Maximum concentrations of limonene in mineral water bottles containing post-consumer PET recyclates without organoleptic deteriorations

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Introduction

The flavor substance limonene is one of the key substances which are used to recognize or identify post-consumer recyclates. Most of the softdrinks contain limonene. Therefore, when the softdrinks are filled in polyethylene terephthalate (PET) bottles, the flavor compounds are absorbed into the bottle wall. As a consequence the recyclates of the PET softdrink bottles contain certain amounts of flavor compounds, especially limonene. But also recyclates of mineral water bottles contain limonene, because during recollection the mineral water bottles are in contact with softdrink bottles. However, recyclates from mineral water bottles show significantly lower limonene concentrations than recyclates from softdrink bottles.

In a European recyclate screening study[1] a maximum concentration of about 20 ppm of limonene was found in conventionally recycled PET. 98% of all investigated recyclate flake samples showed a limonene concentration of below 10 ppm. The average value of limonene in conventional recycled PET flakes was determined to be 2.9 ppm.

Conventionally recycled PET means, that the re-collected softdrink and mineral water bottles are ground and washed. Typically such recyclates are used for fiber and non-food packaging applications. If the recyclates should be re-used in the food packaging area, further deep-cleansing steps are necessary in order to reduce potential contaminants in the recyclates. Within these so-called super-clean recycling steps also the concentration of absorbed flavor substances are reduced.

Headspace gas chromatograms of a typical conventionally recycled PET flake samples and the corresponding super-clean recycled PET pellets are shown in Figure 1. Assuming a cleaning efficiency of 99% for limonene, which is typical for super-clean recycling processes for limonene, the residual concentration of limonene in the final product of the super-clean recycling process will be 29 ppb. The question is now, which bottle wall concentrations of limonene in the recyclate containing PET bottles will result in organoleptic deteriorations of bottled mineral water at the end of the shelf life.

In order to answer this question migration models were used to calculate the maximum bottle wall concentration of limonene at different storage conditions with are corresponding to the taste threshold limit of limonene in water. The taste threshold (retronasal) of D-limonene in water has been determined to 35 ppb[2].

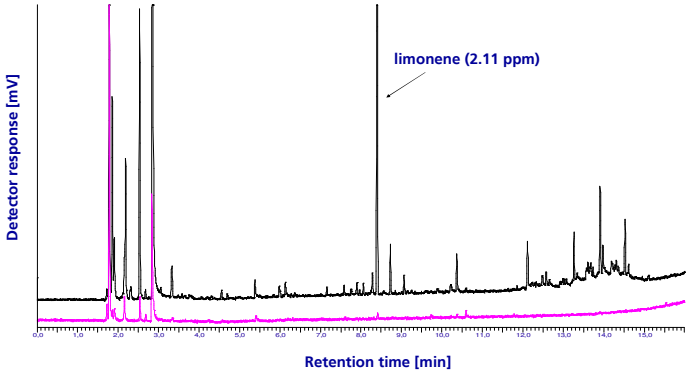

Figure 1: Headspace gas chromatograms of conventionally recycled post-consumer PET flakes (black chromatogram, limonene conc. 2.11 ppm) and super-clean recycled PET pellets from the above flakes (pink chromatogram, limonene conc. 0.03 ppm)

Method

1.0 g of PET samples are sealed in a 22 ml headspace vial and analyzed by headspace gas chromatography (HS GC) with flame ionization detection (FID). Gas chromatograph: Perkin Elmer AutoSystem XL, column: ZB 1, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm. Temperature program: 50 °C (4 min), rate 20 °C min-1, 320 °C (15 min), pressure: 50 kPa helium, split: 10 ml min-1. Headspace autosampler: Perkin Elmer HS 40 XL, oven temperature: 200 °C, needle temperature: 210 °C, transfer line: 210 °C, equilibration time: 1 h, pressurizing time: 3 min, injection time: 0.02 min, withdrawal time: 3 min. Quantification was achieved by external calibration using a limonene standards in toluene at concentrations of 0.1 ppm, 0.48 ppm, 0.97 ppm and 4.84 ppm. Detection limit 0.028 ppm, correlation coefficient r^2 = 0.9999.

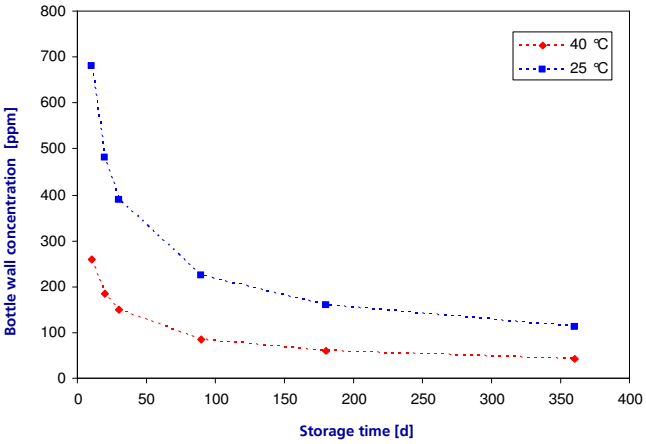

Figure 2: Calculated bottle wall concentrations of limonene corresponding to a migration of 35 ppb (taste threshold limit of limonene in water) into 10% ethanol as a function of the storage time and temperature (bottle volume 1000 ml, bottle wall surface 6 dm²)

Results

Figure 2 shows the correlation between the bottle wall concentration of limonene and the storage time at room temperature and 40 °C. The bottle wall concentration corresponds to a migration of 35 ppb, which is the taste threshold limit of limonene in water. For the calculation the PET specific parameters A_P' = 1 and τ = 1577 was used. The applied A_P value was derived from a comprehensive migration study[3]. The partition coefficient was assumed as K = 1 which represents good solubility of limonene in water (worst case).

As a result, the maximum concentrations of limonene in the PET bottle wall corresponding with the taste threshold limit are above 100 ppm for storage at root temperature and above 40 ppm at storage at 40 °C when the storage time is 1 year. At shorter storage times the maximum concentrations of limonene in the bottle wall are even significantly higher.

Conclusions

The taste threshold of limonene can never be reached from recyclate containing PET bottles. However, due to the fact, that limonene is detectable in nearly every conventionally post-consumer recyclate sample, limonene can be used as an internal indicator for the cleaning efficiency of the super-clean recycling process without artificial contamination (challenge test). The applied headspace GC/FID method is a suitable method for such a routine control of limonene in production.

References

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