COINCIDENCE OF DIFFERENT BROMINATED FLAME RETARDANTS (BFR) IN PLASTIC PARTS OF ELECTRONIC EQUIPMENT – INDICATION FOR INADEQUATE MATERIAL RECYCLING OF WEEE POLYMERS

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Introduction

Numerous brominated flame retardants were identified in polymers from waste electric and electronic equipment (WEEE).[1,2] Among others, tetrabromobisphenol A (TBBP A), octabromodiphenylether (OctaBDE), decabromodiphenylether (DecaBDE) and 1,2-bis(tribromophenoxy)ethane (TBPE) were detected. These polymers are normally excluded from conventional material recycling cycles, since polymers containing DecaBDE, OctaBDE and TBPE were shown to exhibit elevated levels of polybrominated dioxins and furans (PBDD/F) and PBDD/F formation from these three BFR was observed in plastic recycling trials[3]. Several authors described recycling processes[4-6], where extraction procedures remove BFR and PBDD/F from the base polymers to safely recycle the valuable WEEE polymers.

Otherwise, in 2005 about 5 million tons of waste polymers were exported from Europe and the US to China[7]. Only little is known about the fate of these polymers. One third of them are technical polymers which are expected to contain BFR partly. Products of conventional material recycling processes may be expected in plastic parts of new goods, preferably in low-cost articles which are not subjected to extended quality assurance measures. Hence, it was the aim of this study to screen a number of low-cost products for the presence of BFR. Special focus was set on the concurrent presence of different BFR types in homogenous plastic parts, an indication for the inadequate application of conventional material recycling processes to WEEE polymers.

Materials and Methods

40 polymer samples were derived from 20 low-cost electronic goods like drilling machines, vacuum cleaners or planing machines purchased at discounters and do-it-yourself stores in Germany. For each product, one to three homogenous plastic parts were sampled, mainly from casing parts. About 0.5g of polymer was sampled by chopping thin polymer films.

Depending on polymer type about 0.1g of the samples were dissolved or swollen in 5g tetrahydrofuran or toluene and precipitated with 15 g of isopropanol. The extracts were filtered with a PTFE syringe filter and subjected to GC-ECD screening and to GC-MS confirmation analysis, if BFR was detected.

Measurements were conducted on a Carlo Erba GC-ECD using a non-polar chromatographic column (DB-5, J&W, 10m x 0.18 mm, 0.18 µm). Injector temperature was set to 300°C, detector was tempered at 340°C. Temperature programme: 150°C (1 min), 20 K/min, 270°C (5 min), 20 K/min, 340°C (7 min).

Confirmation of GC-ECD identification of BFRs was performed by GC-MS (QP 5000, Shimadzu) in scan mode. Chromatographic conditions were equal to the GC-ECD method. Mass fragments given in Table 1 were used for identification of the following BFRs:

- Tetrabromobisphenol A (TBBPA)
- 1,2-bis(tribromophenoxy)ethane (TBPE)
- Hepta-, octa- and decabromodiphenyl ethers (Hepta-, Octa and DecaBDE).

Table 1: Typical mass fragments of BFR, which were applied for GC-MS confirmation analysis. Dominant fragments are underlined.

BFR	Typical m/z	BFR	Typical m/z
TBBP A	529, 544	OctaBDE	639,641, 643
TBPE	685,687,689	DecaBDE	717, 719, 640, 642
HeptaBDE	561, 563, 483		

Quantification of BFRs was performed by GC-ECD using external calibration standards. These were prepared with technical TBBP A, TBPE, OctaBDE and PentaBDE. PBDE were only quantified if the congener pattern matched that of the technical reference materials.

