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

Frank Welle
Fraunhofer Institute for Process Engineering and Packaging (IVV), Gigenhauser Straße 35, 85354 Freising, Germany, email: welle@iv.fraunhofer.de, phone: ++49 8161 491 724

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 PET softdrink bottles contain certain amounts of flavor compounds, especially limonene. But also recyclates containing 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 recylage 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 final product of the super-clean recycling process will be 29 ppb. The applied migration model was derived from a comprehensive migration study\(^2\). 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 containing 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 recycle 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 headscape GC/FID method is a suitable method for such a routine control of limonene in production.

References

2) A. Buettner, P. Schieberle, Evaluation of aroma differences between hand-squeezed juices from valencia late and naval oranges by quantitation of key odorants and flavor reconstitution experiments, Journal of Agricultural and Food Chemistry, 2001, 49(4), 2387-2394.
3) R. Franz, F. Welle, Migration measurement and modelling from polyethylene terephthalate (PET) into soft drinks and fruit juices in comparison with food simulants, Food Additives and Contaminants, 2008, 25(8), 1033–1046.

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 \(r^2 = 0.9999\).