METHOD DEVELOPMENT FOR THE DETECTION OF ORGANOPHOSPHATE FLAME RETARDANTS AND POLYBROMINATED DIPHENYL ETHERS IN CONSUMER PRODUCTS AND HOUSE DUST

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By

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Introduction

Organophosphate flame retardants (OPFRs) and polybrominated diphenyl ethers (PBDEs) are additive flame retardants frequently found in consumer products and in indoor environments. OPFRs and PBDEs are known to transfer from consumer products, to dust, and ultimately to humans via incidental dust ingestion and inhalation. OPFR metabolites are reported in human urine (1) and PBDE are reported in human serum and breast milk (2). This thesis describes the development and validation of a sonication extraction method for the simultaneous measurement of OPFRs and PBDEs in consumer products and house dust by Gas Chromatography Tandem Mass Spectrometry (GC-MS/MS). Electron ionization (EI) mass spectra and collision cell energy are evaluated for selection of parent and product MS/MS ions. The resultant MS/MS transitions are shown to demonstrate high selectivity and sensitivity in NIST Standard Reference Material 2585, Organic Contaminants in House Dust (National Institute of Standards and Technology, Gaithersburg, MD). Sonication extraction efficiency is evaluated for the two groups of compounds in consumer products and dust using carbon-13 PBDE and deuterated OPFR standards. Dust results are evaluated against NIST certified values and reference literature values. Consumer product results are validated by an inter laboratory collaboration with Duke University (Nicholas School of the Environment, Durham, NC).

Background

Tris(2,3-dibromopropyl) phosphate (TDBPP) was one of the first commercially available flame retardant with a consumer product end point application. It was first

manufactured in the 1950s and reached a U.S. production rate of 5.4 million kilograms in 1975. One of TDBPP's primary initial applications was as an additive flame retardant in children's pajamas. However, in 1977 the Consumer Product Safety Commission banned the use of TDBPP in all children's clothing products due to animal studies that found TDBPP to be a human carcinogen (3). Consumer products, including furniture, electronics and home textiles, are often treated with flame retardant chemicals in response to government fire safety regulations and standards such as California's Technical Bulletin 117. Technical Bulletin 117 requires residential upholstered furniture to meet established fire safety standards that include a one second cover fabric impingement test and a 12 second interior fill material open flame test (4). Consumer product manufacturers have therefore treated both cover fabric and fill materials with flame retardant chemicals. OPFRs and PBDEs represent two major chemical groups that are added to polyurethane foam and or to textile cover fabrics to decrease the flammability of household upholstered furniture products. However, recent studies have provided evidence for PBDE environmental persistence, bioaccumulation, and toxicity and therefore have led to regulatory restrictions on their use (5). Alternative flame retardants such as OPFRs have therefore seen an increased use as replacements for PBDEs and are now more frequently detected (5). Both OPFRs and PBDEs are added to polyurethane foam during the manufacturing process, sprayed onto the surface of textiles, or added through a soaking process. The three different processes allow the flame retardant to be applied at the percent level and provide the treated material a flame resistant property. The application process does not chemically bind the flame retardant

to the host material and therefore allows the flame retardant to escape into the environment (5). Treated consumer products will therefore discharge the additive flame retardant for the life of the product.

Flame Retardant Chemical Compounds

In the current study, a targeted GC-MS/MS method was developed for seventeen different flame retardant chemicals. Table 1 list the chemical name, abbreviation and CAS number for each. Native standards were purchased from AccuStandard Inc. (New Haven, CT, USA) and Wellington Laboratories Inc. (Guelph, ON, Canada). The general structure of an OPFR is shown in Figure 1. The structure is characterized by a central phosphoric acid group where the three hydrogen atoms are replaced by an alkyl, aryl or haloalkyl substituent group (R_1, R_2 and R_3) with the most prominent halogen substituent being chlorine. Due to the three independent linkages, the chemical structure of organophosphate flame retardant can have significant variations and can be synthesized to contain three identical substituent groups or any combination of these three substituent groups. In this study, the alkyl, aryl and haloalkyl substituent groups are not varied on the phosphate, however the method development process presented here can be applied to include additional novel OPFRs. Availability of neat standards, commercial use and the necessity to monitor do to a toxicological hazard would dictate inclusion. Here we focus on the most common OPFRs that are added to fill materials and cover fabrics used to manufacture upholstered consumer products.

