METHODOLOGY TO SCREEN FLAME RETARDANTS IN UPHOLSTERED FURNITURE FOR COMPLIANCE WITH NEW CALIFORNIA LAW (SB 1019)

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Introduction

In 1975, California adopted a flammability standard (TB117, a small open flame plus a smolder test) to protect consumers from house fires. A cost efficient way to meet this standard was the use of chemical flame retardants (FRs). In recent years, however, significant concerns have been raised regarding both the efficacy of FRs to protect from fires and the environmental and health impacts of FRs. As a result, a new standard was developed and published in 2013 (TB 117-2013, a smolder test) [1]. In addition, a new California law (SB1019)[2] requires manufacturers of furniture products to disclose whether those products contain FRs above 1000 ppm. Failure to correctly disclose such information is subject to fines enforced by the California Department of Consumer Affairs (DCA). Our laboratory has been tasked with analyzing samples submitted by DCA for the presence of FRs.

We developed a stepwise approach to screen samples for the presence of brominated (BFR) and phosphorus-based (OPFR) flame retardants in order to limit the number of samples that require quantitation. Screening results from X-Ray Fluorescence (XRF) and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) were validated against measurements by gas chromatography - tandem mass spectrometry (GC-MS/MS) and liquid chromatography/Time-of Flight mass spectrometry operated with electrospray ionization (LC/ESI-QTOF). We addressed the following questions:

1. How homogeneous are the samples?
2. Can screening methods be used to rule out the presence of OPFRs and/or BFRs above 1,000 ppm?
3. What other flame retardants are in the samples?

Materials and methods

Samples of furniture components (polyurethane foam, cover fabric, synthetic fiber pad, batting, beads and plumage) were submitted blindly to our laboratory by DCA. As shown in the flowchart (Fig 1), the samples were screened sequentially by XRF, ICP-OES, GC-MS/MS and LC/ESI-QTOF.

XRF: Screening for Br, Cl, P and Sb was performed using a benchtop Energy Dispersive X-Ray Fluorescence spectrometer (Quant'x, Thermo Scientific) using a VF-50J Rhodium anode X-ray tube and a Peltier Cooled Silicon Lithium-Drifted Detector. The entire sample was placed on the grid in the vacuum chamber and measurements were taken for 30 sec at different voltages and with different filters. Repeated measurements at different points on the grid provided data for the homogeneity of the sample.

ICP-OES: Samples (750 mg) were placed in 50 mL digestion vessels and 10 mL of trace metal grade concentrated nitric acid added. The digestion vessel was covered with a disposable ribbed watch glass and placed in a HotBlock (Environmental Express SC100) at 95 ± 5 °C for 4 hours. The digestate was cooled to room temperature, filtered using Whatman 541 filter paper and rinsed with DI water. The digestate was brought up to 50 mL with DI water and 4 mL were taken and diluted to 10 mL with DI water before analysis. All measurements were performed using a PerkinElmer Optima 7300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) equipped with demountable quartz torch, alumina injector, Gem Cone nebulizer, cyclonic spray chamber, and S10 auto sampler. Data acquisition and processing were performed using PerkinElmer WinLab32 software. The operating conditions of the ICP-OES were as follows: RF power 1300 W, plasma flow 15 L/min, nebulizer gas flow 0.80 L/min, auxiliary flow 0.2 L/min, sample flow 2.0 mL/min, and 2-point background correction. To quantify antimony (Sb) and phosphorus (P) in the samples, yttrium (Y) was selected as an internal standard. Aluminum (Al), calcium (Ca), iron (Fe) and magnesium (Mg) were also monitored because they are known to cause spectral interferences. The wavelengths (nm) used for ICP-OES analysis for each element were as follows: P 214.914, Sb 206.836, and Y 371.029. For all of these wavelengths, radial plasma view was selected.

GC-MS/MS: The extraction method was adapted from Stapleton et al.[3] Briefly, 5 mL of dichloromethane (DCM) were added to the sample (50 mg), vortexed for 1 minute, and then sonicated for 10 minutes. The extraction process was then repeated with 5 mL of fresh dichloromethane and the two extracts pooled. A 20 µL aliquot of the extract was then transferred to an autosampler vial, spiked with deuterated internal standards and diluted to 200 µL. For method blanks, 50 mg of sodium sulfate were carried through the complete extraction process as described above. OPFR and PBDE screening was performed by both full scan and targeted analysis using an Agilent 7000 Series Triple Quad GC-MS/MS operated in electron impact ionization mode. Data acquisition and processing were performed by MassHunter GC/MS Acquisition Software and MassHunter Workstation Software (Qualitative and Quantitative Analysis Version B.06.00). 1 µL sample injections were made onto a DB-5ms column (30 m x 0.25 mm ID, 0.25 µm film thickness; Agilent J&W Inc.). The GC-MS/MS operating conditions were as follows: inlet temperature 250 °C, auxiliary temperature 280 °C, source temperature 250 °C, Quadrupole 1 and 2 temperatures at 150 °C and collision cell gas pressures set to 1.5 psi N_2 and 2.25 psi He for MS/MS operation. The oven temperature was held at 90 °C for 1 minute, followed by a ramp at 15 °C/min to 200 °C with a hold of 3 minutes, followed by a ramp of 5 °C/min to 250 °C, followed by a final ramp of 15 °C/min to 300 °C with a final hold time of 6 minutes. All samples were screened over a scan range of 50-550 amu and each total ion chromatogram peak compared to the NIST Mass Spectral Data Base v2.0. Targeted MS/MS screening was later performed to confirm and quantitate the OPFR and PBDE analytes.

