

Determination of Polychlorinated Biphenyls (PCB) and Phthalates in Waste Polymer Samples Intended for Mechanical Recycling



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Sabine Cleres

***Büchi Labortechnik AG
- Switzerland -***



**SpeedExtractor
E-916**

Introduction



- Polymers intended for use in sensitive products have to comply with certain quality standards
- According to European law, PCB levels must not exceed 50 ppm in consumer products due to their high toxicity and persistence
- Even substances with a lower persistence which however could cause adverse effects are regulated if human exposure is considered to be high (i.e. phthalates)
- Since PCBs have been strictly phased out in many parts of the world, they are not expected to be present in virgin polymers anymore
- However, polymers reclaimed from specific polymer waste streams (i.e. electronic waste or automotive shredder residue) may contain PCBs and phthalates that could enter a new product life cycle

Introduction



- It is important to produce reliable data on such contaminant levels
- Extracts of polymer samples are subjected to highly sophisticated analytical tests using GC-MS or LC-MS
- Complete extractions of contaminants from polymers are necessary but not easy
- A wide range of analytical methods has been developed (i.e. several types of solid liquid extraction)
- Pressurized Fluid Extraction (PFE) is an excellent alternative to classical extraction methods like Soxhlet due to its high grade of automation, reproducibility, short analysis time and low solvent usage
- Büchi's new SpeedExtractor optimizes this approach by enabling a parallel PFE of up to 6 samples

Introduction



- An alternative instrument for PFE is ASE[®] (Accelerated Solvent Extraction) from Dionex with a wide range of accepted applications
- In comparison to the SpeedExtractor this instrument has a sequential extraction set-up
- The use of the parallel pressurized fluid extraction for polymer analysis has not been examined yet

Purpose of this study:

Determination of the levels of PCBs and phthalates in homogenized polymer samples from typical shredder residues intended for mechanical recycling using both PFE instruments in order to investigate the extraction efficacy of the new parallel extraction system

