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Comprehensive characterisation of flame retardants in textile furnishings by ambient high resolution mass spectrometry, gas chromatography-mass spectrometry and environmental forensic microscopy

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ABSTRACT

The presence and levels of flame retardants (FRs), such as polybrominated diphenyl ethers (PBDEs) and organophosphate flame retardants (PFRs), was determined in textile home furnishings, such as carpets and curtains from stores in Belgium. A comprehensive characterisation of FRs in textile was done by ambient high resolution mass spectrometry (qualitative screening), gas chromatography-mass spectrometry (GC-MS) (quantitation), and environmental forensic microscopy (surface distribution). Ambient ionisation coupled to a time-of-flight (TOF) high resolution mass spectrometer (direct probe-TOF-MS) was investigated for the rapid screening of FRs. Direct probe-TOF-MS proved to be useful for a first screening step of textiles to detect FRs below the levels required to impart flame retardancy and to reduce, in this way, the number of samples for further quantitative analysis. Samples were analysed by GC-MS to confirm the results obtained by ambient mass spectrometry and to obtain quantitative information. The levels of PBDEs and PFRs were typically too low to impart flame retardancy. Only high levels of BDE-209 (11–18% by weight) were discovered and investigated in localised hotspots by employing forensic microscopy techniques. Most of the samples were made of polymeric materials known to be inherently flame retarded to some extent, so it is likely that other alternative and halogen-free FR treatments/solutions are preferred for the textiles on the Belgian market.

1. Introduction

Deaths from fires and burns are among the leading causes of fatal home injury. For this purpose, flame retardant chemicals (FRs) are added to a wide range of consumer products typically encountered in the indoor environment. Such products are, for example, foam and textile upholstery, carpets, and curtains. Chemicals, such as polybrominated diphenyl ethers (PBDEs), are commonly added to certain types of textiles to impart flame retardancy. In carpet padding, for example, the commercial "Penta-BDE" technical mixture was used. In the back-coating of curtains, the "Deca-BDE" technical mixture is commonly added. A number of studies have raised serious concerns about the safety of these FRs to humans, when on different model species these chemicals proved to cause endocrine disruption (Lyche et al., 2015; Vonderheide et al., 2008) and to adversely affect the central nervous system and the reproductive system (Lyche et al., 2015). As a result, the production of Penta-BDE mixture has been banned in the European Union in 2003 (EU, 2003) and the Deca-BDE mixture was restricted under RoHS in 2008 (Betts, 2008) and under REACH in 2010 (BSEF, 2010). The Penta-BDE and Octa-BDE technical mixtures are on the Persistent Organic Pollutants (POPs) list of the Stockholm Convention (chm.pops.int) and Deca-BDE is being considered for this list as well.

Another class of FRs used in textiles are organophosphate FRs (PFRs). These multi-use chemicals are considered to be suitable alternatives for the PBDEs (van der Veen and de Boer, 2012), in

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applications such as textile back-coatings (Horrocks et al., 2007). However, studies have indicated that also PFRs pose a health risk by causing endocrine disruption, inducing asthma and allergic rhinitis, skin irritation and dermatitis, adversely affecting the reproductive system and even causing cancer (van der Veen and de Boer, 2012; Wei et al., 2015).

Both BFRs and PFRs are not chemically bound to textiles and the matrix is very soft and flexible, allowing these chemicals to leach out of the materials they were added to (Kajiwara and Takigami, 2013; Kemmlein et al., 2003). The FRs then migrate to indoor air and dust (Kajiwara and Takigami, 2013; Rauert et al., 2014a), and from there are taken-up into the human body (Lyche et al., 2015; Wei et al., 2015).

There has been very little research about the presence of FRs in textiles, their levels, the extent of emissions into the indoor environment and their impact on humans. Kajiwara et al. (2011, 2009) has investigated the presence of hexabromocyclododecane (HBCDD), BDE-209 and PFRs in textiles from Japan. Similarly, Shin and Baek (2012) have described the PBDE levels in flame-retarded textiles present on the South Korean market. In Kemmlein et al. (2003), BFRs and PFRs were studied in textile samples (among others) and emission studies were undertaken to assess their migration into the indoor environment. Different aspects of this phenomenon were also studied by Kajiwara and Takigami (2013), Rauert et al. (2014a, 2014b).

