

Test Report

The results contained in this test report are the property of the client. The publication of this report or the reproduction of extracts thereof is only permitted with prior written consent of the Fraunhofer Institute for Process Engineering and Packaging IVV.

Screening of post-consumer polystyrene towards migration relevant substances

Client:	W. u. H. Fernholz GmbH & Co. KG Folienwerk Schkopau Gebäude F16 06258 Schkopau
IVV Order no.:	PA-1569a-24
Date of order:	30.07.2024
Sample receipt:	30.07.2024
Testing period:	31.07.2024 – 14.08.2024
Date of report:	16.08.2024
Sample storage:	Remaining test material will be stored in the institute for six months.
Total pages:	11

The results relate only to the investigated samples as received.

1 Situation and Aim of the Study

Fernholz is using post-consumer polystyrene (PS) into new food packaging applications. The post-consumer PS will be behind a functional barrier of virgin PS.

Aim of the study was a screening of post-consumer polystyrene for the migration of relevant substances in the input (pellets) and output (multilayer sheets) materials.

2 Sample Material

The customer provided the following material:

- Sample 1: rPS Granulat, rPS 07-2024 Granulat, CO2RE 687 DI30 Charge DE08O2H002, Wareneingang 07-2024, input
- Sample 2: recyclathaltige ABA Folie, internes Kürzel HA8, Fertigungsauftrag 240063113, Herstellungsdatum/Probenahme 04.07.2024 ca. 13.31 Uhr ,Einsatz CO2RE 687 DI30 Charge DE08O2H002 33% Gesamtinhalt ergibt 25.4 rPS bezogen auf Gesamtfolie Foliencarge P00007055591 (Palette 414), output

According to the information provided by the customer, the analysed pair of samples are partially representative for the input / output materials from the decontamination installation.

3 Methods

3.1 Screening for volatile substances

Based on the accredited Fraunhofer IVV Method 1.334:2021-11

For each test 1.0 g of sample material was weighed into a headspace vial and analysed by headspace GC/FID under nitrogen atmosphere. Gas chromatograph: Perkin Elmer Clarus, column: ZB 1 (length 30 m, inner diameter 0.25 mm, film thickness 0.32 µm), temperature program: 50°C (4 min) to 320°C (15 min) with a heating rate of 20°C/min, pre-pressure: 50 kPa helium, split: 10 ml/min. Headspace Autosampler: Perkin Elmer TurboMatrix, oven temperature: 150 °C, needle temperature: 160 °C, transfer line: 170 °C, equilibration time: 1 h, pressurization time: 3 min, injection time: 0.02 min, withdrawal time: 1 min. Quantification of benzene, ethylbenzene, styrene, limonene and acetophenone was achieved by external calibration.

Identification was achieved by mass spectrometry. Mass spectrometer: Perkin Elmer Clarus GC-MS-System with electric ionization (EI), in full scan mode with mass range m/z 35-300. The identification of the mass spectra was done by comparison with the NIST spectra library (NIST/EPA/NIH Mass Spectral Library 2017). A confirmation of the suggested spectra by analysis of a respective standard was not done.

3.2 Screening for medium and low volatile substances

Based on the accredited Fraunhofer IVV method 1.337:2018-02

1.0 g of sample material was extracted with 10 ml of acetone and stored for 3 days at 60 °C. An internal standard of butylated hydroxyanisole (BHA) und Tinuvin 234 was added to an aliquot of the extracts, and analysed by gas chromatography with flame ionisation detection (GC-FID) for semi-volatile compounds. Gas chromatograph: Agilent 6890 GC/FID system, capillary column DB-1 (length 30 m, inner diameter 0.25 mm, film thickness 0.25 µm), temperature programme: 50 °C (2 min up to 340 °C (10 min) with a heating rate of 10 °C/min. Peaks of interest were semi-quantified using the internal standard BHA. This method is valid for organic components with a molecular weight of approximately 150 to 700 g/mol. Quantification of styrene was achieved by external calibration.