Introduction

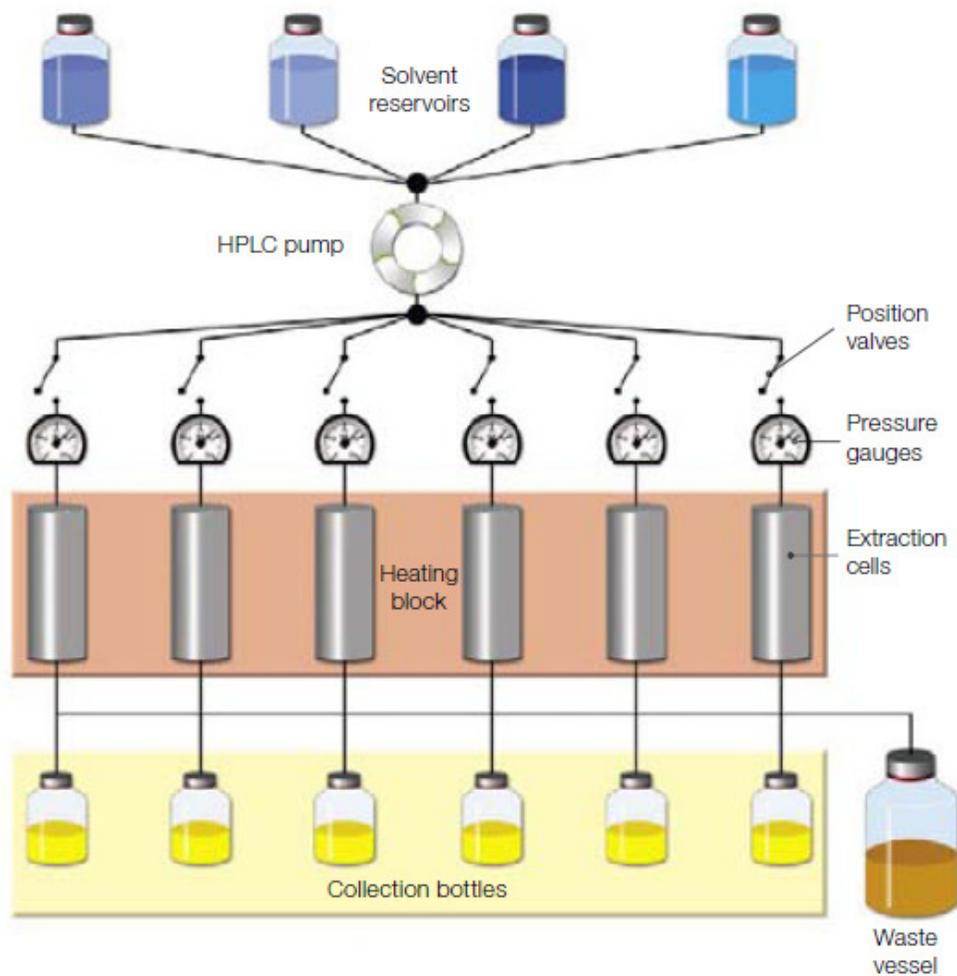


Illustration of the parallel extraction system E-916

Materials and Methods



Instrumentation:

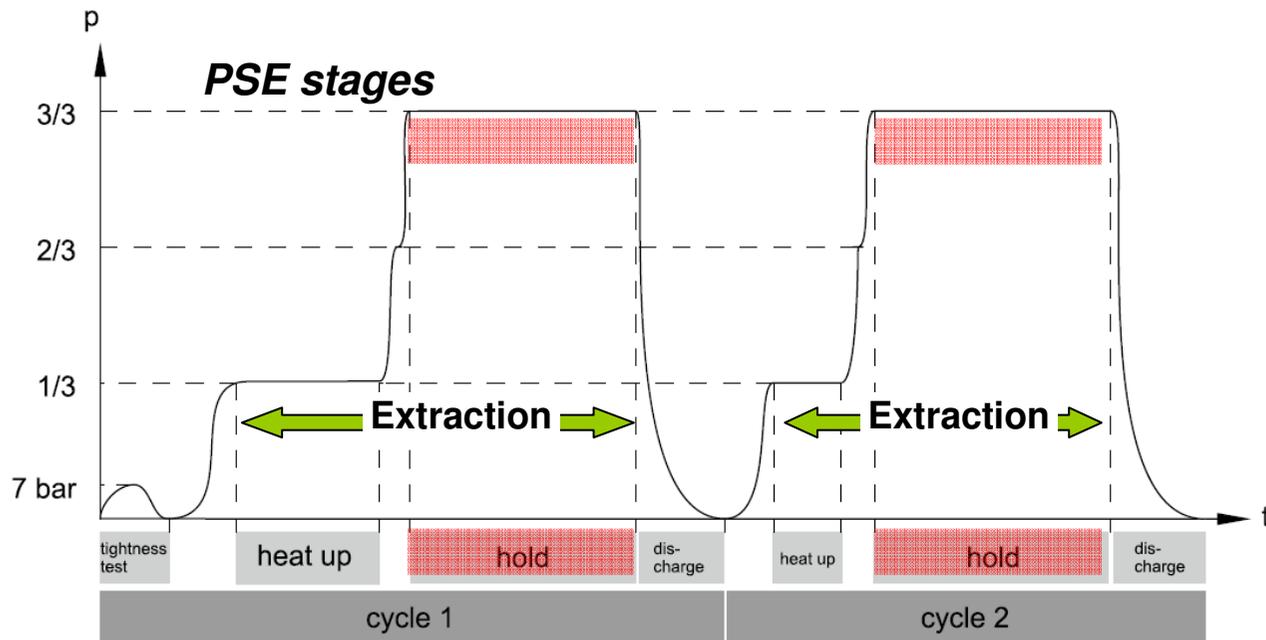
- SpeedExtractor E-916 (Büchi) with 6 extraction cells (20 ml)
- ASE[®] 200 (Dionex), 22 ml extraction cells (sequential)

The work was done by the Fraunhofer Institute for Process Engineering and Packaging, Freising, Germany

Materials and Methods



Example of the extraction stages with the SpeedExtractor



Materials and Methods



Extraction parameters for the determination of PCBs and phthalates in polymers:

