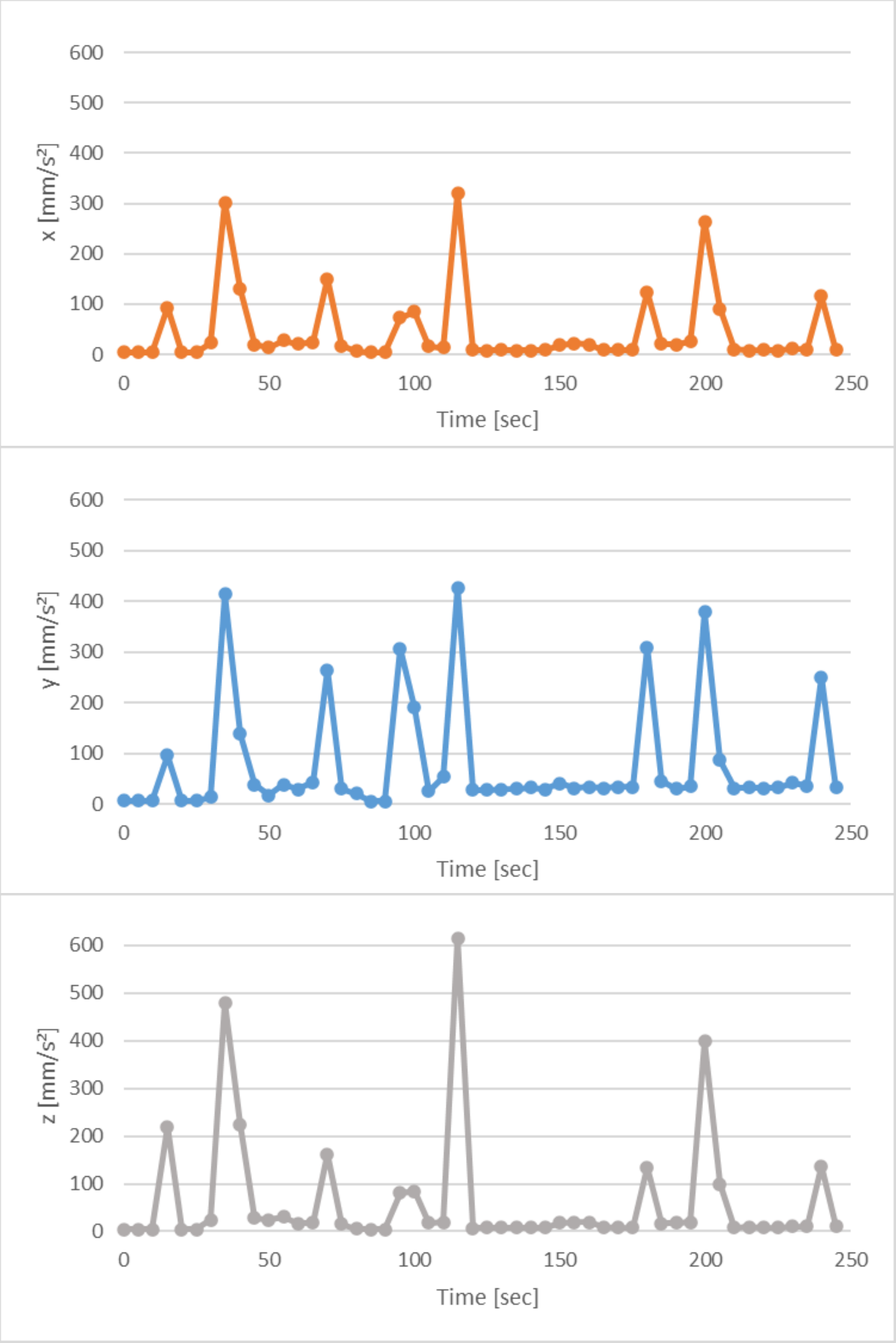

Figure 14: Three-dimensional acceleration measurement in a commercial wine refrigerator.