Table 1. Target compound names, abbreviations and CAS Numbers.

Compound Name	**Abbreviation**	**CAS No.**
Tri-propyl phosphate[1]	TPP	513-08-6
Tri-n-butyl phosphate[1]	TNBP	126-73-8
Tris(2-chloroethyl) phosphate[1]	TCEP	115-96-8
Tris(1-chloro-2-propyl) phosphate[1]	TCIPP	13674-84-5
Tris(1,3-dichloro-iso-propyl) phosphate[1]	TDCIPP	13674-87-8
Triphenyl phosphate[1]	TPHP	115-86-6
2,2',4-Tribromodiphenyl ether[2]	BDE-17	147217-75-2
2,4,4'-Tribromodiphenyl ether[2]	BDE-28	41318-75-6
2,2',4,4'-tetrabromodiphenyl ether[2]	BDE-47	5436-43-1
2,2',3,4,4'-pentabromodiphenyl ether[2]	BDE-85	182346-21-0
2,2',4,4',5-pentabromodiphenyl ether[2]	BDE-99	60348-60-9
2,2',4,4',6-pentabromodiphenyl ether[2]	BDE-100	189084-64-8
2,2',4,4',5,5'-hexabromodiphenyl ether[2]	BDE-153	68631-49-2
2,2',4,4',5,6'-hexabromodiphenyl ether[2]	BDE-154	207122-15-4
2,2',3,4,4',5',6-heptabromodiphenyl ether[2]	BDE-183	207122-16-5
2-Ethylhexyl 2,3,4,5-tetrabromobenzoate[1]	EH-TBB	183658-27-7
Bis(2-ethylhexyl) tetrabromophthalate[1]	BEH-TEBP	26040-51-7

[1]AccuStandard, New Haven, CT, USA, [2]Wellington Laboratories Inc., Guelph, ON, Canada

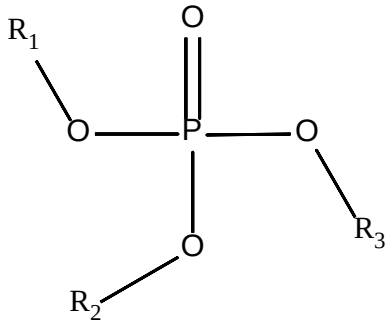

Figure 1. General structure of organophosphate flame retardant (OPFR).

PBDEs are the second chemical class investigated and are legacy flame retardants that are controlled under government regulatory actions including California's Senate Bill 1019 (6), Assembly Bill AB302 (7), European Union's Restriction of Hazardous Substances Directive (RoHS) (8) and the European Commission on Persistent Organic Pollutants (9). Regulatory action was imposed due to their persistence, bio-magnification and risk to human health and the environment. Table 1 list the chemical name, abbreviation and CAS number for nine congeners that have been used to formulate PBDE technical mixtures. The general structure of a PBDE is shown in Figure 2. The structure is composed of two phenyl groups bridged by an ether linkage. Bromo-substitution of the phenyls gives 209 possible structures dependent on the bromine atom ring location and the number of bromine atom substitutions (m and n).

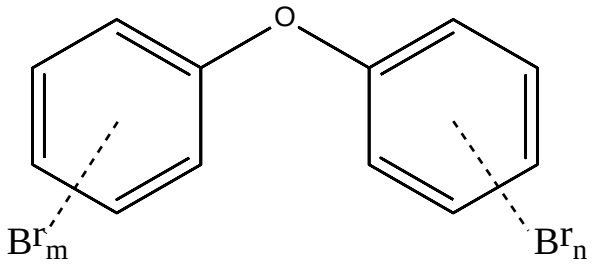

Figure 2. General structure of polybrominated diphenyl ether (PBDE).

Two additional flame retardants, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP) are included do to their reported use in combination with Triphenyl phosphate (TPHP) in commercial flame retardant mixtures (10). The general structure of a benzoate and phthalate is shown in Figures 3 and 4. Both structures can have bromine substitutions on the phenyl or on the

alkyl R groups. For EH-TBB and BEH-TEBP, bromination only occurs on the phenyl group as shown in Figures 5 and 6.

