Test Report

Determination of the cleaning efficiency of the Versalis polystyrene decontamination technology

Client:	Versalis S.p.A. Stabilimento di Mantova, Via Taliercio, 14 46100 Mantova (MN), Italy
Order No.:	PA-1430a-23 rev.
Date of order:	31.05.2023
Samples:	12.06.2023 (100 kg HIPS pellets) 07.09.2023 (Challenge test samples)
Date of the report:	05.12.2023

The results related to the investigated samples as received.

1 Situation and Aim of the Study

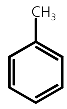
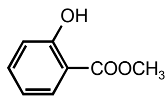
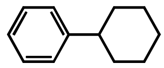
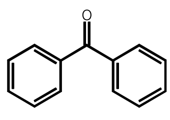
Versalis has developed a decontamination technology for post-consumer polystyrene (PS).

Aim of the study was the determination of the cleaning efficiency of the investigated polystyrene decontamination technology.

2 Sample Material

The cleaning efficiency is usually determined by a so-called challenge test by artificial contamination. The surrogates are summarized in Table 1.

Table 1: Model contaminants for the challenge test

Surrogate	M_W[a]	Structure	Functional Group	Physical properties
Toluene	92.1		aromatic hydrocarbon	volatile, non-polar
Chlorobenzene	112.6	C_6H_5Cl	halogenated aromatic hydrocarbon	volatile, medium-polar
Methyl salicylate	152.2		aromatic ester	non-volatile, polar
Phenyl cyclo-hexane	160.3		aromatic hydrocarbon	non-volatile, non-polar
Benzophenone	182.2		aromatic ketone	non-volatile, polar
Methyl stearate	298.5	$CH_3(CH_2)_{16}COOCH_3$	aliphatic ester	non-volatile, polar

[a]Molecular weight in g/mol

The challenge test was performed with contaminated PS pellets. 100 kg of PS pellets were contaminated according to the following procedure: The 100 kg of pellets were filled into 5 barrels (20 kg each). To each of the barrels, a mixture of 20 ml toluene, 20 ml, chlorobenzene, 20 ml methyl salicylate, 20 ml phenyl cyclohexane, 20 g benzophenone, and 20 g methyl stearate stearate was given. Subsequently the barrels were sealed and stored for 7 d at 50 °C. The sealed barrels were turned/rolled in regular terms. The contaminated PS pellets were combined into one barrel and shipped to Versalis.

3 Sample Material

The investigates samples are summarized in Table 2.

Table 2: Challenge Test samples

sample	Description
Sample C1a-C5b	contaminated PS pellets drawn at Fraunhofer directly after contamination (10 samples)
Sample 0	PS pellets, contaminated input material drawn at Versalis before decontamination
Sample 1	PS strands
Sample 4	PS strands
Sample 7	PS strands
Sample 9	PS strands
Sample 11	PS strands
Sample 11 BIS	PS strands
Sample 21	PS strands

4 Method

Each PS material sample was analyzed twice in the following way: 1.0 g of each PS sample was placed in a 10 ml glass vial. 10.0 ml acetone was given to the PS material and stored for 3d at 60 °C. The extracts were analyzed by GC/FID. Gas chromatograph:Agilent 6890, column: Mx 1 - 25 m - 0.25 mm i.d. - 025 µm film thickness, temperature program: 50 °C (2 min), rate 10 °C min^{-1}, 340 °C (10 min), pressure: 50 kPa hydrogen, split: 10 ml min^{-1}. Quantification was achieved by external calibration using standard solution of the neat surrogates in acetone. The detection limits were determined according to DIN 32645. The results are given in Table 3.

Table 3: Analytical detection limit of the surrogates in PS samples

surrogate	detection limit [mg/l]
toluene	0.1
chlorobenzene	0.1
styrene	0.2
methyl salicylate	1.8
phenyl cyclohexane	0.1
benzophenone	1.7
methyl stearate	1.0

5 Results

5.1 Challenge Test

The surrogate concentrations determined in the investigated challenge test sample are given in Table 4. The mean value of the contaminated samples C1a-C5b was used for the calculation of the cleaning efficiencies.

The gas chromatograms of the investigated samples are given in Figure 1 to Figure 20. Butylated hydroxyanisol (BHA, Retention time R_t = 13.5 min) and Tinuvin 234 (R_t = 30.0 min) were added as internal standards to the extracts.

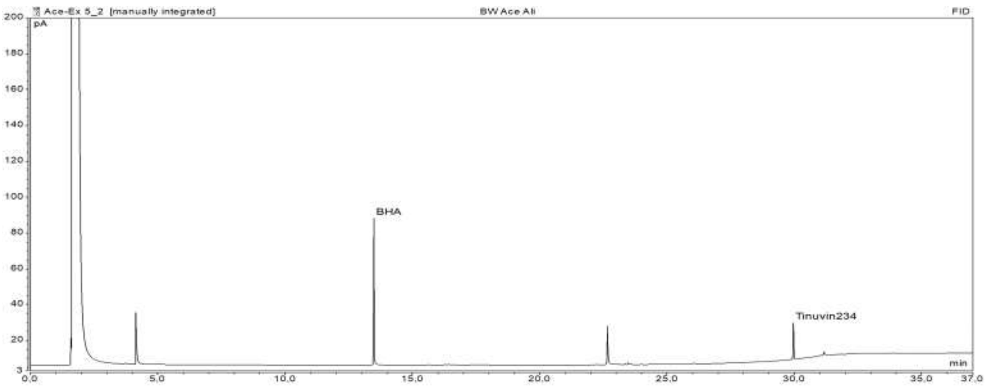


Figure 1: Gas chromatogram of the solvent used for extraction (blank)