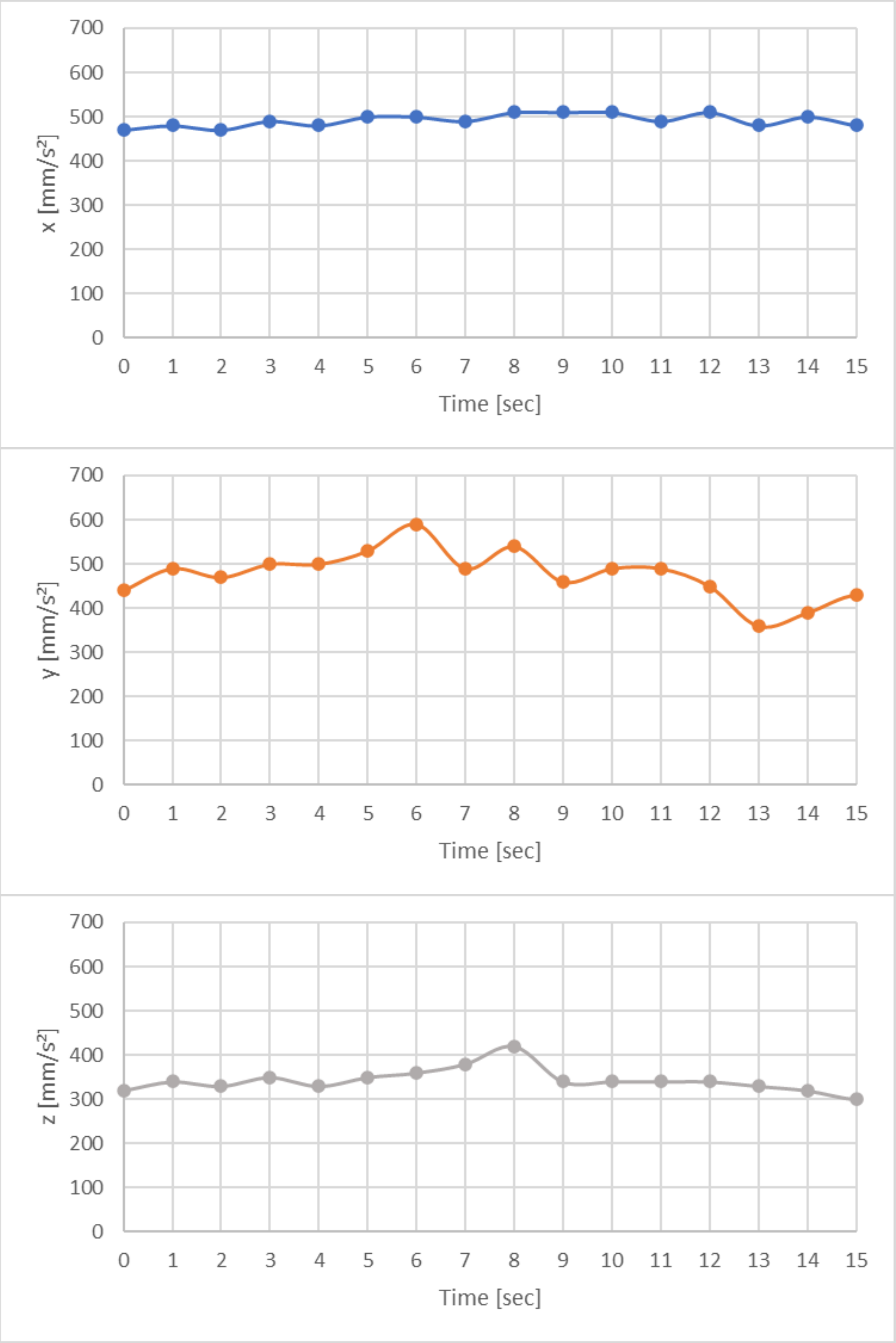

Figure 15: Three-dimensional (x, y, z) acceleration measurement on a bottle stored in the wire mesh container on the vibration plate.

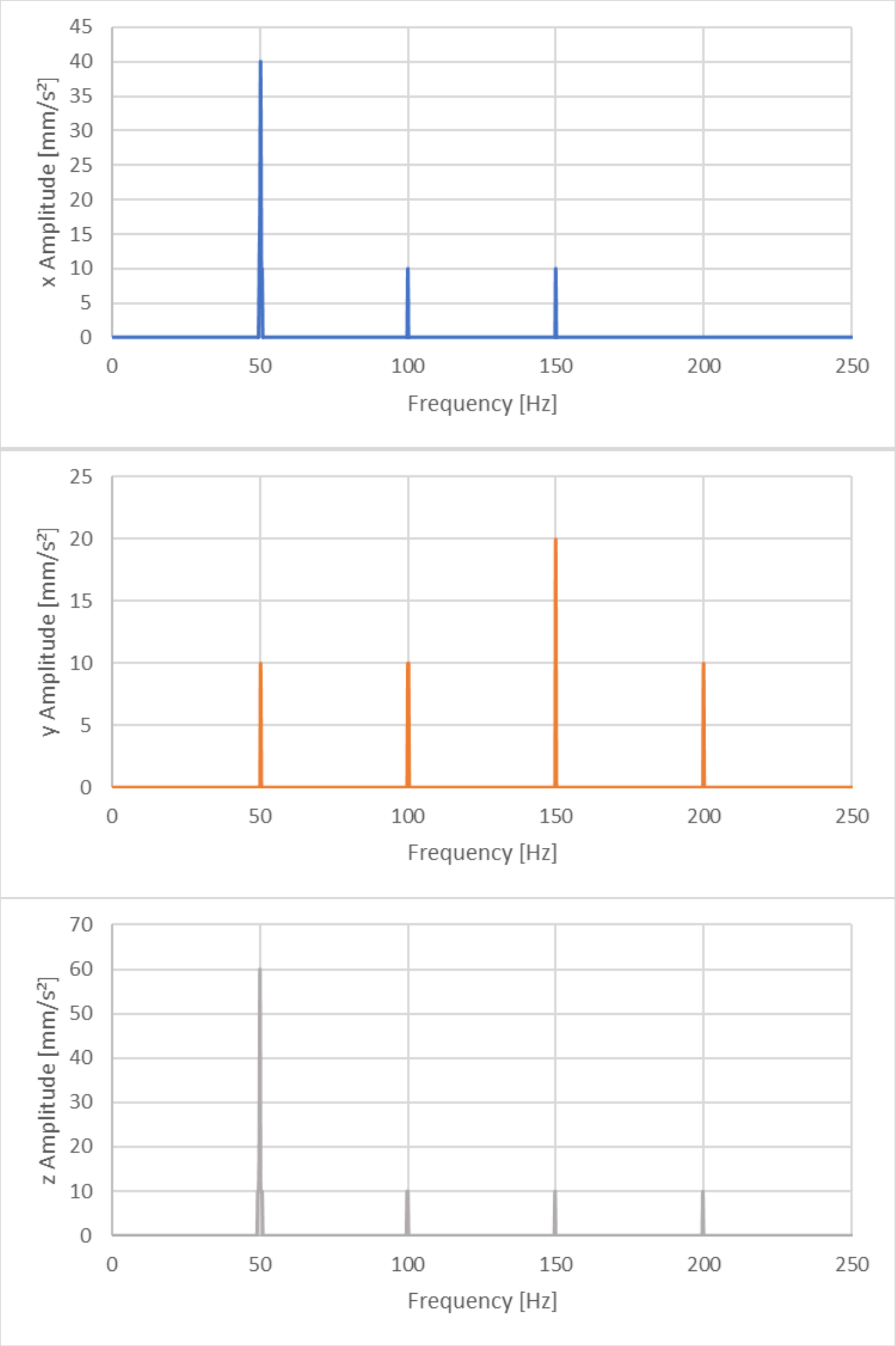

Figure 16: Three-dimensional (x, y, z) signal density during acceleration measurement on a bottle stored in the wire mesh container on the vibration plate.

