IDENTIFICATION OF BROMINATED FLAME RETARDANTS IN FABRICS FROM INTERNATIONAL SOURCES

Alex Konstantinov[a]*, Fiona Utley[a], Dave Potter[a], Colleen Tashiro[a], Thomas F. Webster[b], Ashley K. Miller[b], Nicole Riddell[a], Jeff Klein[a]

Contact Information

[a] Wellington Laboratories Inc., Research Division, Guelph, Ontario, N1G 3M5, Canada

[b] Boston University School of Public Health, Dept. Environmental Health, 715 Albany Street, Boston, MA 02118 USA

IDENTIFICATION OF BROMINATED FLAME RETARDANTS IN FABRICS FROM INTERNATIONAL SOURCES

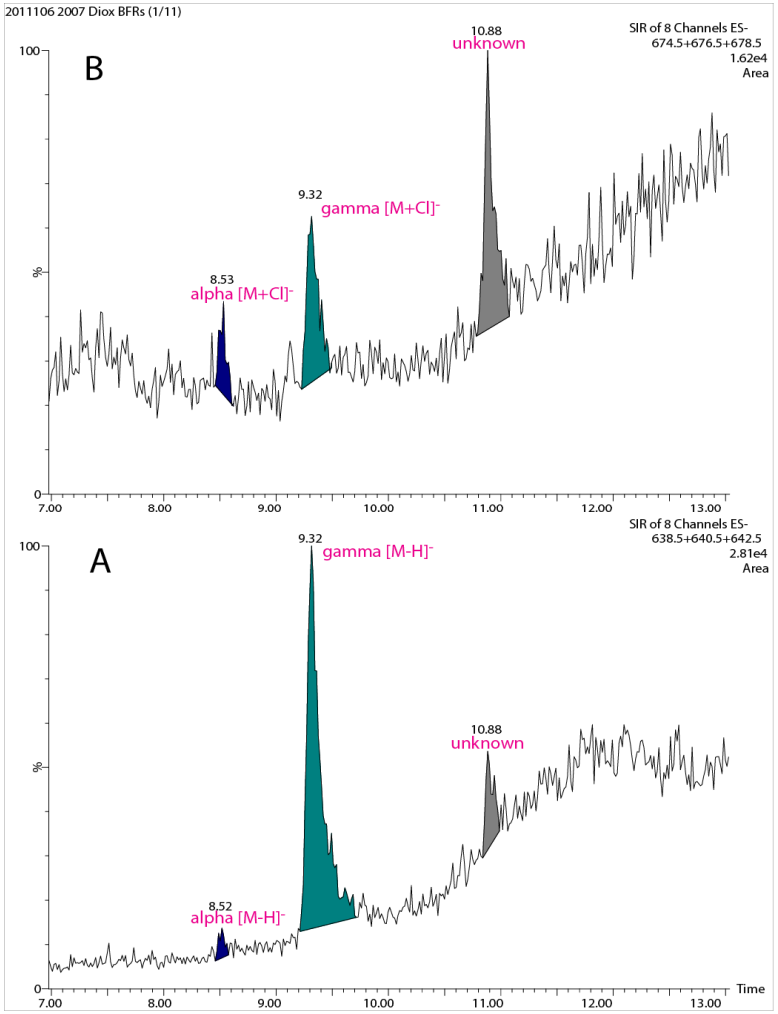

Figure 1: HBCD Molecular ions minus proton (A) and Chloride adducts of HBCD (B) as observed by LC-MS in extract from Dioxin 2007 Conference Bag (fabric).

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.

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 (InnovX 6500 alpha XRF) to determine the extent of halogenated material present in the samples. Three measurements were performed for each piece, in RoHS/WEEE mode for bromine.

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 subjected to a workup, detailed in the abstract for this presentation. Prior to HRGC/HRMS analysis using a Waters AutoSpec Ultima HRMS, a known amount of injection standard was added to each sample (BFR-ISS; Wellington Laboratories Inc., ON).

Results

The x-ray fluorescence pre-screening indicated the presence of brominated flame retardants in all of the samples analyzed (Table 1). Subsequent analysis by HRGC/HRMS supported these preliminary findings with low levels of tetra- though 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; 900 ng/g in the fabric sample obtained from the Dioxin 2006 conference bag, 2,700 ng/g in the BFR 2007 fabric sample, 2,300 ng/g in the Dioxin 2007 fabric sample, 8,300 ng/g in the Dioxin 2004 foam sample, and 180,000 ng/g in the Dioxin 2006 foam sample.