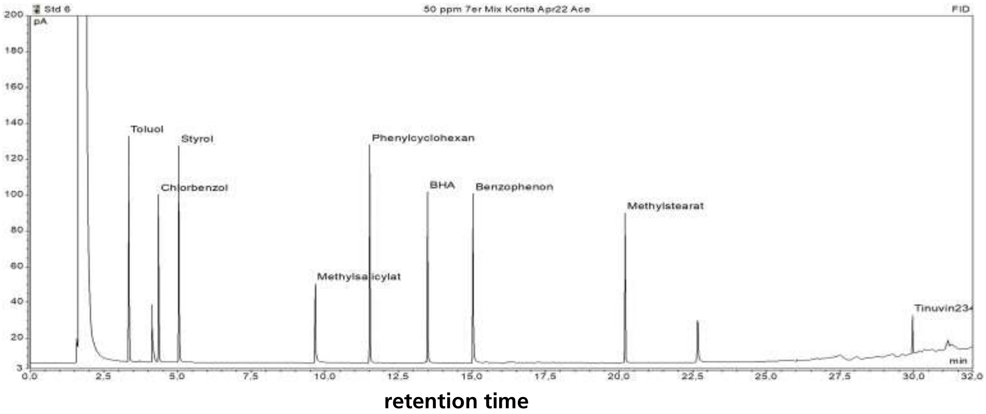


Figure 2: Gas chromatogram of a 50 mg/l standard mixture

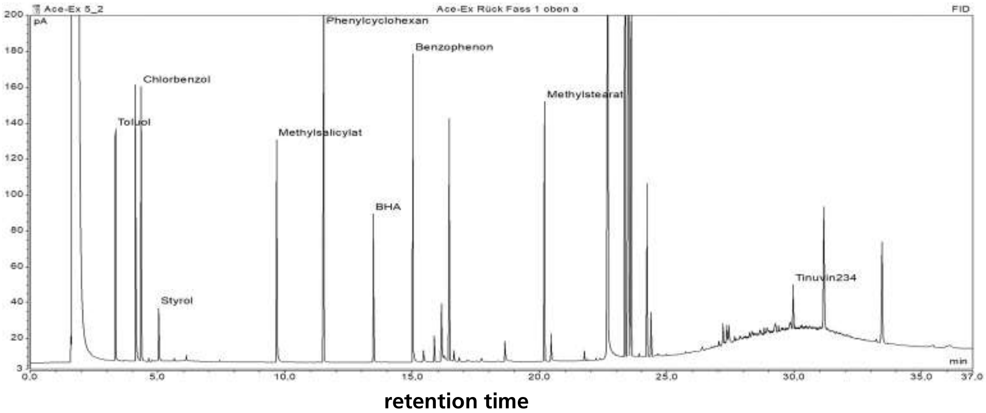


Figure 3: Gas chromatogram of the extract of sample C1a

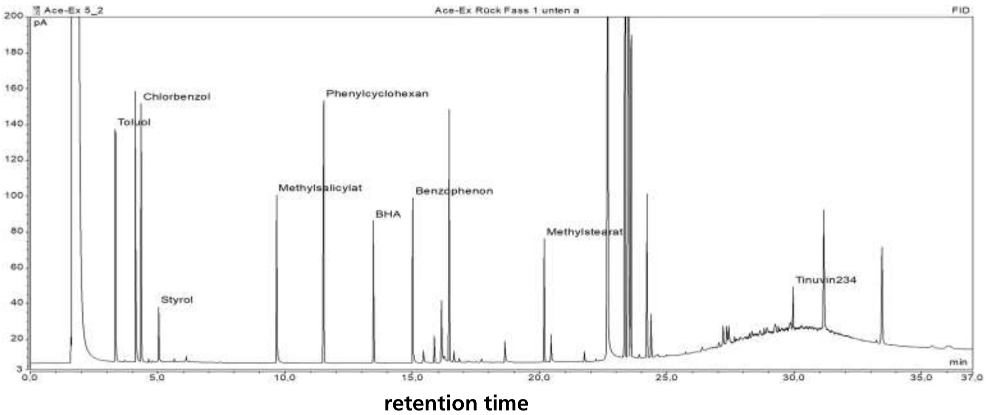


Figure 4: Gas chromatogram of the extract of sample C1b

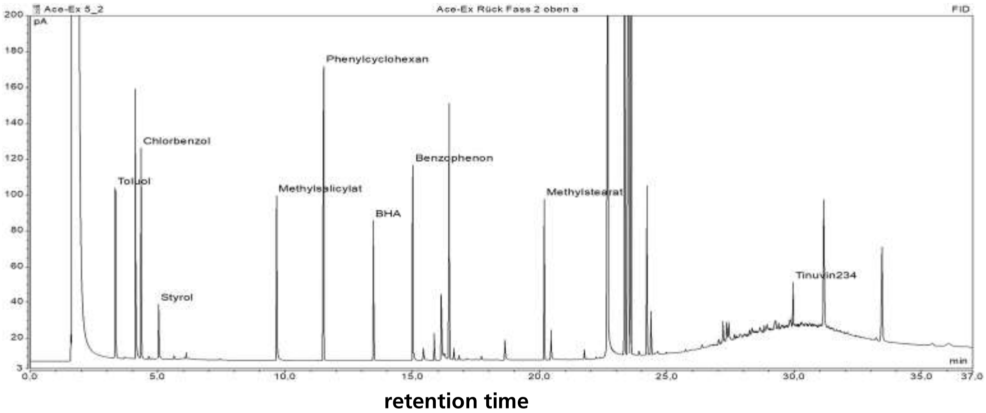


Figure 5: Gas chromatogram of the extract of sample C2a

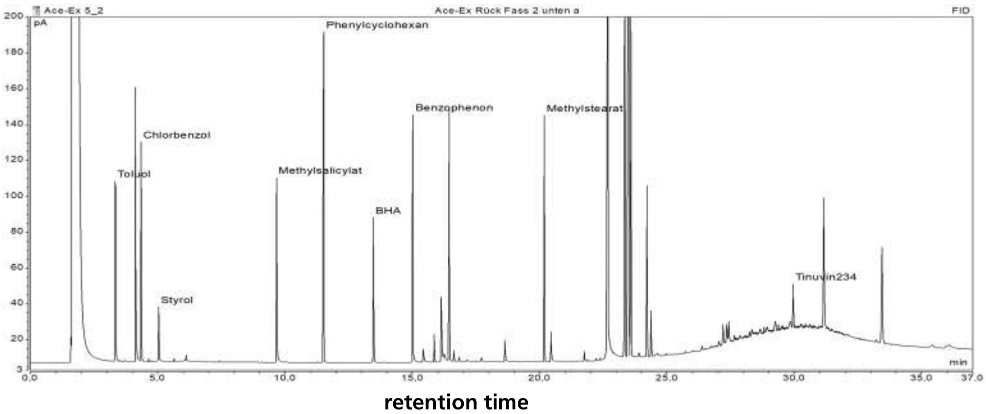


Figure 6: Gas chromatogram of the extract of sample C2b

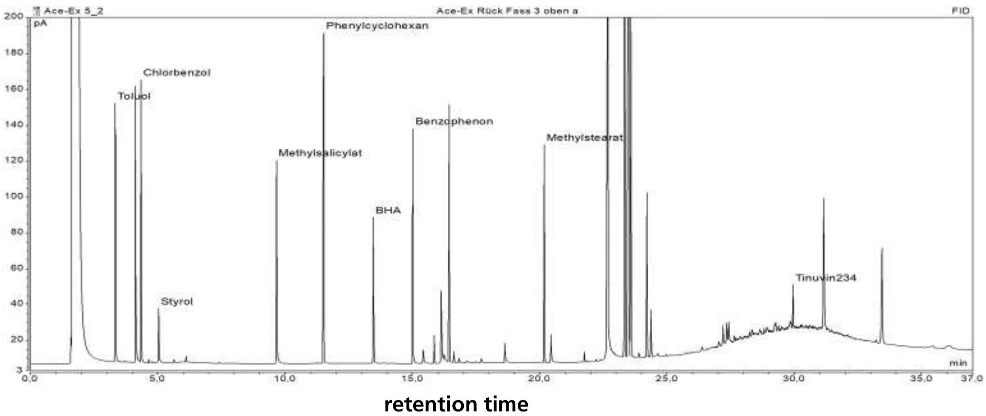
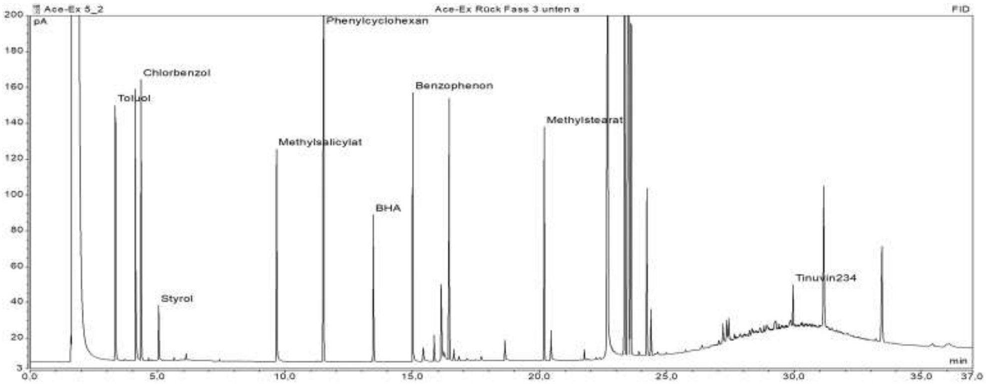
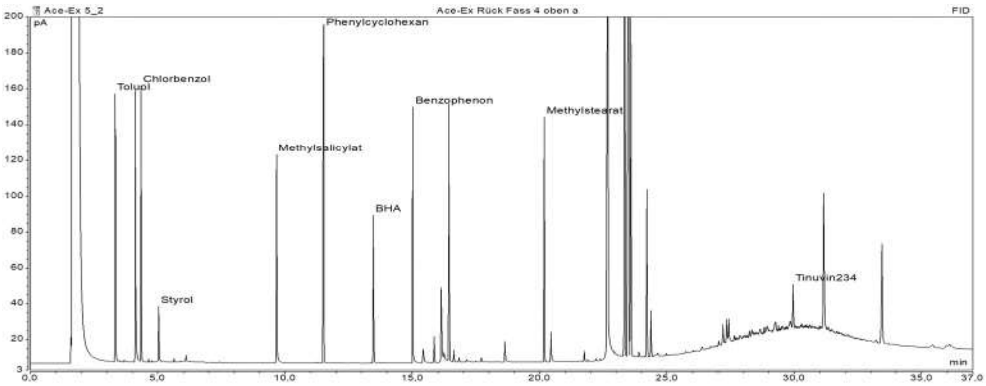


