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ORIGINAL RESEARCH ARTICLE

Improved sealing polymers and cleaning procedures to mitigate aroma carryover during bottling of aromatised and regular wines on the same filling line

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ABSTRACT

Bottling of aromatised wines and regular table wines often takes place on the same bottling line. Installed sealings in the bottling line absorb volatiles from aromatised wines and, due to inadequate cleaning, carryover occurs into the subsequently bottled regular wine. This unintentional carryover can lead to accusations of illegal flavouring of wine. To minimise the carryover risk, sealing materials that absorb less volatiles are beneficial. Incorporating kaolin and micro-cellulose into the ethylene propylene diene monomer rubber (EPDM) network decreased absorption of the critical α-ionone by 51 and 60 %, respectively.

Besides the minimisation of the absorption, a performed cleaning can reduce aroma carryover. So far, knowledge about cleaning parameters that can increase cleaning efficiency is limited since cleaning usually focuses on surficial removal and prevents microbiological cross-contamination. An evaluation of the cleaning parameters, temperature, time and agents clearly revealed a high factor in the considered temperature. The highest cleaning efficiency was seen at 85 °C, whereas the cleaning additives such as citric acid, caustic soda, ozone or dissolved carbon dioxide had no impact. High proportions of the aroma compounds were removed from the polymer in the first 20 min at 85 °C, but none of the performed cleaning sequences was able to remove all compounds.

KEYWORDS: lactones, α-ionone, EPDM, migration, CIP, oxidative cleaning agents, ozone

INTRODUCTION

Wine producers commonly operate with a single bottling line for both aromatised wine-based beverages and regular wine; only for very large or specialised producers, a separate line for aromatised products is economically feasible. Despite the implementation of clean-in-place (CIP) systems, carryover of added aroma compounds from the aromatised product into subsequently bottled wine can occur due to absorption (scalping) and remigration from bottling line sealing polymers (Elss *et al*., 2007, Eckstein, 2011, Vetter, 2012, LUA, 2014, Freund and Seckler, 2016, BMEL, 2019, Beierle *et al*., 2020, Gottmann *et al*., 2021).

Even unintentional carryover of trace aroma compounds can result in prosecution by the EU and other legislation (European Parliament, 2009). Aroma concentrates added for aromatisation are usually of synthetic origin (Mosandl, 2004) and recent developments in enantioselective and isotope ratio analysis allows distinguishing aroma compounds from biological and synthetic sources (Schumacher *et al*., 1998, Langen *et al*., 2013, Lampe, 2015, Langen *et al*., 2016). So far, any detection of aroma compounds of chemical origin is illegal, regardless of their sensory relevance. The German Federal Ministry of Nutrition and Agriculture (Bundesministerium für Ernährung und Landwirtschaft, BMEL), in cooperation with the German food control authorities and wine industry, developed good manufacturing practices (GMP) to reduce the risk of aroma carryover (BMEL, 2019). If a bottling company complies with this guideline and aroma compounds used to aromatise are detected but have, more importantly, no sensory significance, these compounds will be classified as technically unavoidable, consequently not resulting in prosecution.

Literature exploring the uptake of aroma compounds into sealing polymers and their release during cleaning and contact within subsequently bottled wine is scarce. Cleaning procedures usually focus on the mechanical removal of residue from previous products as well as sterilisation of the bottling line to prevent microbial cross-contamination (Englezos *et al*., 2019), while the removal of aroma compounds from sealing materials has been largely neglected. To date, cleaning efficacy and its economic efficiency depend on each company's experience and are based on their experimental trials (Changani *et al*., 1997, Seiberling, 2008, Basso *et al*., 2017).

The achieved cleaning effect is primarily influenced by a combination of several factors: time, temperature, mechanical effects and the concentration and chemical nature of cleaning agents (Sinner, 1960, Tamime, 2009). Mechanical cleaning is limited to the polymer surface and can be neglected in terms of cleaning efficiency on absorbed aroma compounds. The aroma carryover risk was firstly described for aroma compounds including limonene and myrcene from orange lemonade bottled in reusable polyethylene terephthalate (PET) bottles, whereas the conducted basic bottle washing at 70 °C removed only 31 % and 45 %, respectively (Nielsen, 1994). Furthermore, Safa and Bourelle (1999) reported a sensorial perceptible carryover of 250–300 µg/L limonene from reusable PET bottles into water, despite prior cleaning. Within in the scope of our recent study, the GMP-oriented cleaning of ethylene propylene diene monomer rubber (EPDM) sealings polymers removed only 11–62 % of absorbed marker aroma compounds in a model system and further assessment of each cleaning parameter were required (Gottmann *et al*., 2021).

Besides frequent use of water, acidic and alkaline agents, oxidants such as peracetic acid, ozone and chlorine dioxide are widely applied to remove organic compounds and to sterilise bottling lines, hoses, barrels and other winery equipment (Sonntag and Gunten, 2012, Rincon-Delgadillo *et al*., 2013, Englezos *et al*., 2019, Pandiselvam *et al*., 2019, Kim and Huang, 2020, Gan *et al*., 2020, Stadler *et al*., 2020, Stadler and Fischer, 2020). Improved cleaning efficacy was shown for a 60 min treatment of enriched water with 2 mg/L ozone for the removal of D-limonene from EPDM and silicone sealings (Nishijima *et al*., 2014).

To minimise the risk of aroma carryover, less absorptive sealing materials are of interest. The chemical nature of a sealing polymer defines its absorptive behaviour. Commonly used polymers are EPDM and highly fluorinated rubber (FKM), which vary in their flexibility, inertness, stability, application field and temperature tolerance (Vetter, 2012, Freund and Seckler, 2016). However, the cost is often the deciding factor for industry usage, with EPDM being the more economical option over FKM (Abts, 2010). EPDM polymers available on the market differ in their formulation, particularly with the incorporation of filling materials such as minerals, talc, natural organics and synthetic inorganics into the polymer mesh to reduce costs and control physical properties (Müller *et al*., 2022). The absorption behaviour of the polymers usually becomes secondary or even redundant. However, importantly, the selected filler influences the crystallite formation of the polymer. With increasing crystallinity, the migration of molecules diminishes, as movement is more restricted in crystalline phases than in amorphous phases and aroma absorption can be influenced (Charara *et al*., 1992, Richter and Schacker, 2016).

This work addresses how novel fillers in EPDM polymers influence the absorption of aroma compounds and how different cleaning methods affect their release. We used seven aroma coumpounds previously characterised in their sensory properties, which are commonly used in high concentrations in aromatised cocktails with the aroma of peach (γ-decalactone, δ-decalactone and γ-undecalactone), apple (ethyl 2-methylbutanoate) and raspberry (α-ionone), as well as mulled wines with clove (eugenol) and cinnamon (*trans*-cinnamaldehyde) (Gottmann *et al*., 2022). Using a recently developed model system (Gottmann *et al*., 2021), aroma absorption was studied by monitoring experimental EPDM polymers enriched with nine different fillers in comparison with two commercial sealings. Moreover, the impact of cleaning temperature, time and chemical additive on cleaning efficacy was investigated in this model system.

MATERIALS AND METHODS

1. Chemicals

Aroma compounds were purchased from Sigma-Aldrich KGaA (Darmstadt, Germany) with purities as follows: ethyl 2-methylbutanoate (99 %), α-ionone (≥ 96 %), γ-decalactone (≥ 98 %), δ-decalactone (≥ 98 %), γ-undecalactone (≥ 98 %), eugenol (99 %) and *trans*-cinnamaldehyde (≥ 99 %). Sodium hydroxide (98 %) and citric acid (99.5 %) were obtained from Merck KGaA (Darmstadt, Germany) and D-glucose (p.a.), D-fructose (> 99.5 %), L-tartaric acid (≥ 99 %), D-malic acid (≥ 99.5 %), L-lactic acid (≥ 95 %), sodium chloride (≥ 99 %) and glycerol (≥ 99 %) from Carl Roth GmbH + Co. KG (Karlsruhe, Germany). Ethanol (96 %) was purchased from Berkel AHK (Ludwigshafen, Germany) and sodium chlorite (10 %) and hydrochloric (10 %) from ASiRAL GmbH & Co. KG (Neustadt, Germany). Hydrosan SinQ cleaning agent with 50 g/kg peracetic acid was purchased from Wigol (Worms, Germany).