LC/ESI-QTOF: Preliminary suspect screening for an array of FRs was conducted using a LC/MS method adapted from Van den Eede et al.[4] Samples (50 mg) were extracted with 10 mL methanol. A portion of the extract was diluted 1:100 in methanol and 10 µL of the dilution were then injected into a HPLC (Agilent 1290) with an Extend C18 column (50 mm x 2.1 mm x 1.8 µm), coupled to a quadrupole time of flight instrument (Agilent, 6550 iFunnel QTOF) with an electrospray ionization source (ESI). Mobile phases consisted of 5 mM ammonium acetate buffer (A) and methanol (B) with a gradient program of 15.5 min and a post time of 5 min, with a flow rate of 0.3 mL/min. Triplicate extracts were analyzed in both ESI positive and ESI negative mode. The "find by formula" algorithm in Masshunter Qualitative analysis (B.06.00) was used for data analysis requiring an accurate mass match within 5 ppm and a quality score of 70. Hits were evaluated for their presence in replicates, corresponding retention times, and area counts exceeding the blanks by at least an order of magnitude.

Results and Discussion

We investigated 40 samples of foam, fabric, batting and other fill material (feathers, beads, etc.). Table 1 shows results from the first batch of foam samples we investigated. We found no FRs in samples A and B by any of the techniques used. XRF detected P in samples C, D and E; Br in sample C and Cl in sample D and E. Total P content was quantitated by ICP-OES in samples C, D and E (MDL=17 ppm). No Sb was found in any of the samples above 17 ppm. Specific OPFRs and PBDEs were measured by GC-MS/MS and the total P content in the identified OPFRs matched pretty well the total P measured by ICP-OES. Analysis by LC/ESI-QTOF confirmed the presence of the identified FRs. Additional FRs (including TMPP isomers and melamine) were tentatively identified via LC/ESI-QTOF.

These data are consistent with information released by DCA after receiving our results: Sample A was a Standard PUF Substrate that DCA uses in their TB117-2013 flammability testing and is free of FRs. Sample B came from a newer product (2013) that met the new TB117-2013 standard without any FRs in it. Sample C was from the late 1990s, it contained both PBDEs and OPFRs and had met the open flame part of TB117. Sample D was from 2012, contained OPFRs and had met both the open flame and the smolder part of TB117. The heterogeneous sample E was from 2012, contained OPFRs, had not passed the open flame part of TB117 and had not been tested for the smolder part of TB117. Overall, the data are consistent with Cooper at al.[5] reflecting patterns of use of FRs over time, with the phasing out of PBDEs and their replacement by OPFRs.

Sample E was a heterogeneous sample (re-bonded PUF). Not surprisingly, it showed the highest variability for P (RSD=29% by ICP-OES, in contrast to RSD=1.4-3.3% in samples C and D). XRF measurements along a grid showed RSD of 35% and 32% for Cl and P in sample E, respectively, while Sample D showed RSD=4% for Cl and P. Total P content in Sample E ranged from ~1,000 ppm by ICP-OES to 1,840 estimated by GC-MS/MS, probably due to sample heterogeneity.

Our preliminary data from 45 samples of furniture components indicate that XRF can screen for Br, P and Sb and ICP-OES can screen for P and also provide the total P content. Screening techniques help reduce the number of samples requiring confirmatory analysis by GC-MS/MS. The sensitivity and selectivity of each screening test were calculated from the True and False Positives and Negatives. As Shown in Table 2, screening for P by ICP correctly identified all samples containing OPFRs. Similarly, all samples containing BFRs were correctly identified by XRF. This screening approach utilizes equipment used by most commercial laboratories analyzing environmental samples, enabling manufacturers and retailers to easily have their products tested to ensure compliance with the law.

Table 1. FRs[*] measured and physical characteristics of polyurethane foam products tested

	A	B	C	D	E
Appearance	homogeneous	homogeneous	homogeneous	homogeneous	heterogeneous
XRF					
Br, Cl, P, Sb	ND	ND	Br, P	Cl, P	Cl, P
ICP-OES					
P (ppm) [a]	<17	<17	1,500	8,830	995
Sb (ppm)	<17	<17	<17	<17	<17
GC-MS/MS					
OPFRs (ppm)	ND[b]	ND[b]	15785 TPHP	92452 TCEP	6540 TCPP, 20970 TDCIPP
PBDEs (ppm)	ND[b]	ND[b]	28,000 BDE47, 34,360 BDE99, 5,400 BDE100	ND[b]	ND[b]
P[c] (ppm)	ND	ND	1,040	8,880	1,840
LC/ESI-QTOF [d]	ND	ND	TPHP TMPP Melamine	TCEP TPHP	TCPP TPHP TDCIPP TCEP Melamine
Year sampled	2014	2013	1990s	before 2012	2012
Passed TB117-2013?	NO	YES	N/A	N/A	N/A
Passed TB117 Open Flame?	N/A	N/A	YES	YES	NO
Passed TB117 Smolder?	N/A	N/A	N/T	YES	N/T

[*] Abbreviations based on Bergman et al[6]. [a] Mean of triplicate measurements; [b] MDLs varied by congener (0.16 for PBDEs; 0.6 for TCEP, TCPP; 1 for TDCIPP; 4 for TPHP; 8 for TEHP); [c] Total P based on individual OPFRs measured; [d] Tentative identification; N/A: Not Applicable; N/T: Not Tested

Table 2. Sensitivity and Selectivity of Screening Tests

	Sensitivity	Selectivity	Predictive Value (+)	Predictive Value (-)
P by ICP for OPFRs	1	0.79	0.38	1
P by XRF for OPFRs	0.9	0.77	0.53	0.96
Br by XRF for BFRs	1	0.81	0.2	1

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Figure 1. Screening Scheme