

Scalping of Hop Volatiles from Beer into Crown Cork Liner Polymers and Can Coatings

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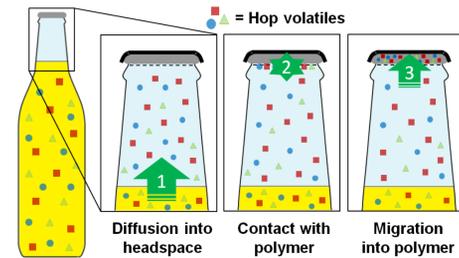
INTRODUCTION

Hop Aroma changes rapidly during storage and next to racemization, isomerization, and oxidation reactions, flavor scalping may be one of the culprits for these flavor changes.

Thermodynamically, scalping in beer systems can be divided into three phases, as shown in the figure. Consequently, the migration into the crown cork is mainly limited by two factors:

1. Volatility of the compound
2. Liability to migrate into the polymer

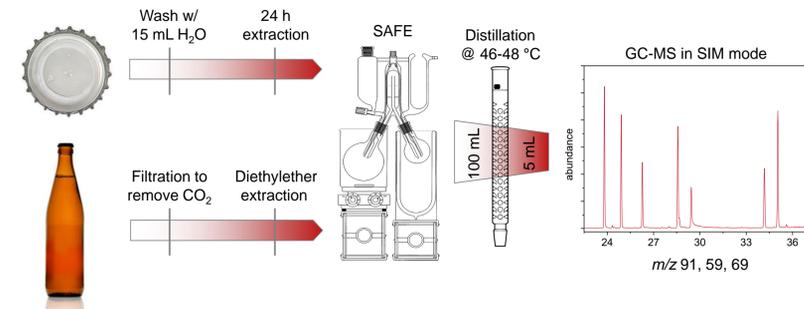
Object of the present study was to assess the sorption kinetics and liability of individual hop volatiles to migrate into polyethylene (PE) crown cork liner polymers and can coatings.



ANALYTICS

Hop essential oils in beers were quantitated using solvent-assisted flavor evaporation (**SAFE**) followed by GC-MS.

Crown liner and can coating polymers were carefully washed with bidistilled water to remove residual adhering liquid, extracted in diethyl ether for 24 h, and then also purified and analyzed using SAFE-GC-MS.

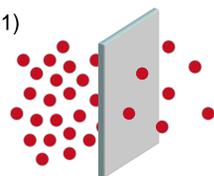


MODELLING APPROACH

The **aroma sorption kinetics** into crown cork liner polymers were modeled by applying Fick's Second Law of Diffusion for a Plane Sheet (eq. 1). The diffusion coefficient D can then be easily deduced from the equation.

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-D(2n+1)^2 \pi^2 t/l^2\} \quad (\text{eq. 1})$$

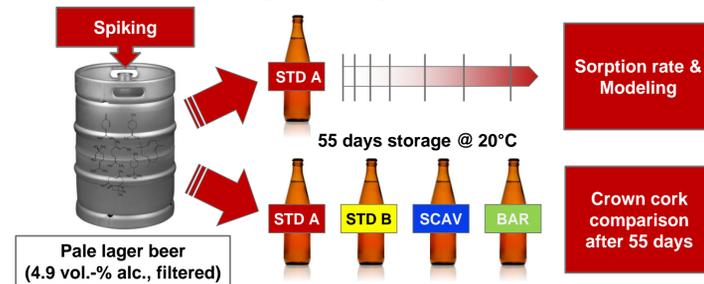
M_t : Total amount of components by a sheet at time t
 M_∞ : Equilibrium absorbed mass after infinite time
 D : Diffusion coefficient
 l : Film thickness of the polymer
 t : Time



EXPERIMENTAL I: SORPTION KINETICS & LINER COMPARISON

Pilsner beer low in hop aroma (all hop constituents < 5 µg/L) was spiked with a mixture of 500 µg/L of myrcene, limonene, linalool, α-terpineol, geraniol, t-caryophyllene, and α-humulene, bottled, and capped with low-density polyethylene (LDPE) crown cork liners. Hop volatiles were monitored then periodically during storage at room temperature.

Different liners were also tested: LDPE liner from a manufacturer A (**STD A**), LDPE liner from a manufacturer B (**STD B**), oxygen barrier high-density polyethylene (HDPE) liner (**BAR**), and an oxygen scavenger LDPE liner (**SCAV**).