The identification of the main compounds was done by GC analysis coupled with mass spectrometry. GC/MS-System: ThermoFinnigan SSQ, column: Optima-5-MS (length 30 m, inner diameter 0.25 mm, film thickness 0.25 µm), temperature programme: 50 °C (2 min up to 340 °C (10 min) with a heating rate of 10 °C/min. Full scan mode, mass range m/z 40 - 800. The identification of the spectra was done by comparison with the NIST spectra library (NIST/EPA/NIH Mass Spectral Library 2017). A confirmation of the suggested spectra by analysis of a respective standard was not done.

4 Results

4.1 Screening for volatile substances

The screening for volatile organic compounds in the investigated samples was achieved by headspace gas chromatography. The applied method is able to detect substances up to about 250 g/mol. The headspace gas chromatograms are shown in Figure 1 to Figure 2.

Neat standard substances were used for quantification of benzene, ethylbenzene, styrene, limonene and acetophenone. Their concentrations are summarized in Table 1. These concentrations were derived from a standard addition calibration.

For all other substances determined in the recyclate samples the following semi-quantification procedure was applied. The limonene standard was used to semi-quantify the substance peaks determined in the investigated recyclate samples by external calibration. For this purpose, the counts per ppm (mg/kg) were calculated from a standard calibration curve of limonene. These counts per ppm were subsequently applied to the area counts of all other substance peaks. By following this procedure it is possible to quantify also substance peaks which cannot be identified or in case that standard substances are not available. The results of the semi-quantification are given in Table 2.

It is important to note, that this quantification is a semi-quantification of the substance peaks determined in the headspace gas chromatograms. The method is over-estimative for substances with retention times smaller than that of limonene. The over-estimative factors for benzene, ethylbenzene and styrene can derived from the comparison with the results from Table 1 (standard addition method). For limonene the results of the semi-quantification are in good

agreement with the standard addition method. For substances with greater retention times like acetophenone the semi-quantification method is slightly under-estimative. Substance peaks with retentions time greater than 10 min cannot be semi-quantified with this semi-quantification method.

The results in Table 1 have to be considered more accurate.

Sample 1 (pellets) shows lower amounts of substances compared to Sample 2 (sheet). The additional substances peaks which are in most cases related to degradation of the PS polymer. It should be noted, that sample 2 is a multilayer sheet and the food contact side is virgin PS.

Table 1: **Quantification** of benzene, ethylbenzene, styrene, limonene and acetophenone in the investigated recycle samples

	Concentration [mg/kg]	
	Sample 1	Sample 2
benzene	<0.07	<0.07
ethylbenzene	19.0 ±0.3	48.1 ±3.4
styrene	185 ±3	244 ±4
limonene	<0.2	<0.2
acetophenone	1.2 ±0.1	2.0 ±0.5

Table 2: Results of the identification / characterisation and **semi-quantification** of volatile substances in the investigated recycle samples

R _t [min]	Identification	Semi-quantification [mg/kg]	
		Sample 1	Sample 2
1.72	2-methyl-1-propene (isobutene)	<1	4.2
1.82	ethoxy ethene*	<1	6.1
3.08	2-butenal	<1	1.0
3.84	toluene*	2.9	1.6
4.50	hexanal	<1	1.2
5.20	not identified (no peak in MS)	<1	1.5
5.60	ethylbenzene*	29.2	71.6
5.75	1,3-dimethylbenzene	1.4	<1
6.04	styrene*	216	290
6.12	2-heptanone	1.6	<1
6.64	isopropylbenzene*	2.6	1.7
6.92	benzaldehyde	<1	2.5
7.08	n-propylbenzene*	1.7	<1
7.62	beta-myrcene	<1	1.3

R _t [min]	Identification	Semi-quantification [mg/kg]	
		Sample 1	Sample 2
13.73	styrene dimer*	/	/
13.92	styrene dimer*	/	/