2. Polymer materials

EPDM discs of 2 mm thickness were manufactured by the Institut für Kunststofftechnik Westpfalz (IKW, Pirmasens, Germany) at the University of Applied Sciences, Kaiserslautern. EPDM consisted of 100 parts per hundred rubber (phr) KEP 510 from (Weber&Schaer, Hamburg, Germany), 15 phr white oil (Weber&Schaer, Hamburg, Germany), 8 phr Peroxan DC (Thermo Fischer, Karlsruhe, Germany) and 2 phr TAC-70 XP (Pergan, Bocholt, Germany). The fillers incorporated into the polymer during manufacturing were: Aktivit VM, a silicate mineral (Hoffmann Mineral, Neuburg, Germany), micro-cellulose (Acros Organics, Darmstadt, Germany), glass flakes (Mühlmeier Mahltechnik, Bärnau, Germany), kaolin (Thiele Kaolin Company, Sandersville, USA), talcum (Bassermann Minerals GmbH&Co.KG, Mannheim, Germany), cork (Kork-Handel GmbH & Co. KG, Igel, Germany), polyethylene (PE) wax (TH. C. Tromm GmbH, Köln, Germany), Carbon Black N220 and Carbon Black N990 (Heinrich Heller GmbH, Wuppertal, Germany) (Supplemental Table 1). For comparison, a standard commercial EPDM (70 EPDM 291) and an FKM (75 Fluoroprene XP41) were optimised by the supplier for their minimised aroma absorption (Freudenberg Process Seals GmbH, Weinheim, Germany).

3. Model wine

As prescribed by the German wine control authorities, the model wine consisted of 12 % v/v ethanol, 2.5 g/L D-glucose, 2.5 g/L D-fructose, 1.5 g/L L-tartaric acid, 1.5 g/L D-malic acid, 1.5 g/L L-lactic acid and 6 g/L glycerol. The pH was adjusted to 3.5 using 10 N sodium hydroxide (Lampe, 2015). The model wine was aromatised to various concentrations in the experiments using an ethanolic stock solution.

4. Direct quantitation of absorbed aroma compounds in polymer material with TD-GC-MS

A recently published thermal desorption gas chromatography and mass spectrometry method (TD-GC-MS) allows direct analysis of aroma compounds (Gottmann *et al*., 2021) such as ethyl 2-methylbutanoate, α-ionone, γ-decalactone, δ-decalactone, γ-undecalactone, eugenol and *trans*-cinnamaldehyde and their ab- and desorption in different polymers. The analytical system consisted of an Agilent 6890 GC equipped with an Agilent 5975 C MS, thermo desorption unit (TDU), cold injection system (CIS) and a multi-purpose sampler (MPS), all provided by Gerstel (Mühlheim, Germany). For calibration, four stamped untreated polymer samples were placed into a TDU liner with glass wool, after which the MPS pipetted 1 µL of each calibration standard solution (0.1–300 µg/cm^3) directly into the TDU liner. Calibration standards were prepared in methyl *tert*-butyl ether (MTBE). 3-Methylbutyl acetate (9 µg/L) was used as an internal standard.

The separation of volatiles was achieved with a ZB-WAXplus™ column of 30 m × 0.25 mm internal diameter and 0.5 µm film thickness (Phenomenex, Germany). The oven program started at 40 °C for 2 min, followed by a 3 °C/min increase to 60 °C. The temperature rose further by 20 °C/min until 180 °C was reached, followed by a slower increase of 5 °C/min up to 240 °C, which was maintained for 9 minutes. The total runtime was 35.6 min. The transfer line temperature was set to 250 °C and the helium carrier gas flow rate was constant at 1.2 mL/min. The MS was operated in electron impact ionisation mode with an electron energy of 70 eV, the source temperature was set to 230 °C and total ion chromatograms were recorded over 30–300 *m/z*. The initial TDU temperature of 30 °C was held for 1 min and heated up at a rate of 720 °C/min to the final extraction temperature of 150 °C and kept constant for 30 min in splitless mode. The TDU transfer line was kept at 280 °C. The cryo-focusing temperature was set to 0 °C and a CIS-liner with Tenax TA™ filling was chosen. After thermal extraction, the CIS was heated at a rate of 12 °C/min to 250 °C and held for 5 min. The GC inlet was run in solvent vent mode. The total flow was set to 24 mL/min while the purge flow to the split vent was set to 20 mL/min at 0.01 min, corresponding to a split ratio of 1:20. The gas saver was set to 15 mL/min after 20 min until the end of the GC analysis. The vent flow was 25 mL/min with a vent pressure of 20 kPa until 0.01 min. Chromatograms obtained were processed with MassHunter Qualitative Analysis software (ver. B.05.00, Agilent Technologies) and PARADISe (ver. 3.9).

5. Quantitation of aroma compounds in water with HS-SPME-GC-MS

Quantitative analysis of ethyl 2-methylbutanoate, α-ionone, γ-decalactone, δ-decalactone, γ-undecalactone, eugenol and *trans*-cinnamaldehyde was achieved using an established headspace solid phase microextraction (HS-SPME)-GC-MS method for the determination of volatiles in Riesling and model wine (Schwinn *et al*., 2019; Gottmann *et al*., 2022). The analytical system consisted of a Finnigan TRACE DSQ GC-MS (Thermo Fisher Scientific, Waltham, MA, USA) with a CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland). A 2 mL sample and 8 mL of a saturated sodium chloride solution were pipetted in a 20 mL headspace vial and closed with a screw cap. As an internal standard,

10 µL of a 2-heptanol stock solution (10 g/L in ethanol) was added with a microliter syringe, resulting in a final concentration of 50 µg/L. Volatiles were separated on a ZB-5ms 30 m × 0.25 mm column with a film thickness of 0.5 µm (Phenomenex, Aschaffenburg, Germany). Sample pre-incubation took place at 40 °C for 10 min, followed by a headspace extraction with a polydimethylsiloxane (PDMS) fibre for 20 min (FIB-P-100/10, CTC Analytics, Zwingen, Swiss). Volatiles were desorbed from the SPME fibre at 240 °C in the GC injector for 2 min in splitless mode and purged after 2 min. The flow rate of the helium carrier gas was held constant at 1.0 mL/min. The oven temperature was held initially for 2 min at 30 °C, then increased to 150 °C at a rate of 3.5 °C/min, followed by a further increase to 300 °C at a rate of 25 °C/min. Ionisation by electron impact (EI+) was done at 70 eV and total ion chromatograms were recorded from 29–300 *m/z*. Extracted ion chromatograms were obtained with the following *m/z* (quantifier; qualifier) for each compound: ethyl 2-methylbutanoate (102; 85), α-ionone (136; 121), γ-decalactone (128; 85), δ-decalactone (99; 114), γ-undecalactone (128; 85), eugenol (164; 149) and *trans*-cinnamaldehyde (131; 132). Chromatograms were processed with Xcalibur 2.2 (Thermo Fisher Scientific).

6. Experimental design

Polymer plates with a diameter of 39 mm and a height of 2 mm were clamped into a customary stainless-steel bracket (Gottmann *et al*., 2021) and immersed in aromatised model wine. This setup ensured that only one side of the polymer was exposed to the wine. Storage in model wine and cleaning solutions in Experiments 2 and 3 were done in a closed 1 L glass beaker equipped with a magnetic stirrer (350 rpm). Prior to analysis, the polymer plates were dismounted and rinsed with deionised water and then dried with cellulose tissue. Four disks (∅ 2 mm) were stamped out of the polymer plate to obtain a representative sample. These 4 disks were placed together into one TDU liner. Before TD-GC-MS analysis, 1 µL of 3-methylbutyl acetate (9 µg/L in MTBE) was automatically pipetted by the MPS into the TDU liner as an internal standard.

