

TNO Report

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**Challenge test of the PTP modified PET-M
recycling system**

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Summary

PTP Plastic technologies and products has asked TNO Quality of Life to perform a challenge test for their recycling system. In this recycling system post consumer PET is recycled to a modified food grade PET material (PET-M granules).

To investigate the cleaning effect of the different processing steps and to find out if the output of the process meets the legal food packaging demands, a challenge test has been carried out with surrogate contaminants. This is a generally accepted procedure that anticipates formal legislation that will be implemented in Europe in the very near future. Basis for this procedure are the so called ILSI guidelines (Guidelines of the International Life Sciences institute (ILSI); Recycling of plastics for food contact use; edited by the ILSI Europe Packaging Material Task Force; Brussels, Belgium, May 1998) and the FDA threshold of regulation procedure (Code of Federal Regulations 21CFR170.39, Threshold of regulation for substances used in food-contact, Revised as of April 1, 2003).

For this challenge test ground and cleaned, post consumer PET (flakes) were contaminated with a cocktail of surrogate contaminants. This cocktail contained the following compounds: phenylcyclohexane, benzophenone, toluene, mono chlorobenzene, R(+)-limonene, 1,1,1-trichloroethane, 2,4-pentanedione, ortho-cresol (2-methyl phenol) and methylstearate (octadecanoic acid, methyl ester). To impregnate the PET flakes they were submerged in this cocktail during 10 days at 40°C. After this storage period the cocktail was removed and the flakes were rinsed, dried and processed in the PTP recycling system.

During the contamination and during the different steps of the recycling process samples were taken for analyses at TNO. The granules produced in this process were used for the production of 1.5 l bottles on site. These bottles were tested for the presence of the surrogate contaminants. Migration tests were performed using the standard 3% acetic acid food simulant by exposure during 10 days at 40°C. The simulants were analyzed for contaminants.

The contamination liquids, PET flakes samples, pellets, the produced PET bottles and migration extracts were analyzed for contaminants by using GC-MS.

The test results show that the system removes the surrogate contaminants very well. Moreover, the results show that migration of the residual surrogates into the food simulant acetic acid is low enough to conclude that the capabilities of the system meets the demands of de USA FDA (dietary concentration <0.5 µg/l) and the informal EU ILSI guideline limit of 10 µg/l.

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1 Introduction

A new European regulation (EC 1935/2004) covering all food contact materials was adopted by the Council of Ministers on October 14, 2004. This regulation states that the use of recycled materials and goods should be favored for environmental reasons, provided that strict requirements are established to ensure food safety and consumer protection. To that end, rules are being drawn up for recycled plastics, expanding on the general requirements contained in the new framework regulation.

The following are some of the important requirements captured in the draft regulation:

- The recycling process should be authorized by relevant European authorities;
- The plastic material being recycled must be manufactured in accordance with 2002/72/EC, and must have been in contact with foodstuffs only;
- The output of the recycling process must comply with 2002/72 EC;
- The recycled product must be accompanied by a declaration of compliance;
- The recycling must be performed under an appropriate quality assurance system.

The output of a recycling process should be a plastic material that complies with the plastics directive. In practice, this means that the recycling process must be capable of removing any chemical contamination from the plastic input in such a way that a food-grade material results. Recycling processes therefore have to be evaluated via 'challenge tests'.

In a challenge test, the plastic input is exposed to selected surrogate contaminants. These are compounds that represent any possible contaminant in practical situations, with the exception of carcinogenic and mutagenic substances. After exposure, the plastic is subjected to the recycling process, with subsequent analysis of the plastic for those contaminants demonstrating the efficacy of that process.

Formal EU legislation on recycling for food contact applications is still under way. A formal evaluation procedure is therefore not yet available. For this reason, present test set-up is based on the FDA threshold of regulation procedure and the ILSI guidelines. These guidelines serve thus far as unofficial EU procedure.

The surrogate contaminants and concentrations advised in these procedures, supplemented with some surrogates that are advised by the 'Agence Française de Sécurité Sanitaire des Aliments' are used by TNO for challenge testing (Saisine n° 2001-SA-0315, CES MCDA, March 2004). Therefore, the TNO study can be considered a real worst case study.

PTP Plastic technologies and products asked TNO Quality of Life to perform such a challenge test for their recycling process. In this recycling procedure PET is recycled to a modified PET material (PET-M granules). To investigate the cleaning effect of the different processing steps and to find out if the final output of the process meets the legal food packaging demands, a challenge test has been carried out with above mentioned surrogate contaminants.

2 Procedure

The entire procedure for the challenge test consists of the following steps:

- a. Pre-study to validate the analysis of the surrogate contaminants in the PET-M material and if necessary develop an adapted methodology to ensure reliable analytical data;
- b. Contamination of a batch of PET-flakes with a cocktail of surrogate contaminants at TNO under standard conditions;
- c. Subjecting the contaminated PET-flakes to the recycling process;
- d. Analysis of the concentration of contaminants in the PET samples taken at different points in the process
- e. Modelling of migration from residual contaminants in PET bottles
- f. Actual Migration measurement in food simulant.

