Detection of Polybrominated Diphenylethers (PBDE), Dibenzofurans (PBDF) and Dibenzodioxins (PBDD) in Scrap of Electronics and Recycled Products

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1. Introduction

In addition to chlorinated dioxines, brominated compounds are also focussed on in legislative, scientific and toxicological investigations.

While sources for chlorinated dioxins and furans were thoroughly sought over the last years, sources for brominated compounds, brominated hydrocarbons, were mostly ignored.

Brominated hydrocarbons are applied as flame retardants in plastics and textiles. Plastics are widely distributed and used in our modern world. Especially in electronic appliances, plastics have to contain flame retardants in order to prevent the flammable material from burning in case of an electronic malfunction.

The most common additives over the last decades have been polybrominated diphenylethers PBDE (additive flame retardants, not linked to the polymer network) and brominated bisphenols (tetrabromo-bisphenol-A TBBA, reactive flame retardants forming part of the polymer structure). Japan for example produced and used about 6000 tons of PBDE and 14000 tons of TBBA in 1987[1]. PBDE easily react to produce brominated dioxins and furans[2].

As a consequence of the proposal for the so called "Electronic Scrap Ordinance" issued by the German Federal Department of Environment, Nature Conservation and Reactor Safety in 1991[3], obsolete electronic devices, printed circuit boards and electronic components, are subjected to various recycling activities. Printed circuit boards with electronic components consist of metals (25 - 30 wt%), glass and ceramics (about 45 wt%) and flame retarded plastics (20 - 25 wt%). These plastics contain flame retardants to a maximum of 20 wt%[4].

In 1994 the German law concerning chemical substances[5] was expanded to cover a wider range of substances, especially eight brominated dioxins and furans. In order to evaluate electronic devices as a source for dioxins, electronics and recycled of obsolete electronics were subjected to detailed analytical investigations.

2. Experimental

Samples from industrial scale mechanical processing, lab-scale pyrolysis, pilot-scale pyrolysis and lab-scale solvolysis were investigated. The samples were identified as follows:

a. TBBA-containing plastics (epoxy-resin-FR4-material) after mechanical processing (hammer mill).

b. Residues after quartz-flask pyrolysis of chopped printed circuit boards and electronic components in N_2/H_2-atomosphere at 1100°C.

c. Condensed phase from quartz-flask pyrolysis b.

d. Flotable material from pilot-scale pyrolysis (T=800°C) of mixed printed circuit boards (epoxy-resin-FR4-material and phenolic-resin-material with electronic components) and mixed flame retarded plastics (mainly thermoplastics).

e. Non-flotable material from d.

f. High pressure extraction of epoxy-resin-FR4-material with ethylacetate (N_2-atmosphere, T=280°C, p=30 bar)[6]

g. Normal-pressure extraction of chopped printed-circuit-boards and electronic components (chopped to a grain-size < 1000µm) with propylenecarbonate (T=240°C).

The residues and the extracts from a. - g. were mixed with an internal mixture of 2,3,7,8-$^{13}C_{12}$-TBDD, 1,2,3,7,8-$^{13}C_{12}$-PBDD, 1,2,3,4,7,8-$^{13}C_{12}$-H_6BDD, 2,3,7,8-$^{13}C_{12}$-TBDF, 2,3,4,7,8-$^{13}C_{12}$-PBDF. After extraction with toluene, sample preparation analogous to Hagenmaier et al[7] and cleaning the samples were analysed by GC/MS.

3. Results

a. Sample a: no PBDE/PBDD/PBDF could be detected

b. Sample b: no PBDE/PBDD/PBDF could be detected

b. Sample c: Small amounts of tri- tetra- and pentabrominated diphenylethers could be detected.

In the SIM-mode PBDF could be detected at the following concentrations:

	ng/kg
sum TBDF	7035000
sum PBDF	5470000
sum H_6BDF	213000
sum H_7BDF	31000
2,3,7,8-TBDF	28860
2,3,4,7,8-PBDF	23900

d. Sample d: Small amounts of mono- and dibromodibenzofurans could be detected

e. Sample e: Small amounts of tri- and tetrabromodiphenylethers could be detected

f. Sample f: Small amounts of brominated diphenylethers could be detected

g. Sample g: Scan-mode GC/MS indicated high concentrations of brominated diphenylethers.
In addition, PBDD and PBDF could be detected at the following concentrations:

	ng/kg
sum TBDD	233
sum PBDD	201
sum H_6BDD	1980
2,3,7,8-TBDD	64
sum TBDF	230000
sum PBDF	308900
sum H_6BDF	97500
sum H_7BDF	920
2,3,7,8-TBDF	4962
2,3,4,7,8-PBDF	12600

4. Discussion

The results prove that brominated diphenylethers are still present additives in plastics, although they were banned by European electronics producers since the mid-eighties. In accordance with Dumler[2], pyrolysis of flame retarded material, especially of printed circuit boards and electronic components (laboratory scale), produces high amounts of brominated dioxins and furans located in the condensed material. These dioxins and furans can be seen as direct reaction products of diphenylethers implemented in the

material.
In addition pilot scale processing of scrap material in a pyrolysis reactor gives products still contaminated with brominated diphenylethers, partially converted to furans.
Brominated diphenylethers can be extracted from plastics using propylcarbonate. The origin of the brominated dioxins and furans detectable in the propylcarbonate extract is still to be investigated. Dioxins and furans are either generated from the diphenylethers at the extraction temperatures of 240°C, or have to be seen as contaminants of the flame retardants.
As a consequence, brominated diphenylethers must be seen as perfect reagents for the generation of dioxins and furans and should not be used any longer as additives in plastics.
Recycling activities which process flame retarded plastics might produce hazardous products, an aspect that has to be investigated more closely.

5. References

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