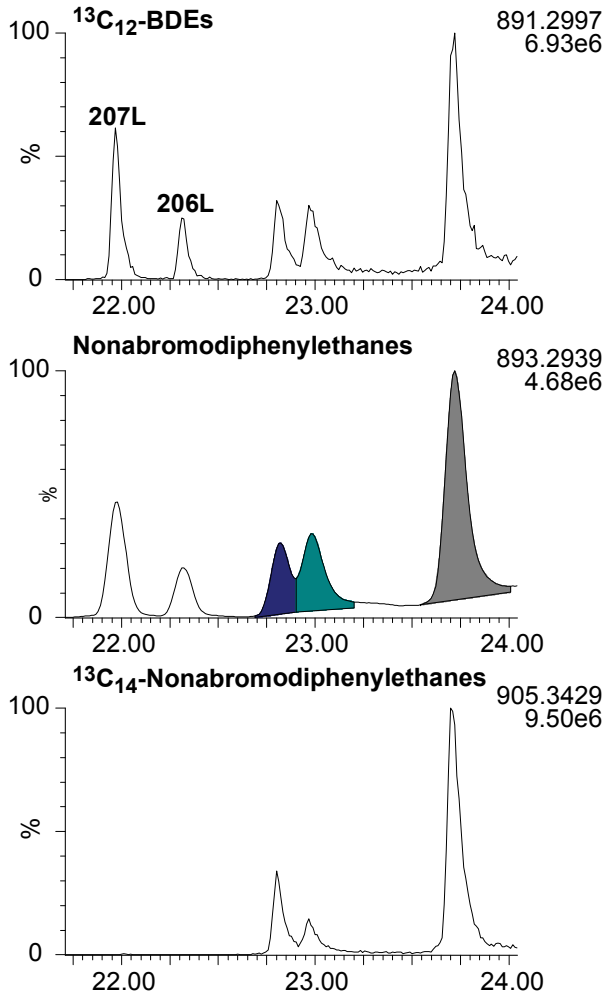

Figure 2: Nonabromodiphenyl ethanes (identified as shaded peaks) found in the surrogate nona-BDE channels during the HRGC/HRMS analysis of the Dioxin 2007 conference bag fabric sample.

Results continued

Similarly, decabromodiphenylethane (DBDPE) was found to be present in three fabric samples at concentrations ranging from 300 to 1,900 ng/g and the gamma isomer HBCD (Figure 1) was detected at 3,000 ng/g 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). HBCD was monitored for $[M-H]^-$ and $[M+Cl]^-$ adducts. In both channels there was observed an unknown peak, which eluted significantly later then any HBCD isomer to which we have access. Appearance of the unknown peak in both channels indirectly confirms that this is also an HBCD isomer because like HBCDs it can form an adduct with Cl^-.

It is interesting to note that three peaks of another 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 2) and were identified as nonabromodiphenyl ethanes by a co-injection with surrogate nonabromodiphenyl ethane mixture.

Yet another unknown halogenated compound was found in the fabric sample from Dioxin 2007 (Figure 3). It appears to have 6 chlorines with the exact mass of 383.8651.

IDENTIFICATION OF BROMINATED FLAME RETARDANTS IN FABRICS FROM INTERNATIONAL SOURCES

Conference	Lab Blank	2007 BFR Amsterdam	2009 BFR Ottawa	1996 Dioxin Amsterdam	2004 Dioxin Berlin	2004 Dioxin Berlin
BDEs:\Sample type		Fabric	Fabric	Fabric	Fabric	Foam
						
XRF [Br] (RoHS/WEEE)		5,000,000	2,000,000	176,000,000	348,000,000	382,000,000
Total BDEs	883	3,020,000	33,900	54,800	68,000	13,200,000
DBDPE	ND (724)	374,000	1,650	2,680	ND (547)	ND (17,400)
HBB	NDR (5.5)	22,700	345	2,120	NDR (1,500)	1,320
PBEB	ND (0.7)	8,540	ND (1.6)	233	63	ND (93)
BB153	ND (1.9)	5,170	ND (3.6)	ND (4.3)	ND (3.2)	ND (145)
BTBPE	no rec	no rec	no rec	109	825	no rec
Total BFRs	**723**	**3,430,000**	**35,880**	**59,900**	**69,100**	**13,200,000**