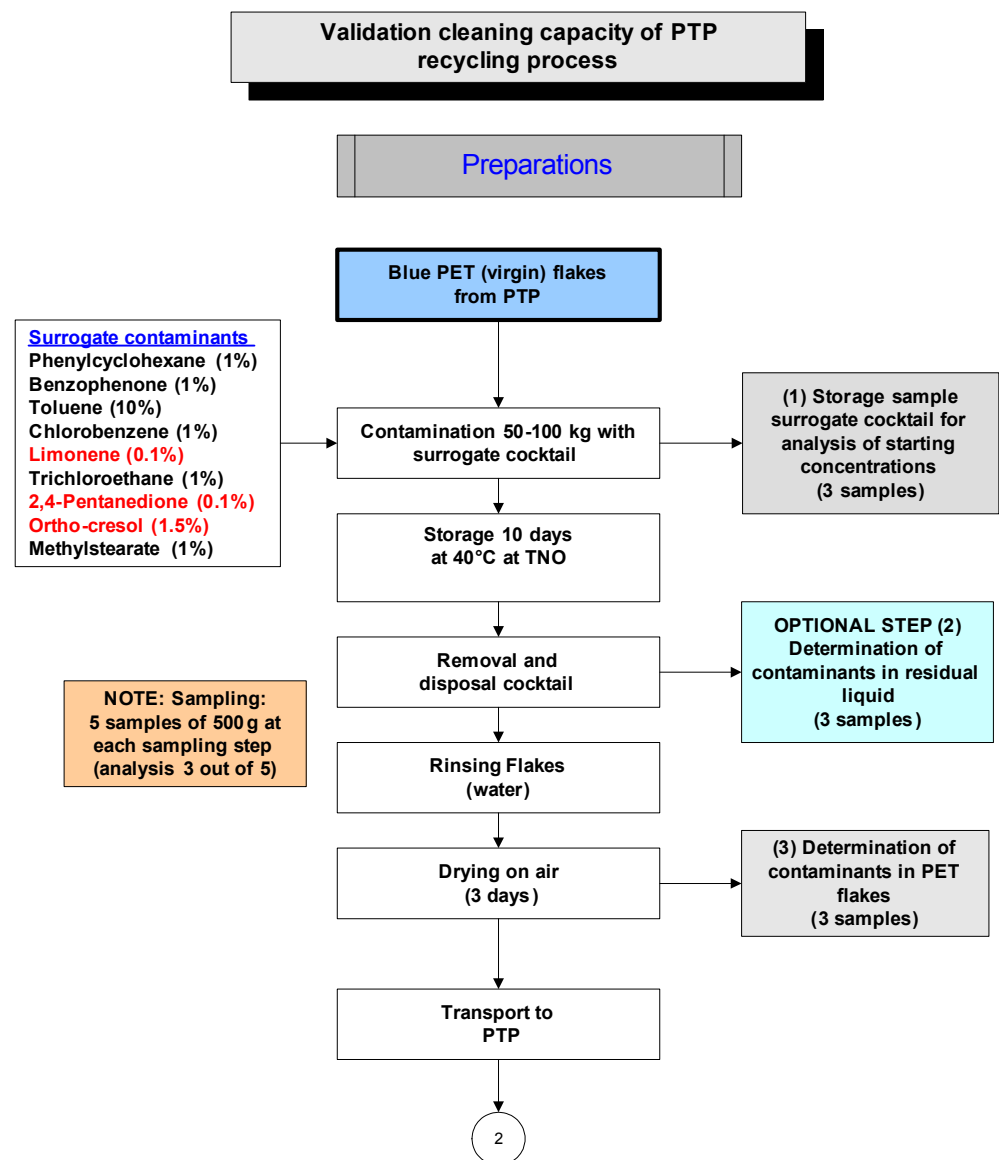
The timing of the project was as follows:

Time schedule

Monday July 18, 2005	Start contamination and storage
Thursday July 28, 2005	Removal contaminant cocktail, sampling rinsing and drying on air
Monday August 1ste, 2005	Transport to the Czech Republic by courier
Wednesday August 3, 2005	Start of the challenge test; sampling in plant
Thursday August 4, 2005	Production of the bottles
Friday August 5, 2005	Transport samples to TNO by courier
Monday August 8, 2005	Start of the analysis at TNO

A schematic overview of the challenge test procedure is presented in the next figure.

Figure 1 Schematic overview of the procedure is presented in below.



2.1 Contamination

For the challenge test blue PET flakes (ground bottles, weight 75 kg) were contaminated with a cocktail of surrogate contaminants in two large metal drums. The cocktail contained nine compounds in hexane (see next table). To impregnate the PET flakes they were submerged in this cocktail during 10 days at 40°C.

Table 1 Surrogate contaminants used for contamination

Compound	Cas no.	Conc. (w/w)	Properties	Guidelines
Cyclohexylbenzene	827-52-1	(1 %)	non-volatile, non-polar; aromatic/alicyclic hydrocarbon	EU ¹⁾
Benzophenone	119-61-9	(1 %)	non-volatile, polar; aromatic ketone	EU
Toluene	108-88-3	(10 %)	volatile, non-polar; aromatic hydrocarbon	EU
Chlorobenzene	108-90-7	(1 %)	volatile, non-polar, swelling agent; halogenated aromatic hydrocarbon	EU
Limonene	138-86-3	(0.1 %)	volatile, non-polar; main compound of citrus	France ²⁾
1,1,1-Trichloroethane	25323-89-1	(1 %)	Very volatile, polar; halogenated aliphatic hydrocarbon substitute	EU
2,4-Pentanedione	123-54-6	(0.1 %)	Very volatile, polar	France
o-cresol	95-48-7	(1.5 %)	volatile, polar, swelling agent	FDA ³⁾
Methyl stearate	112-61-8	(1 %)	organometallic compound substitute	EU

These contaminants represent different classes of compounds and are a combination of contaminants recommended in:

1) *The ILSI guidelines (Guidelines of the International Life Sciences institute (ILSI) Recycling of plastics for food contact use; edited by the ILSI Europe Packaging Material Task Force; Brussels, Belgium, May 1998);*

2) *Contaminants recommended in the guidelines initiated by the 'Agence Française de Sécurité Sanitaire des Aliments';*

3) *Contaminants recommended by the US FDA in the threshold of regulation (Code of Federal Regulations 21CFR170.39, Threshold of regulation for substances used in food-contact, Revised as of April 1, 2003).*

Figure 2 PET flakes



Although it is yet unknown if the surrogates, recommended by the French authorities, actually are required, it is decided to include them in the test to make sure that the full range of possible surrogates is covered in this challenge test. As an example the following cocktail can be prepared

Table 2 Example: cocktail composition in about 75 liter hexane (total weight 60 kg)

Contaminant	Kg	% (w/w)
Toluene	6	10
R(+)-Limonene	0.06	0.1
Monochlorobenzene	0.6	1
Cyclohexylbenzene	0.6	1
Benzophenone	0.6	1
1,1,1 trichloro-ethane	0.6	1
2,4-pentanedione (acetyl acetone)	0.06	0.1
o-cresol	0.9	1.5
Methyl stearate	0.6	1

During storage the flakes and the surrogate cocktail in the drums were mixed at regular time intervals. After 10 days the cocktail was removed and the flakes were rinsed to remove adhering contaminants. To that end the contents of each drum was quickly rinsed with 20 liter hexane and not with water as should have been done according to the protocol. This was done because of the time for drying was relative short and a too high water content of PET flakes may cause degradation of PET in the extrusion stage of the recycling process.