Figure 7: Gas chromatogram of the extract of sample C3a



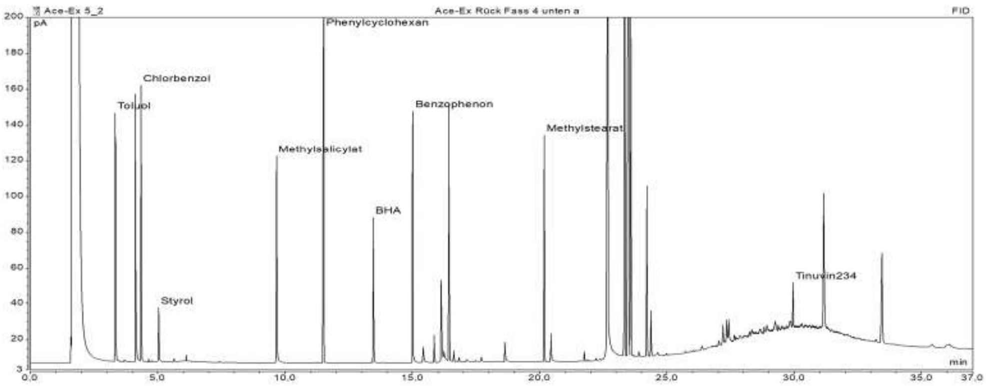
retention time

Figure 8: Gas chromatogram of the extract of sample C3b



retention time

Figure 9: Gas chromatogram of the extract of sample C4a



retention time

Figure 10: Gas chromatogram of the extract of sample C4b

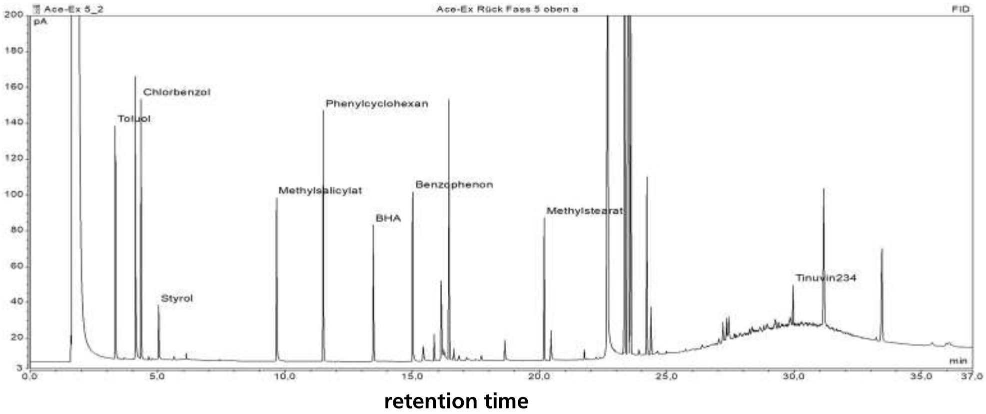


Figure 11: Gas chromatogram of the extract of sample C5a

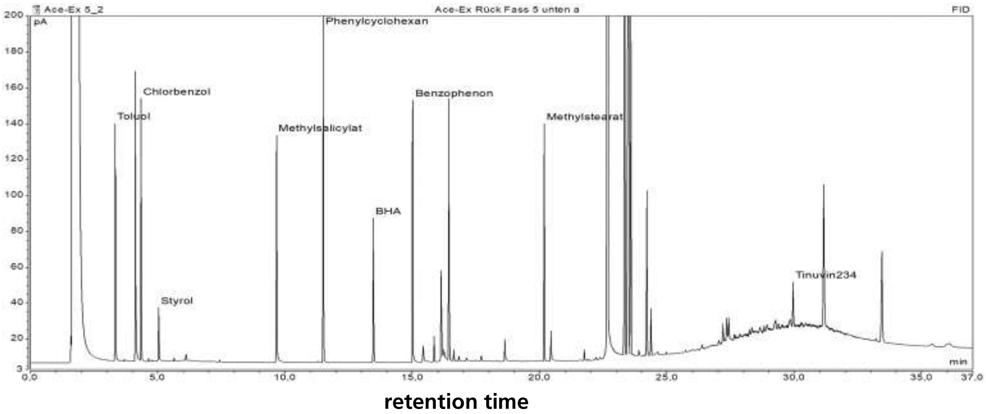


Figure 12: Gas chromatogram of the extract of sample C5b

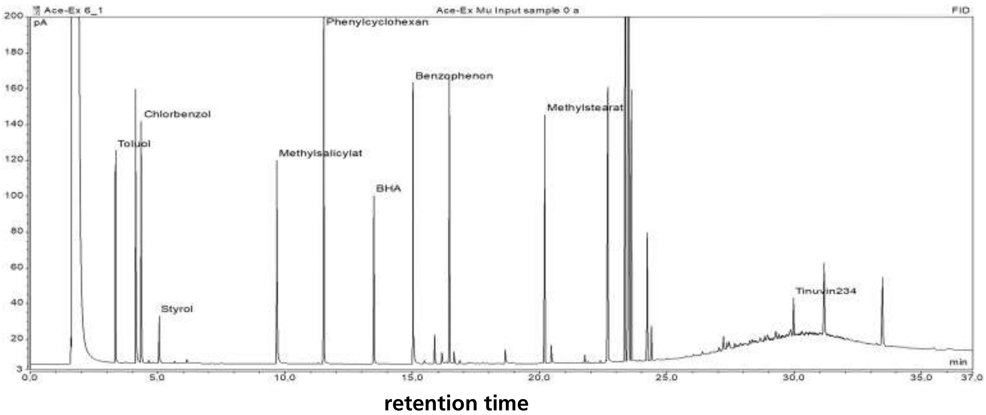


Figure 13: Gas chromatogram of the extract of sample 0

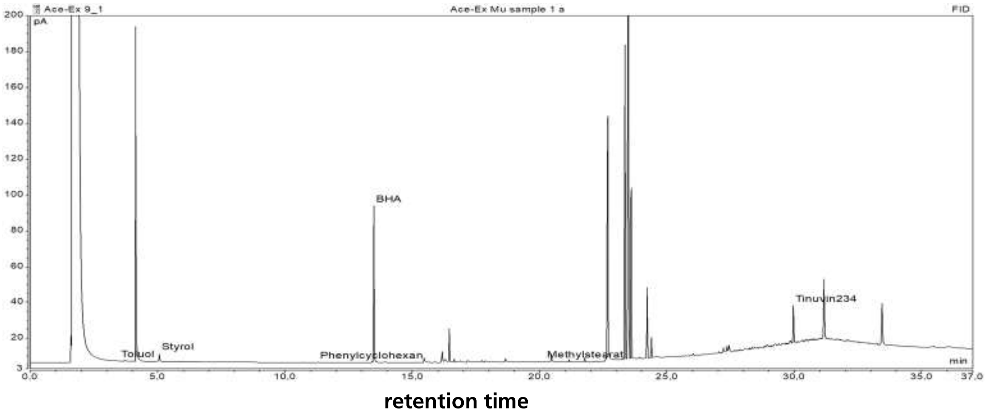


Figure 14: Gas chromatogram of the extract of sample 1

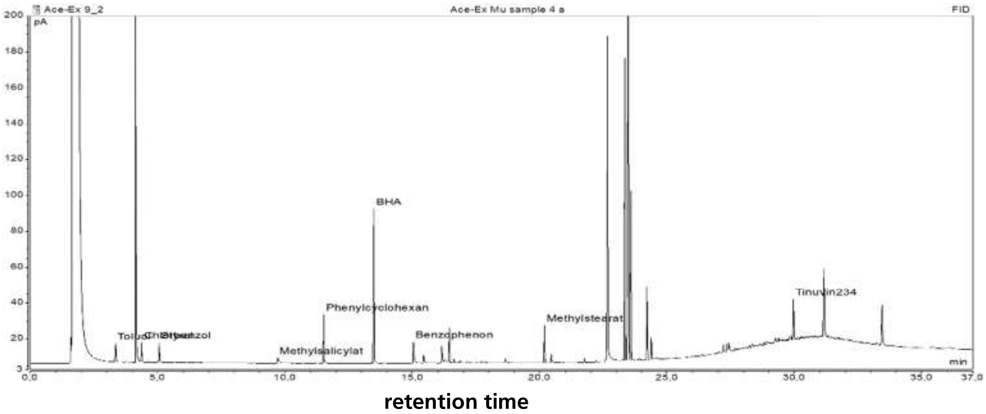


Figure 15: Gas chromatogram of the extract of sample 4

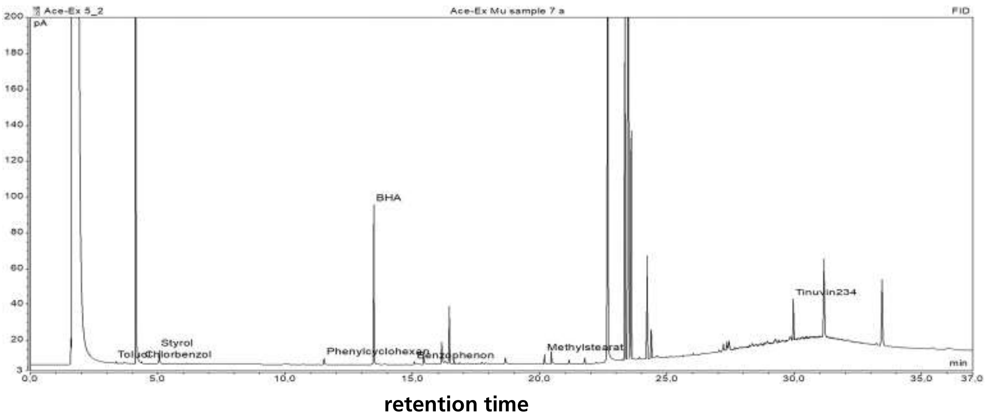


Figure 16: Gas chromatogram of the extract of sample 7

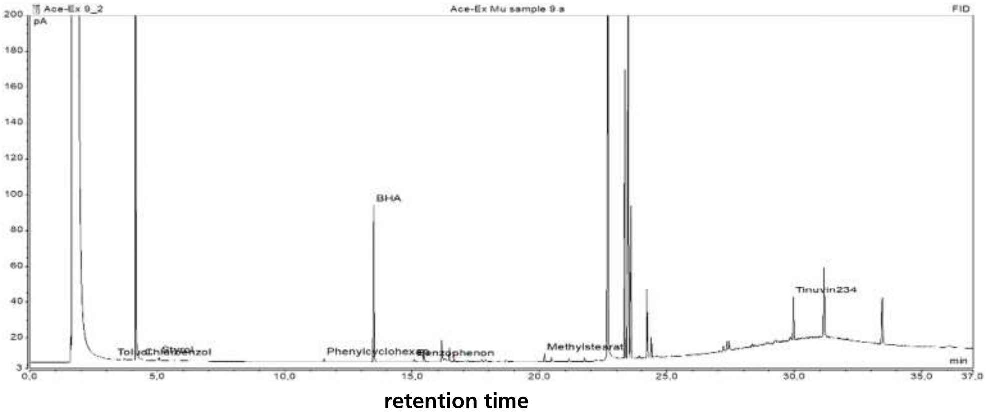


Figure 17: Gas chromatogram of the extract of sample 9

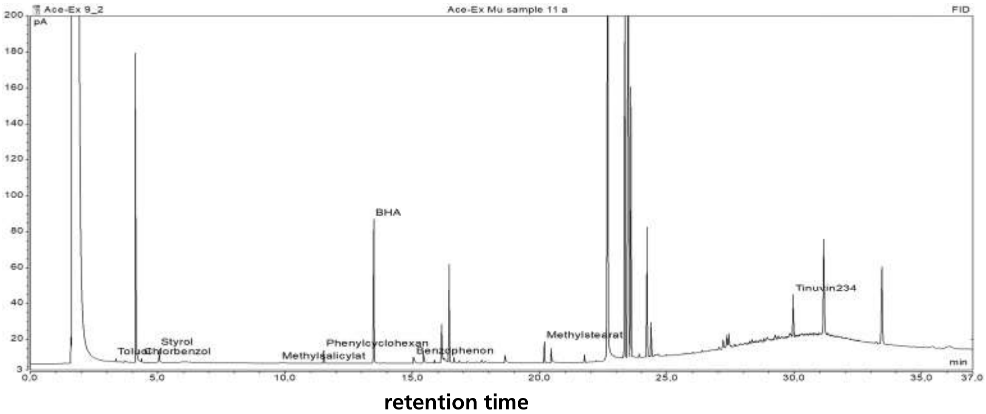


Figure 18: Gas chromatogram of the extract of sample 11

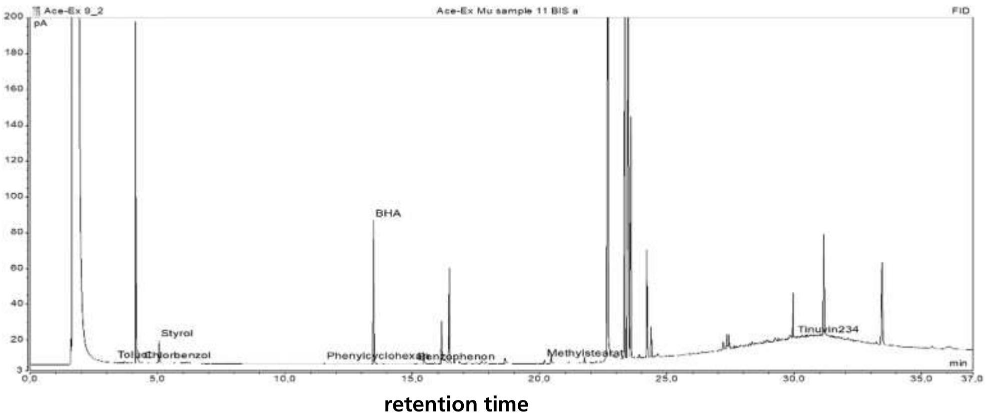


Figure 19: Gas chromatogram of the extract of sample 11 BIS

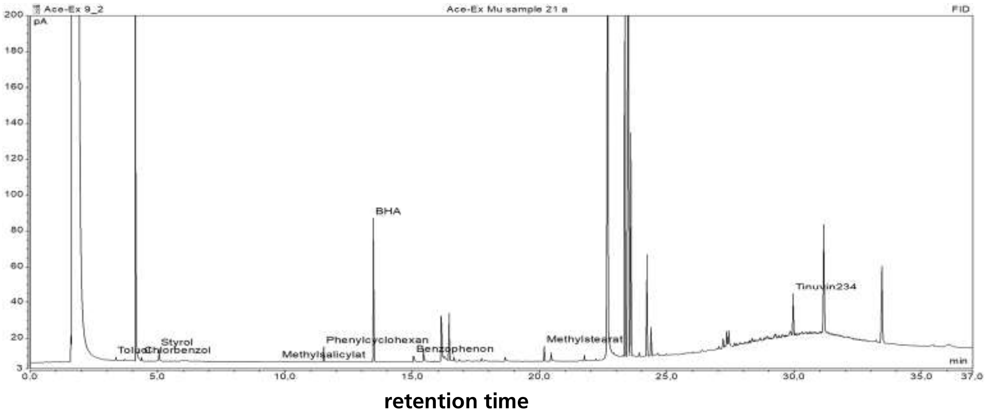