Results and Discussion

Until now BFRs were detected and confirmed in 7 out of 40 samples, with DecaBDE or TBBPA as dominant BFR types. In one case, OctaBDE has been detected as the dominant BFR. No investigated sample exceeded the 1000 ppm level for OctaBDE of the European RoHS directive yet.[9]

However, there were samples, which contain significantly amounts of different BFRs. In figure 1 this is referenced by ECD chromatograms for two samples, which were superimposed with the chromatogram of a BFR reference standard. Figure 2 depicts the mass spectra of the detected BFR in sample B. They confirm the coincidence of TBBP A, TBPE, DecaBDE and OctaBDE. In this regard it is important to note that technical OctaBDE contains dominant HeptaBDE and OctaBDE congeners, besides less significant Hexa-, Nona- and DecaBDE congeners.[8]

Coincidence of two or more flame retardant systems is outmost unusual for new products and is interpreted as strong indication for the presence of recycled polymers. Since the four detected BFR in sample B are typical for polymers of WEEE,[1,3] it can suggested that inadequate material recycling of WEEE polymers is the source. Conventional material recycling processes without removal of BFR and PBDD/F from the base polymers seemed to be used also for polymers of WEEE. Household products made of these improperly recycled materials provide an uncontrolled source of human exposure to BFRs. European RoHS[9] directive was implemented in order to prohibit such a practise.

In consequence of our findings, it is planned to extend the material screening and to include PBDD/F measurements.

References

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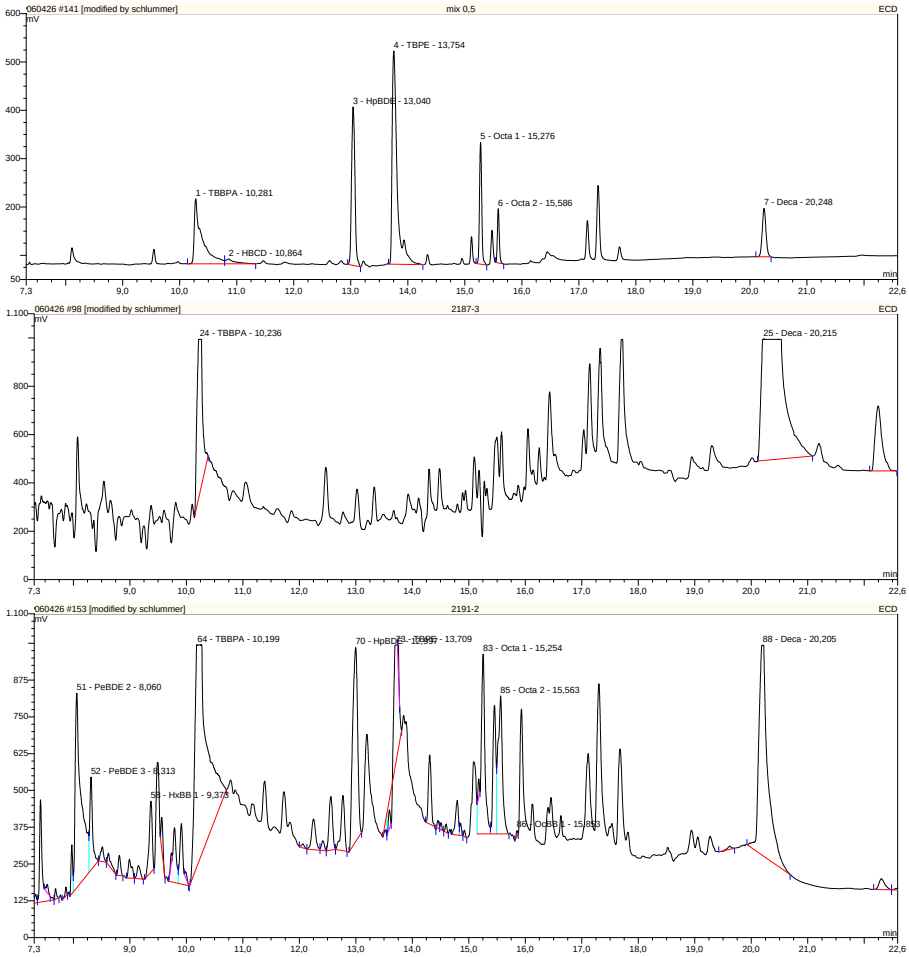

BFR reference mix

Sample A

Sample B

Figure 1: ECD chromatograms of samples A and B with more than one BFR type, superimposed with a BFR reference mix.

