IDENTIFICATION OF IMPURITIES OF PHOSPHATE AND BROMINATED FLAME RETARDANTS

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INTRODUCTION

In the last years, new flame retardants (FRs) have been identified for the first time in products and in environmental samples by using mainly liquid chromatography coupled to high resolution mass spectrometry. For example, 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate), known commercially as "V6",[1] or a triazine-based flame retardant [2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine, TTBP-TAZ][2] were recently reported. Not only FRs, but also their byproducts, impurities or degradation products have been very recently identified, such as those derived from tetrabromobisphenol-A (TBBP-A) or tetrabromobisphenol-S.[3,4] The persistency and toxicity of these impurities or related compounds, as well as their presence in the environment is still largely unknown. We present and discuss here an overview of our results on the investigations of impurities and degradation products of FRs, namely from TTBP-TAZ[2], RDP[5], TBBPA and TBBPA-based products[6] and the impurity diphenyl phosphate (DPHP) that derives from a variety of phosphorus flame retardants (PFRs).

MATERIALS AND METHODS

Wide-scope solvent extraction methods were employed without further clean-up to prevent losses of compounds that could be of interest in the screening step. The samples were mainly plastics from electronic equipment casings and indoor dust collected from electronics (to assess the possible migration into the environment). After a pre-concentration step (only in the case of dust), we analyzed the extracts with liquid chromatography (LC) and high resolution time-of-flight (TOF) mass spectrometry. Atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) were employed to cover a wide polarity range. Both target and non-target approaches were used for screening. For suspect screening, home-made databases for the screening of metabolites helped to identify impurities, mainly for those compounds that arose from cleavage of bonds of the main structure, such as 2,4,6-tribromophenol from TTBP-TAZ and meta-*HO*-triphenylphosphate (meta-HO-TPHP) from RDP. For brominated compounds, a script based on mass defect plots and isotope pattern recognition was developed in order to highlight the target unknowns. Formulas were calculated on the basis of mass accuracy (below 5 ppm) and isotopic pattern fit.

RESULTS AND DISCUSSION

1. 2,4,6-TRIBROMOPHENOL (2,4,6-TBP) AND TBBP-TAZ

2,4,6-TBP was detected in almost all plastic samples that contained TTBP-TAZ. It was higher than in the TTBP-TAZ standards (0.02-0.09 % weight/weight, w/w) and ranged from 0.02 to 0.7 % w/w. There was a strong direct correlation between the concentration of both compounds (Pearson correlation, r = 0.951, p < 0.001). The higher concentrations of 2,4,6-TBP in the plastic samples could be due to the lower purity of the TTBP-TAZ formulations used in the preparation of the plastic polymers. Furthermore, 2,4,6-TBP can be used alone as a FR and as an additive/intermediate in formulations of other FRs or could even be a degradation product due to the high temperatures employed during the processing of the plastics. On the basis of these results, we could conclude that the use of TTBP-TAZ is a potential source of contamination of 2,4,6-TBP.

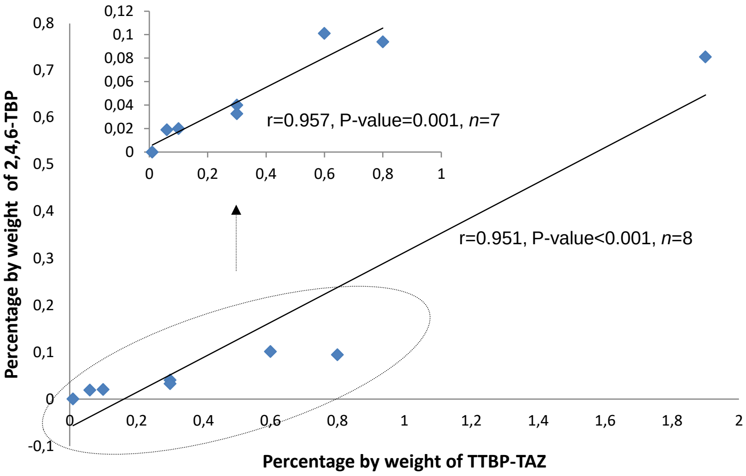

Figure 1. Correlation between the concentration of 2,4,6-TBP (*x axis*) and TTBP-TAZ (*y axis)* in the plastic samples.

2. TBBPA AND TBBPA POLYMERS IMPURITIES

Plastics casings containing TBBPA and TBBPA-based polymers were analyzed. A variety of TBBPA and TBBPA-derivatives related compounds (*n*=14) were identified in the consumer electronics as shown in Figure 2. The *m/z* values (most abundant isotopomer) of these compounds were between 292.88631 and 928.5424 and bromine atoms were in the range 2-7.