Figure 20: Gas chromatogram of the extract of sample 21

Table 4: Concentrations of the surrogates in the investigated PS samples

Sample	Concentration [mg/kg] (cleaning efficiency)						
	Toluene	Chloro-benzene	Styrene[a]	Methyl salicylate	Phenyl cyclohexane	Benzophenone	Methyl stearate
Sample C1a	550.6 ±14.7	844.4 ±20.6	123.9 ±7.2	917.5 ±77.6	740.5 ±106.7	623.7 ±133.2	636.1 ±172.0
Sample C1b	539.8 ±8.9	824.2 ±16.2	129.9 ±1.6	826.7 ±58.3	618.4 ±67.9	482.8 ±75.2	462.3 ±106.1
Sample C2a	389.0 ±10.3	653.1 ±22.3	129.7 ±1.3	739.7 ±70.3	567.4 ±82.9	406.6 ±83.8	377.8 ±110.1
Sample C2b	403.6 ±10.0	678.6 ±21.6	129.2 ±0.7	800.9 ±45.5	652.3 ±52.3	534.2 ±73.9	573.8 ±124.4
Sample C3a	590.3 ±8.8	881.9 ±14.0	128.5 ±2.4	940.5 ±36.5	735.5 ±43.4	635.4 ±54.9	679.5 ±57.6
Sample C3b	585.6 ±5.5	870.1 ±13.6	129.3 ±2.0	925.6 ±61.6	716.3 ±62.0	598.7 ±52.9	644.6 ±64.7
Sample C4a	577.1 ±4.0	850.6 ±8.0	129.7 ±1.0	859.7 ±59.7	661.8 ±89.1	523.6 ±110.6	429.2 ±313.8
Sample C4b	579.6 ±22.3	853.8 ±31.8	129.1 ±1.0	877.0 ±67.0	681.1 ±67.8	554.5 ±65.7	405.5 ±277.8
Sample C5a	513.8 ±15.5	784.4 ±18.4	126.7 ±4.5	744.0 ±22.1	531.2 ±19.5	403.1 ±14.4	385.0 ±26.9
Sample C5b	531.3 ±2.5	811.2 ±6.7	128.4 ±2.4	903.4 ±126.3	656.3 ±116.0	524.3 ±124.3	530.0 ±165.9

