BROMINATED AROMATICS IN MATERIALS FROM A CAR SCRAP PLANT

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Introduction

There exist a huge number of possible halogenated, chlorine and/or bromine containing, aromatics which can be suspected to cause some environmental hazards; biphenyls, diphenylethers, benzenes, phenols, dibenzo-p-dioxins, dibenzofurans etc. Brominated organic compounds are widely used as flame retardants in various products at high concentrations [1]. Most common are polybrominated diphenylethers (PBDEs), polybrominated diphenyls (PBBs), tetrabromobisphenol and hexabromocyclododecane. Commercial PBDE flame retardants contain mainly penta-, octa- and decabromodiphenylethers (PeBDEs, OBDEs and DeBDE) [2].

Polybrominated dioxins and furans are formed by thermal reactions from brominated flame retardants [3]. For example oxidative thermal decomposition of 1,2.bis-(tribromophenoxy)ethane can produce TeBDDs in yields up to 5 % [4]. Commercial 2,4,6-tribromophenol and tetrabromobisphenol preparations have been reported to contain PBDDs and PBDFs [5].

Due to releases from many processes PBDEs are ubiquitous environmental pollutants. Very scarce data on eventual emissions to the environment or environmental concentrations of PBDFs or PBDDs could be found in the literature. Monobromopolychlorodibenzo-p-dioxins and dibenzofurans, not PBDD/F with only bromine, were found in fly as from a MSW incinerator [6]. Significant amounts of bromo-PAH and bromochloro-PAH, dioxins and dibenzofurans were identified in fly ash from a US municipal incinerator [7]. DBDF, TriBDD/F, TeBDD/F and PeBDF have been found in vehicle exhaust [8].

In this work samples of scrap raw materials from electronic equipments were screened for the occurrence of polybrominated aromatics. Originally, it was obvious that the material contains brominated flame retardants, but more details on their structures and amounts was needed for selection of optimal waste treatments.

Materials and methods

Four recycling material samples were investigated: R1 (electronics plastics), R2 (filter dust from electronics crusher), R3 (cyclone dust from electronics crusher) and R4 (light fluff from car chopper). After extraction, sample clean-up and Florisil and carbon column fractionation, the samples were screened by low resolution GC/MS in electron impact (EI) mode. Fisons AutoSpec mass spectrometer connected to HP 5890 Series II gas chromatograph equipped with a 25 m long, 0.2 mm inner diameter fused silica column coated with 0.11 μm layer of HP-5 stationary phase was used. The electron ionization potential was 70 eV or 30eV. Low resolution mode with total MS

Scans was used. For the analyses of the higher brominated (hepta- to decabromo) diphenyl ethers a HP-5 comumn was shortened to 10 m because of the very slow elution of these.

Results and conclusions

Inhomogenity of the samples made any reliable quantitation of analytes impossible. However, a large number of bromo-organic substances could be identified and their relative amounts approximated. All samples R1-R4 contained polybrominated aromatic compounds known as flame retardants in high amounts and in only slightly variable profiles. The most abundant (up to per cents) polybrominated aromatics observed were 1,1-bis(2,4,6-tribromophenoxy) ethane, tetrabromobisphenol A and tri- to decabromodiphenylethers. Hexabromo- and pentabromobenzene seemed to be the most abundant bromobenzenes, and ethylpentabromobenzene and and dimethyltetrabromobenzene the most abundant alkylbromobenzenes.

PBDEs were recognised by their EI mass spectra. All PBDEs have a very strong M^+ ions and major, often base peak fragment ions $M^+ - Br_2$ (M^+ -158) with the typical clusters due to two bromine isotopes. These latter ions have the same exact mass and number of bromine atoms as PBDF with two bromines less.

In some preliminary tests PBDD/Fs were not observed in these scrap samples. All EI mass spectra of PBDDs and PBDFs show a relatively intense M^{+*} cluster. In EI/selected ion monitoring (SIM) MS at least three members of this cluster should be monitored. For more reliability fragment ions due to losses of Br*, COBr*, (Br*+COBr*) and (2Br*+COBr*) can be checked. Additionally, doubly charged ions like M^{2+}, $(M-Br)^{2+}$ and $(M-2Br)^{2+}$ are found [9-10].

All samples contained remarkably high concentrations of polychlorobiphenyls and polychlorinated naphthalenes. Chlorinated (nona- deca- and undeca-) terphenyls in high concentrations were observed in some samples.

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