6.1. Quantitative analysis of absorbed aroma compounds in polymer materials (Experiment 1)

The influence of different filling materials in EPDM on the absorption of aroma compounds into sealings was investigated with nine different fillers compared to a commercial EPDM and FKM (XP41). Experimentally polymers were manufactured with Aktivit VM, micro-cellulose, glass flakes, kaolin, talcum, cork, polyethylene wax, Carbon Black N220 and Carbon Black N990 with low and high parts per hundred rubber (Supplemental Table 1). Polymer plates were immersed for 48 h in aromatised model wine containing ethyl 2-methylbutanoate (500 µg/L), α-ionone (180 µg/L), γ-decalactone (900 µg/L), δ-decalactone (2300 µg/L), γ-undecalactone (550 µg/L), eugenol (1000 µg/L) and *trans*-cinnamaldehyde (600 µg/L). After immersion, polymer samples were analysed.

6.2. Removal of aroma compounds from EPDM by different cleaning parameters (Experiment 2)

The effects of the cleaning agent, temperature and time on cleaning efficiency were evaluated with an EPDM plate clamped into the bracket. Prior to this evaluation, EPDM plates were immersed for 24 h in an aromatised model containing ethyl 2-methylbutanoate (1300 µg/L), α-ionone (2400 µg/L), γ-decalactone (12300 µg/L), δ-decalactone (6500 µg/L), γ-undecalactone (1200 µg/L), eugenol (800 µg/L) and *trans*-cinnamaldehyde (1000 µg/L). Plates

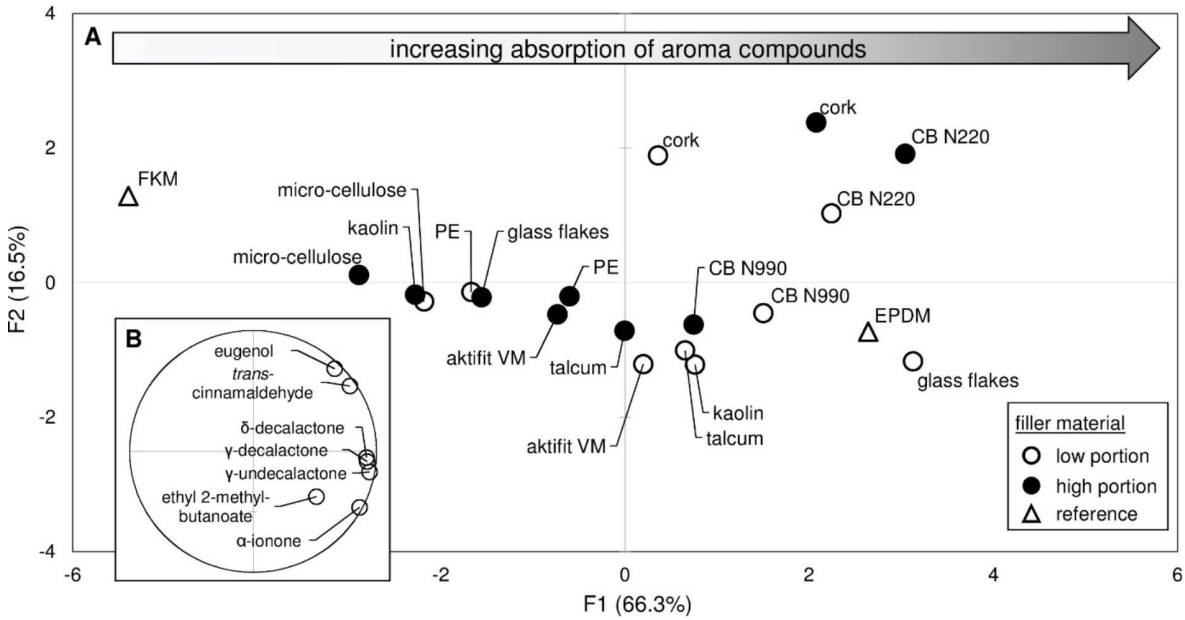


FIGURE 1. Observations (A) and loadings (B) of the principal component analysis of aroma compounds absorbed into different experimental EPDM and one commercial EPDM and FKM (XP41) (n = 4). Polyethylene wax (PE), Carbon Black N220 (CB N220), Carbon Black N990 (CB N990).

were rinsed with deionised water at room temperature before and after the cleaning step to remove residues. Water, sodium hydroxide (1.5 % w/v), citric acid (1.5 % w/v), ozonised water (5 mg/L), chlorine dioxide (5 and 500 mg/L) and peracetic acid (1 % v/v) were used as cleaning agents. The ozonised water was prepared using a univog ozone generator (Zickler, Böchingen, Germany). The chlorine dioxide solution was prepared according to the hydrochloric acid–chlorite procedure, and the resulting concentration was controlled by photometric determination of chlorine dioxide with an MD 100 photometer (Lovidbond, Dortmund, Germany) (Kuke, 2005). All cleaning agents were applied at 22 °C for 30 min, while water, sodium hydroxide and citric acid were additionally evaluated at increased temperatures of 50 and 85 °C. A further time-dependent evaluation of the cleaning efficiency of water at 85 °C was carried out from 0 to 60 min in seven steps. A long-term cleaning at room temperature for 24 h at 22 °C was conducted with water, carbonated water (6 g/L CO_2), model wine (8, 12 and 16 % v/v), a red wine (12 % v/v) and white wine (12 % v/v).

6.3. Decomposition of aroma compounds by oxidative agents (Experiment 3)

All seven aroma compounds of interest were exposed to the oxidative agent's ozone (5 mg/L), chlorine dioxide (5 and 500 mg/L) and peracetic acid (1 % v/v) in a watery system of 20 mL. Water functions as a control without any added agents. The fate of aroma compounds was determined after 30 min and 3 days by HS-SPME-GC-MS.

7. Statistical analysis

Principal component analysis (PCA) was done based on mean centring (co-variance) and no rotation was applied to study the impact of EPDM filling material and cleaning parameters on the uptake and removal of aroma compounds. Agglomerative hierarchical clustering was conducted with Euclidean distance and ward's method. Mean values were compared using a one-way analysis of variance (ANOVA, $p < 0.05$) with Tukey's honestly significant difference (HSD, $p < 0.05$) post-hoc test. Values provided in the charts and tables are given as the mean ± standard deviation of the sample. These analyses were done using XLStat (Addinsoft, Paris, France).

RESULTS

We previously reported the principles of the uptake of aroma compounds from model wine into EPDM sealing material and their incomplete desorption during cleaning, which bear the risk of subsequent contamination (Gottmann *et al*., 2021). It is the objective of this study to mitigate the absorption of aroma compounds by improved polymer materials and to enhance their removal through improved cleaning procedures. Studying the behaviour in sealings, we report concentrations of aroma compounds per volume (µg/cm^3). Due to different fillers, the density of the polymers varied by a factor of two (Supplemental Table 1).