	SpeedExtractor	ASE®
Solvent	<i>n</i> -hexane 90%, 2-propanol 10%	<i>n</i> -hexane 90%, 2-propanol 10%
Temperature	80 °C	80 °C
Pressure	100 bar	100 bar
Cells	20 ml	22 ml
Cycles	3	3
Hold	5 min	5 min
Discharge	2 min	-
Flush with solvent	1 min	40%
Flush with gas (N ₂)	2 min	120 s

Analysis



1. Determination of phthalates:

- 0.5 ml to 1.0 ml of the extract was used directly for the determination
- Determination was done with a GC-MS (Shimadzu QP-5000) in single ion monitoring mode
- Quantification was based on an internal standard method with deuterated standards

2. Determination of PCBs:

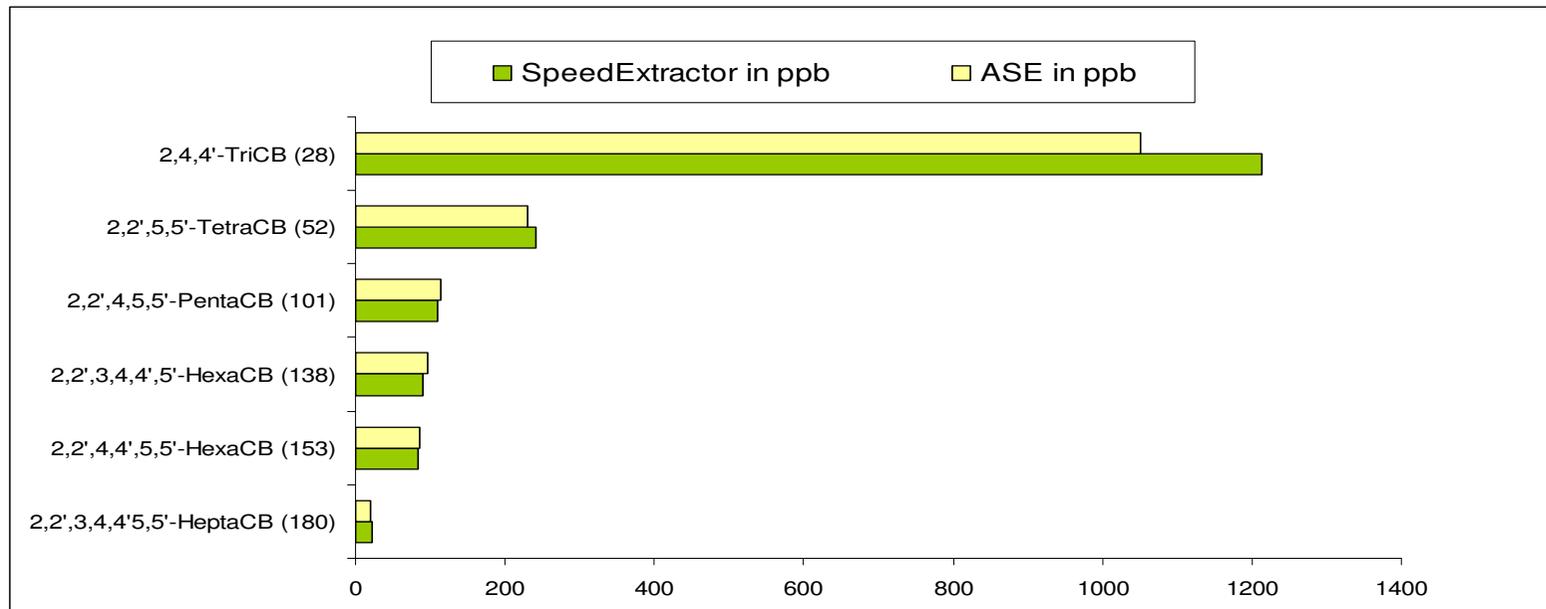
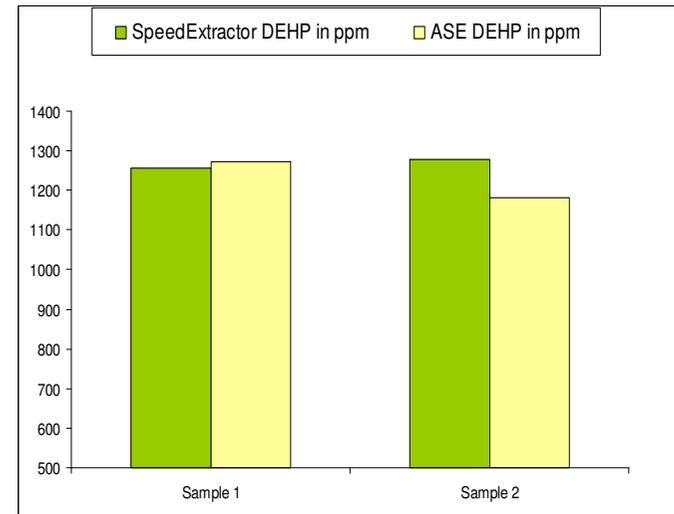
- Residual extracts were cleaned with a mixed column containing acid and basic modified silica
- Concentration to 1 ml was done under a gentle stream of nitrogen
- Detection of PCBs was performed by a GC-MS (HP 5890 Series II coupled to Thermo Finnigan TSQ 7000) in SIM mode
- Quantification of 6 indicator PCBs (#28, #52, #101, #138, #153, #180) was based on isotope dilution