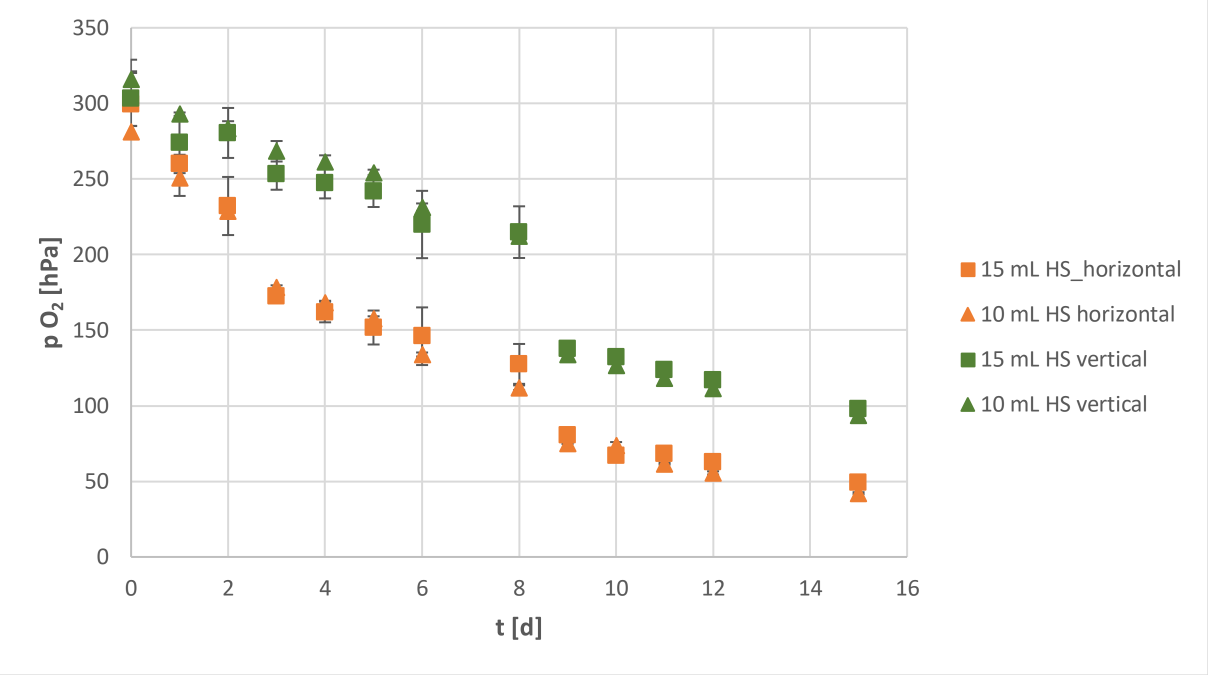

Figure 17: Influence of horizontal and vertical bottle storage on the decrease in headspace oxygen over 15 days in bottles with 15 mL and 10 mL headspace volume sealed with screw caps (n=2).