* substance also detectable in virgin HIPS

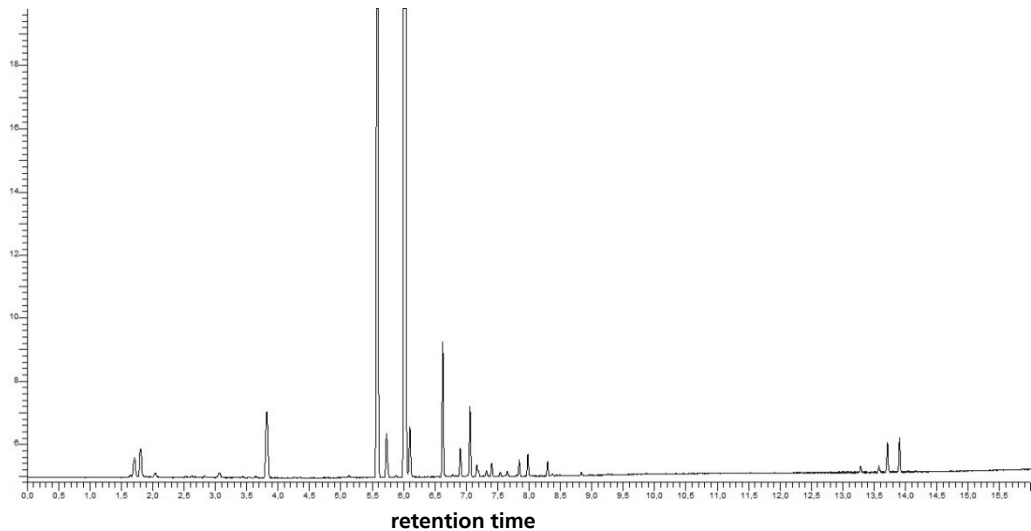


Figure 1: Headspace gas chromatogram of sample 1

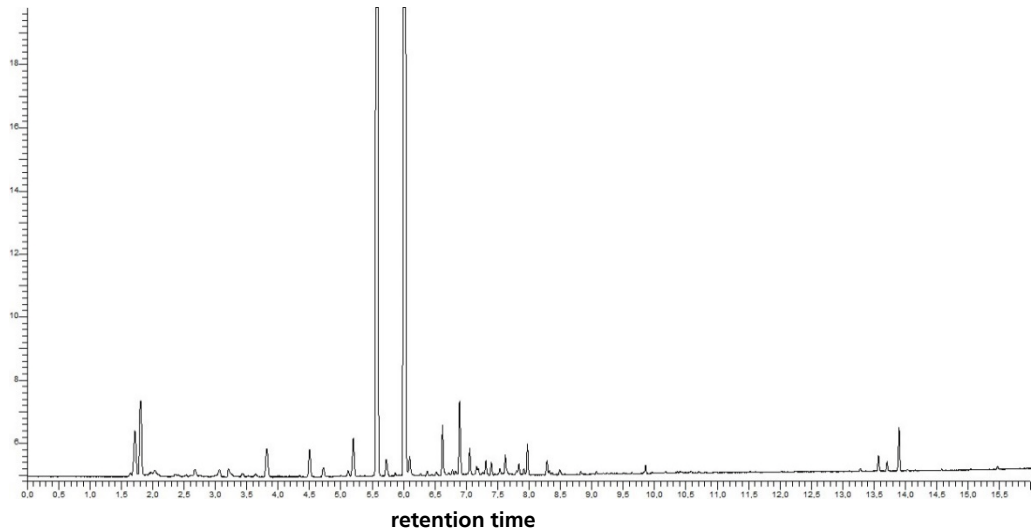


Figure 2: Headspace gas chromatogram of sample 2

4.2 Screening for medium and low volatile substances

In addition to the headspace measurements, the extracts of the sample materials were analysed for medium and low volatile substances. The applied method is able to detect substances between 150 g/mol and about 750 g/mol. Semi-quantification was achieved by comparison of the detector response of the internal standard BHA compared to the area counts of the substance peaks.

Styrene monomer was additionally quantified via external calibration. The results are given in Table 3.