After 3 days drying on air (no significant hexane smell anymore) the flakes were transported in hermetically sealed plastic drums to PTP in the Czech Republic for the evaluation of their recycling system.

Sampling

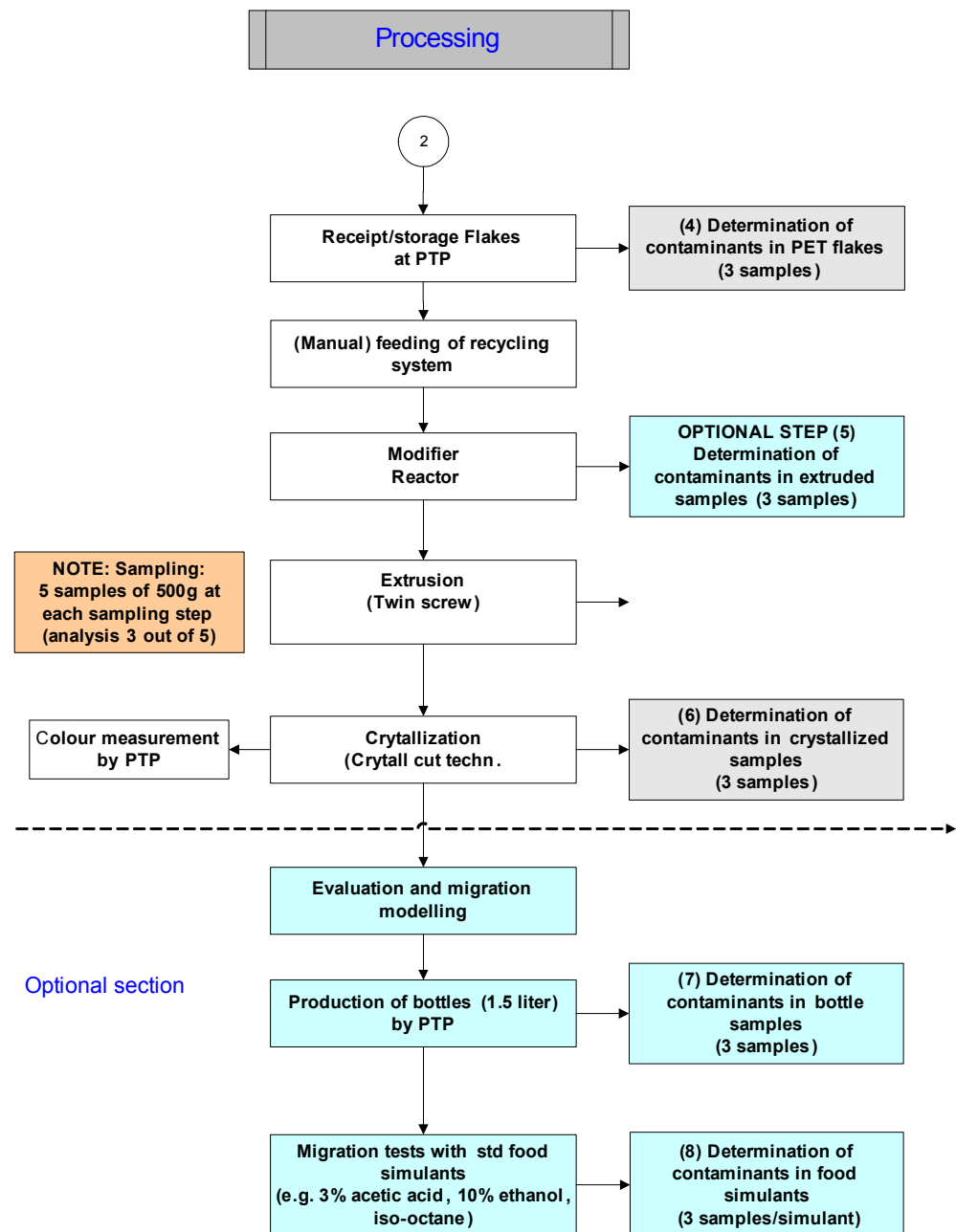
Before and after exposure, samples of the cocktails liquid phase were taken to verify the concentration of the surrogates in the drum at the start and the end of the flake contamination. Before transport samples of the dry contaminated PET flakes were taken and stored until analysis in hermetically sealed glass jars at 5°C.

2.2 Sampling and processing

In this section of the report the PTP recycling process is described briefly and all relevant technical parameters are included. The details were provided by PTP technologies BV and relevant conditions were recorded during processing of the contaminated PET. Prior to the challenge test, the line produced white (clear) PET to allow visible identification of the start of the blue colored contaminated material, used in the challenge test.

The scheme below describes the sampling protocol at the plant of PTP in the Czech Republic.

Figure 3



Sampling

The plastic containers that contained the contaminated PET were opened by a TNO employee and immediately samples (about 500 gram solid material) were taken and stored in glass jars. The PET material from the individual containers was mixed before processing. During each of the next process steps samples were taken for analysis at TNO.