Since some FRs have been proven to be harmful to humans (Lyche et al., 2015; van der Veen and de Boer, 2012; Vonderheide et al., 2008), in this study we have investigated the presence and levels of these chemicals in textiles from the Belgian market. To streamline this process, we have investigated the usefulness of the time-of-flight (TOF) high resolution mass spectrometer (direct probe-TOF-MS) technique as a quick, cheap and reliable method to screen for these chemicals in a high number of samples. This technique, along with a gas chromatography-mass spectrometry (GC-MS) and forensic microscopy, can be used as a comprehensive approach to elucidate if and what type of FR is present in a given sample.

2. Materials and methods

2.1. Samples

47 curtain samples and 14 carpet samples were collected from four different stores from Antwerp, Belgium in 2013 (Table SI-1). Environmental contamination was removed from the samples by wiping their surface with paper tissues impregnated with Milli-Q water.

2.2. Materials

Detailed information about the materials employed in this study is available in Supporting information.

2.3. Target compounds

FRs and plasticisers that have been known to be added to textile materials were targeted during the Direct Probe-TOF-MS screening. For a full list, see Table SI-2. For the analytes which were detected with this procedure, trace analysis by GC-MS was done (Table 1). More information about the analytical standards used in this study is available in Supporting information.

2.4. Direct probe screening (ambient mass spectrometry). procedure and parameters

The samples were submitted to a rapid screening for FRs employing a direct probe (DP) assembly (Fig SI-1), mounted on an atmospheric pressure chemical ionisation (APCI) II source, connected to a Bruker Daltonik microTOF II mass spectrometer (mass accuracy <2 ppm and resolution $>16{,}500$ FWHM).

Table 1
Overview of the detection frequencies (DF, %) and concentrations of analytes of interest (ng/g) measured in the textile samples by GC-MS ($n=61$). Values rounded to significant digits.

Analyte	DF (%)	10th Percentile	90th Percentile	Max
BDE 28	2	0.3	0.3	0.3
BDE 47	26	0.3	1	3
BDE 66	0	–	–	–
BDE 100	3	0.2	0.4	0.4
BDE 99	28	0.2	2	5
BDE 85	8	0.1	1	2
BDE 154	8	0.3	1	1
BDE 153	16	0.3	2	3
BDE 183	13	0.5	3	4
BDE 209	56	10	25,922	560,000
EHTBB	2	10	10	10
DBDPE	13	14	7644	25,000
TNBP	18	30	470	1000
TCEP	28	48	686	1800
TCPP*	54	15	368	1000
TBOEP	41	48	2480	4300
TEHP	23	37	1125	1700
TPHP	72	10	2630	95,000
EHDPHP	41	34	702	4200
TMPPs**	8	94	2820	3300

* Sum of 2 isomers.
** Sum of 4 isomers.

The procedure followed was similar to the one described in Ballesteros-Gómez et al. (2014, 2013). A small amount of sample was introduced in the glass capillary, a drop of calibration solution was added to the wall of the capillary, which was then slid into the ionisation source. A temperature programme was developed in order to gradually vaporise both volatile and less volatile analytes, before the matrix becomes carbonised and background noise increases enough to prevent detection. As such, the initial vaporiser temperature was set at 225 °C, then increased to 260 °C after 1 min and 300 °C after 3.5 min and held at this temperature until 5 min. To prevent cross-contamination, the source was "baked-out" for 5 min at 400 °C between analyses. The detector had the following parameters: dry gas 2 L/min, nebuliser 4 bar, dry heater 220 °C, capillary voltage 1000 V (both polarities), corona −8000 nA (negative) and +5000 nA (positive) and end plate offset of −1000 V (positive) and −500 V (negative).

This provided basic information about the FR content of the samples quickly and with minimal consumable use. The limit of detection (LOD) was determined by searching for the lowest level of analyte, determined by GC-MS and detected with the direct probe-TOF-MS. The values were rounded down to the nearest value dividable by 10, if the number was lower than 1000 and down to the nearest value dividable by 100, if the number was between 1000 and 100,000 (Table SI-2). This approach was used to take advantage of the availability of accurate quantitative levels, determined by GC-MS and to give a more accurate and realistic estimation of the LOD for our analytes of interest in the matrix studied (by compensating for varying spectral noise levels). In some samples which generate less spectral noise during the direct probe-TOF-MS analysis, the analytes can be tentatively detected at even lower levels, but setting the LOD to lower levels can further increase the number of false positive results, some of which can be due to background levels from the environment where the analysis is being conducted.