Conference	2006 Dioxin Oslo	2006 Dioxin Oslo	2007 Dioxin Tokyo	2008 Dioxin Birmingham	2000 Enviroanalysis Ottawa	2001 Pittcon New Orleans
BDEs:\Sample type	Fabric	Foam	Fabric	Fabric	Fabric	Fabric
						
XRF [Br] (RoHS/WEEE)	136,000,000	506,000,000	339,000,000	n/a	4,000,000	72,000,000
Total BDEs	992,000	214,000,000	2,530.000	356,000	102,000	17,200
DBDPE	9,800	ND (85,500)	755,000	ND (7550)	ND (1,790)	9,820
HBB	378	ND (814)	1,740	ND (50.5)	1,570	3,270
PBEB	103	ND (293)	ND (47.9)	ND (21.9)	NDR (26.1)	48
BB153	ND (56.3)	ND (416)	ND (12.2)	ND (26.8)	ND (28.8)	NDR (5)
BTBPE	no rec	ND (10,800)	3,040	no rec	475	ND (103)
Total BFRs	**1,002,000**	**214,000,000**	**3,290,000**	**356,000**	**104,000**	**30,300**

Table 1: Concentrations of BFRs detected in Conference bags (pg/g) by XRF and HRGC/HRMS.

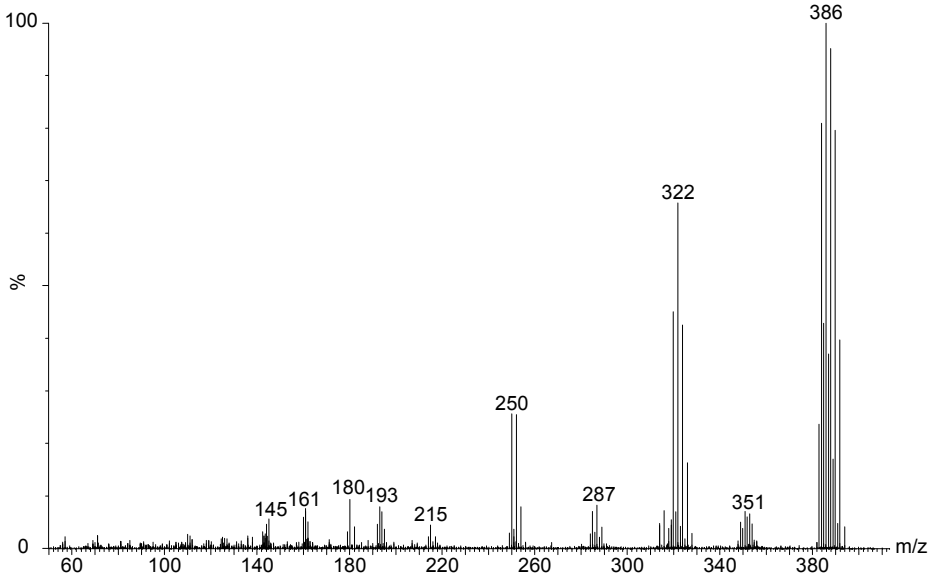

Figure 3: TIC Trace of the unknown halogenated compound from Dioxin 2007 conference bag fabric sample.

Conclusions

The amounts 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 two 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.

References

1. de Wit CA. (2002); *Chemosphere* 46: 583-624
2. Trudel D, Scheringer M, von Goetz N, Hungerbühler K. (2011); *Environ. Sci. Technol*. 45: 2391-2397
3. Covaci A, Gerecke AC, Law RJ, Voorspoels S, Kohler M, Heeb NV, Leslie H, Allchin CR, De Boer J. (2006); *Environ. Sci. Technol.* 40(12): 3679-3688
4. Prevedouros K, Jones KC, Sweetman AJ. (2004); *Environ. Sci. Technol.* 38(12): 3224-3231
5. Marsh G, Hu J, Jakobsson E, Rahm S, Bergman A. (1999); *Environ. Sci. Technol*. 33(17): 3033-3037
6. Betts K. (2009); *Environ. Sci. Technol.* 43(9): 2998
7. Kajiwara N, Sueoka M, Ohiwa T, Takigami H. (2009); *Chemosphere* 74:1485