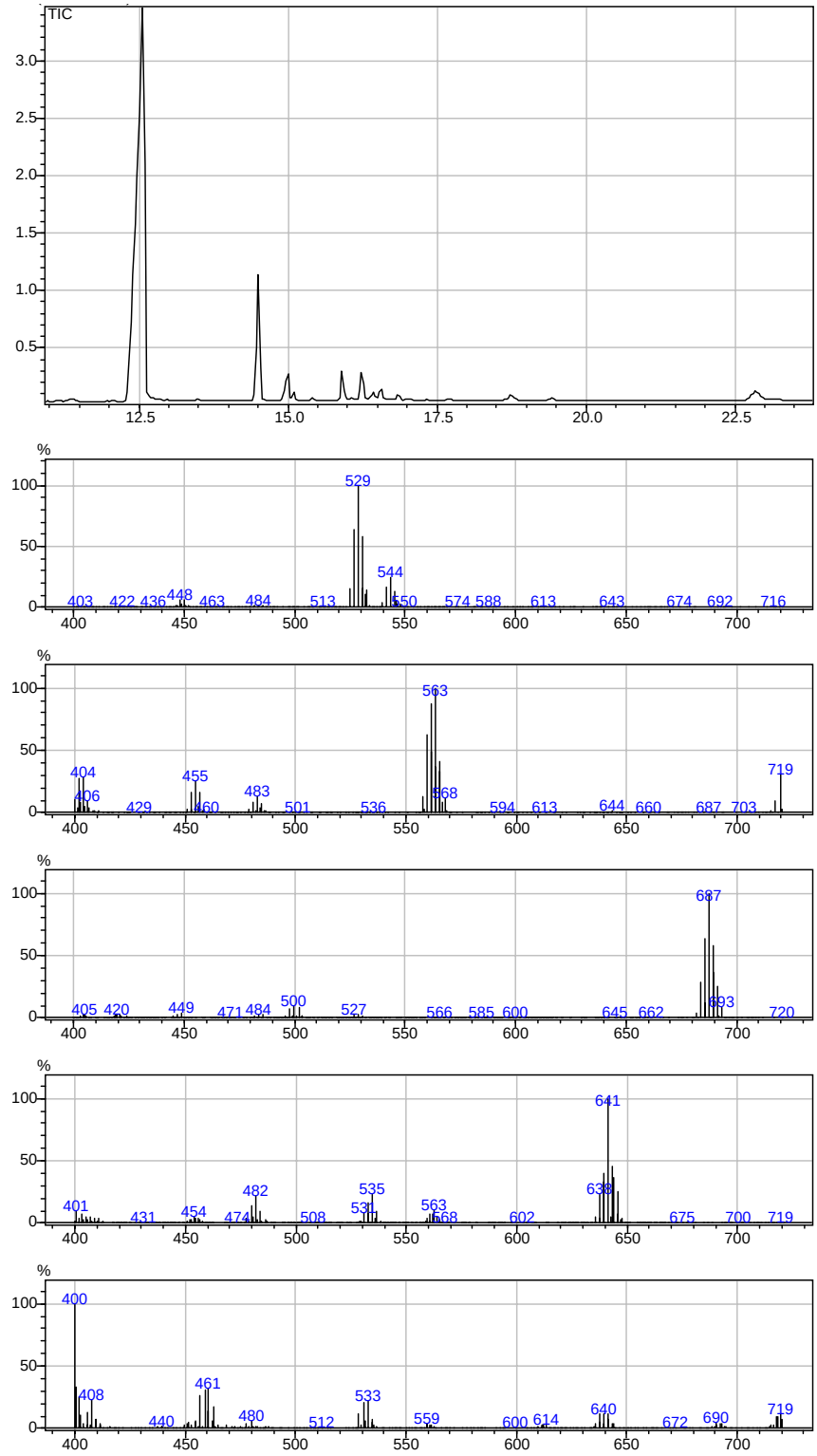

Figure 2: Total ion chromatogram and mass spectra of the detected BFR in sample B.