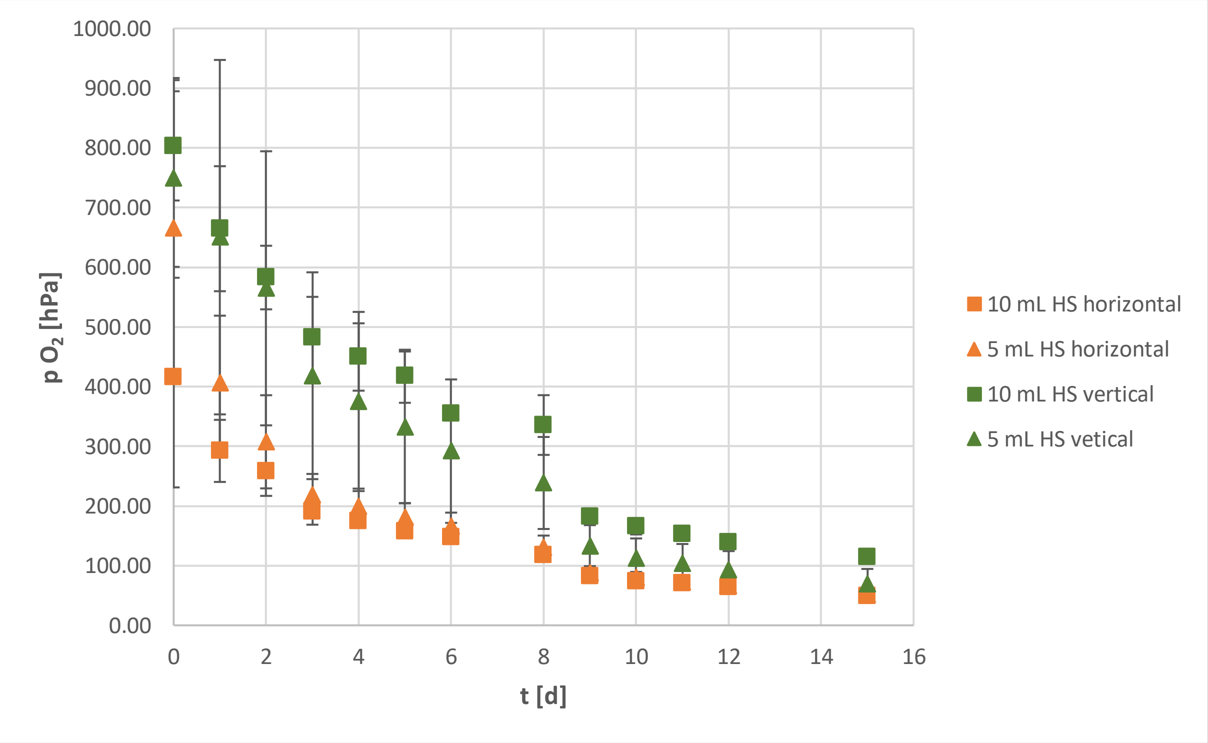

Figure 18: Influence of horizontal and vertical bottle storage on the decrease in headspace oxygen over 15 days in bottles with 10 mL and 5 mL headspace volume sealed with cork closure (n=2).

8.2. Supporting information on: Influence of vibration on volatile compounds, color, SO_2 and CO_2 of Riesling sparkling wine and white wine:

Table 7: Relative responses and standard deviations of TDN, linalool, and 3-methyl butyl acetate for non-vibrated (0 mm/s²) and vibrated (500 mm/s^2 and 1000 mm/s^2) wine 1 over a period of 6 months (n=2). The responses at time point 0 were set to 1.00.

Month	**Vibration level [mm/s²]**	**TDN**		**Linalool**		**3-methyl butyl acetate**	
		Relative response	**SD**	**Relative response**	**SD**	**Relative response**	**SD**
1	**0**	0.93	0.13	1.50	1.27	1.78	1.17
	500	0.96	0.04	1.90	0.54	0.89	0.13
	1000	0.82	0.02	1.03	0.03	1.07	0.09
2	**0**	1.07	0.16	1.55	1.08	0.60	0.01
	500	1.08	0.15	2.13	0.69	0.55	0.06
	1000	0.85	0.21	0.78	0.02	0.81	0.07
3	**0**	1.07	0.03	0.83	0.19	1.17	0.59
	500	1.06	0.02	0.99	0.33	1.00	0.46
	1000	0.80	0.23	0.60	0.09	0.55	0.02
4	**0**	0.11	0.15	0.96	0.50	0.03	0.04
	500	1.26	0.09	0.61	0.33	1.48	0.47
	1000	0.96	0.07	0.75	0.02	0.57	0.01
5	**0**	0.91	0.22	1.00	0.53	0.47	0.18
	500	1.20	0.01	1.34	0.21	0.53	0.11
	1000	0.79	0.03	0.67	0.08	0.74	0.01
6	**0**	0.98	0.36	0.91	0.35	0.60	0.05
	500	1.26	0.02	1.34	0.01	0.54	0.29
	1000	0.67	0.05	0.50	0.02	0.37	0.01

Table 8: Supporting information on Figure 3. Mean values for the relative change in TDN, linalool and 3-methyl butyl acetate and standard deviations for Wine 2 non-vibrated (0 mm/s²) and vibrated (500 mm/s^2 and 1000 mm/s^2) stored over a period of 6 months (n=2). Initial value (Time point 0) was set to 1.

Month	**Vibration [mm/s²]**	**TDN**		**Linalool**		**3-Methyl butyl acetate**	
		Relative response	**SD**	**Relative response**	**SD**	**Relative response**	**SD**
1	**0**	1.58	0.47	0.59	1.17	0.82	0.35
	500	0.56	0.28	0.60	0.13	0.82	0.16
	1000	0.98	0.20	0.62	0.09	1.14	0.00
2	**0**	1.55	0.34	0.42	0.01	0.87	0.04
	500	1.25	0.00	0.31	0.06	0.77	0.00
	1000	1.52	0.23	0.43	0.07	1.11	0.02
3	**0**	2.08	1.59	0.25	0.59	0.54	0.23
	500	1.12	0.08	0.27	0.46	0.61	0.04
	1000	3.37	0.84	0.28	0.02	0.87	0.23
4	**0**	3.37	1.40	0.20	0.04	0.64	0.29
	500	1.55	0.00	0.20	0.47	0.44	0.13
	1000	4.23	0.00	0.24	0.01	0.90	0.13
5	**0**	3.17	2.24	0.18	0.18	0.59	0.25
	500	0.88	0.15	0.18	0.11	0.50	0.05
	1000	4.65	0.05	0.16	0.01	0.76	0.03
6	**0**	3.83	2.20	0.11	0.05	0.54	0.28
	500	2.10	0.33	0.17	0.29	0.40	0.03
	1000	6.82	2.95	0.12	0.01	0.88	0.22

Table 9: Supporting information on Figure 3. Mean values for the relative change in TDN, linalool and 3-methyl butyl acetate and standard deviations for Wine 3 non-vibrated (0 mm/s²) and vibrated (500 mm/s^2 and 1000 mm/s^2) stored over a period of 6 months (n=2). Initial value (Time point 0) was set to 1.

