IDENTIFICATION OF BROMINATED FLAME RETARDANTS IN FABRICS FROM INTERNATIONAL SOURCES

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Introduction

Our exposure to Brominated Flame Retardants (BFRs) from fabric or textile sources is often associated with furniture upholstery and the polyurethane foams that they contain[1-5]. The additive manner in which many textiles are treated with halogenated flame retardants makes their release into the environment and our exposure through repeated contact a real concern.[4,6] The use of additive flame retardants such as polybrominated diphenyl ethers (PBDEs) and Hexabromocyclododecane (HBCD) in the treatment of textiles is evaluated herein through pre-screening with x-ray fluorescence, soxhlet extraction, and quantification by HRGC/HRMS. This study examines the brominated flame retardant content of fabrics obtained from international sources that are not related to clothing or upholstery.

Materials and methods

Fabric samples were selected from nine bags obtained from international conferences over the course of 14 years (BFR, Dioxin, EnviroAnalysis, and Pittcon – see Table 1). Two of the bags contained a small amount of polyurethane foam which was also sampled and analyzed for brominated flame retardants. The fabric samples were pre-screened using X-ray fluorescence to determine the extent of halogenated material present in the samples.

Table 1: A summary of the type and age of conference bag samples obtained from international conferences.

Conference	Year	Sample Type
BFR	2007	Fabric
BFR	2009	Fabric
Dioxin	1996	Fabric
Dioxin	2004	Fabric
Dioxin	2004	Foam
Dioxin	2006	Fabric
Dioxin	2006	Foam
Dioxin	2007	Fabric
Dioxin	2008	Fabric
EnviroAnalysis	2000	Fabric
Pittcon	2001	Fabric

In order to obtain true representative samples of the fabric, at least 5 sub-samples were taken from random parts of the fabric and combined. The samples and a lab blank were spiked with 50 µl of a surrogate mixture containing a variety of mass-labelled brominated flame retardants (BFR-LCS; Wellington Laboratories Inc., ON) and soxhlet-extracted for 17 hours at a rate of 3-4 cycles per hour using toluene. The samples were then treated with sulfuric acid and cleaned-up using a multi-layer column. The column was composed of layers of silica gel, base-treated silica gel, and acid-treated silica gel and the analytes were eluted with hexane (distilled-in-glass grade; Caledon, ON). The hexane fractions were then rotovapped to 200 µl, transferred to a microvial using DCM/pentane (distilled-in-glass; Caledon, ON), evaporated again to approximately 10 µl and finally reconstituted in 50 µl of toluene for HRGC/HRMS analysis. Prior to HRGC/HRMS analysis using a Waters AutoSpec Ultima HRMS, a known amount of injection standard was added to each the sample (BFR-ISS; Wellington Laboratories Inc., ON).

Results and discussion:
The x-ray fluorescence pre-screening indicated the presence of brominated flame retardants in all of the samples analyzed. Subsequent analysis by HRGC/HRMS supported these preliminary findings with low levels of tetra-, penta-, and hepta-brominated diphenyl ethers (BDEs; pg/g to ng/g levels) being found in all of the samples analyzed. Significant amounts of other BDEs were found in several samples.

Four of the conference bag fabric samples contained 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47) at levels ranging from 2 – 250 ng/g as well as 2,2′,4,4′,5-pentabromodiphenyl ether (BDE 99) at concentrations of 2 – 60 ng/g. Decabromodiphenyl ether (BDE-209) was found to be present at significant levels in multiple samples; 0.9 µg/g in the fabric sample obtained from the Dioxin 2006 conference bag, 2.7 µg/g in the BFR 2007 fabric sample, 2.3 µg/g in the Dioxin 2007 fabric sample, 8.3 µg/g in the Dioxin 2004 foam sample, and 180 µg/g in the Dioxin 2006 foam sample.

Similarly, decabromodiphenylethane (DBDPE) was found to be present in three fabric samples at concentrations ranging from 0.3 to 1.9 µg/g and the gamma isomer HBCD was detected in the fabric sample from Dioxin 2007 (the identity of the predominant HBCD isomer in the sample was determined through LCMS retention time comparison to characterized standards).

It is interesting to note that three peaks of unknown compounds were observed in the surrogate (^{13}C) Nona-BDE channels during HRGC/HRMS analysis. These unknown peaks eluted between BDE-206 and BDE-209 (Figure 1) and the ratio of their peak areas in the two channels equalled that of $^{13}C_{12}$-BDE-206 (206L) and $^{13}C_{12}$-BDE-207 (207L). This suggests that the compounds are halogenated and may contain nine bromines. However, their structures and origin have not yet been determined. They could, for example, be hydroxylated nonabromodiphenyl ethers.

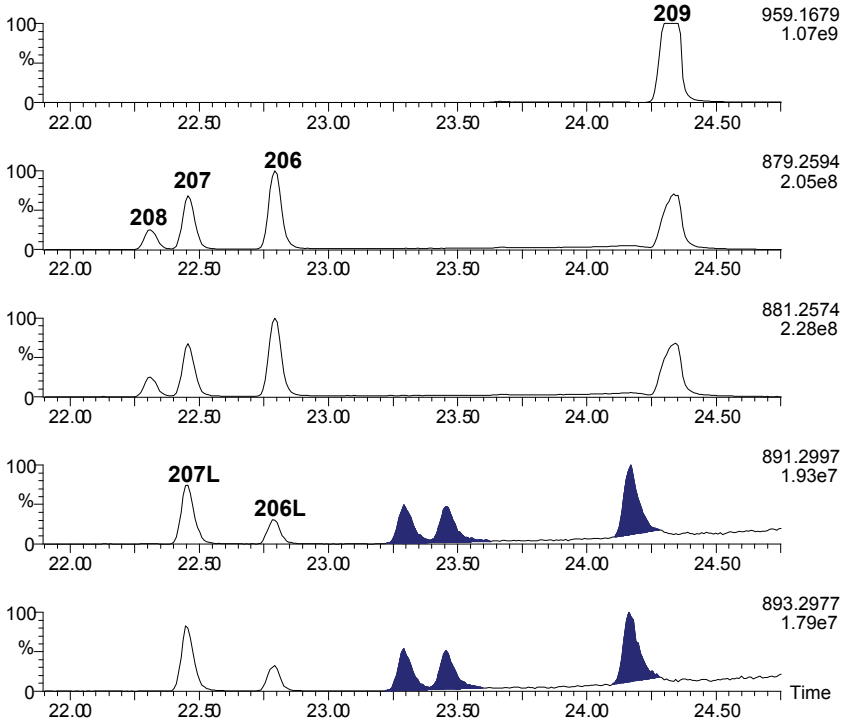

Figure 1. Unknown halogenated compounds (identified as shaded peaks) observed in the surrogate nona-BDE channels during the HRGC/HRMS analysis of the Dioxin 2007 conference bag fabric sample.

The amount of brominated flame retardants detected in the fabric samples were significantly lower than expected based on percentages reported in the scientific literature.[7] The use of the multi-layer column was not a source of concern because, with the exception of 2 components in BFR-LCS, the percent recoveries in the lab blank ranged from 32% to 98%. According to the scientific literature, HBCD is the most frequently added BFR to textiles manufactured in Japan followed by BDE-209 and DBDPE.[7] This may explain the occurrence of high levels of BDE-209 and DPDPE in several samples.

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