The identified compounds were most probably impurities, byproducts or degradation products of TBBPA and TBBPA-derivatives and they could have been originated during the synthesis or during the processing of the final plastic product. Ten of these identified compounds have previously been reported as degradation products of TBBPA formed during pyrolysis processes and also in the environment^{6} as photolysis or biodegradation products of TBBPA, but to the best of our knowledge most of them have been never reported in consumer products. Nineteen other lower intensity brominated compounds with calculated molecular formulas or number of bromine atoms, were also present in the plastic samples.

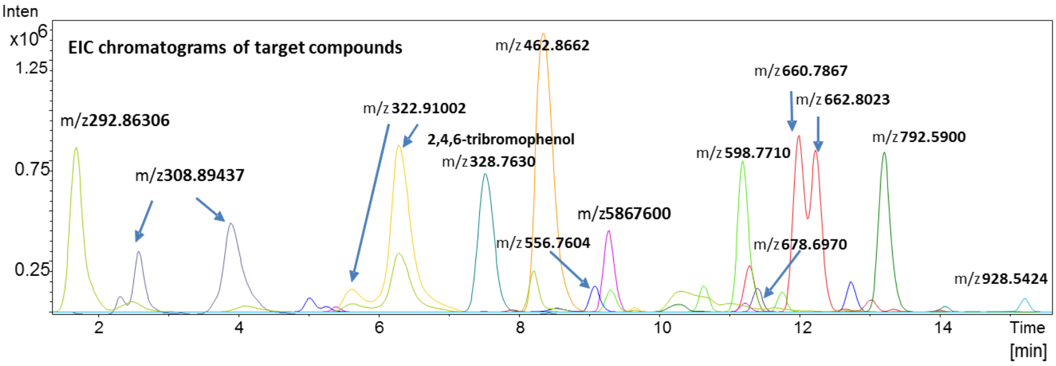

Figure 2. Extracted ion chromatograms (LC-TOF-MS) of the target brominated compounds

3. ARYL PHOSPHATE FLAME RETARDANTS

The impurities of resorcinol bis(diphenyl phosphate) (RDP) were investigated in plastics and dust collected on electric/electronic material. Di- and triphenyl phosphate, di- and mon-hydroxylated TPHP, RDP with the loss of a phenyl ring and oligomers were detected. The most frequently detected impurity, *meta*-HO-TPHP after TPHP was quantified in the range 20-14,227 ng/g in dust collected on electronics. The concentrations of meta-HO-TPHP in dust were much higher than those that could be expected taking into account that it is only a minor impurity in RDP commercial formulations. The higher polarity and smaller molecular weight of *meta*-HO-TPHP could lead to an easier migration of this compound than RDP into the dust or possibly a chemical or biological hydrolysis of RDP could have taken place.

The presence of DPHP, a common impurity of RDP and other aryl PFRs, was also investigated in plastic products and in indoor dust. DPHP has been used as biomarker of several aryl PFRs, since it has been detected as main metabolite of these compounds *in vitro* studies.[7] External routes and sources of exposure to DPHP are important to understand the levels monitored in the human body and its role as biomarker. Concentrations of DPHP were in the range 218-6488 ng/g and 151-4189 ng/g in dust collected from electronics and in floor dust, respectively, and were 2-4 times lower than TPHP in the same samples. DPHP was present at very low concentrations in plastics known to contain relevant amount of aryl-PFRs and many times undetected, this suggesting that the relative high levels found in indoor dust may be due to the degradation of aryl PFRs. The ingestion of dust could be a source of DPHP influencing the levels measured in urine and not only the metabolism of aryl-PFRs. A strong correlation was found between TPHP and DPHP in dust as shown in Figure 3.

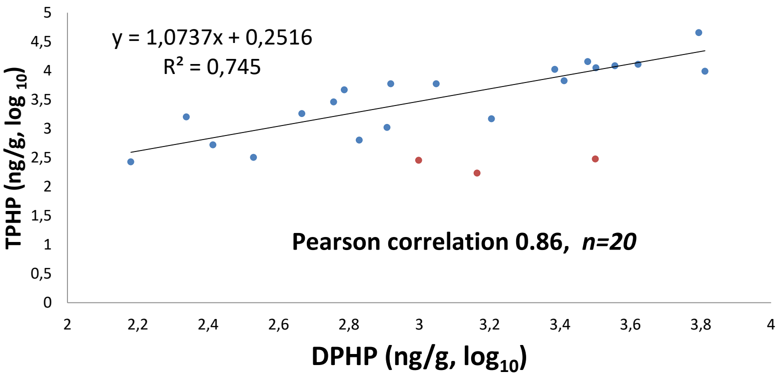

Figure 3. Correlation between the concentrations of 2,4,6-TBP (*x axis*) and TTBP-TAZ (*y axis)* in the plastic samples

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