Time point	**Vibration [mm/s²]**	**TDN**		**Linalool**		**3-Methyl butyl acetate**	
		Relative response	**SD**	**Relative response**	**SD**	**Relative response**	**SD**
1	**0**	0.70	0.00	0.69	0.40	1.25	0.46
	500	0.96	0.12	0.53	0.00	1.49	0.11
	1000	0.34	0.13	0.47	0.27	0.61	0.41
2	**0**	0.69	0.00	0.44	0.06	0.89	0.00
	500	0.28	0.01	0.19	0.00	0.89	0.07
	1000	1.83	0.13	0.50	0.01	0.66	0.10
3	**0**	0.17	0.00	0.13	0.00	0.60	0.06
	500	0.32	0.04	0.19	0.01	0.91	0.07
	1000	1.82	0.34	0.38	0.01	0.65	0.13
4	**0**	0.76	0.21	0.32	0.24	0.68	0.15
	500	0.31	0.01	0.18	0.00	0.65	0.03
	1000	1.65	0.37	0.38	0.02	0.50	0.06
5	**0**	1.08	0.25	0.30	0.21	0.66	0.09
	500	0.15	0.03	0.15	0.00	0.62	0.05
	1000	2.66	0.25	0.44	0.09	0.62	0.02
6	**0**	0.30	0.19	0.23	0.13	0.61	0.05
	500	0.61	0.06	0.14	0.00	0.63	0.06
	1000	2.59	0.10	0.30	0.00	0.61	0.02

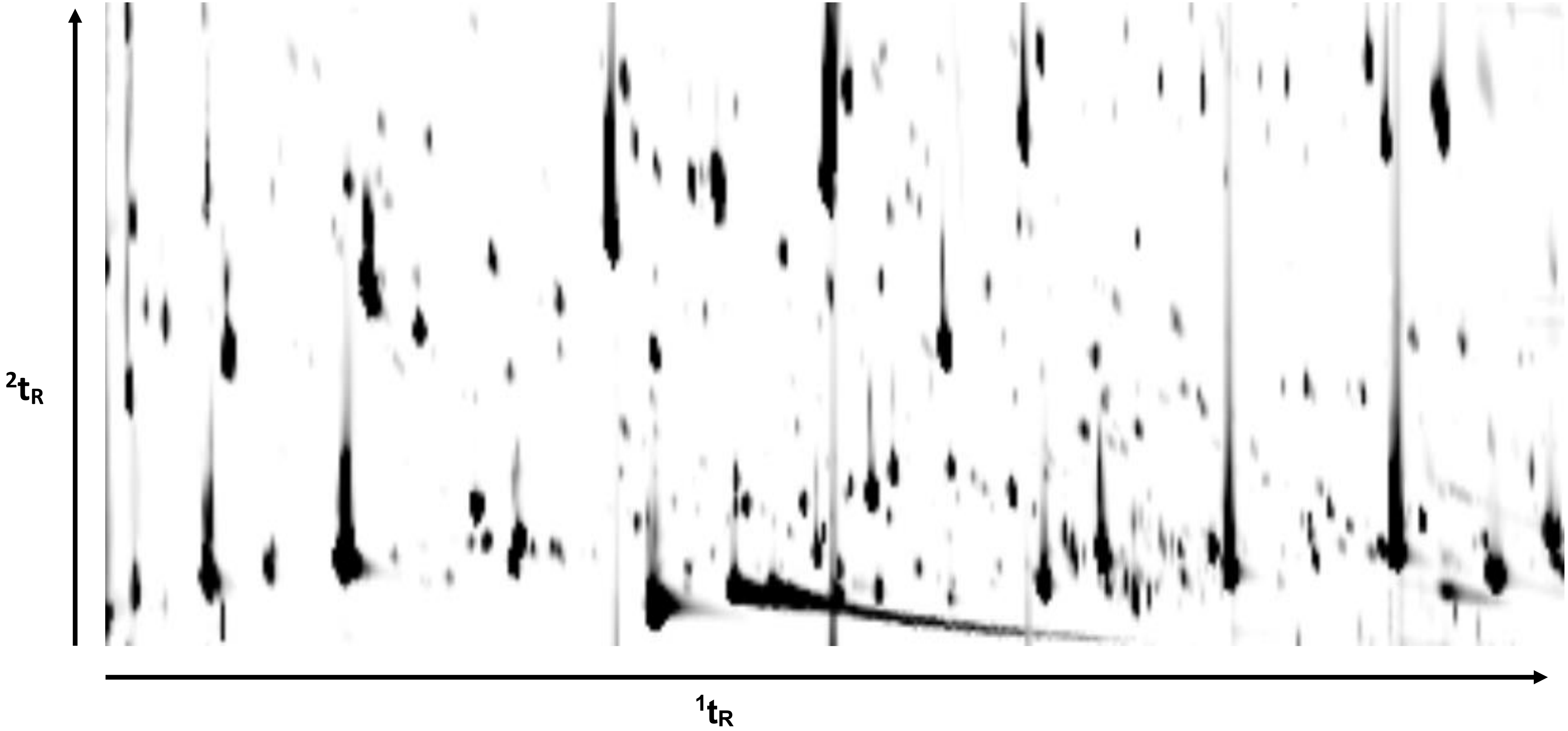

Figure 19: Grey scale image in GasPedal (version 1.0, Decodon, Greifswald, Germany) resulting from HS-SPME-GC×GC-qMS analysis of wine 2.

Table 10: Standard analytical parameters of the three used wines prior to the experiments.