1. Impact of added filling materials in EPDM (Experiment 1)

Aroma absorption from model wine into 18 experimentally manufactured EPDMs and in comparison to commercially available EPDM and optimised FKM (XP41) polymers is reported after 48 h (Supplemental Table 2). The first two principal components in Figure 1 explain 83 % variation of the studied aroma compounds. Examining the loading plot in the small Figure 1B, all aroma compounds behave in a similar way, with a strong correlation between eugenol and trans-cinnamaldehyde as well as among lactones, the ester and α-ionone. The first dimension in the score plot in Figure A describes primarily high absorption of aroma compounds on the right and low on the left side. Incorporation of Aktivit VM, kaolin, talcum, micro-cellulose, Carbon Black N990 and glass flakes into EPDM triggered a decreasing uptake as the filler proportion increased. The inverse effect was observed for Carbon Black N220, cork and PE. EPDM materials with high portions of micro-cellulose and kaolin revealed the lowest absorption of aroma compounds. According to Table 2 addition of fillings diminished the uptake of the least polar compounds α-ionone and γ-undecalactone by a factor of two. None of the customised EPDM materials could reach the low level of absorption shown by the optimised FKM (XP41), which diminished the uptake of aroma compounds compared to the commercial EPDM by 85 to 99 %.

2. Evaluation of Cleaning Parameters (Experiments 2 and 3)

The impact of duration and temperature of each cleaning agent prescribed by the GMP (BMEL, 2019) was studied using the commercial EPDM sealing.

2.1. Cleaning temperature and cleaning agent

The first PC in (Figure 2A) explains already 92.6 % of the total variation. It is mainly governed by the cleaning temperature with the hot (85 °C) agents on the left side, the moderate temperature of 55 °C in the middle and the cool treatments (22 °C) on the right side. Applying a long contact time of 24 h, exposure to alcoholic model wines (8 to 16 %), carbonised (6 g/L) and pure water achieved a comparable removal of aroma compounds as the hot but short treatments. The smaller loading plot in Figure 2B shows only minor differences among the seven aroma compounds, which only varies along PC2, explaining only 4 % of the total variance.

Agglomerative hierarchical clustering (Figure 2C) yielded four significant different clusters: The first two clusters are the non-treated sealing and the short cold treatment (30 min, 22 °C) with peracetic acid (PAA). The next cluster comprises all other cold treatments and short exposure to water and caustic soda at 55 °C, respectively. The exposure to oxidative additives for 30 min in 22 °C water did not improve the cleaning efficacy versus the commonly used citric acid and caustic soda. The most efficient 4th cluster comprises all hot (85°C and all 24 h lasting treatments as well as the citric acid solution at 55 °C.

The potential mitigation effect of oxidative agents was proven by the direct exposure to a watery solution of aroma compounds (Table 1). At 22 °C, α-ionone, *trans*-cinnamaldehyde and eugenol vanished completely after 30 min in the presence of chlorine dioxide and peracetic acid. Upon ozone exposure, sluggish degradation was observed over 3 days. On the contrary, for the three lactones and the ester, no significant changes occurred even after 3 days.

Studying the efficacy of different cleaning procedures at three temperature levels for 30 min, both the temperature and the cleaning agents themselves were highly significant (Table 2). However, the *F*-values for temperature exceeded, in general, the *F*-value for the cleaning agents by far.

In the case of the α-ionone, the temperature had only a minor enhancing effect (factor 2.5), while for the other aroma compounds, the factor rose to 15 (ethyl 2-methylbutanoate) and up to 100 (γ-undecalactone) or 133 (eugenol). This deviation is also backed by the highly significant interaction temperature × agent for all studied aroma compounds, indicating that the effect of temperature varies for different agents. Overall, the largest removal down to 12 % of the original aroma concentration within the EPDM polymer was observed for δ-decalactone and *trans*-cinnamaldehyde treated with 85 °C hot caustic soda solution, followed by a removal down to 17 % for eugenol. The least removal, only to 42 % of the original concentration, was measured for least polar α-ionone.

Although the removal of aroma compounds from EPDM polymers by oxidants was significant or highly significant except for the ester (Table 2), the low *F*-values and the infrequent significant mean comparisons show the overall limited effect of oxidants. Compared to water control, none of the oxidative additives achieved a significantly better removal than exposure to water. Only peracetic acid was often significantly less effective than pure water or oxidant enriched water.

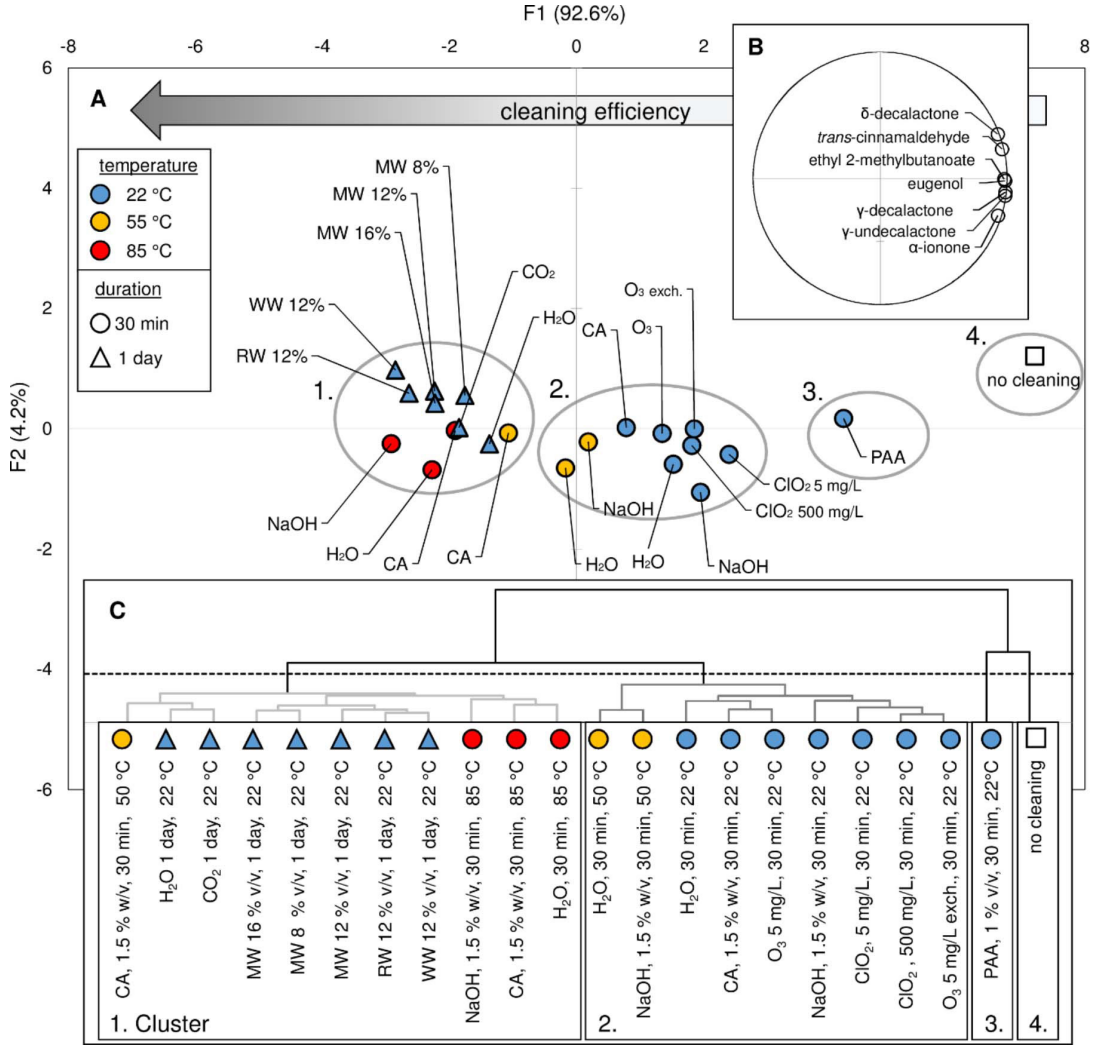


FIGURE 2. Observations (A) and loadings (B) of the principal component analysis of aroma compounds removed from EPDM using different cleaning agents, temperatures and times (n = 3). Grouping of cleaning parameters by agglomerative hierarchic clustering (C). Caustic soda solution (NaOH), citric acid solution (CA), ozonised water (O_3), chlorine dioxide solution (ClO_2), peracetic acid solution (PAA), model wine (MW), red wine (RW), white wine (WW) and carbonised water (CO_2).