Step 1

The contaminated washed post-consumer PET flakes (particle size (average) 4 – 8 mm, bulk density (average) 250 - 400 kg / m³ ,dust content < 1 %, moisture < 2,0 %, Polyolefin < 1%, metal max. 10 ppm, label / paper < 100 ppm, are loaded into the preliminary mixing bunker where the flakes are mixed with modifying agent. During that process the surface of flakes is coated with the modifying agent during several minutes. [Temperature: room temperature]

Step 2

After the preliminary mixing, the contaminated flakes, coated with modifying agent, are transported into a specially designed rotating infrared reactor (in figure 1 and 2 referred to as modifying reactor), where the flakes are being mixed and dried at a temperature of 150° C under normal atmospheric condition. The process of mixing of flakes at high temperature is also necessary for initiation of the modification reaction between PET flakes and modifying agent on the surface of the flakes. [Recorded conditions: processing ca. 60 minutes at 150°C for 75 kg; residence time in dryer is about 13.5 minutes]

Step 3

Under normal operation conditions the dried PET is transported by the means of a vacuum conveying system into the hopper of the twin-screw extruder. During the challenge test transport was done manually. The extruder has 2 degassing zones, a melt pump and a screen changer with 58 micron filters. During the extrusion, the modification reaction between (molten) PET and modifying agent is completed throughout the whole volume of the material.

Figure 4 Extruder conditions



After passing the screen of the filter, the melt of modified PET flows through the underwater pelletizing system. The pellets are then passing through a mechanical dryer where they are separated from water and fall on the surface of a vibrating conveyor. The temperature of the pellets at the exit of the mechanical dryer is about 135°-150° C.

Figure 6 Crystallizing PET granules on vibrating table



2.3 Samples for investigation

As mentioned above, all samples were taken by a TNO employee (see also figures 1 and 3) and delivered at TNO. Upon receipt at TNO the samples were provided with a unique TNO code and stored at 4°C until start of the analysis. In appendix 2 an overview of all samples and their codes are given. The next table provides a summary.

Table 3 Samples for analyses

Sample/sampling time or date	Description	TNO Code 0941/01/xx	Received at TNO
18/07/2005	Surrogate cocktail drums 1 and 2, before addition of flakes,	5686-1 to 3	18-07-2005
28/07/2005	Surrogate cocktail drums 1 and 2, after exposure of flakes	Drum1 A/B Drum2 A/B	28-07-2005
03/08/2005	Air dry PET flakes, taken at PTP plant	5752-5755	11-08-2005
03/08/2005	Modifier reactor (IR Dryer)	5756-5558	11-08-2005
03/08/2005	Granules from crystallizer	5759-5761	11-08-2005
01/08/2005	Air dry Contaminated flakes before transport to PTP	5762-5764	11-08-2005
18 /07/05	Blank flakes 1	5765-5767	11-08-2005
04/08/2005	PET bottles from recycled contaminated flakes	5768-5777	11-08-2005
03/08/2005	Preform from recycled contaminated flakes	5778-5787	11-08-2005

2.4 Analytical procedure

2.4.1 *Sample pre-treatment*

20 g of sample material was transferred to a 100 ml flask and dichloromethane (DCM; Sigma/Aldrich purity $\geq 99.8\%$) was added. To the samples of flakes 100 ml, to the samples after the modifier reactor 80 ml, to the crystals 30 ml and to the PET-bottle samples 90 ml of DCM was added. The samples were extracted for 24 h at room temperature which proved to be the optimal condition. 1 ml of the final extracts was transferred to a 2 ml GC vial and 25 μl of the internal standard (IS, dodecane 443.52 mg/l in DCM) was added.

The 3% acetic acid food simulant migration extracts were extracted two times with DCM (800 ml of extracts with 2 time 40 ml of DCM). The DCM extracts were pooled. To the pooled extract DCM was added to a final volume of 100 ml. Furthermore, sodium sulfate and sodium bicarbonate were added for drying purposes. DCM was decanted and the DCM was evaporated under a vigreux column at 50°C to a final volume of 1 ml. To this final extract 25 μl of internal standard solution containing 443.52 mg/l of dodecane in DCM was added.

All samples were analyzed in triplicate.

2.4.2 *Standard solutions*

The stock solutions of trichloroethane, toluene, 2,4-pentanedione, monochlorobenzene, limonene, o-cresol, cyclohexylbenzene, benzophenone and methylstearate were prepared by dissolving ca. 65 mg of the standards in 100 ml DCM. These stocks were diluted 10 times by transferring 1 ml to a volumetric flask of 10 ml.

The standard solutions containing ca. 65 mg/l (Std-1) of each contaminant were used as the highest calibration solutions.

Table 1 and 2 of the appendix present the calibration solutions used for the construction of the calibration curves. Depending on the concentration of the compounds in the sample the 'high' or the 'low' calibration curve was used.

Internal standard was prepared by the solution of 44.3 mg dodecane in 100 ml of DCM (443.5 mg/l; IS-1). This solution was diluted 20 times by the addition of 9.5 ml of DCM to 500 μl of IS-1. This resulted in a IS solution named IS-3 containing 22.2 mg/l.

2.4.3 *GC-MS analysis*

The final extract, blanks and calibration solutions obtained under 2.4.1 and 2.4.2 were analyzed by GC-MS for the concentrations of contaminants. The GC-MS conditions were as follows:

Analyses were performed on a ThermoQuest Trace GC and MS used in electron impact mode. The GC-MS conditions and equipment were as follows:

- Injection volume: 1 or 2 μl (split mode)
- Column: DB-5MS (J&W) 60 m x 0.32 mm (df = 0.25 μm)
- Injector: Optic-2 (ATAS) programmed: 70°C \rightarrow 10°C/sec \rightarrow 300°C
- Transfer line/source: 250°C/200°C
- Carrier: He (200 kPa); constant pressure
- Oven: 40°C (3 min) \rightarrow °C/min \rightarrow 100°C \rightarrow 10°C/min \rightarrow 280°C (5min)
- Detection mode: full scan (m/z 40 to m/z 300)

Compounds were quantified by dividing the peak height of three specific ions with the peak height of the internal standard ion (m/z 57) using the linear regression method. The final results were calculated by the average of the three quantification results. n-Dodecane was used as an internal standard (ion 57) for correction of the injection volume (added right before injection). Quantification was performed using an equivalent calibration line or a single close by calibration point.