Results and Discussion



Two PFE extracts from two waste polymer samples were analyzed

The data show that the SpeedExtractor delivered results equivalent to those obtained with the ASE[®] system



Results and Discussion



PCBs

- Measured PCBs were found to be in the lower and sub ppm range
- They were used to calculate total PCB threshold value according to the German LAGA norm (5 times the sum of the 6 indicator PCBs)
- No sample exceeded the 50,000 ppb threshold value but the value of sample 1 was much higher than expected

PCB results of waste polymer samples



	Sample 1 [ppb]		Sample 2 [ppb]	
	SpeedExtractor	ASE®	SpeedExtractor	ASE®
2,4,4'-TriCB (28)	6,192	5,436	1,214	1,051
2,2',5,5'-TetraCB (52)	1,172	1,063	241	230
2,2',4,5,5'-PentaCB (101)	222	217	110	115
2,2',3,4,4',5'-HexaCB (138)	98.0	113	90.3	95.6
2,2',4,4',5,5'-HexaCB (153)	79.4	95.2	82.7	85.3
2,2',3,4,4',5,5'-HeptaCB (180)	18.5	21.7	21.1	19.7
Total PCB <i>(German LAGA norm)</i>	38,907	34,726	8,799	7,986

Results and Discussion



Phthalates

- For the phthalates, DEHP dominates the phthalate pattern as expected
- Both samples exceeded the 0.1% level, 1,000 ppm respectively, set by the U.S. Consumer Product Safety Improvement Act for Toys

Phthalate results of waste polymer samples



	Sample 1 [ppm]		Sample 2 [ppm]	
	SpeedExtractor	ASE®	SpeedExtractor	ASE®
DiBP (Diisobutylphthalate)	8.56	7.84	21.4	22.1
DBP (Dibutylphthalate)	5.72	5.82	22.7	21.4
DEHP (Diethylhexylphthalate)	1,257	1,272	1,278	1,180

Conclusion



Determination of PCBs and Phthalates in polymer waste:

- The results show the necessity to monitor the levels of PCBs and phthalates in certain polymer waste streams intended for mechanical recycling
- No sample exceeded the PCB threshold value but the margin of safety of one sample was much smaller than expected
- For the phthalates, both samples exceeded the 0.1% level set by the U.S. Consumer Product Safety Improvement Act for Toys

Conclusion



Comparison of the two PFE instruments:

- The concentration values obtained with the SpeedExtractor E-916 and the Dionex ASE[®] 200 were comparable
- Both instruments delivered high recoveries and reproducibility and used little amounts of solvent
- The SpeedExtractor is faster than ASE[®] 200 in terms of sample processing time
- In this study, the extraction time with the SpeedExtractor was 5 times shorter than the extraction time with the ASE[®]

Acknowledgements



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Conclusion



The new SpeedExtractor delivered high-quality results

SpeedExtractor

High accuracy and extraction speed for routine environmental analysis

Quality in your hands



Thank you for your attention !



Quality in your hands