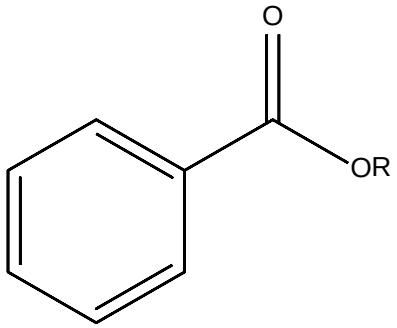

Figure 3. General structure of a benzoate.

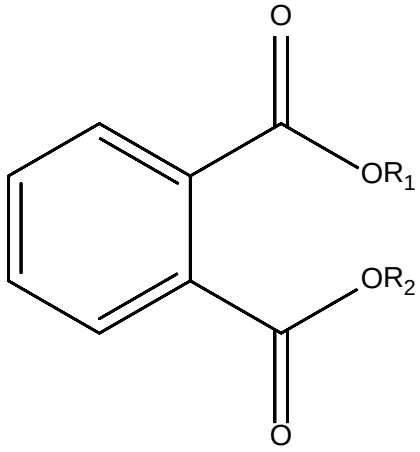

Figure 4. General structure of phthalate.

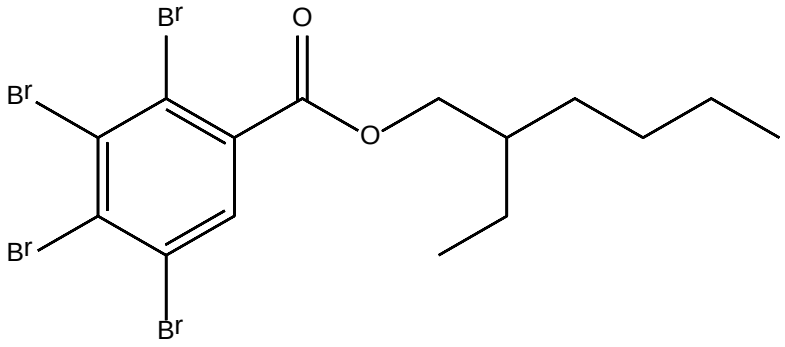

Figure 5. Chemical structure of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB).

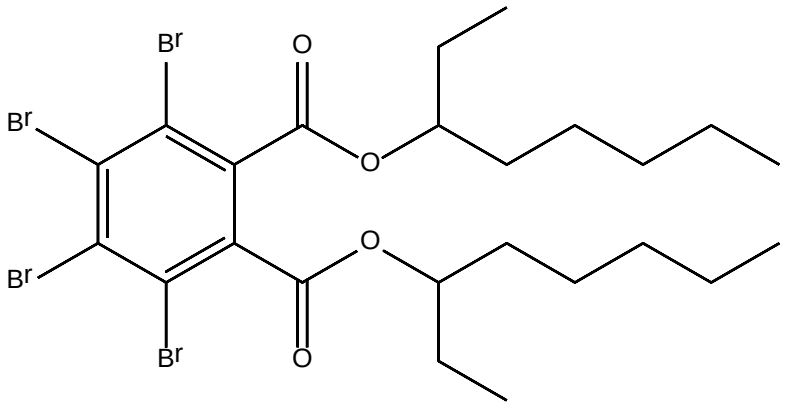

Figure 6. Chemical structure of bis(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP).

As part of the method development process deuterated OPFR (d-OPFRs) standards and Carbon-13 (^{13}C) PBDE standards were included for isotope dilution quantitation. Table 2 lists the labelled standard names and abbreviations. Chemical abstract service numbers are not available for these labelled compounds. OPFR labeled standards are deuterated with replacement of all alkyl hydrogen atoms with deuterium. Deuterium substitution provides both a chromatographic retention time shift and a mass spectra off set equal to the number of deuterium atom substitutions. PBDE labeled standards, are synthesized with ^{13}C rather than ^{12}C carbon atoms at all carbon positions in

the two phenyl groups. ^{13}C substitution provides a mass spectra off set of twelve amu but does not provide a shift in retention time with respect to the native ^{12}C species. The difference in molecular mass between the isotopically labeled compounds therefore allows unique GC-MS/MS transitions to be developed. The use of isotopically labeled compounds also allows accurate quantification and recovery determinations. This is true in theory and practice due to the equivalences between the physicochemical properties of structurally similar isotope compounds.