Wine	**Density**	**Alcohol [g/L]**	**Reducing sugar [g/L]**	**Glucose [g/L]**	**Fructose [g/L]**	**Total acidity [g/L]**	**pH**	**Volatile acidity [g/L]**	**Tartaric acid [g/L]**	**Lactic acid [g/L]**	**Malic acid [g/L]**	**Glycerin [g/L]**	**Sugarfree extract [g/L]**
Wine 1	0.994	105.2	7.1	3.0	3.8	7.9	3.0	0.3	2.7	0.0	3.5	6.4	22.0
Wine 2	0.992	99.3	1.7	0.0	2.1	7.9	2.8	0.5	4.8	0.2	1.5	5.5	18.6
Wine 3	0.994	101.6	5.7	2.7	3.2	7.3	3.1	0.5	2.8	0.2	2.9	6.6	20.1

Table 11: List with all volatile compounds which were identified from HS-SPME-GC×GC-qMS analysis and significant different according to one way ANOVA ($p \leq 0.05$). Identification based on MS: Comparison of mass spectra against those from the NIST 11 library; LRI Comparison of LRIs with literature.

$^{1}t_{R}$ *[min]*	**$^{2}t_{R}$ *[s]***	**Name**	**CAS-Nr.**	**^{1}LRI$_{WAX}$ (Reference)**	**^{1}LRI$_{WAX}$ ^{1}D**	**Identification**
10	2.7	3-Methylbutyl acetate	123-92-2	1125^{a}	1120	MS, LRI
11.1	0.8	Butanol	71-36-3	1150^{b}	1153	MS, LRI
13.1	0.9	3-Methylbutanol	123-51-3	1211^{a}	1214	MS, LRI
13.7	3.3	Ethyl hexanoate	123-66-0	1223^{c}	1233	MS, LRI
15	2.9	Hexyl acetate	142-92-7	1268^{c}	1272	MS, LRI
16.5	3.9	Propyl hexanoate	626-77-7	1321^{d}	1319	MS, LRI
16.6	**1.4**	**Heptan-2-ol (ISTD)**	543-49-7		**1323**	
17	3.6	Ethyl heptanoate	106-30-9	1342^{e}	1335	MS, LRI
17.5	1	Ethyl lactate	687-47-8	1349^{f}	1352	MS, LRI
17.7	1	Hexanol	11-27-3	1356^{a}	1358	MS, LRI
18.4	0.9	3-Ethoxypropanol	111-35-3	1389^{g}	1381	MS, LRI
18.7	2.8	Nonan-2-one	821-55-6	1392^{h}	1390	MS, LRI
18.7	3.2	Methyl octanoate	111-11-5	1378^{c}	1390	MS, LRI
20	3.9	Ethyl octanoate	106-32-1	1428^{c}	1434	MS, LRI
20.4	5.2	Linalyl propionate	144-39-8	-	1448	MS
21.2	2.7	Nerol oxide	1786-08-9	1468^{i}	1475	MS, LRI
21.3	0.3	Acetic acid	64-19-7	1465^{c}	1478	MS, LRI
22.2	4.3	Geranyl ethyl ether	40267-72-9	1519^{j}	1509	MS, LRI
22.9	4.3	Vitispirane	65416-59-3	1525^{i}	1535	MS, LRI
23.3	1.2	Ethyl (2-hydroxy-4-methyl) pentanoate	10348-47-7	1547^{k}	1549	MS^{N}, LRI
23.3	1.6	Linalool	78-70-6	1552^{l}	1549	MS, LRI
23.3	4.9	2-Methylpropyl octanoate	1300784	1561^{m}	1549	MS, LRI
23.6	1.3	Octanol	111-87-5	1547^{n}	1560	MS, LRI
25.1	1.3	Hotrienol	29957-43-5	1616^{o}	1615	MS, LRI
25.7	4.3	Ethyl decanoate	110-38-3	1624^{c}	1638	MS, LRI
25.8	3.2	Riesling acetal	129601-94-1	1637^{p}	1641	MS, LRI

27.3	1.2	4-Butoxybutanol	4161-24-4	1701[q]	1698	MS, LRI
27.4	1.6	α-Terpineol	98-55-5	1692[l]	1702	MS, LRI
28.3	2.8	3-Tridecanone	1534-27-6	1755[r]	1738	MS
28.8	2.7	TDN	30364-38-6	1748[p]	1758	MS, LRI
29.8	1.7	Ethyl phenyl acetate	101-97-3	1768[e]	1798	MS, LRI
30.8	4.9	Ethyl dodecanoate	106-33-2	1844[c]	1840	MS, LRI
31.4	0.6	Hexanoic acid	142-62-1	1857[s]	1865	MS, LRI
32.9	0.9	Phenethyl alcohol	60-12-8	1923[a]	1929	MS[N], LRI
33.8	2.2	Dodecanol	112-53-8	1953[t]	1968	MS, LRI
35.5	5.3	Ethyl tetradecanoate	110-27-0	2043[m]	2045	MS, LRI
36.2	0.8	Octanoic acid	124-07-2	2070[a]	2077	MS, LRI
40.3	2.8	Pentadecanol	629-76-5	2272[u]	2275	MS, LRI
40.6	0.8	Decanoic acid	334-48-5	2279[v]	2290	MS, LRI

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8.3. Supporting information on: The impact of temperature fluctuations on the composition, colour and flavour properties of wine during two years storage:

Table 12: Sensory evaluation of Riesling wine stored at constant 12°C (CT_{Iso}), uniform temperature fluctuation of 0.5°C around 12°C (FT_{LA}), uniform temperature fluctuation of 1.5°C around 12°C (FT_{HA}), alternating temperature which changed in 6 months intervals from constant 6°C to 18°C (CT_{ALT}) and irregular temperature fluctuation which increased the wine temperature every six hours to 14°C (FT_{IR}); Descriptive analysis (n=16 × 3 replicates), statistical evaluation with three-way ANOVA (p < 0,05) and Fisher (LSD) Post hoc analysis, different letters show significant differences within the attributes, n.s.: not significant.