Sample	Concentration [mg/kg] (cleaning efficiency)						
	Toluene	Chloro-benzene	Styrene[a]	Methyl salicylate	Phenyl cyclohexane	Benzophenone	Methyl stearate
mean samples C	**478.2 ±173.1**	**732.0 ±254.1**	**116.8 ±38.8**	**775.9 ±266.6**	**596.4 ±208.3**	**480.6 ±176.9**	**465.8 ±189.4**
Sample 0	491.2 ±6.1	771.0 ±13.7	125.8 ±3.5	955.3 ±49.7	753.7 ±74.1	656.5 ±93.8	661.8 ±129.9
Sample 1	<0.1 (>99.9%)	<0.1 (>99.9%)	18.1 ±0.1 (84.5%)	<1.8 (>99.8%)	<0.1 (>99.9%)	<1.7 (99.6%)	3.4 ±0.7 (99.3%)
Sample 4	20.3 ±18.1 (95.8%)	28.9 ±25.0 (96.1%)	34.4 ±16.3 (70.5%)	32.0 ±36.5 (95.9%)	62.6 ±50.1 (89.5%)	46.6 ±39.6 (90.3%)	63.7 ±44.0 (86.3%)
Sample 7	2.1 ±1.4 (99.6%)	4.0 ±4.1 (99.5%)	26.8 ±13.7 (77.1%)	<1.8 (>99.8%)	12.2 ±4.8 (98.0%)	11.3 ±4.3 (97.6%)	24.0 ±7.5 (94.8%)
Sample 9	0.8 ±0.4 (99.8%)	2.2 ±2.4 (99.7%)	8.1 ±4.4 (93.1%)	<1.8 (>99.8%)	10.3 ±2.1 (98.3%)	12.0 ±2.4 (97.5%)	25.1 ±2.9 (94.6%)
Sample 11	3.9 ±3.1 (99.2%)	5.9 ±6.0 (99.2%)	50.1 ±9.9 (57.1%)	3.8 ±5.9 (99.5%)	16.4 ±15.6 (97.3%)	14.8 ±12.7 (96.9%)	40.0 ±25.2 (91.4%)
Sample 11 BIS	1.2 ±0.1 (99.7%)	<0.1 (>99.9%)	59.4 ±1.4 (49.1%)	<1.8 (>99.8%)	2.9 ±0.5 (99.5%)	3.6 ±1.3 (99.3%)	9.3 ±3.3 (98.0%)

Sample	Concentration [mg/kg] (cleaning efficiency)						
	Toluene	Chloro-benzene	Styrene[a]	Methyl salicylate	Phenyl cyclohexane	Benzophenone	Methyl stearate
Sample 21	6.0 ±2.3 (98.7%)	8.3 ±4.0 (98.9%)	33.0 ±1.3 (71.7%)	8.2 ±6.4 (98.9%)	32.3 ±12.1 (94.6%)	25.0 ±8.8 (94.8%)	38.0 ±12.6 (91.8%)

[a]Styrene is the monomer and not artificially contaminated.

5.2 Safety Evaluation of the Decontamination Technology

Diffusion models provide a scientific tool for establishing a correlation between the migration into contact media and the corresponding concentration $C_{P,0}$ of a migrant (surrogates) in the final product of the super-clean decontamination technology. In this way maximum surrogate concentrations in PS can be established which would not lead to exceeding a certain migration value of interest.

All calculations were based on the modelling parameters for HIPS (A_P' =1.0 and τ = 0 K). In addition, all calculation were done for a food package with 1 l volume and 600 cm^2 surface area ("EU cube"), a density of 1.04 g/cm^3 and high solubility for the surrogates (partition coefficient $K_{Polymer/Food}$ = 1).

Remark: The input material of the decontamination technology is PS, mainly high impact polystyrene (HIPS), because most of the yogurt cups are made from HIPS. However, the sorting processes might not distinguish between general purpose polystyrene (GPPS) and therefore also GPPS might be also in the input stream. From a migrational point of view, GPPS shows a lower diffusivity compared to HIPS. For both polymers, modelling parameters are available. We choose the modelling parameters of HIPS, because these parameters are the worst-case compared to GPPS.

The safety evaluation was done based on an initial contamination level of 3 mg/kg and the cleaning efficiency data of samples 11 BIS.

Within the study the following scenarios were evaluated:

- pot for cold filled yogurt, 250 g yogurt per day for a toddler, storage for 40 d at 6 °C
- pot for hot filled yogurt, 250 g yogurt per day for a toddler, 2 h 70 °C followed by 40 d at 6 °C
- tray for meat, fish or cheese, 150 g meat, fish or cheese per day for a toddler, 30 d at 6 °C
- tray for fruit or vegetables, 500 g fruit or vegetables per day for a toddler, 30 d at 25 °C
- cup for cold drinks, 750 ml cold drinks per day for a toddler, 1 d at 25 °C (cold drinks)
- cup for hot drinks, 750 ml hot drinks per day for a toddler, 2 h at 70 °C (hot drinks)

<u>Scenario 1: rPS in yogurt pots (cold filled)</u>

For the evaluation of the decontamination technology, the following exposure scenario was used:

- A toddler with 10 kg b.w. consumes **250 g** yogurt per day. This leads to a maximum migration of 0.1 µg/kg (0.0025*10/0.250 = 0.1).
- Due to the fact, that migration models for a low diffusive polymer like HIPS overestimated the migration by at least a factor 5 the maximum migration was set to **0.5 µg per kg** foodstuff.
- The maximum contamination level of post-consumer recyclates is assumed to be 1 mg/kg in conventionally recycled PS flakes before super-cleaning.
- The recyclate content in the packaging material is 100%.
- The calculation was done for a maximum shelf life of **40 d at 6 °C**.

The results are visualized in Figure 21 and Figure 22. In conclusion the above mentioned application can be considered as safe up to 100% recyclate.

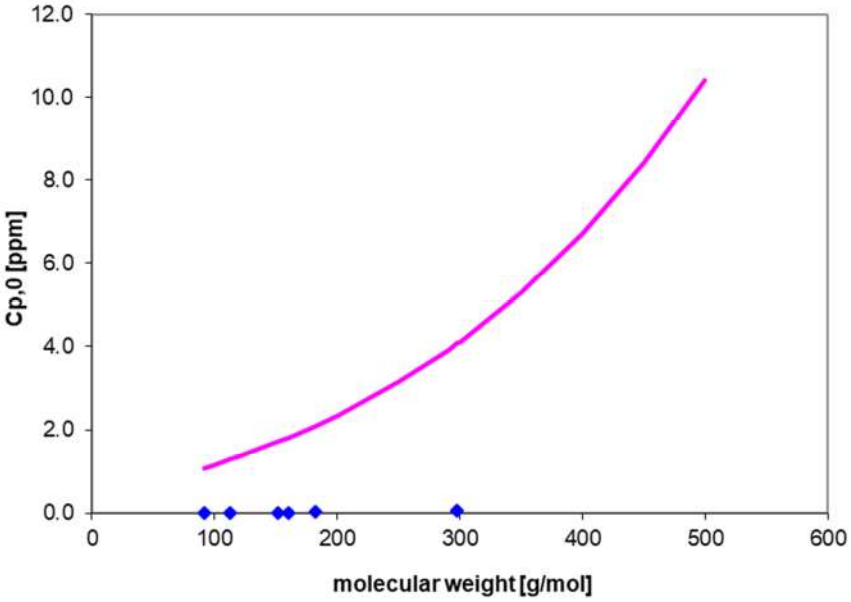


Figure 21: Residual concentrations corresponding to a migration of **0.5 µg/kg** of surrogates adjusted to **3 mg/kg** initial concentration, storage conditions: **40 d at 6 °C**. Pink line: maximum concentration, blue dots: experimental data (C_{res})