2.2. Cleaning time

Due to the major effect of high temperature, the desorption over time was only studied at 85 °C over 60 min in pure water. For all aroma compounds, the decrease within the studied sealing lasted only for 20 min and reached a stable equilibrium (Figure 3). The percentage of removed aroma compounds varied between 62 % for α-ionone and 90 % for *trans*-cinnamaldehyde and was highly significant for all aroma compounds (Table 2). Exchanging the water after 30 min for another 30 min cleaning step at 85 °C did not trigger any further significant removal of aroma compounds from the sealings, except for the significant decrease from 34 % down to 27 % of the original concentration of γ-decalactone (Table 2).

Comparing the percentage of removed aroma compounds due to exposure to pure water for 30 min (control) and 24 hours, the delta varied significantly between 36 % further removal for ethyl 2-methylbutanoate and 12 % for δ-decalactone. Supplementing the water with alcohol by using model or commercial wine for the 24 h exposure, a further significant improvement was observed except for ethyl 2-methylbutanoate and δ-decalactone. The addition of 6 mg/L CO_2 to the water yielded only for ethyl 2-methylbutanoate and γ-undecalactone a further significant removal.

DISCUSSION

Diffusion phenomena in solid material are strongly dependent on the concentration gradient and are governed according to the first Fick's law (1) by the diffusion flux (*J*), the diffusion coefficient (*D*), the concentration (*c*) being active along the length and thickness of the matrix (*x*) (Sajilata *et al*., 2007, Licciardello *et al*., 2009, Karbowiak *et al*., 2010, Číhal *et al*., 2015).

(1) $J = -D\frac{\partial c}{\partial x}$

To minimise the diffusion flux *J* of aroma compounds into and within sealing polymers, the diffusion coefficient *D* is the only factor which can be freely modified. The concentration of aroma compounds is predetermined by the composition of the bottled aromatised beverage, while *x* is defined by the dimensions of the sealings which are installed within a bottling machine. To alter the diffusion coefficient *D,* we incorporated different filler substances into the polymer, which should mitigate best aroma absorption, but have as little as possible impact on material properties such as durability and flexibility. Increased crystallinity of the polymer due to interaction with appropriate filler substance diminishes absorption because, in crystalline phases, diffusion of aroma compounds is more hindered, as it is the case in amorphous phases in polymers (Charara *et al*., 1992, Richter and Schacker, 2016). Due to their nonpolar properties the incorporation of PE wax and cork into EPDM enlarged the absorption of volatiles, which is contradictory to the mitigation objective (Barker *et al*., 2001, Brajkovich *et al*., 2005, Blake *et al*., 2009, Karbowiak *et al*., 2010, Adams *et al*., 2019). The observed difference between Carbon Black N220 and N990 is rationalised by the fact that Carbon Black N220 consists of small particles with a larger surface per unit of weight, which enhances absorption versus the larger-sized N990 particles. Uptake of aroma compounds decreased largely by incorporation of micro-cellulose or kaolin into the EPDM polymer and absorption declined more effectively with a larger portion of both materials.

TABLE 1. Impact of contact time and oxidative agents on the concentration of aroma compounds dissolved in cleaning water.

		water mg/L	$O_{3\ aq}$ (5 mg/L) mg/L	$ClO_{2\ aq}$ (5 mg/L) mg/L	$ClO_{2\ aq}$ (500 mg/L) mg/L	PAA_{aq} (1 % v/v) mg/L
ethyl 2-methylbutanoate	30 min	1.3 ± 0.2 ab	1.5 ± 0.5 a	1.3 ± 0.2 abc	1.3 ± 0.1 abc	0.8 ± 0.7 bcd
	3 days	1.0 ± 0.1 abc	0.8 ± 0.2 bcd	1.6 ± 0.3 a	0.2 ± 0.1 d	0.7 ± 0.5 cd
α-ionone	30 min	2.4 ± 0.1 a	1.5 ± 0.2 b	nd [a]	nd	nd
	3 days	1.9 ± 0.1 b	0.6 ± 0.1 c	nd	nd	nd
trans-cinnamaladehyde	30 min	1.0 ± 0.1 a	0.5 ± 0.2 bc	1.0 ± 0.1 a	nd	nd
	3 days	0.8 ± 0.1 ab	0.4 ± 0.3 c	0.9 ± 0.1 a	nd	nd
eugenol	30 min	0.8 ± 0.1 a	0.3 ± 0.1 b	nd	nd	nd
	3 days	0.9 ± 0.1 a	0.3 ± 0.3 b	nd	nd	nd
γ-decalactone	30 min	12.3 ± 1.7 a	8.2 ± 1.1 a	9.2 ± 0.4 a	10.3 ± 0.5 a	8.4 ± 1.1 a
	3 days	9.3 ± 0.1 a	10.2 ± 0.3 a	8.6 ± 0.8 a	9.3 ± 1.8 a	7.8 ± 0.6 a
δ-decalactone	30 min	6.5 ± 3.1 a	5.2 ± 1.2 a	8.1 ± 1.6 a	7.7 ± 0.6 a	6.8 ± 0.9 a
	3 days	6.1 ± 0.1 a	2.5 ± 0.6 a	4.1 ± 0.9 a	5.9 ± 1.6 a	3.5 ± 0.5 a
γ-undecalactone	30 min	1.2 ± 0.2 a	0.9 ± 0.1 a	0.9 ± 0.0 a	1.1 ± 0.1 a	0.9 ± 0.1 a
	3 days	0.9 ± 0.1 a	0.8 ± 0.1 a	0.8 ± 0.0 a	0.8 ± 0.1 a	0.8 ± 0.1 a

[a] below the detection limit of the applied method (10 µg/L);
Mean values compared with Tukey HSD-test (α = 95 %); significant difference is indicated by different letters.

TABLE 2. Aroma compounds removal from EPDM during different cleaning steps (n = 3). Part 1/2