	CT_{ISO}	**FT_{LA}**	**FT_{HA}**	**CT_{ALT}**	**FT_{IR}**	***p*-value**
Color***	4.0 b	4.5 ab	4.8 a	4.6 ab	4.0 ab	0.0019
Ripe fruit, n.s.	4.4	4.9	5.0	4.9	5.1	0.2613
Honey, n.s.	4.1	4.2	4.8	4.8	4.7	0.2713
Petrol**	3.05 b	3.4 ab	4.1 a	4.0 a	3.4 ab	0.0183
sweet, n.s.	3.9	3.9	3.6	3.6	3.6	0.4964
sour, n.s.	5.3	5.1	5.0	5.1	5.1	0.9539
Body, n.s.	4.6	4.6	4.6	4.5	4.7	0.9628
Mouthfeel, n.s.	4.4	4.2	4.6	4.2	3.9	0.0129
bitter, n.s.	3.4	3.6	3.7	3.7	3.3	0.4880

$^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$

Table 13: Results from HS-SPME-GC-MS of volatile compounds in model wine (n=3), which was stored for eight months at constant 12°C (CT_{Iso}), uniform temperature fluctuation of 0.5°C around 12°C (FT_{LA}), uniform temperature fluctuation of 1.5°C around 12°C (FT_{HA}), and irregular temperature fluctuation which increased the wine temperature every six hours to 14°C (FT_{IR}).

Volatile compound	**In**	**CT_{ISO}**	**FT_{LA}**	**FT_{HA}**	**FT_{IR}**
	Concentration [µg/L]				
Ethyl butanoate	403.8	263.5	170.7	0.2	306.1
2,3-Methyl butyl acetate	1254.0	912.5	678.1	48.8	1132.3
Ethyl hexanoate	288.7	200.6	143.5	8.0	264.6
Hexyl acetate	275.6	165.0	122.1	8.3	212.3
Linalool	232.8	204.2	182.5	160.3	192.2
2-Phenylethyl alcohol	393.3	464.1	489.9	493.7	463.4
Ethyl octanoate	2493.9	1790.8	1147.3	145.3	2309.8
2-Phenethyl acetate	445.9	374.5	403.5	354.2	399.9
ß-Damascenone	48.44	41.81	43.73	35.86	43.58

Table 14: Calibration range and functions, coefficient of determination (R^2), limit of detection (LOD) and limit of quantification (LOQ) of the HS-SPME-GC-gMS method.

Substance	**Internal standard**	**Calibration range [µg/L]**	**Calibration function**	**R^2**	**LOD [µg/L][d]**	**LOQ [µg/L][d]**
Ethyl butanoate	Ethyl hexanoate - d$_5$	6 - 330	Y = 0.0271766+0.000905385*X	0.998	1.35	3.74
2,3-Methyl butyl acetate	Hexyl acetate - d$_3$	20 - 976	Y = 0.000297395+0.00136326*X	0.9977	2.76	7.38
Ethyl hexanoate	Ethyl hexanoate - d$_5$	15 - 754	Y = 0.0306895+0.00497477*X	0.9986	1.6	4.43
Hexyl acetate	Hexyl acetate - d$_3$	11 - 538	Y = 0.0113607+0.00899087*X	0.9988	1.01	2.79
Linalool	Linalool - d$_5$	7 - 326	Y = 0.00863314+0.0177028*X	0.9984	1.42	3.92
2-Phenethyl alcohol	2-Phenethyl alcohol - d$_5$	303 - 15147	Y = -0.0409183+0.000693957*X	0.9988	96.1	266
Ethyl octanoate	Ethyl hexanoate - d$_5$	15 - 746	Y = -27.0807119 46.09771691*X	0.9961	1.6	4.44
2-Phenethyl acetate	2-Phenethyl alcohol - d$_5$	20 - 1022	Y = 0.266558+0.0673452*X	0.998	3.07	8.51
ß-Damascenone	ß-Damascenone - d$_4$	0.2 - 11	Y = 0.0207974+0.179248*X	0.9986	0.26	0.73

[d] Calibration curve method DIN3264

Table 15: List with all volatile compounds which were identified from HS-SPME-GC×GC-qMS analysis and significant different according to one way ANOVA ($p \leq 0.05$). Identification based on MS: Comparison of mass spectra against those from the NIST 11 library; LRI Comparison of LRIs with literature.

$^{1}t_R$ *[min]*	$^{2}t_R$ *[s]*	**Name**	**CAS-Nr.**	**$^{1}LRI_{WAX}$ (Reference)**	**^{1}LRI ^{1}D**	**Identification**
13.7	3.3	Ethyl hexanoate	123-66-0	1223[a]	1233	MS^N, LRI
16.6	**1.4**	**Heptan-2-ol (ISTD)**	543-49-7		**1323**	
21.4	4.6	3-Methyl butyl octanoate	2198-61-0	1452[b]	1458	MS^N, LRI
22.2	4.3	Geranyl ethyl ether	40267-72-9	1519[c]	1509	MS^N, LRI
22.9	4.3	Vitispirane	65416-59-3	1525[b]	1535	MS^N, LRI
23.3	1.6	Linalool	78-70-6	1552[d]	1549	MS^N, LRI
25.7	4.3	Ethyl decanoate	110-38-3	1624[a]	1638	MS^N, LRI
26.9	1.4	Diethyl succinate	123-25-1	1679[e]	1683	MS^N, LRI
28.8	2.7	TDN	30364-38-6	1748[f]	1758	MS^N, LRI
30.8	4.9	Ethyl dodecanoate	106-33-2	1844[a]	1840	MS^N, LRI
31.4	0.6	Hexanoic acid	142-62-1	1857[g]	1865	MS^N, LRI
32.9	0.9	Phenethyl alcohol	60-12-8	1923[h]	1929	MS^N, LRI
40.6	0.8	Decanoic acid	334-48-5	2279[i]	2290	MS^N, LRI
41.2	4.1	Ethyl 9-hexadecenoate	54546-22-4	2283[b]	2290	MS^N, LRI