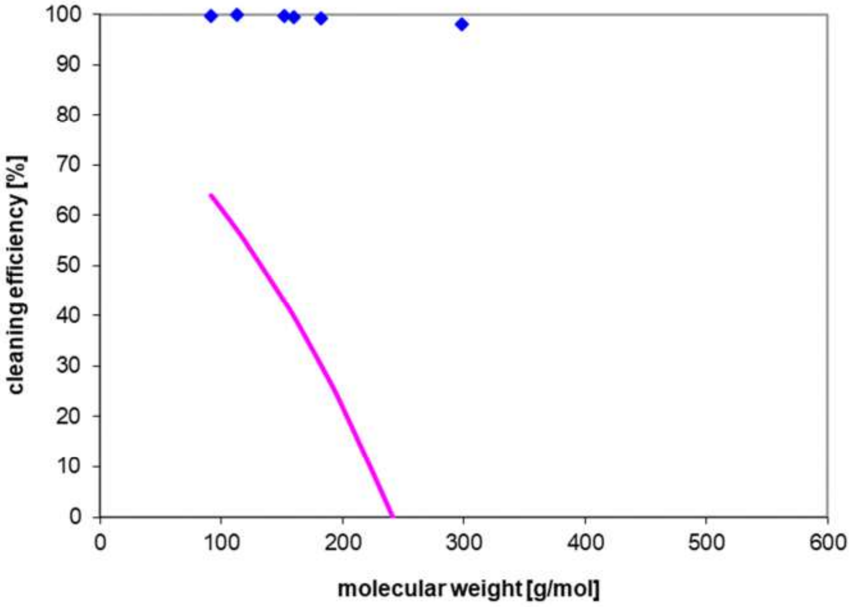


Figure 22: Cleaning efficiencies of surrogates in the challenge test, pink line: Minimum cleaning efficiency. Pink line: minimum cleaning efficiency, blue dots: experimental data

Scenario 2: rPS in yogurt pots (hot fill)

For the evaluation of the decontamination technology, the following exposure scenario was used:

- A toddler with 10 kg b.w. consumes **250 g** yogurt per day. This leads to a maximum migration of 0.1 µg/kg (0.0025*10/0.250 = 0.1).
- Due to the fact, that migration models for a low diffusive polymer like HIPS overestimated the migration by at least a factor 5 the maximum migration was set to **0.5 µg per kg** foodstuff.
- The maximum contamination level of post-consumer recyclates is assumed to be 1 mg/kg in conventionally recycled PS flakes before super-cleaning.
- The recyclate content in the packaging material is 100%.
- The calculation was done for a maximum shelf life of **2 h at 70 °C followed by 40 d at 6 °C**.

The results are visualized in Figure 23 and Figure 24. In conclusion the above mentioned application can be considered as safe up to 100% recyclate.

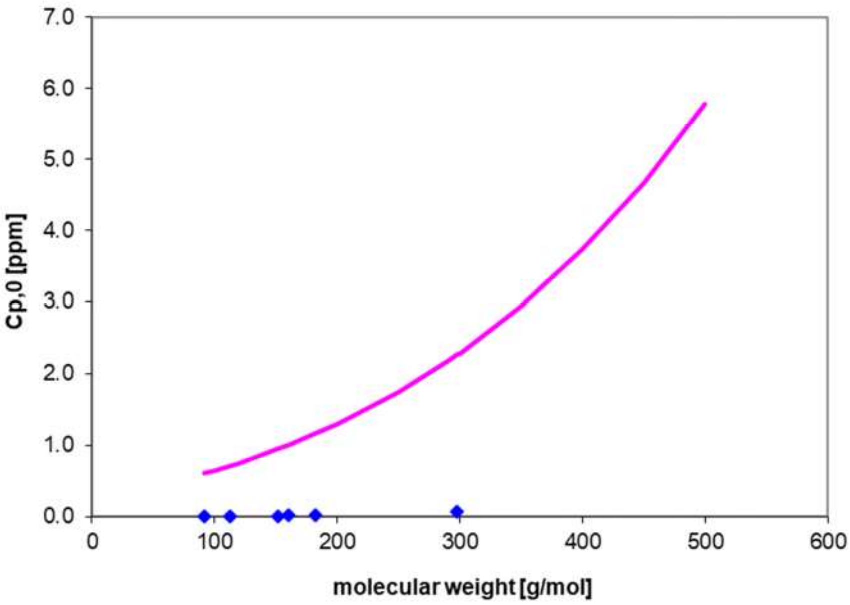


Figure 23: Residual concentrations corresponding to a migration of **0.5 µg/kg** of surrogates adjusted to **3 mg/kg** initial concentration, storage conditions: **2 h at 70 °C followed by 40 d at 6 °C**. pink line: maximum concentration, blue dots: experimental data (C_{res})

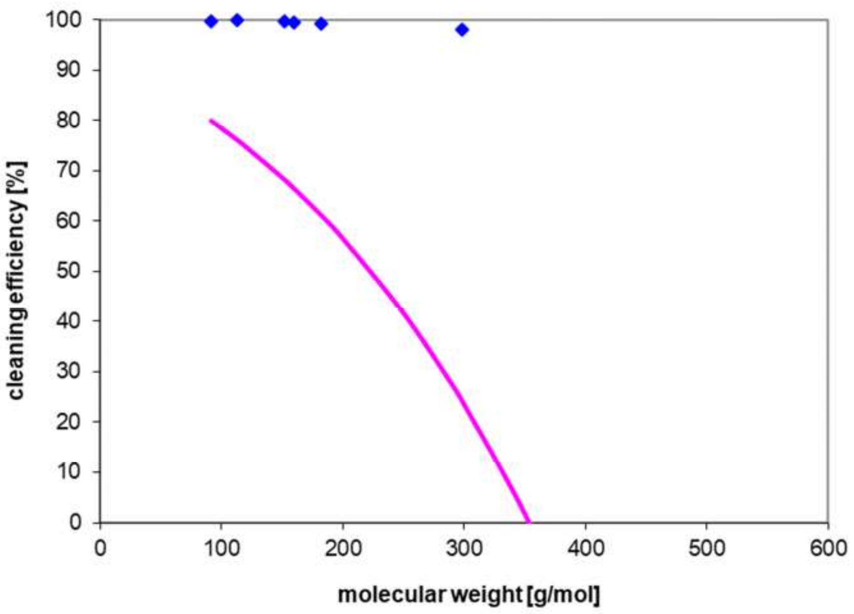


Figure 24: Cleaning efficiencies of surrogates in the challenge test. Pink line: Minimum cleaning efficiency, blue dots: experimental data

Scenario 3: rPS in trays for meat, fish and cheese

For the evaluation of the decontamination technology, the following exposure scenario was used:

- A toddler with 10 kg b.w. consumes **150 g** meat, fish or cheese per day. This leads to a maximum migration of 0.1 µg/kg (0.0025*10/0.150 = 0.167).
- Due to the fact, that migration models for a low diffusive polymer like HIPS overestimated the migration by at least a factor 5 the maximum migration was set to **0.833 µg per kg** foodstuff.
- The maximum contamination level of post-consumer recyclates is assumed to be 1 mg/kg in conventionally recycled PS flakes before super-cleaning.
- The recyclate content in the packaging material is 100%
- The calculation was done for a maximum shelf life of **30 d at 6 °C**.

The results are visualized in Figure 25 and Figure 26. In conclusion the above mentioned application can be considered as safe up to 100% recyclate.