The relative response factors for more than 50 substances versus the response of BHA using a non-polar column (such DB 1) was investigated in a previous published study^[1]. These were found between 0.41 and 1.36 at a mean of 0.89 ± 0.28 (without alcohols). The response factor between styrene and BHA was determined as 1.31; this explain the difference in the quantitative and semi-quantitative results for styrene showed in Table 3 and Table 4.

The results in Table 3 have to be considered more accurate.

Looking at the (semi-)quantification values for styrene obtained by headspace analysis (Table 1 and Table 2) it can be noted that these are significantly lower compared to the values obtained by solvent extraction. These could be explained by an incomplete extraction of the residual monomer from the analysed granulate (not milled) when using headspace. Therefore the results showed in Table 3 have to be considered more accurate.

The gas chromatograms of the representative gas chromatograms of the acetone extracts of the samples are shown in Figure 4 to Figure 5. Identified substance peaks are given in Table 4. The concentrations of the other substances were too low for an unambiguous identification.

Table 3: **Quantification** of styrene in the investigated recycle samples

	Concentration [mg/kg]
Sample 1	363 ± 7
Sample 2	340 ± 2

It is important to note, that acetone was used as an extraction solvent. Acetone is very aggressive and significantly swells polystyrene which leads to an exhaustive extraction of the samples. The results of the semi-quantification are given in Table 4. The results for the samples are given as mean values with the standard deviation of investigated samples, which are analysed each twice.

Most of the identified substance peaks in the samples were well-known polystyrene substances e.g. oligomers, which are typical also for virgin polystyrene samples.

^[1] Anita Gruner, Chan Suk Yoon, Angela Störmer, Roland Franz. Semi-quantitative determination of potential migrants in food packaging materials - Part 2: Semi-volatile compounds. Poster presentation at the ILSI Food Packaging Conference 2008.

Table 4: Results of the identification / characterisation and **semi-quantification** of medium and non-volatile substance substances in the investigated recycle samples

Peak	Identification	Concentration [mg/kg]	
		Sample 1	Sample 2
styrene	styrene (monomer)	528 ±8	489 ±3
A	dimer, not clearly identified but styrene oligomer masses	18.0 ±1	15.5 ±2
oligo 1	dimer, not clearly identified but styrene oligomer masses	28.7 ±3	62.1 ±1
oligo 2	dimer, not clearly identified but styrene oligomer masses	143 ±8	135 ±22
oligo 3	dimer, not clearly identified but styrene oligomer masses	205 ±5	254 ±1
B	hexadecanoic acid	63.4 ±8	248 ±9
C	octadecanoic acid	38.7 ±15	131 ±6
oligo 4	isomer of 1-phenyl-4-(1'-phenylethyl)tetraline (trimer)	1312 ±13	1419 ±16
oligo 5	isomer of 1-phenyl-4-(1'-phenylethyl)tetraline (trimer)	2650 ±53	2823 ±32
oligo 6	isomer of 1-phenyl-4-(1'-phenylethyl)tetraline (trimer)	731 ±6	801 ±8
oligo 7	isomer of 1-phenyl-4-(1'-phenylethyl)tetraline (trimer)	331 ±3	376 ±4
oligo 8	isomer of 1-phenyl-4-(1'-phenylethyl)tetraline (trimer)	70 ±46	104 ±1
D	trimer, not clearly identified but styrene oligomer masses	60.1 ±1	48.0 ±7
E	trimer, not clearly identified but styrene oligomer masses	58.5 ±1	45.3 ±10
F	Irgafos 168	4.0 ±2	74.8 ±6
G	oxidized Irgafos 168 and Irganox 1076 (co-eluting)	<1	<1
H	1,3,5-triphenylcyclohexane	336 ±25	373 ±16