EXPERIMENTAL II: CROWN CORKS VS. CAN LININGS

Bottled and canned highly-hopped ale beer both filled in 330 mL containers, were obtained from a Scottish brewery.

It was assured that the samples originated from the same bright beer tank. After the samples were obtained, they were stored for 46 days at room temperature under dark conditions and then analyzed.



RESULTS I: SORPTION KINETICS

All volatiles migrated into to liner polymer but to varying rates and maximum amounts. Already after one day of storage, contents ranged from 0.3 µg (geraniol) to 40.7 µg (limonene). After ca. 21 days, a maximum was reached for most of the volatiles.

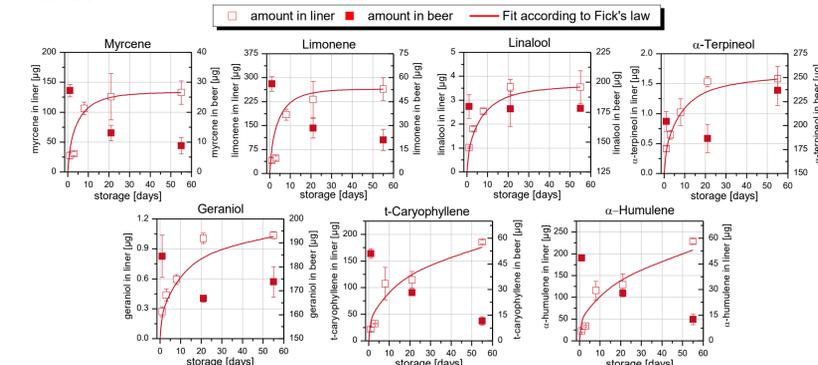


Figure 1: Hop monoterpene, sesquiterpene and terpene alcohol amounts absorbed into an LDPE liner polymer and amounts in beer as a function of storage time. Note that absolute amounts per bottle/crown cork and not concentrations are displayed. $N = 3$.

RESULTS I: SORPTION KINETICS (CONTINUED)

The **depletion** of myrcene, limonene, t-caryophyllene, and α-humulene in the beers can be traced back to scalping, while the decrease or increase of geraniol or α-terpineol, respectively, may be traced back to other reactions, such as proton-catalyzed isomerization. The amount of linalool remained unchanged but racemization (R-linalool → S-linalool) may have occurred.

The **absorption kinetic** was additionally modeled by fitting Fick's second law (eq. 1) to the experimental data. Table 2 depicts the deduced diffusion coefficients D , the amounts found at maximum M_{max} , and the root mean square error (RMSE).

Table 2: Model parameters as deduced from Fick's second law.

Polymer-volatile	Diff. Coeff. [cm ² /day]	M_{max} [µg]	RMSE/ M_{max} ×100 [1/µg]
LDPE-myrcene	1.17×e ⁻⁵	144.0	13.3
LDPE-limonene	1.32×e ⁻⁵	275.8	19.1
LDPE-linalool	0.84×e ⁻⁵	3.9	3.1
LDPE-α-terpineol	0.72×e ⁻⁵	1.6	2.3
LDPE-geraniol	0.49×e ⁻⁵	1.1	6.0
LDPE-t-caryophyllene	0.32×e ^{-5*}	184.4*	9.7
LDPE-α-humulene	0.26×e ^{-5*}	227.0*	9.7

*: because M_{max} was not reached, data was derived from linear fitting.

Table 1: Hop volatile changes in beer and crown corks.

Compound	Changes in liner	Changes in beer	Possible explanation
Myrcene	↑	↓	Scalping
Limonene	↑	↓	Scalping
Linalool	(↑)	→	(Racemization)
α-Terpineol	(↑)	↑	Isomerization
Geraniol	(↑)	↓	Isomerization
t-Caryophyllene	↑	↓	Scalping
α-Humulene	↑	↓	Scalping

- All substances diffused into the liner polymer
- Diffusion occurred according to Fick's 2nd law
- M_{max} dependent on polarity
- Diffusion coefficients dependent on other factors

RESULTS I: CROWN CORK COMPARISON

All liners displayed similar scalping tendencies with the exception of the oxygen barrier liner where myrcene and limonene were found at significantly higher levels.