Ions used for quantification were:

1,1,1-Trichloroethane:	m/z 61, 97 and 99
Toluene:	m/z 65, 91 and 92
2,4-Pentanedione:	m/z 43, 85 and 100
Chlorobenzene:	m/z 77, 112 and 114
Limonene:	m/z 68, 93 and 136
o-cresol	m/z 90, 107 and 108
Cyclohexylbenzene:	m/z 104, 117 and 160
Benzophenone:	m/z 77, 105 and 182
Methyl stearate:	m/z 74, 87 and 298

2.5 Migration experiments

To test the possible migration of contaminants from the recycled PET-M bottles to food two PET-M bottles of 1.5 l (end product of the recycling process) were filled with a food simulant *viz.* 3% acetic acid and saved for 10 days at 40°C. After 10 days the simulants were extracted with DCM as described in section 2.4.1 and the final extracts were analyzed for contaminants.

Recovery experiments:

A sample of 3% acetic acid was fortified with the cocktail of surrogate contaminants at the level 2 µg/l and a sample at the level of 20 µg/l. These samples analyzed by the same procedure as the migration extracts.

3 Results and discussion

3.1 Contamination of the samples with the cocktail of surrogate contaminants

The total batch of ca. 75 kg of virgin PET material received from PTP was divided over two drums. To each drum a specific amount (in kg) of the contaminants were added. The actual amounts added are described below

Table 4 Composition of surrogate contaminant cocktail

Contaminant	Total [kg] drum 1	Total [kg] drum 2
Toluene	7.3000	7.4000
Limonene	0.0737	0.0734
Monochlorobenzene	0.7350	0.7360
Cyclohexylbenzene	0.5050	0.5010
Benzophenone	0.7380	0.7360
1,1,1-Tricloro-ethane	0.7380	0.7360
2,4-Pentanedione (acetyl acetone)	0.0754	0.0740
o-Cresol	0.5040	0.5000
Methyl stearate	0.7365	0.7360
Total amount of contaminants	11.4056	11.4924
Added hexane for solution	63.29	63.21
Total amount of PET	37.50	37.50

3.2 Calibration curves

For all calibration curves constructed (see Table 1 and Table 2 of appendix 1) the correlation coefficient R^2 was >0.99 , the only exceptions were 2,4-pentanedione and methyl stearate. For 2,4-pentanedione none of the calibration curves (set of ions selected) could be used and the quantification for this compound was based on the calibration standard which was most near the concentration in the sample. For methyl stearate the calibration curve of the ion set of m/z 298/57(I.S) showed R^2 of 0.94. This calibration curve was included in the quantification of the samples.

3.3 Analytical results

The results obtained for the analysis of all the samples collected are presented in Table 3 and Table 4 of the appendix. Table 3 presents the measured concentrations of the surrogate contaminant in the cocktail before and after storage with the PET flakes. The results of the concentration measurements right after preparation of the cocktail show some inhomogenities and one sample was taken before addition of the pentanedione. The results of the measurements after storage show that the composition of the cocktails of drum 1 and 2 was well comparable and balanced. Furthermore, the average results of each sample set of three samples are given in Table 4 of the appendix. For each sample point three samples were analyzed and finally three different samples of recycled PET

bottles were analyzed for containing contaminants. The average results are calculated by using three different ion pairs (as described in section 2.4.3).

In the Table 5 (see below) a summary of the average results of each polymer sample is given. The relative standard deviations (RSD), with a few exceptions, are very good considering the variation in quality of the PET used for the test (different bottles, different origin). For limonene and pentanedione the concentrations are already very low after the IR drying step.

Table 5 Summary of results

TNO codes	5752-5754		5756-5758		5759-5761		5774-5777	
Sample	Air dry PET flakes (n=9)		IR dryer (n=9)		Crystallized PET (n=9)		PET-bottles (n=4)	
	µg/kg	RSD%	µg/kg	RSD%	µg/kg	RSD%	µg/kg	RSD%
1,1,1-trichloro Ethane	50705	6.50%	1341	1.90%	133	2.00%	96	3.80%
Toluene	881737	3.30%	25181	6.00%	4468	2.10%	3616	9.00%
2,4-Pentanedione	87997	1.90%	2653	3.20%	429	1.80%	<400	n
Chlorobenzene	201893	4.50%	5242	5.20%	992	3.30%	967	11.60%
Limonene	3556	4.10%	92	9.60%	152	2.50%	211	17.40%
o-Cresol	1872706	9.20%	123182	1.90%	26229	4.60%	26800	9.30%
Cyclohexyl benzene	141440	11.20%	3814	30.50%	1637	2.50%	1496	4.30%
Benzophenone	786429	5.90%	230945	4.80%	152263	3.00%	198315	5.50%
Methyl stearate	493639	10.30%	95393	5.80%	58881	1.90%	64418	4.90%

Analysis of a blank sample (see appendix) shows that none of the compounds is present above the limit of detection, except for limonene. This compound is present at a level of 420 µg/kg. This is not unusual because the flakes originate from washed post consumer bottles and very likely have been used for citrus containing beverages.

Table 6 shows the effects of the different process steps on the removal of the surrogate contaminants. The tumbling IR dryer shows to be very effective as it removes about 97% of both the volatile and the less volatile compounds. Only for the least volatile compounds benzophenone (BP 305.4°C) and methyl stearate (BP 442 - 443°C) the removed amounts are lower (70% and 80%). Extrusion with the twin screw extruder is less effective. The results clearly show that this process step is very effective for very volatile compounds such as trichloroethane that has a boiling point of 75°C (removes 90% from the dried material) and much less effective for non volatile compounds such as methyl stearate (only 38% removed).