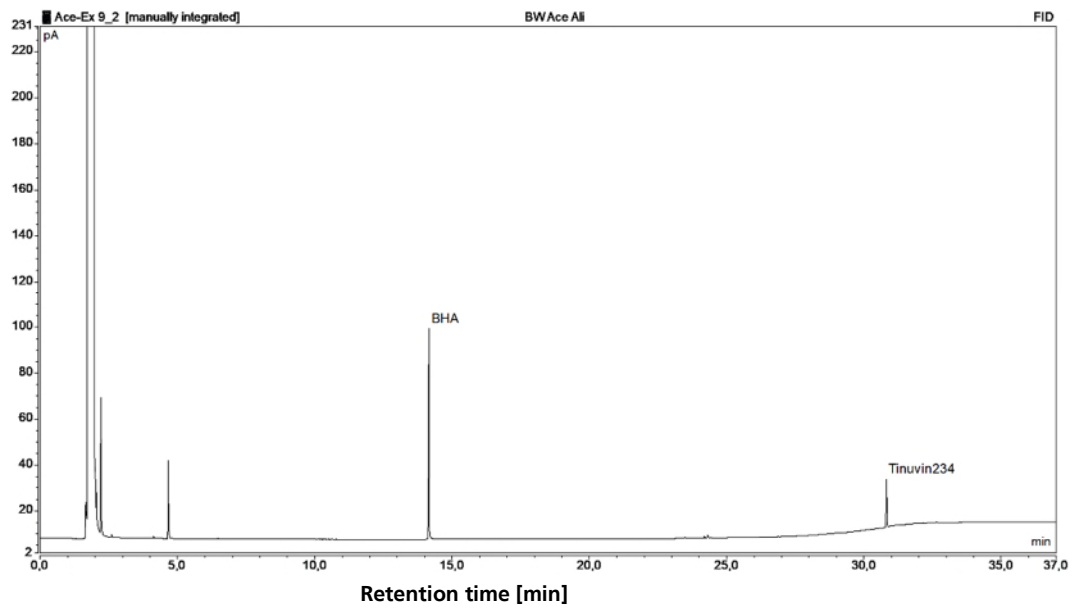


Figure 3: Gas chromatogram of the acetone solvent blank

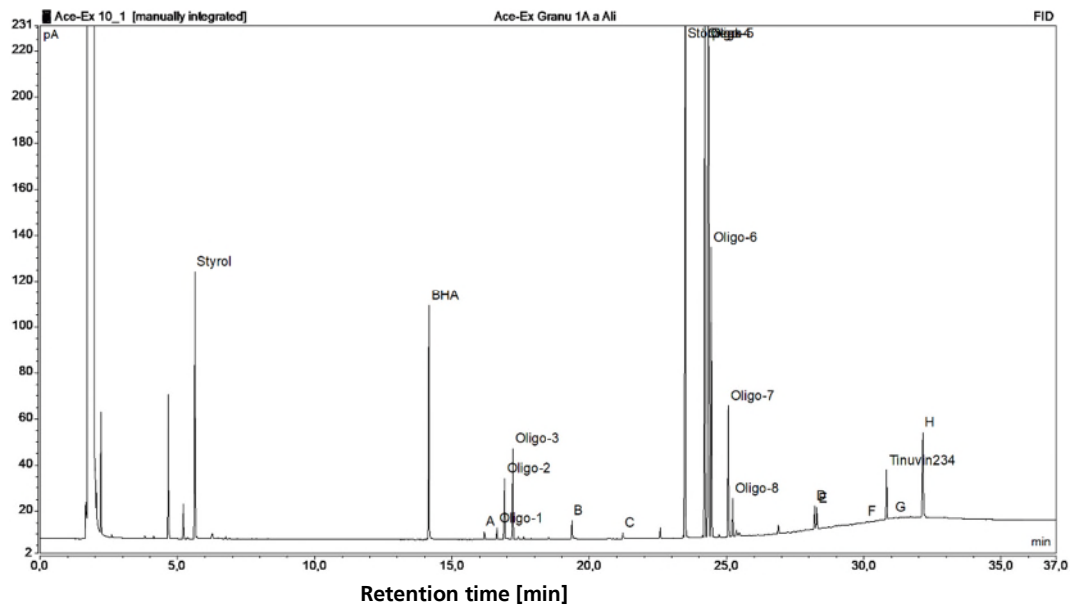


Figure 4: Gas chromatogram of the acetone extracts of sample 1

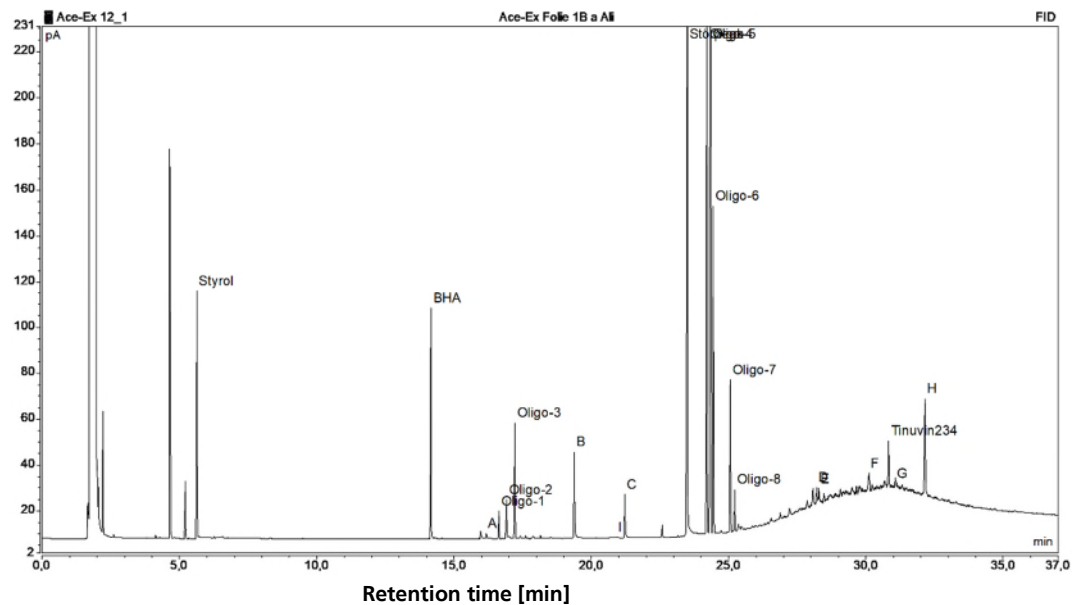


Figure 5: Gas chromatogram of the acetone extracts of sample 2

5 Discussion

Within this study, impurities of input materials and output materials of a PS super-clean recycling process were monitored regarding to migration relevant substances. The investigated samples were analysed by use of non-target screening methods. The substance peaks were semi-quantified by use of standard substances like limonene (headspace GC) and BHA (extraction followed by GC). These multi-standards are necessary, because it is impossible to calibrate each of the substance peaks with neat standard substances of each of the individual peaks.

To determine the threshold limits for each of the individual substances in the material, the maximum concentration in the recyclates was calculated, which corresponds to the maximum migration (concentration in food at the end of shelf life) for genotoxic compounds with a toxicological threshold limit of $0.0025 \mu\text{g}$ per kg body weight per day. This approach is similar to the evaluation of post-consumer PET in direct food contact published by EFSA^[2].

The maximum concentration of substances peaks in post-consumer recyclates corresponding to a migration limit were calculated after storage for 40 days at 6°C for a toddler with 10 kg body weight consuming 250 g yogurt per days for a PS cup with 100% recyclate. This results in a migration threshold limit of $0.1 \mu\text{g/l}$. In the final step, the maximum concentration in PS were calculated which

^[2] EFSA CEF Panel (EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids). Scientific Opinion on the criteria to be used for safety evaluation of a mechanical recycling process to produce recycled PET intended to be used for manufacture of materials and articles in contact with food. *EFSA Journal*, **2011**, 9, 2184.

corresponds to the migration threshold limit of 0.1 µg/l. The results are given in Table 5.