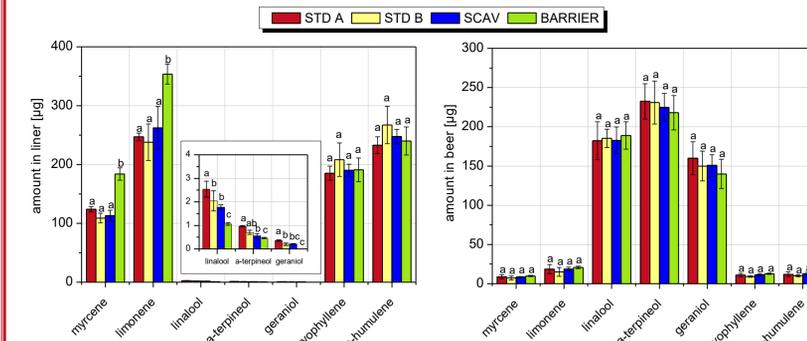


Figure 2: Hop volatiles in different crown cork liner polymers and in beers after 55 days of storage. Mean values are presented and error bars represent ± 1 standard deviation. Letters above bars indicate statistical significance at $p < 0.05$. $N = 3$.

Interestingly, in the beers none of the applied crown cork liner materials yielded significantly different amounts of hop constituents after 55 days of storage.

RESULTS II: CROWN LINER VS. CAN LINING

No variation on terpenoid sorption pattern between cans and bottles could be observed. No to very little geraniol, linalool and α-terpineol were detected in either packaging polymer. For both containers, myrcene was drastically reduced; however, the can coating polymer exhibited a significantly lower migration ($p < 0.05$) than the crown liner matrix. The low concentrations of limonene, t-caryophyllene and α-humulene may be traced back to the hop bill used for production.

Table 3: Hop volatiles found and percent absorption in beers, crown corks, and can coatings after 46 days of storage. $N = 3$.

Compound	Bottled Beer		Canned Beer	
	Beer [µg]	Polymer [µg]	Beer [µg]	Polymer [µg]
Myrcene	8.9 ± 1.0	279.4 ± 34.8	41.0 ± 1.1	101.6 ± 13.0
Limonene	0.3 ± 0.0	2.3 ± 0.2	0.5 ± 0.0	0.6 ± 0.0
Linalool	200.9 ± 8.9	1.2 ± 0.2	169.4 ± 7.7	0.7 ± 0.1
α-Terpineol	6.0 ± 0.1	< 0.3	5.6 ± 0.4	< 0.3
Geraniol	71.5 ± 4.5	0.8 ± 0.2	69.2 ± 6.7	0.5 ± 0.4
t-Caryophyllene	< 0.3	1.3 ± 0.1	< 0.3	8.7 ± 0.2
α-Humulene	< 0.3	5.3 ± 0.1	0.4 ± 0.0	0.8 ± 0.1

The sum of all individual volatiles examined in the liner materials or can lining and bottled beer or canned beer, respectively, was significantly higher in the beers from the bottles than from the cans with the exception of geraniol where no significant difference ($p < 0.05$) was found.

It is noteworthy that a 0.33 L beer can possesses a lining surface area of ca. **312.6 cm²** while a crown cork lining has a 'sorbing' surface area of ca. **2.25 cm²**. When taking the surface to volume ratios into consideration, it can be stated that the total amounts of hop volatiles sorbed per cm² are considerably lower in the beer can than in the crown cork liner.

Can linings and crown cork liner polymers were both susceptible to aroma scalping!

CONCLUSIONS

This study demonstrates the significance of flavor scalping in both, bottle-crown cap and can-coating beer systems. Especially the analyzed hydrocarbon fraction is susceptible to quick sorption by all closures or containers tested, whereas terpenoids showed little to minor migration tendency. The migration proceeds rapidly via the head space and no direct contact is necessary.

- Scalping leads to an aroma imbalance of originally adjusted hop aroma!
- There is clearly a need to improve closures to enhance flavor consistency!
- Be aware of this phenomenon when assessing (hop) aroma in beer!

See also: Philip C. Wietstock, Richard Glattfelder, Leif-Alexander Garbe, and Frank-Jürgen Methner
 Characterization of the Migration of Hop Volatiles into Different Crown Cork Liner Polymers and Can Coatings
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