Table 6 Efficacy of process steps compared with previous steps

Sample	Air dry PET flakes µg/kg	After dryer (=reactor) µg/kg	Lost by drying	After extrusion µg/kg	Lost by extrusion	PET- bottle µg/kg	Lost by blowing
1,1,1-Trichloroethane (BP 72 - 75°C)	50705	1341	97.4%	133	90.1%	96	28.2%
Toluene (BP 110.6°C)	881737	25181	97.1%	4468	82.3%	3616	19.1%
2,4-Pentanedione (BP 140.4 °C)	87997	2653	97.0%	429	83.8%	<400	nd
Chlorobenzene (BP 130°C)	201893	5242	97.4%	992	81.1%	967	2.5%
Limonene (BP 176°C)	3556	92	97.4%	152	0%	211	0%
o-Cresol (BP 191°C)	1872706	123182	93.4%	26229	78.7%	26800	0%
Cyclohexylbenzene (BP 239°C)	141440	3814	97.3%	1637	57.1%	1496	8.6%
Benzophenone (BP 305.4°C)	786429	230945	70.6%	152263	34.1%	198315	0%
Methyl stearate (BP 442 - 443°C)	493639	95393	80.7%	58881	38.3%	64418	0%

The highest concentration in the PET bottles, being the food contact product, is observed for benzophenone (about 200 mg/kg). Theoretically, this compound can migrate into a bottled beverage or other food product. The ISLI guidelines state that recycled PET is considered safe for food contact if the migration into a food simulant is less than 10 µg/l. In fact the dietary intake must be less than 10 µg/l. According to the FDA this limit is 0.5 µg/l. The dietary concentrations (DC) are calculated with the formula:

$$Dc = (C_{pack} \times W \times C_f \times F_t \times R \times M_{max})/V$$

In this formula correction factors of FDA related to the use of products and a correction factor for 100% migration are used. For details of correction factors see the explanations below.

Formula description:

- Dc = dietary concentration in µg/L
- C_{pack} = measured concentration of benzophenone in the bottle (µg/kg)
- W = bottle weight (kg)
- V = volume of the bottle (in liter)
- C_f = Consumption factor (=0.05) taken from Table 1 FDA regulation 21 CFR 170.39.
- F_t = Food distribution factor (=0.97) for acidic liquids taken from Table II FDA regulation 21 CFR 170.39.
- R = Ratio of contaminated/uncontaminated bottles at a level of 1:2500 (see below)
- M_{max} = Maximal migration obtained by using migration modeling software program (Swiss Federal Office of Public health, Division of Food Science, *Advanced Kinetics and Technology Solutions* (AKTS A6) SML Standard version 4)
M_{max} = 33 % (factor of 0.33)

In the EU-Project FAIR-CT98-4318 "Recyclability" that has been carried out between January 1999 and April 2002 information on contamination levels have been collected. One of the objectives of this study was to provide a statistical overview of the nature and extent of contaminants in PET recovered from the food packaging market, in order to establish an evaluation platform for the quality and safety-in-use of recycled PET plastics for food packaging. In this study about 900 PCR PET flake samples from all over Europe were collected at commercial washing plants and analyzed. The results of this study showed that about 0.03 – 0.04% of the collected post consumer bottles is being misused with non-food contaminants (so R = 1: 2500 or 0.0004).

This gives the following calculation of the dietary concentration:

$$Dc = 200 \cdot 10^5 \cdot 44 \cdot 10^{-3} \cdot 5 \cdot 10^{-2} \cdot 0,97 \cdot 4 \cdot 10^{-4} \cdot 0,33 = 0,056 \mu\text{g/L}$$

This value is well below the limit of 0,5 $\mu\text{g/L}$. The values of Dc of all other tested challenge chemicals will be lower.

To verify these results also an actual migration study has been made using the standard food simulant 3% acetic acid. In practice this simulant is considered a worst case. The results of this investigation are described in the next paragraph.

3.4 Migration experiments

The results obtained for the determination of the contaminants in food simulant 3% acetic acid are presented in Table 7. The presented results are without I.S. or recovery correction.

Table 7 Concentrations ($\mu\text{g/l}$) of surrogates in food simulant 3% acetic acid (HAc) after 10 days exposure at 40°C*

TNO code	5768B	5769A	Avg.	RSD%	Blank HAc	Recovery at 2 ppb and 20ppb level (%)	
1,1,1-Trichloroethane	< 0,1	< 0,1	< 0,1	n	< 0,1	31.3	32.5
Toluene	2.1	2.3	2.2	6.4%	1.9**	63.0	78.1
2,4-Pentanedione	< 1,2	< 1,2	< 1,2	n	< 1,2	126.1	129.3
Chlorobenzene	0.2	0.2	0.2	0.0%	< 0,1	80.6	90.1
Limonene	0.1	0.1	0.1	0.0%	< 0,1	78.0	85.5
o-Cresol	2.3	2.5	2.4	5.9%	< 0,1	58.3	63.1
Cyclohexylbenzene	< 0,1	< 0,1	< 0,1	n	< 0,1	73.3	77.5
Benzophenone	2.7	2.6	2.7	2.7%	< 0,1	80.2	98.7
Methyl stearate	< 0,1	< 0,1	< 0,1	n	< 0,1	91.2	132.9

*results are not corrected by IS or for recovery.

** Verified contamination in glass work

The concentration of contaminants in the 3% acetic acid food simulant obtained after incubation for 10 days at 40°C were below 3 $\mu\text{g/l}$ for all contaminants under investigation this is below the Dc limit of 10 $\mu\text{g/l}$ set by the ILSI guidelines.

If the FDA Cf and Ft factors are considered the Dc is also well below the limit of 0.5 $\mu\text{g/kg}$.

4 Conclusions

TNO has performed an investigation into the suitability of a recycling method known as “Modification Technology”, for the production of food grade PET-M material from post consumer PET bottles. This technology consists of a system to clean and modify PET flakes by means of modifier reactor/ infrared drier, a twin screw extruder and a crystallization system (Crystal Cut technology) to produce ready to use PET-M granules.

The system has been challenged by TNO, using the most severe challenge test available to date, during which PET flakes are contaminated with an extended set of surrogate contaminants that covers chemicals, demanded by the procedures of FDA, ILSI and French authorities.

Present test results show that the system removes the surrogate contaminants very well. Moreover, the results show that migration of the residual surrogates into the food simulant acetic acid is low enough to conclude that the capabilities of the system meets the demands of de USA FDA (dietary concentration <0.5 µg/l) and the informal EU ILSI limit of 10 µg/l.