medium | temperature | duration	ethyl 2-methylbutanoate		α-ionone		*trans*-cinnamaladehyde		eugenol		γ-decalactone		δ-decalactone		γ-undecalactone	
	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³
no cleaning	100	(6.5 ± 0.6)	100	(41.4 ± 2.5)	100	(4.2 ± 0.2)	100	(2.9 ± 0.2)	100	(6.6 ± 0.1)	100	(2.8 ± 0.2)	100	(19.8 ± 0.3)
cleaning for 30 min														
water (22 °C) (control)	69	(4.5 ± 0.5) a	72	(29.8 ± 1.0) ab	40	(1.7 ± 0.1) ab	59	(1.7 ± 0.1) b	61	(4.0 ± 0.1) b	37	(1.0 ± 0.0) ab	62	(12.3 ± 0.2) b
water (50 °C)	50	(3.3 ± 0.3) b	62	(25.7 ± 1.9) bc	27	(1.2 ± 0.0) d	43	(1.3 ± 0.1) c	47	(3.1 ± 0.0) d	27	(0.7 ± 0.0) c	54	(10.7 ± 0.2) d
water (85 °C)	31	(2.0 ± 0.2) c	56	(23.1 ± 2.4) cde	11	(0.5 ± 0.1) e	21	(0.6 ± 0.1) ef	26	(1.7 ± 0.0) f	17	(0.5 ± 0.1) d	35	(6.9 ± 0.5) g
CA_{aq} 1.5 % w/v, (22 °C) [a]	56	(3.7 ± 0.2) b	58	(23.9 ±3.4) bcde	38	(1.6 ± 0.1) b	56	(1.7 ± 0.1) b	56	(3.7 ± 0.1) c	40	(1.1 ± 0.0) a	58	(11.4 ± 0.1) c
CA_{aq} 1.5 % w/v, (50 °C)	38	(2.5 ± 0.5) c	47	(19.5 ± 3.3) ef	26	(1.1 ± 0.1) d	38	(1.1 ± 0.3) d	40	(2.7 ± 0.1) e	26	(0.7 ± 0.1) c	47	(9.3 ± 0.5) f
CA_{aq} 1.5 % w/v, (85 °C)	35	(2.3 ± 0.2) c	50	(20.5 ± 2.8) def	14	(0.6 ± 0.0) e	23	(0.7 ± 0.0) e	27	(1.8 ± 0.0) f	30	(0.8 ± 0.0) bc	37	(7.4 ± 0.1) g
$NaOH_{aq}$ 1.5 % w/v, (22 °C)	54	(3.5 ± 0.4) b	84	(34.5 ± 1.0) a	41	(1.7 ± 0.0) a	65	(1.9 ± 0.2) a	71	(4.7 ± 0.0) a	38	(1.1 ± 0.0) a	71	(14.1 ± 0.1) a
$NaOH_{aq}$ 1.5 % w/v, (50 °C)	55	(3.6 ± 0.3) b	61	(25.4 ± 5.4) bcd	33	(1.4 ± 0.0) c	45	(1.3 ± 0.1) c	48	(3.2 ± 0.0) d	34	(1.0 ± 0.1) ab	51	(10.1 ± 0.3) e
$NaOH_{aq}$ 1.5 % w/v, (85 °C)	33	(2.1 ± 0.2) c	42	(17.3 ± 1.6) f	12	(0.5 ± 0.1) e	17	(0.5 ± 0.1) f	21	(1.4 ± 0.0) g	12	(0.3 ± 0.2) d	26	(5.1 ± 0.1) h
ANOVA														
temperature: *F*-value | *p*-value	155.2	***	45.8	***	1595.9	***	1589.3	***	1598.1	***	134.5	***	2040.0	***
medium: *F*-value | *p*-value	10.1	***	17.8	***	23.6	***	11.9	***	36.8	***	13.3	***	21.4	***
temperature × medium: *F*-value | *p*-value	16.4	***	11.2	***	16.6	***	26.1	***	47.2	***	27.1	***	139.5	***
oxidative cleaning agents for 30 min at 22 °C														
water (control)	69	(4.5 ± 0.5) a	72	(29.8 ± 1.0) ab	40	(1.7 ± 0.1) b	59	(1.7 ± 0.1) bc	61	(4.0 ± 0.1) b	37	(1.0 ± 0.0) b	62	(12.3 ± 0.2) b
PAA_{aq} (1 % v/v) [a]	79	(5.1 ± 0.4) a	81	(33.7 ± 0.9) a	55	(2.3 ± 0.2) a	86	(2.5 ± 0.6) a	85	(5.6 ± 0.2) a	73	(2.0 ± 0.2) a	85	(16.9 ± 1.8) a
$O_{3\,aq}$ (5 mg/L)	61	(4.0 ± 0.7) a	59	(24.3 ± 4.4) b	40	(1.7 ± 0.1) b	64	(1.9 ± 0.1) bc	63	(4.2 ± 0.1) b	41	(1.1 ± 0.0) b	65	(12.8 ± 0.4) b
$O_{3\,aq}$ (5 mg/L.), 6 x exch. [b]	60	(3.9 ± 0.4) a	65	(26.8 ± 3.8) ab	44	(1.8 ± 0.3) b	67	(2.0 ± 0.6) bc	66	(4.4 ± 0.3) b	48	(1.3 ± 0.3) b	68	(13.5 ± 1.9) b
$ClO_{2\,aq}$ (5 mg/L)	65	(4.2 ± 0.6) a	76	(31.4 ± 2.7) ab	46	(2.0 ± 0.1) ab	72	(2.1 ± 0.3) c	70	(4.7 ± 0.0) ab	47	(1.3 ± 0.0) b	71	(14.1 ± 0.4) ab
$ClO_{2\,aq}$ (500 mg/L)	60	(3.9 ± 0.8) a	68	(28.0 ± 2.3) ab	43	(1.8 ± 0.0) b	54	(1.6 ± 0.2) c	72	(4.8 ± 0.1) ab	47	(1.3 ± 0.1) b	73	(14.5 ± 0.1) ab
ANOVA														
medium: *F*-value | *p*-value	1.9	n.s.	4.2	*	7.6	**	7.3	**	14.1	***	17.6	***	6.5	**

Part 2/2

medium | temperature | duration	ethyl 2-methylbutanoate		α-ionone		*trans*-cinnamaladehyde		eugenol		γ-decalactone		δ-decalactone		γ-undecalactone	
	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³	%	µg/cm³
cleaning with water at 85 °C for														
5 min	58	(3.8 ± 0.3) a	72	(29.8 ± 1.7) a	35	(1.5 ± 0.0) b	59	(1.7 ± 0.0) a	63	(4.2 ± 0.0) a	43	(1.2 ± 0.0) a	69	(13.7 ± 0.4) a
10 min	51	(3.3 ± 0.4) a	63	(26.1 ± 2.6) ab	44	(1.9 ± 0.1) a	36	(1.1 ± 0.2) b	37	(2.4 ± 0.1) b	48	(1.3 ± 0.0) a	45	(8.8 ± 1.0) b
15 min	39	(2.5 ± 0.1) b	48	(19.8 ± 3.8) bcd	17	(0.7 ± 0.1) c	31	(0.9 ± 0.1) c	36	(2.4 ± 0.0) b	20	(0.6 ± 0.0) b	44	(8.8 ± 0.1) b
30 min	31	(2.0 ± 0.2) bc	56	(23.1 ± 2.4) abc	11	(0.5 ± 0.1) d	21	(0.6 ± 0.1) de	26	(1.7 ± 0.0) cd	17	(0.5 ± 0.1) b	35	(6.9 ± 0.5) c
45 min	36	(2.3 ± 0.2) b	55	(22.8 ± 1.6) abcd	14	(0.6 ± 0.0) cd	23	(0.7 ± 0.0) d	28	(1.9 ± 0.0) c	19	(0.5 ± 0.0) b	38	(7.6 ± 0.4) bc
60 min	25	(1.6 ± 0.0) c	45	(18.8 ± 2.3) cd	12	(0.5 ± 0.0) d	19	(0.6 ± 0.1) de	23	(1.5 ± 0.0) de	16	(0.5 ± 0.0) b	34	(6.8 ± 0.1) c
60 min, 1 x exch. [c]	21	(1.4 ± 0.0) c	38	(15.8 ± 2.7) d	10	(0.4 ± 0.0) d	16	(0.5 ± 0.1) e	20	(1.3 ± 0.0) e	17	(0.5 ± 0.1) b	27	(5.4 ± 0.3) d
ANOVA														
duration: *F*-value | *p*-value	44.0	***	10.2	***	327.9	***	246.9	***	237.5	***	220.4	***	86.8	***
storage for 1 day at 22 °C with														
water (control)	33	(2.2 ± 0.3) a	55	(22.9 ± 4.3) a	25	(1.1 ± ± 0.1) a	31	(0.9 ± 0.1) ab	31	(2.1 ± 0.1) a	25	(0.7 ± 0.2) a	43	(8.6 ± 0.8) a
water (6 g/L CO_2)	25	(1.6 ± 0.2) b	51	(21.2 ± 1.9) ab	23	(1.0 ± ± 0.0) ab	28	(0.8 ± 0.1) bc	28	(1.9 ± 0.0) a	27	(0.8 ± 0.1) a	37	(7.4 ± 0.1) b
model wine (8 % v/v)	35	(2.3 ± 0.2) a	37	(15.2 ± 1.3) bc	25	(1.0 ± ± 0.0) a	33	(1.0 ± 0.0) a	30	(2.0 ± 0.1) a	30	(0.8 ± 0.1) a	36	(7.2 ± 0.3) b
model wine (12 % v/v)	30	(1.9 ± 0.3) ab	39	(16.1 ± 2.2) bc	23	(1.0 ± ± 0.1) a	26	(0.8 ± 0.0) c	23	(1.5 ± 0.1) b	30	(0.8 ± 0.0) a	29	(5.7 ± 0.2) cd
model wine (16 % v/v)	32	(2.1 ± 0.2) ab	33	(13.8 ± 1.4) c	23	(0.9 ± ± 0.1) ab	32	(0.9 ± 0.1) ab	29	(1.9 ± 0.1) a	22	(0.6 ± 0.1) a	30	(6.0 ± 0.1) c
red wine (12 % v/v)	31	(2.0 ± 0.1) ab	35	(14.6 ± 1.2) c	18	0.8 ± 0.0) c	22	(0.6 ± 0.0) d	21	1.4 ± 0.0) b	27	0.7 ± 0.1) a	24	4.8 ± 0.1) de
white wine (12 % v/v)	27	(1.8 ± 0.1) ab	30	12.3 ± 1.0) c	19	0.8 ± 0.0) bc	19	0.6 ± 0.0) d	18	1.2 ± 0.0) c	30	0.8 ± 0.0) a	23	4.6 ± 0.1) e
ANOVA														
medium: *F*-value | *p*-value	4.3	*	9.9	***	11.1	***	43.9	***	64.0	***	2.4	n.s.	53.4	***