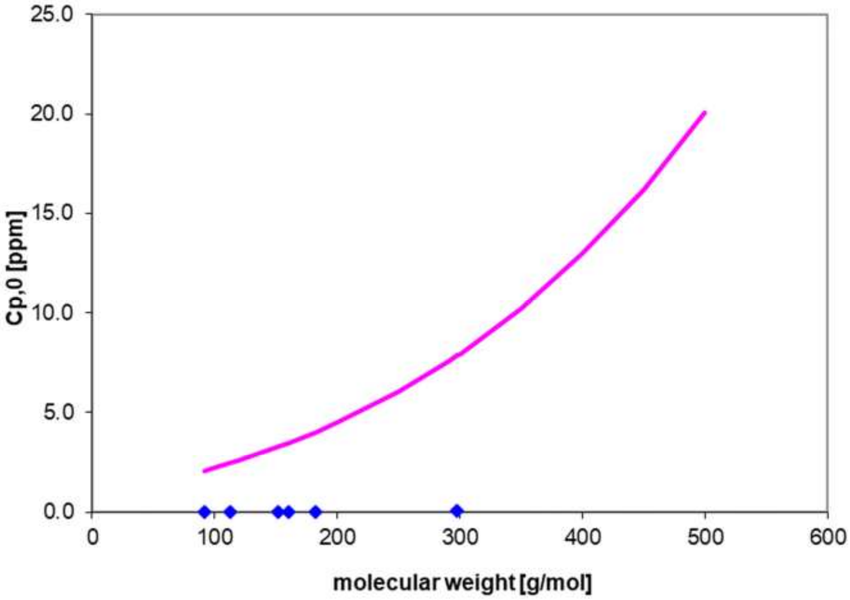


Figure 25: Residual concentrations corresponding to a migration of **0.833 µg/kg** of surrogates adjusted to **3 mg/kg** initial concentration, storage conditions: **30 d at 6 °C**. pink line: maximum concentration, blue dots: experimental data (C_{res})

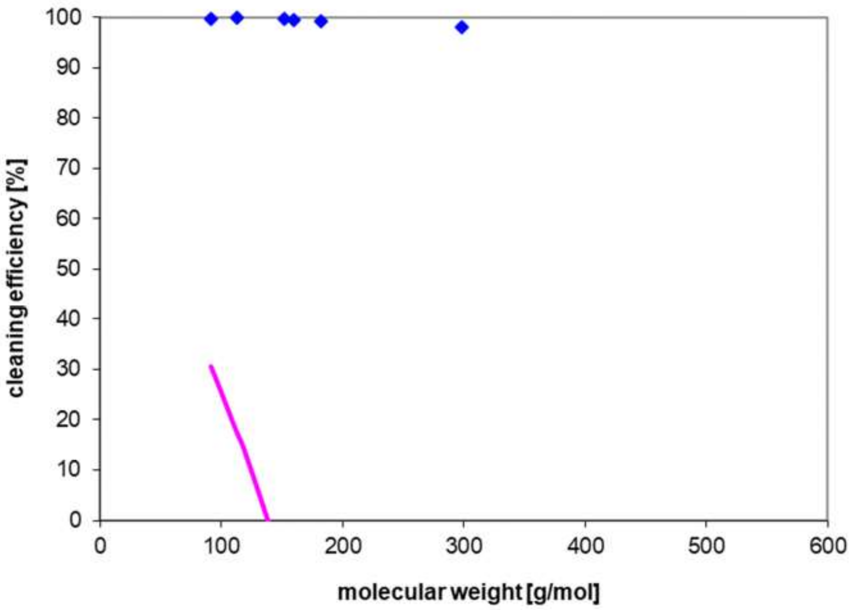


Figure 26: Cleaning efficiencies of surrogates in the challenge test. Pink line: minimum cleaning efficiency, blue dots: experimental data

<u>Scenario 4: rPS in trays for fruits and vegetables</u>

For the evaluation of the decontamination technology, the following exposure scenario was used:

- A toddler with 10 kg b.w. consumes **500 g** fruit or vegetables per day. This leads to a maximum migration of 0.1 µg/kg (0.0025*10/0.500 = 0.05).
- Due to the fact, that migration models for a low diffusive polymer like HIPS overestimated the migration by at least a factor 5 the maximum migration was set to **0.25 µg per kg** foodstuff.
- The maximum contamination level of post-consumer recyclates is assumed to be 1 mg/kg in conventionally recycled PS flakes before super-cleaning.
- The recyclate content in the packaging material is 100%
- The calculation was done for a maximum shelf life of **30 d at 25 °C**.

The results are visualized in Figure 27 and Figure 28. In conclusion the above mentioned application can be considered as safe up to 100% recyclate.

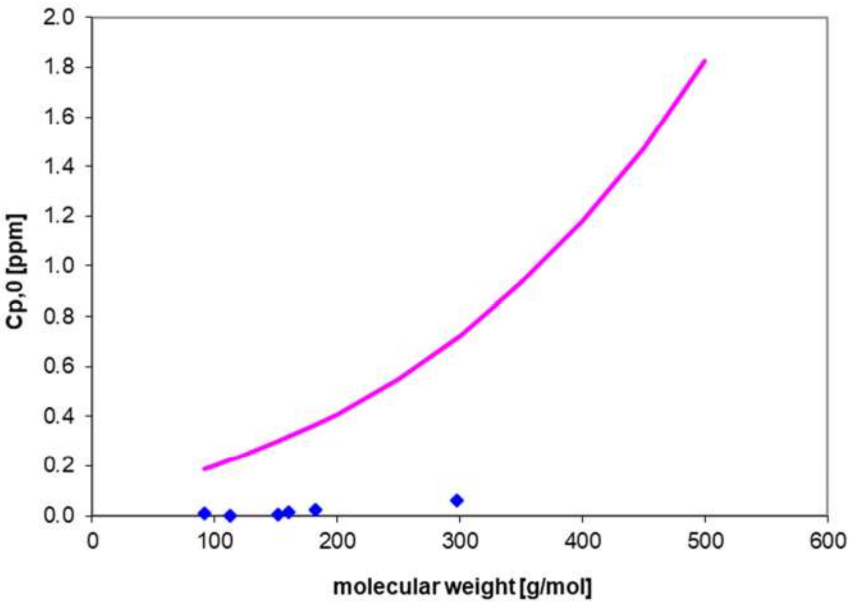


Figure 27: Residual concentrations corresponding to a migration of **0.25 µg/kg** of surrogates adjusted to **3 mg/kg** initial concentration, storage conditions: **30 d at 25 °C**. pink line: maximum concentration, blue dots: experimental data (C_{res})

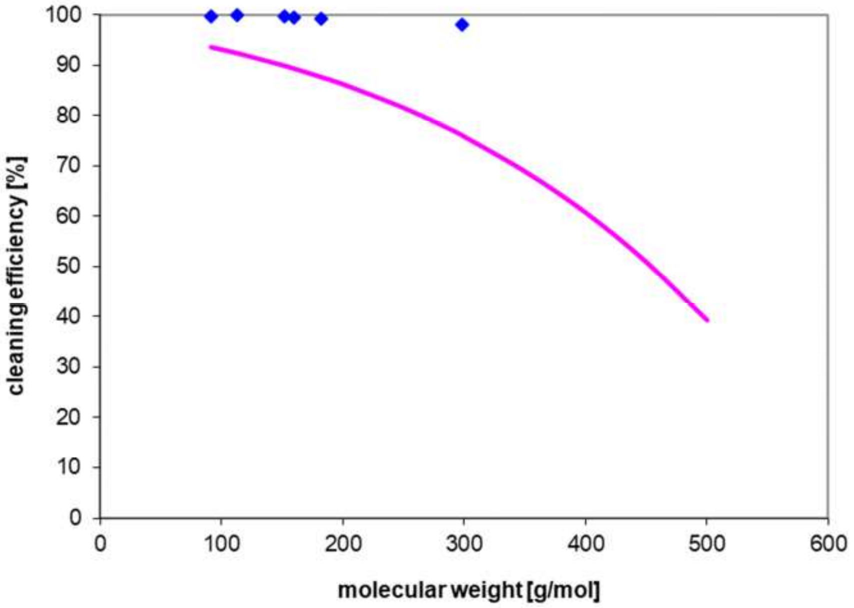


Figure 28: Cleaning efficiencies of surrogates in the challenge test, pink line: Minimum cleaning efficiency, blue dots: experimental data

Scenario 5: rPS in drinking cups (cold drinks)

For the evaluation of the decontamination technology, the following exposure scenario was used:

- A toddler with 10 kg b.w. consumes **750 ml** cold drinks per day. This leads to a maximum migration of 0.1 µg/kg (0.0025*10/0.750 = 0.033).
- Due to the fact, that migration models for a low diffusive polymer like HIPS overestimated the migration by at least a factor 5 the maximum migration was set to **0.167 µg per kg** foodstuff.
- The maximum contamination level of post-consumer recyclates is assumed to be 1 mg/kg in conventionally recycled PS flakes before super-cleaning.
- The recyclate content in the packaging material is 100%
- The calculation was done for a maximum shelf life of **1 d at 25 °C**.

The results are visualized in Figure 29 and Figure 30. In conclusion the above mentioned application can be considered as safe up to 100% recyclate.