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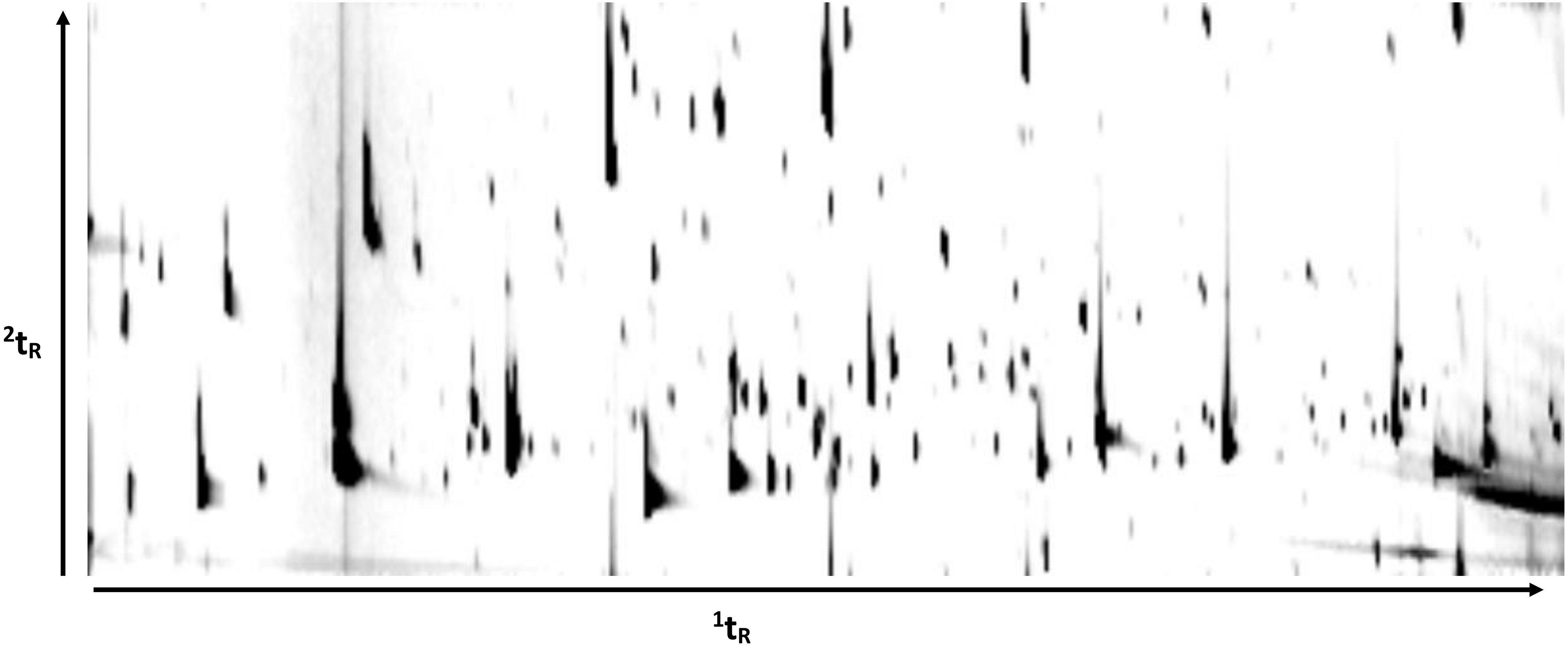

Figure 20: Grey scale image in GasPedal (version 1.0, Decodon, Greifswald, Germany) resulting from HS-SPME-GC×GC-qMS analysis of the Riesling wine used for the experiment.

Table 16: List of analyzed reference substances with HS-SPME-GC×GC-qMS.

Name	**$^{1}t_R$ [min]**	**$^{2}t_R$ [s]**	**^{1}LRI ^{1}D^{a}**
Heptan-2-ol (ISTD)	**16.6**	**1.4**	**1323**
Ethyl butanoate	8.5	2.5	1082
Ethyl acetate	10.3	1.9	1099
3-Methyl-1-butyl acetate	11.2	2.8	1125
Hexyl acetate	16.2	3	1276
trans Rose oxide	18.7	3.8	1356
trans Hex-2-enol	20.5	0.9	1415
Ethyl octanoate	21.3	3.9	1442
Ethyl decanoate	21.3	3.9	1442
Nerol oxide	22.4	2.8	1480
Linalool	24.5	1.6	1554
α-Terpeniol	28.7	1.7	1711
Citronellol	30.4	1.4	1774
TDN	31.1	2.8	1806
Nerol	31.2	1.3	1810
2-Phenethyl aceate	31.8	2.8	1835
β-Damascenone	31.9	2.4	1840
Geraniol	32.3	1.3	1856
2-Phenethyl ethanol	34.2	0.8	1937
β-Ionone	34.6	2.5	1955
cis Hex-2-enol	19.6	0.9	1420
Fufural	21.3	0.8	1487

[a] Linear retention index based on n-alkanes

9. List of figures

10. Lebenslauf

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