[a] citric acid solution (CA), caustic soda solution (NaOH), Peracetic acid solution (PAA);

[b] after 30 min, water was exchanged with fresh hot water at 85 °C;

[c] after every 5 min, the ozonised water was exchanged with fresh ozonised water;

Mean values compared with Tukey HSD-test (α = 95 %); the significant difference is indicated by different letters for each group considered: 1. 30 min cleaning; 2. oxidative cleaning agents; 3. time-dependent evaluation; 4. one-day storage.

Significance of the parameters cleaning temperature, cleaning medium and cleaning duration is indicated with n.s. (not significant), *p < 0.05), **p < 0.01 and ***p < 0.001.

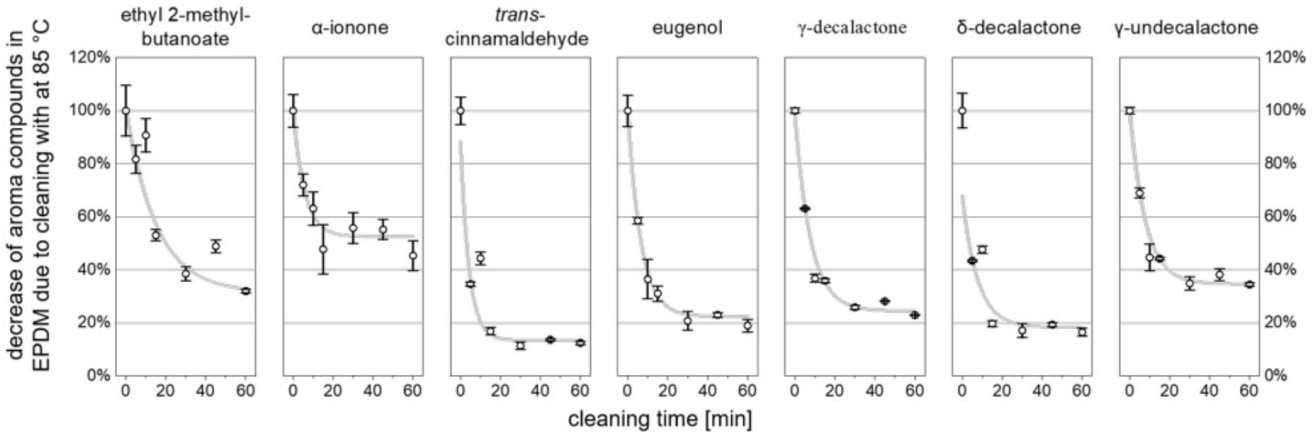


FIGURE 3. Depletion of absorbed aroma compounds from EPDM plates cleaned with hot water (85°C) over time (n = 3). Corresponding concentrations are listed in Table 2.

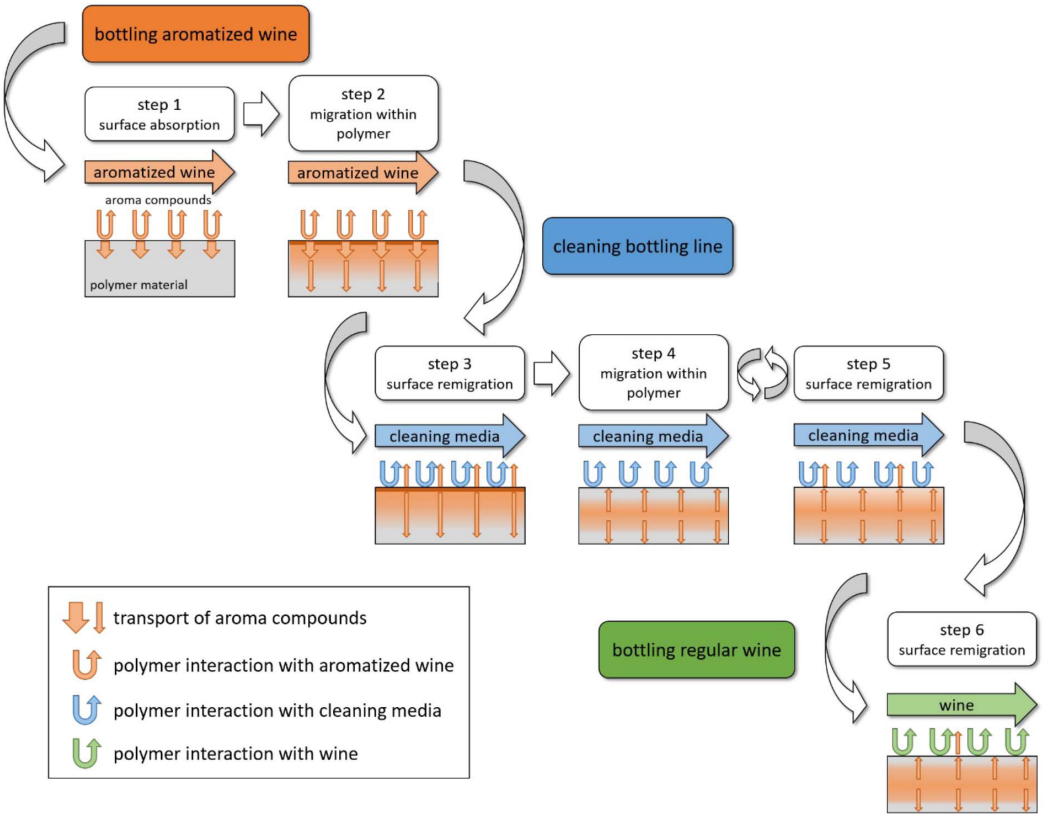


FIGURE 4. Model of the diffusion of aroma compounds in the sealing polymers during the bottling of aromatised wine and regular wine on the same bottling line, with an intermedial cleaning sequence.

This beneficial effect can be explained by the crystalline nature of cellulose and the layered silicate mineral kaolin ($Al_2Si_2O_5(OH)_4$). However, as displayed in Figure 1, this improvement could not achieve the same inertness towards the absorption of aroma compounds as it was measured for fluorine-based rubber (FKM). FKM sealings feature excellent thermal and chemical stability due to the high binding energy of the carbon-fluorine bond and the high density of the polymer. The linear molecular structure also favours semi-crystalline structures with high melting points, which hinders diffusion within the sealing (Abts, 2010). Although aroma carryover can be efficiently decreased by implementing FKM sealings into bottling equipment, FKM is not commonly used due to its approximately ten times higher price as well as its low fatigue resistance, which severely restricts its use in sealing moving parts of the bottling machine. The merits of FKM to mitigate the migration of several aroma compounds as reported in this paper has been so far only published in German technical literature, studying aroma carryover during simulated bottling of flavoured water just by sensory evaluation and no chemical analysis of aroma compounds in the sealing itself (Eckstein, 2011, Vetter, 2012, Freudenberg Sealing Technologies, 2016, Freund and Seckler, 2016, Beierle *et al*., 2020).