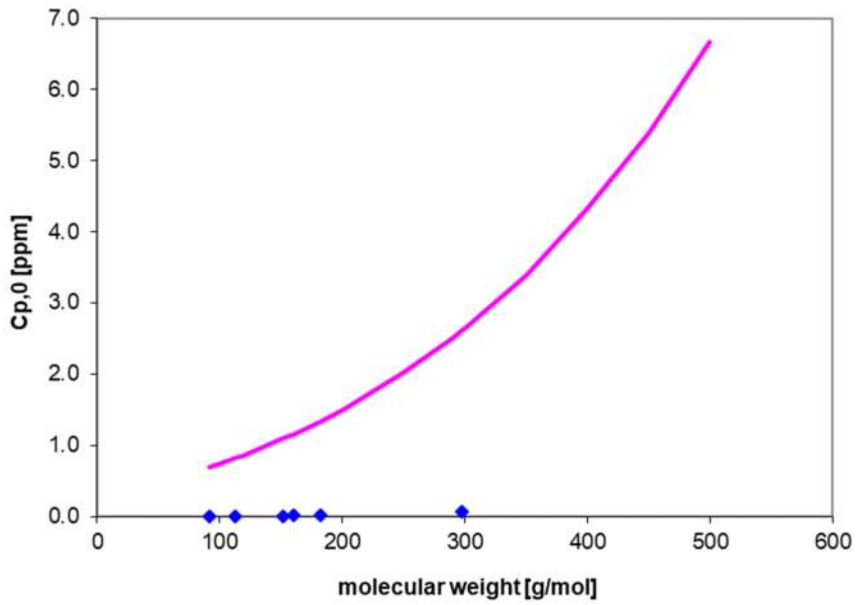


Figure 29: Residual concentrations corresponding to a migration of **0.167 µg/kg** of surrogates adjusted to **3 mg/kg** initial concentration, storage conditions: **1 d at 25 °C**. , pink line: maximum concentration, blue dots: experimental data (C_{res})

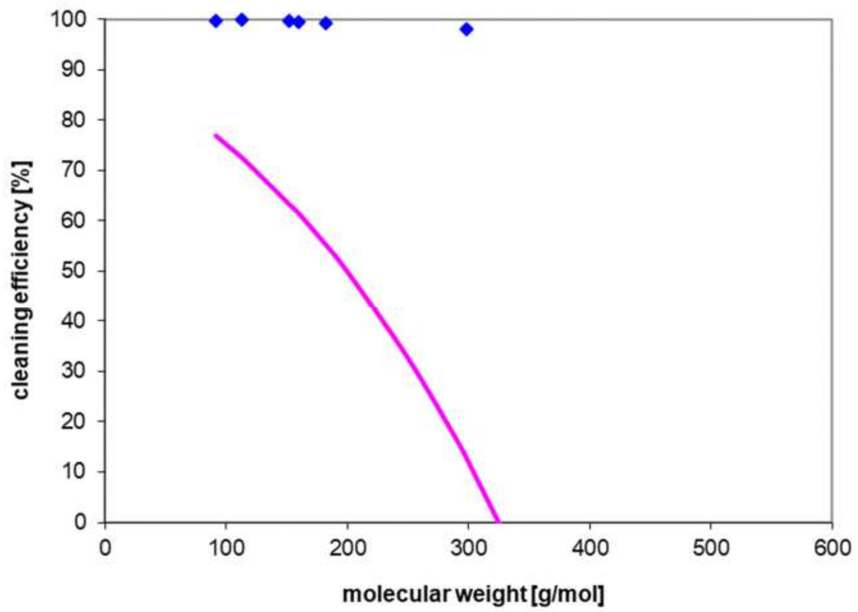


Figure 30: Cleaning efficiencies of surrogates in the challenge test, pink line: Minimum cleaning efficiency, blue dots: experimental data

Scenario 6: rPS in drinking cups (hot drinks)

For the evaluation of the decontamination technology, the following exposure scenario was used:

- A toddler with 10 kg b.w. consumes **750 ml** hot drinks per day. This leads to a maximum migration of 0.1 µg/kg (0.0025*10/0.750 = 0.033).
- Due to the fact, that migration models for a low diffusive polymer like HIPS overestimated the migration by at least a factor 5 the maximum migration was set to **0.167 µg per kg** foodstuff.
- The maximum contamination level of post-consumer recyclates is assumed to be 1 mg/kg in conventionally recycled PS flakes before super-cleaning.
- The recyclate content in the packaging material is 100%
- The calculation was done for a maximum shelf life of **2 h at 70 °C**.

The results are visualized in Figure 31 and Figure 32. In conclusion the above mentioned application can be considered as safe up to 100% recyclate.

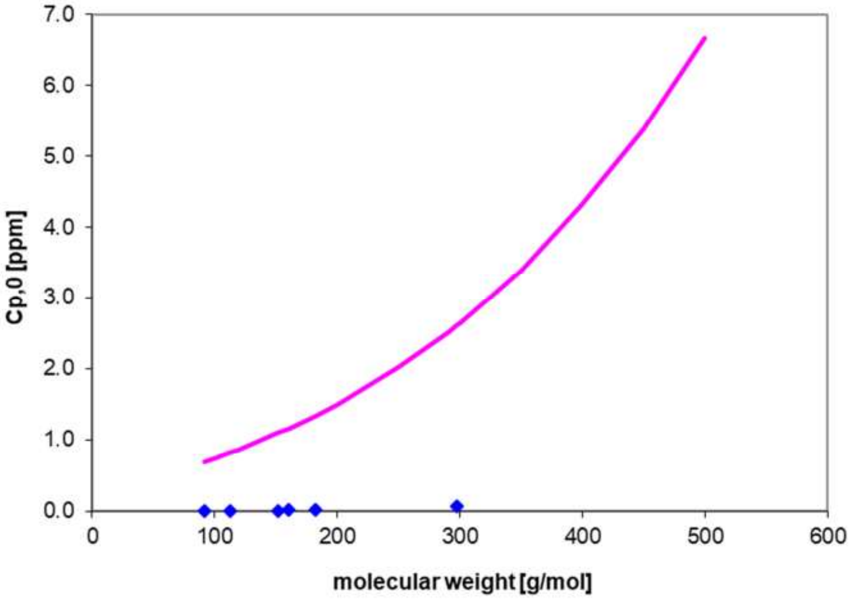


Figure 31: Residual concentrations corresponding to a migration of **0.167 µg/kg** of surrogates adjusted to **3 mg/kg** initial concentration, storage conditions: **2 h at 70 °C**. pink line: maximum concentration, blue dots: experimental data (C_{res})

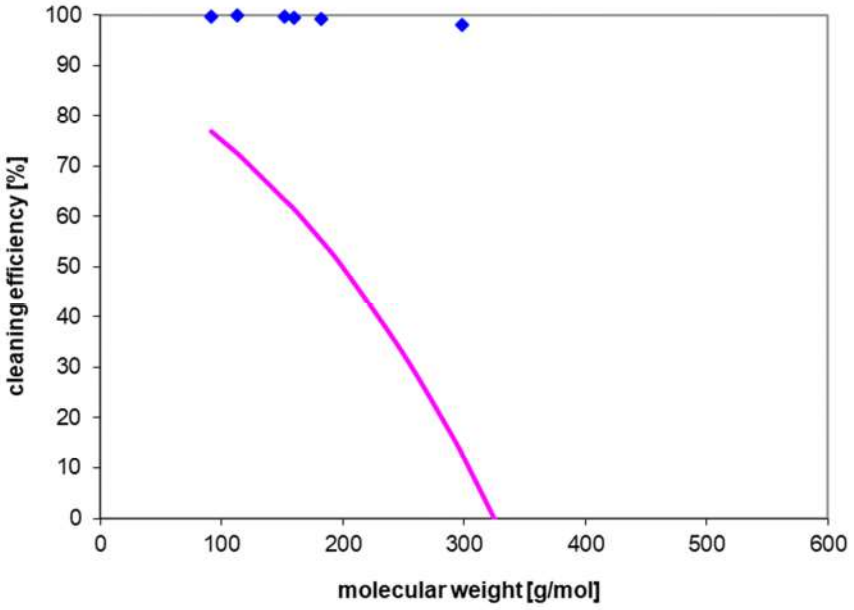


Figure 32: Cleaning efficiencies of surrogates in the challenge test, pink line: Minimum cleaning efficiency, blue dots: experimental data

6 Signatures

Fraunhofer-Institut
für Verfahrenstechnik und Verpackung

Freising, December 5, 2023

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Annotation: This report replaces the Fraunhofer IVV report PA-1430a-23 from 05.12.2023. Some errors were corrected, two samples were excluded and the process parameters were deleted.