Investigation into migration relevant compounds in plastic stoppers for wine

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Introduction

Since about one decade traditional cork or cork-agglomerate stoppers for wine have been increasingly substituted by metal caps, plastic stoppers or glass stoppers with a silicone sealant. One reason for that development is the transfer of a corky, musty off-flavor from contaminated cork stoppers (e.g. 2,4,6-trichloroanisole) into the bottled wine. The alternatives minimizes the risk of corky off-flavors in bottled wine. However, metal caps and glass stoppers need new filling technology whereas the plastic stoppers can be used with the same filling equipment used for cork stoppers, which is one reason for the success of plastic stoppers on the market.
The plastic stoppers usually are manufactured from thermoplastic elastomers (TPE), which are blends of several polyolefins (PO) of different molecular weight and density. In some cases the polyolefins are blended with polyethylene vinyl acetate (EVA) or other polymer types. The physical behavior of such TPEs is between rubber and plastics. Thermoplastic elastomers behave at room temperature like rubber but are thermoformable under exposure to heat. Due to the rubber like behavior, on the other hand, thermoplastic elastomers are expected to be high diffusive polymers. Due to this fact, additives, oligomers, slip agents and polymer impurities from the polymerization or the manufacturing process might migrate from the plastic stopper into the wine. Therefore the control of migration relevant substances in plastic stoppers is important.
Within the study, 35 plastic stoppers were investigated regarding migration relevant compounds. The plastic stoppers are used for glass bottled wine and were purchased from local super markets.

Method

0.5 g of the plastic stoppers were cut into small pieces and extracted with 5 ml of dichloromethane at 40 °C and with 5 ml of 95% ethanol at 60 °C, respectively. The extracts were stored overnight at 4 °C, decanted from the polymer and analyzed by gas chromatography (GC/FID). Butylhydroxyanisol (BHA) and Tinuvin 234 were used as internal standards added to the solutions before GC analysis. Gas chromatograph: HP 6890, column: DB 1, length: 20 m, inner diameter: 0.18 mm, film thickness: 0.18 µm, temperature program: 50 °C (2 min), rate 5 °C min^{-1}, 340 °C (10 min), pressure: 50 kPa helium, split: 10 ml min^{-1}. In addition the plastic stoppers were investigated for high volatile compounds by headspace gas chromatography. Identification was achieved by gas chromatography with mass spectrometric (MS) coupling.

Results

The inner surfaces of the stoppers were in direct contact to the bottled wine, which might lead to a sorption of wine compounds. Especially flavor compounds from the wine might migrate into the polymer during storage. Therefore minimum of 1 cm of the inner contact surface was cut off before extraction of the polymer.

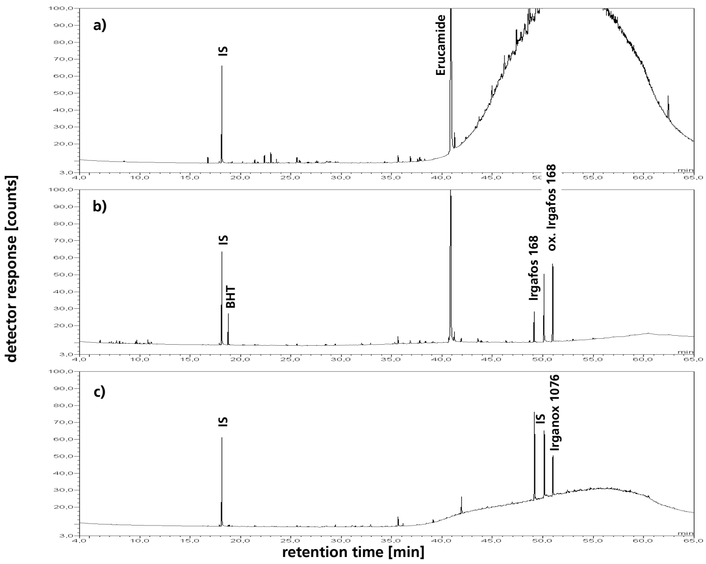

Figure 1: Example chromatograms of the dichoromethane extracts of cork stoppers

95% ethanol and dichloromethane were used as solvents for extraction of migration relevant compounds. Both solvents are suitable for such purposes and gave similar results for the quantification of additives. However, dichloromethane was more aggressive towards the extraction of the oligomers. Figure 1 shows three example chromatograms of the dichloro-methane extracts of the plastic stoppers. The upper gas chromatogram shows a high amount of oligomers resulting in a peak cluster between retention time of 40 min and 65 min. The compounds could not be separated with the applied method. However only mass fragments typically found in alkanes or alkenes were found. Such a signal pattern was found for three samples within the 35 investigated plastic stoppers. Most of plastic stopper samples (24) show a medium concentrated oligmers signal pattern as shown in Figure 1c. Eight samples shows no significant oligomeric signal pattern as shown in Figure 1b. In two samples, also siloxane oligomers could be determined.
The additives found in the investigated cork stoppers are listed in Table 1. The plastic stoppers contain antioxidant additives (e.g. di-*tert*-butylhydroxytoluene (BHT), Irgafos 168 or Irganox 1076) and in some cases the slip agent erucamide. In some case trace amounts of styrene and nonylphenol (isomeric mixture) were found. Plastic additives like phthalates were not determined in the investigated plastic stoppers.

Conclusions

The major difference in the investigated plastic stopper materials is the amount and concentration of oligomers. The signal pattern can be used to distinguish between different plastic stopper materials.

Table 1: Substances found in the investigated plastic stoppers (marked in yellow, if the compound was found in the polymer)

	BHT	Erucamide	Irgafos 168	Irganox 1076	additional compounds, remarks
1		X			
2					Irganox 1330
3			X	X	Figure 1, bottom
4		X			Figure 1, top
5	X	X	X	X	
6	X				Figure 1, middle
7	X				Only oxidized Irgafos 168
8			X	X	
9			X	X	
10				X	Traces of styrene
11			X	X	Traces of styrene
12	X	X	X	X	
13			X	X	
14			X	X	
15			X	X	
16			X	X	
17			X	X	
18			X	X	Traces of nonylphenol
19			X	X	Traces of nonylphenol, Tinuvin 326
20				X	Traces of nonylphenol
21			X	X	
22			X	X	
23			X		
24			X		
25			X		
26		X	X		
27			X		
28		X			
29			X		
30			X		
31					
32			X		
33			X		
34				X	Oleic acide amide
35	X			X	

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