DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCB) AND PHTHALATES IN WASTE POLYMER SAMPLES INTENDED FOR MECHANICAL RECYCLING

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Abstract

The purpose of this study was to determine the levels of polychlorinated biphenyls (PCBs) and phthalates in homogenized polymer samples from polymer waste streams using two different pressurized liquid extraction (PLE) instruments (ASE® and SpeedExtractor). Both extraction methods showed very similar results..

Measured PCB levels were in the lower and sub ppm range. Calculated total PCB levels using the German LAGA norm do not exceed the 50 ppm (50,000 ppb) threshold value; however, the margin of safety is much smaller than expected. In both samples, diethylhexylphthalate (DEHP) dominates the phthalate pattern and exceeds the 0.1% level set by the US Consumer Product Safety Improvement Act for toys. The results indicate that it may be useful to monitor the levels of PCBs and phthalates in certain polymer waste streams to prevent them from entering a new product life cycle when reused in production.

Introduction

Polymers intended for use in sensitive products have to comply with quality standards set by governments and non-governmental organizations. Some of these standards include maximum levels of chemicals; if exceeded, these chemicals could cause adverse effects to humans or the environment. For example, according to European law, PCB levels must not exceed 50 ppm in consumer products due to high toxicity and persistence[1,2]. However, even substances that could cause adverse effects but have a lower persistence than phthalates are regulated if human exposure is considered to be high[3].

Since PCBs are considered to be persistent organic pollutants (POPs) and have therefore 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 (waste electronics or automotive shredder residue) may contain both, PCBs and phthalates[4], and enter a new product life cycle when reused in production.

Analytical laboratories are responsible for producing reliable data on such possible contaminant levels. Therefore, polymer samples are extracted and extracts are subjected to highly sophisticated analytical tests using tools such as GC-MS or LC-MS. However, a complete extraction of contaminants from polymers is not easy and a wide range of analytical methods has been developed including dissolution and precipitation and several types of solid liquid extraction.

In this regard, PLE may present a good analytical alternative not only due to its high grade of automation and reproducibility but also for economic reasons (short analysis time and low solvent usage). Buchi's new SpeedExtractor further optimizes this approach by enabling a parallel PLE of up to 6 samples (Figure 1). However, the use of this new analysis tool for polymer analysis has not been examined yet, while the alternative PLE instrument, the ASE® (Dionex), has a wide range of accepted applications.

Thus, the purpose of this study was to determine the levels of PCBs and phthalates in homogenized polymer samples from typical shredder residues intended for mechanical recycling using both PLE instruments in order to judge the extraction efficacy of the new parallel extraction unit.

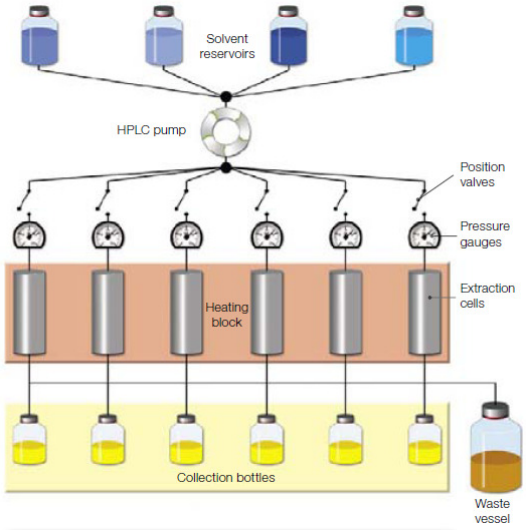

Fig. 1: Illustration of the parallel extraction system E-916

Materials and Methods

Parallel pressurized solvent extraction of PCBs and phthalates was performed with the SpeedExtractor E-916 with 6 extraction cells (20 ml). Sequential accelerated solvent extraction was conducted with the Dionex ASE 200 (22 ml extraction cells). Two grinded polymer samples (< 0.7 mm) from automotive waste streams containing high polymer content were used as test material.

Polymer waste samples (about 0.6 g) were mixed with pumice stone and filled into the extraction cells. ^{13}C labelled internal PCB standards and 2 deuterated internal phthalate standards (D4-DBP and D4-DEHP) were added, and the extraction process was performed according to the parameters given in Table 1. 0.5 ml of the extract (about 1% of its volume) was used for phthalate analysis; the residual extracts were cleaned with a mixed column containing acid and basic modified silica and reduced to 1 ml.

Table 1: Extraction parameters chosen for both PLE instruments

	SpeedExtractor	**ASE®**
Solvent	*n*-hexane/2-propanol (9/1)	*n*-hexane/2-propanol (9/1)
Temperature	80 °C	80 °C
Pressure	100 bar	100 bar
Cells	20 ml	22 ml
Cycles	3	3 (40% flush)
Extraction time (static)	5 min (hold time)	5 min
Discharge	2 min	-
Flush / Purge time	1 min solvent / 2 min N_2	2 min N_2

Detection of PCB was performed by GC-MS (HP 5890 Series II coupled to Thermo Finnigan TSQ 7000) operated in single ion monitoring mode. Quantification of 6 indicator PCBs (#28, #52, #101, #138, # 153, #180) was based on isotope dilution. Phthalates were analyzed with GC-MS (Shimadzu QP-5000) in SIM mode. Quantification was based on an internal standard method with deuterated standards.

Results and Discussion

Two PLE extracts from two waste polymer samples were analyzed for PCB and phthalates. Results are shown in terms of ppb (µg/kg) and indicate very similar results for both extraction methods.

Table 2: Analytical results for PLE extraction. Samples (containing waste polymer) were analyzed twice each.

	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	112.8	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 (German LAGA norm)	38,907	34,726	8,799	7,986
DiBP (Diisobutylphthalate)	8,565	7,837	21,369	22,134
DBP (Dibutylphthalate)	5,716	5,821	22,657	21,408
DEHP (Diethylhexylphthalate)	1,257,000	1,272,000	1,278,000	1,180,000

Measured PCB levels are in the lower and sub ppm range. They were used to calculate total PCB levels using the German LAGA norm (5 times the sum of #28, #52, #101, #138, #153 and #180). Based on this, no sample exceeded the 50 ppm (50,000 ppb) threshold value; however, the margin of safety was much smaller than expected.

For the phthalates, DEHP dominates the phthalate pattern as expected. Both samples exceed the 0.1% level set by the US Consumer Product Safety Improvement Act for toys.

The results indicate that it may be useful to monitor the levels of PCBs and phthalates in certain polymer waste streams intended for recycling.

Acknowledgements

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