5 Signatures

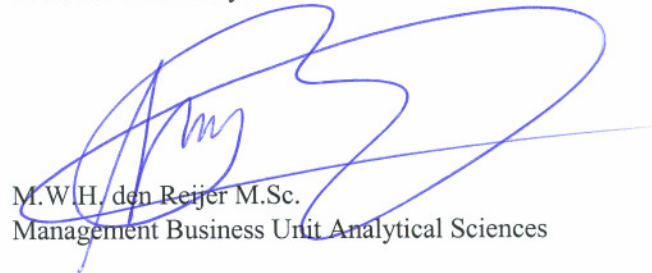
In absence



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6 Addendum

6.1 **V6633 B01 Tables**

Table 1 Concentrations of calibration solutions (mg/L) for the calibration curve (HIGH)

Calibration curve HIGH	Std-1 (0V)	Std-2 (2V)	Std-3 (4V)	Std-4 (8V)	Std-5 (16V)	Std-6 (32V)
1,1,1-Trichloroethane	65.72	32.86	16.43	8.22	4.11	2.05
Toluene	65.32	32.66	16.33	8.17	4.08	2.04
2,4-Pentanedione	63.18	31.59	15.80	7.90	3.95	1.97
Chlorobenzene	62.49	31.25	15.62	7.81	3.91	1.95
Limonene	65.05	32.53	16.26	8.13	4.07	2.03
o-cresol	64.89	32.45	16.22	8.11	4.06	2.03
Cyclohexylbenzene	66.61	33.31	16.65	8.33	4.16	2.08
Benzophenone	65.01	32.51	16.25	8.13	4.06	2.03
Methyl stearate	65.24	32.62	16.31	8.16	4.08	2.04
Prepared by dilution of:	4 mL 0V	2 mL 0V	1 mL 0V	500 µL 0V	250 µL 0V	125 µL 0V
	+ 100 µL IS-1	+ 2 mL DCM	+ 3 mL DCM	+ 3.5 mL DCM	+ 3.75 mL DCM	+ 3.875 mL DCM
		+ 100 µl IS-1	+ 100 µl IS-1	+ 100 µl IS-1	+ 100 µl IS-1	+ 100 µl IS-1

* IS-1 = internal standard solution containing 443.5 mg/l dodecane in DCM (dichloromethane)

Table 2 Concentrations ($\mu\text{g/L}$) of calibration solutions for the calibration curve (LOW)

Calibration curve LOW	Std-7 (32V)	Std-8 (128V)	Std-9 (512V)	Std-10 (1600V)	Std-11 (6400V)
1,1,1-Trichloroethane	2053.75	513.44	128.36	41.08	10.27
Toluene	2041.25	510.31	127.58	40.83	10.21
2,4-Pentanedione	1974.38	493.59	123.40	39.49	9.87
Chlorobenzene	1952.81	488.20	122.05	39.06	9.76
Limonene	2032.81	508.20	127.05	40.66	10.16
o-cresol	2027.81	506.95	126.74	40.56	10.14
Cyclohexylbenzene	2081.56	520.39	130.10	41.63	10.41
Benzophenone	2031.56	507.89	126.97	40.63	10.16
Methyl stearate	2038.75	509.69	127.42	40.78	10.19
Prepared by dilution of:	250 μL 0V	1 mL 32V	250 μL 32V	80 μL 32V	20 μL 32V
	+ 7.75 mL DCM	+ 3 mL DCM	+ 3.75 mL DCM	+ 3.92 mL DCM	+ 3.98 mL DCM
	followed by	+ 100 μl IS-3	+ 100 μl IS-3	+ 100 μl IS-3	+ 100 μl IS-3
	4 mL 32V				
	+100 μL IS-3*				

* IS-3 = internal standard solution containing 22.2 mg/l dodecane in DCM (dichloromethane)

Table 3 Concentrations of surrogates in cocktail stored in drums 1 and 2, before and after submersion of the flakes for 10 days at 40 °C

TNO code	Sample	1,1,1-Trichloroethane	Toluene	2,4-Pentanedione	Chloro benzene	Limonene	O-Cresol	Cyclohexyl benzene	Benzo phenone	Methyl stearate
5686-1-3	drum 1 (no pentadione) before exposure	6869	70505	65	6970	706	4756	4691	6904	6753
5686-4-5	drum 2 before exposure	4009	37509	455	4075	444	2797	2122	3540	3304
5686-6	drum 1 (with pentanedione) before exposure	6699	58851	840	6578	674	4290	4449	6521	5887
Drum-1A and B	drum 1 after exposure	6446	54555	702	5999	685	3161	3787	5380	5141
Drum-2A and B	drum 2 after exposure	6787	55986	665	6620	670	3692	4401	6014	5121

Table 4 Summary of the average results ($\mu\text{g}/\text{kg}$) bases on 3 or 4 individual measurements (n=3 or n=4)