A comprehensive evaluation of the efficacy of removing aroma compounds from sealings by commonly applied cleaning agents, temperatures and duration of treatments for bottling equipment did not reveal any significant improvement toward pure water at the same temperature (Figure 2C). All cleaning agents by themselves, as well as their dissolvent water, are highly polar compounds. Deviating absorption of aroma compounds of varying polarity in the same EPDM sealing revealed that only 1 % of the most polar *trans*-cinnamaldehyde could be absorbed from a solution, while the least polar α-ionone was absorbed by 25 % (Gottmann *et al*., 2021). As cleaning agents such as citric acid, caustic soda and water exceed by large the polarity of the studied aroma compounds, it is obvious that neither the cleaning agents nor the water enter the sealing and, thus, cannot interact directly with absorbed aroma compounds in deeper layers of the polymer.

Oxidative cleaning additives commonly used in sterilisation and sanitation, such as ozone, peracetic acid (PAA) or chlorine dioxide, are discussed in the industry to enhance the removal of aroma compounds from sealings. Indeed, oxidative additives oxidise volatiles according to the Criegee mechanism resulting in an oxygen-substitution or a ring cleavage leading to a rise in polarity of the educts (Staehelin *et al*., 1984, Mvula and Sonntag, 2003, Sonntag and Gunten, 2012, Wenk *et al*., 2013). This effect was proven to be effective in the water by the direct exposure of aroma compounds to oxidative agents (Table 1). The unsaturated aroma molecules α-ionone, eugenol and *trans*-cinnamaldehyde were partially or completely degraded by oxidants, while the saturated lactones and ester remained unaffected in their concentration even throughout three days of contact. The observation that none of the treatments with added oxidants in this study could significantly enhance the depletion of aroma compounds from the sealings in comparison to water (Table 2) is another proof that these highly polar agents do not migrate into the EPDM polymers at all. In an earlier study, ozonated water (2 mg/L, 60 min, 20 °C) enhanced the removal of limonene from EPDM and silicone sealings, while for 1-hexanol, furfural and 4-vinylguaiacol only minor effects were observed (Nishijima *et al*., 2014). Our findings are corroborated by Stadler *et al*. (2020), who did not observe any change in oak volatiles in wine barrels using a short 2 min treatment with 10 mg/L ozonated water, although ozone penetrates porous oak better than solid EPDM polymers.

The fact that elevated temperature is by far the most effective cleaning parameter to remove aroma compounds is rationalised by the comprehensive definition of the diffusion coefficient D in Fick's law (2). D is determined by the maximum diffusion (D_0), the activation energy (E_A) required to initiate diffusion, the universal gas constant (R) and temperature (T). Besides the fixed R, D_0 depends on the matrix and E_A on the compound studied. Thus, the only parameter that can be freely varied is temperature.

(2) $D = D_0 \times exp^{-\frac{E_A}{RT}}$

The rising temperature warms up the sealing polymer and stimulates the diffusion of aroma compounds in the polymer matrix according to the Arrhenius equation with the rate constant (k) and the pre-exponential factor (A).

(3) $k = A \times exp^{-\frac{E_A}{RT}}$

As a result, depletion of aroma compounds close to the surface of the sealing will increase compared to a cleaning temperature at 55 °C or even 22 °C with lower diffusion coefficients for the aroma compounds in the polymer.

A more holistic approach can be considered using the second Fick's law. Derived from the first law with a static approach, the second Fick's law (4) predicts the change in concentration in a given area as a function of time (Sajilata *et al*., 2007, Licciardello *et al*., 2009, Karbowiak *et al*., 2010, Číhal *et al*., 2015).

(4) $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$

Studying the time-dependent depletion of aroma compounds at 85 °C in Figure 3, an equilibrium was revealed between absorption and depletion established after 20 minutes of cleaning. Bearing in mind that cleaning agents can only interact directly with aroma compounds remaining or emerging from deeper polymer layers on the surface of the sealing, diffusion of aroma compounds from deeper layers to the surface of the polymer seems to be the limiting step for the depletion of aroma compounds during the cleaning process. This diffusion is governed by the concentration gradient in the polymer matrix, the polarity of the aroma compounds and the density and crystallinity of the sealing polymer, which is a function of the polymer composition and added fillers. Any cleaning or oxidative agents are by far too polar to penetrate the sealing; only ethanol seems to be nonpolar enough to exert a minor depletion enhancement, but only after 24 h of exposure (Canals *et al*., 2005, Coelho *et al*., 2019). Highly nonpolar compounds such as α-ionone and γ-undecalactone seem to benefit more from this small effect which is confirmed by a two-fold increase in depletion. According to the principles of Le Chatelier, the exchange of the cleaning agents during the cleaning process should improve the cleaning efficacy to a large extent due to newly established equilibria. Surprisingly, exchanging the hot cleaning water after 30 min did not lead to further significant removal of the aroma compounds from the polymer.

We integrated all diffusion processes and equilibria in a general picture in Figure 4. Exposing the sealings to different aromatised wine-based beverages, absorption of aroma by the sealing is a function of their concentration in the liquid as well as a function of the chemical and physical features of the polymer such as polarity, crystallinity and density. The factor of time and temperature further governs how deep aroma compounds migrate into deeper layers of the polymer. As shown, cleaning agents and oxidative additives only act at the surface of the sealing. Primarily rising temperature and, to a smaller extent, time accelerate diffusion in the polymer and trigger a faster diffusion of aroma compounds from deeper layers towards the surface. Vice versa, enhanced diffusion

can also lead to a further migration into even deeper layers. Aroma compounds that migrate over a longer period of time due to the concentration gradient into deeper layers cannot be removed directly and need to migrate back to the polymer surface, which is exposed to the cleaning media.

Bottling the subsequent wine, desorption of aroma compounds from the polymer only occurs at the surface of the sealing. Relative cold bottling temperatures between 15-20 °C hinder a fast diffusion and, thus, limits the migration of aroma compounds from deeper layers of the polymer towards the sealing surface. Large volumes passing through the bottling machine facilitate a strong dilution of the few desorbed aroma compounds in the bottled wine.

CONCLUSIONS

The comprehensive study of aroma compounds varying in chemical structure and polarity revealed their absorption and desorption behaviour within the sealing polymer. A first strategy to mitigate aroma carryover is to increase the crystallinity and density of the sealing polymer to restrict the uptake and diffusion within the polymer. The most promising kaolin and cellulose fillers did not modify the physical properties of the sealing polymers. Statistical analysis of all cleaning parameters clearly proved temperature as the most important and effective factor, which was rationalised by different physical laws. None of the cleaning agents were able to improve the depletion of aroma compounds for the simple reason that they only act on the surface because they are too polar to penetrate the nonpolar sealing polymers. Only exposure to ethanol solution over a long time of 24 hours showed a minor benefit in aroma depletion. Based on the developed model, aroma compounds will never be completely removed from a sealing polymer because diffusion has no spatial orientation and only follows a concentration gradient. Thus, depletion of aroma compounds ceased after 20 minutes at high temperature, as diffusion to the sealing surface was too slow to deliver further aroma compounds from deeper layers and also led to diffusion in the contrary direction. Energy-consuming high cleaning temperatures can only be partially compensated by very long exposure periods of 24 h or even longer.

Considering the fact that complete depletion of aroma compounds from sealings is not possible, aroma carryover into the subsequently bottled wine cannot be prevented to 100 %. Thus, it requires further studies to determine the sensory relevance of aroma carryover through sensory tests and the application of odour-thresholds of aroma compounds determined in a wine matrix.

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