As can be seen from the gas chromatograms several substance peaks were detected in the samples. However, only substance peaks are relevant, which have concentrations above a threshold concentration in the material. Most of the detected substance have concentrations below or far below of such a threshold concentration. The threshold concentration depends on the storage conditions of the recycle containing packaging material and the exposure scenario applied.

EFSA is using the A_p prediction model for the calculation of the maximum concentration on the material. This A_p model is over-estimative and a general over-estimative factor of 5 is considered by EFSA. In a scientific publication, the over-estimative factors for HIPS has been experimentally determined^[3]. Within this publication, it could be shown that the over-estimative factors of the A_p model are much higher than 5 applied by EFSA for PET. The over-estimative factors at 5 °C were determined to 20.8 (toluene), 14.2 (chlorobenzene), 16.1 (styrene), 456 (phenyl cyclohexane), 271 (benzophenone) and >1130 (methyl stearate). The maximum concentration in the recycle was also calculated with a worst-case over-estimative factor of 14.2.

It is important to note, that the maximum concentrations in Table 5 are for genotoxic compounds or non-identified substance, where structural information for a toxicological classification are lacking. All identified substances, where a genotoxic alert can be excluded, have significantly higher threshold limits (Cramer class II substances). Applying the threshold of toxicological concern (TTC) concept, the threshold limit is by a factor of 600 higher.

For the worst-case calculation, it can be concluded, that substance peaks with a concentration below of 3 mg/kg in the PS material are not of interest, because they cannot exceed the migration threshold for genotoxic substances at the end of the shelf life. Therefore, only substance peaks with concentrations above 3 mg/kg are relevant for exposure evaluation and should be included into the monitoring report. It is important to note, that the 3 mg/kg threshold limit is for small substances like toluene. Higher molecular weight substances have much higher threshold limits due to the lower mobility in applied diffusion model and their consequent higher over-estimative factors.

Therefore only substance peaks with concentrations above 3 mg/kg are relevant for exposure evaluation and should be included into the monitoring report. In addition, it gets obvious that only low molecular weight substances are relevant for migration. Similar to PET, the cut off is around 200 g/mol. Therefore screening for volatile substances by use of headspace gas chromatography should be the method of choice for the monitoring of post-consumer PS recycles.

Taking into account the modelling of the migration and the over-estimative factors, no criticalities were determined in either the input material or the final product. In addition sample 2 is a multilayer sheet and the food contact side is virgin PS.

^[3] F. Welle, Recycling of post-consumer polystyrene packaging waste into new food packaging applications – Part 1: Direct food contact. *Recycling*, **2023**, 8(1), 26

Table 5: Maximum concentration of substances peaks in post-consumer PS recyclates corresponding to a migration limit of 0.10 µg/l after storage for 40 days at 6 °C for a toddler with 10 kg body weight consuming 250 g yogurt per days for a PS cup with 100% recycle

Molecular weight [g/mol]	Substance	Maximum concentration [mg/kg]		
		genotoxic, over-estimative factor of 5	genotoxic, over-estimative factor of 14.2	Cramer III, over-estimative factor of 5
92	toluene	1.082	3.074	649
100	fictive	1.156	3.284	694
113	chlorobenzene	1.283	3.643	770
119	chloroform	1.344	3.816	806
152	methyl salicylate	1.709	4.853	1025
160	phenyl cyclohexane	1.803	5.119	1082
182	benzophenone	2.087	5.928	1252
200	fictive	2.339	6.642	1403
250	fictive	3.143	8.926	1886
298	methyl stearate	4.074	11.570	2444
350	fictive	5.303	15.059	3182
400	fictive	6.712	19.063	4027
450	fictive	8.411	23.888	5047
500	fictive	10.410	29.563	6246

6 Signature

Fraunhofer Institute for
 Process Engineering
 and Packaging IVV

Freising, 16.08.2024

Dr. Frank Welle
 Head of Department Product Safety and Analytics

Dr. Valeria Guazzotti
 authorized Scientist Migration