TNO code 941-01-xxxx	Sample	1,1,1- trichloroethane	Toluene	2,4-Pentane dione	Chloro benzene	Limonene	o-Cresol	Cyclohexyl benzene	Benzo phenone	Methyl stearate
5752*	Air dry PET flakes-1 (n=3)	54016	926266	78912	193288	2887	1770236	78029	692606	376128
RSD%		8.4%	9.0%	6.3%	8.2%	13.9%	18.4%	3.6%	13.4%	28.4%
5753	Air dry PET flakes-2 (n=3)	48496	932404	94359	213438	5012	1987344	219323	867796	610022
RSD%		13.7%	2.6%	5.9%	9.7%	13.7%	1.4%	24.0%	3.1%	16.6%
5754	Air dry PET flakes-3 (n=3)	49603	786541	90720	198952	2768	1860537	126968	798886	494768
RSD%		0.9%	7.0%	9.5%	1.2%	6.6%	3.6%	6.0%	3.2%	7.8%
Average		50705	881737	87997	201893	3556	1872706	141440	786429	493639
RSD%		6.5%	3.3%	1.9%	4.5%	4.1%	9.2%	11.2%	5.9%	10.3%
5756	modifier reactor-1 (IR dryer)	1375	24308	3245	4952	35	99176	1955	110092	36564
RSD%	(n=3)	11.6%	14.9%	9.9%	12.6%	-	4.0%	65.4%	12.3%	17.2%
5757	modifier reactor-2 (IR dryer)	1431	26476	2742	5552	93	134144	2891	235394	83633
RSD%	(n=3)	8.8%	3.6%	5.0%	3.4%	20.7%	0.4%	8.7%	3.8%	6.4%
5758	modifier reactor-3 (IR dryer)	1217	24760	1973	5222	146	136227	6596	347348	165982
RSD%	(n=3)	7.9%	6.1%	4.0%	4.1%	34.3%	3.4%	17.5%	11.9%	15.3%
Average		1341	25181	2653	5242	92	123182	3814	230945	95393
RSD%		1.9%	6.0%	3.2%	5.2%	9.6%	1.9%	30.5%	4.8%	5.8%
5717	crystallizer PET-3 (n=3)	143	4942	443	1097	162	27617	1763	153979	57462
RSD%		4.5%	6.5%	8.2%	3.6%	5.7%	11.4%	0.4%	9.8%	6.7%
5760	crystallizer PET-2 (n=3)	133	4283	419	938	144	26301	1595	150093	57441
Stdev%		4.3%	8.6%	4.7%	7.6%	4.8%	3.7%	5.2%	11.7%	3.7%
5761	crystallizer PET-4 (n=3)	124	4178	424	941	148	24771	1552	152718	61741
Stdev%		1.0%	4.5%	7.0%	1.0%	1.0%	3.0%	1.5%	5.7%	7.3%
Average		133	4468	429	992	152	26229	1637	152263	58881

Stdev%		2.0%	2.1%	1.8%	3.3%	2.5%	4.6%	2.5%	3.0%	1.9%
5774-5777	PET-bottle (n=4)	96	3616	n.d**	967	211	26800	1496	198315	64418
Stdev%		3.8%	9.0%	n.d	11.6%	17.4%	9.3%	4.3%	5.5%	4.9%
5776	Blank flakes	<100	<100	<100	<100	420	<100	<100	<100	<100

*each result is the average of the quantification results obtained for three different ions (see section 2.4.3); ** n.d. = not detected

Overview of samples

Sample/sampling time or date	Description	TNO Code 0941/01/xx	Received at TNO
18-07-2005	Blank flakes	5765-5767	12-07-2005
18-07-2005	Surrogate cocktail drum 1 before addition of flakes, no acetyl acetone	5686-1	18-07-2005
18-07-2005	Surrogate cocktail drum 1 before addition of flakes, no acetyl acetone	5686-2	18-07-2005
18-07-2005	Surrogate cocktail drum 1 before addition of flakes, no acetyl acetone	5686-3	18-07-2005
18-07-2005	Surrogate cocktail drum 2 before addition of flakes, no acetyl acetone	5686-4	18-07-2005
18-07-2005	Surrogate cocktail drum 2 before addition of flakes, no acetyl acetone	5686-5	18-07-2005
18-07-2005	Surrogate cocktail drum 2 before addition of flakes, with acetyl acetone	5686-6	18-07-2005
28-07-2005	Surrogate cocktail drum 1 after exposures to flakes	A and B	28-07-2005
28-07-2005	Surrogate cocktail drum 2 after exposures to flakes	A and B	28-07-2005
03/08/2005, 11.30 h	Air dry PET flakes 1, taken at PTP plant	5752	11-08-2005
03/08/2005	Air dry PET flakes 2, taken at PTP plant	5753	11-08-2005
03/08/2005	Air dry PET flakes 3, taken at PTP plant	5754	11-08-2005
03/08/2005	Air dry PET flakes 4, taken at PTP plant	5755	11-08-2005
03/08/2005, 12.15 h	Modifier reactor (IR Dryer) 1	5756	11-08-2005
03/08/2005, 12.30 h	Modifier reactor(IR Dryer) 2	5757	11-08-2005
03/08/2005, 12.50 h	Modifier reactor(IR Dryer) 3	5758	11-08-2005
03/08/2005	Crystallizer PET 1	5759	11-08-2005
03/08/2005, 12.50 h	Crystallizer PET 2	5760	11-08-2005
03/08/2005	Crystallizer PET sample 4	5761	11-08-2005
01/08/2005	Air dry Contaminated flakes before transport to PTP, Sample 1	5762	11-08-2005
01/08/2005	Air dry Contaminated flakes before transport to PTP, Sample 2	5763	11-08-2005
01/08/2005	Air dry Contaminated flakes before transport to PTP, Sample 3	5764	11-08-2005
18 /07/05	Blank flakes 1	5765	11-08-2005

18 /07/05	Blank flakes 2	5766	11-08-2005
18 /07/05	Blank flakes 3	5767	11-08-2005
04/08/2005	PET bottle 1	5768	11-08-2005
04/08/2005	PET bottle 2	5769	11-08-2005
04/08/2005	PET bottle 3	5770	11-08-2005
04/08/2005	PET bottle 4	5771	11-08-2005
04/08/2005	PET bottle 5	5772	11-08-2005
04/08/2005	PET bottle 6	5773	11-08-2005
04/08/2005	PET bottle 7	5774	11-08-2005
04/08/2005	PET bottle 8	5775	11-08-2005
04/08/2005	PET bottle 9	5776	11-08-2005
04/08/2005	PET bottle 10	5777	11-08-2005
03/08/2005	Preform 1	5778	11-08-2005
03/08/2005	Preform 2	5779	11-08-2005
03/08/2005	Preform 3	5780	11-08-2005
03/08/2005	Preform 4	5781	11-08-2005
03/08/2005	Preform 5	5782	11-08-2005
03/08/2005	Preform 6	5783	11-08-2005
03/08/2005	Preform 7	5784	11-08-2005
03/08/2005	Preform 8	5785	11-08-2005
03/08/2005	Preform 9	5786	11-08-2005
03/08/2005	Preform 10	5787	11-08-2005