Table 2. Carbon-13 and deuterated standard names and abbreviations.

Compound Name	**Abbreviation**	**CAS No.**
Tri-propyl phosphate-d_{21}[3]	dTPP	-
Tri-n-butyl phosphate-d_{27}[2]	dTNBP	-
Tris(2-chloroethyl) phosphate-d_{12}[2]	dTCEP	-
Tris(2-chloroisopropyl) phosphate-d_{18}[3]	dTCIPP	-
Tris(1,3-dichloro-2-propyl) phosphate-d_{15}[3]	dTDCIPP	-
Triphenyl phosphate-d_{15}[3]	dTPHP	-
2,4,4'-Tribromo[$^{13}C_{12}$]diphenyl ether[2]	^{13}C-BDE-28	-
2,2',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether[2]	^{13}C-BDE-47	-
3,3',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether[2]	^{13}C-BDE-77	-
2,2',4,4',5-pentabromo[$^{13}C_{12}$]diphenyl ether[2]	^{13}C-BDE-99	-
2,2',4,4',5,6'-hexabromo[$^{13}C_{12}$]diphenyl ether[2]	^{13}C-BDE-154	-
2,2',4,4',5,5'-hexabromo[$^{13}C_{12}$]diphenyl ether[2]	^{13}C-BDE-153	-

[2]Wellington Laboratories Inc., Guelph, ON, Canada, [3]Cambridge Isotope Laboratories, Inc., Andover, MA, USA

Gas Chromatography

Gas chromatography was performed on an Agilent Technologies 7890B gas chromatograph equipped with a 7693 autoinjector system. A 0.25 mm ID x 30 m fused silica capillary column with a 0.25 µm phenyl arylene polymer film was used for analyte separation (J&W DB-5ms, Agilent Technologies, Santa Clara, CA). The structure of the phenyl arylene polymer film is shown in Figure 7. The DB-5ms column provides an inert non-polar analyte contact surface therefore polar OPFRs were found to have short retention times while the non-polar PBDEs were found to have longer retention times. A list of retention times is included in Table 4. This was expected due to the diphenyl structure of PBDEs and the 5% phenyl structure of the stationary phase. It was also observed that as the substituent groups on the OPFRs increase in alkyl chain length retention time also increases. Tris(1,3-dichloro-iso-propyl) phosphate (TDCIPP) and triphenyl phosphate (TPHP) are noted to have the longest residence times do to the large nonpolar groups. An iterative approach was applied to develop the GC temperature program. Little or no peak overlap was desired between the native OPFRs, deuterated OPFRs, ^{12}C-PBDEs and ^{13}C-PBDEs. Based on the similar chemical structure of the labeled and unlabeled compounds it was initially hypothesized that retention times would not be different. However, upon investigation it was found that OPFRs and their corresponding deuterated counterparts have a 6 to 15 second difference in retention time. TPP and dTPP was determined to have the smallest retention time difference of 6 seconds while TDCIPP and dTDCIPP had the largest retention time difference of 15 seconds. It was also determined that ^{12}C-PBDEs and there corresponding ^{13}C-PBDE equivalents

have no difference in chromatographic retention time. The difference in behavior is associated with the placement of the labeled deuterium on the peripherals of the molecular structure of the OPFRs where the deuterium atoms have an altered molecular vibration do to a difference in reduce mass. PBDEs do not show this same behavior because the ^{13}C atoms are placed on the interior of the molecule (phenyl groups) where the individual molecular vibrations of the ^{13}C atoms have minimal direct interaction with the phenyl arylene polymer film. The iterative approach resulted in a final GC temperature program where the oven was first 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. Ultra high purity grade helium (99.999%) was used as the carrier gas and set at a flow rate of 1.5 ml/min.

Inlet temperatures from 150 ˚C to 300 ˚C were investigated for analyte vaporization. It was concluded that injector temperatures of 150 ˚C, 175 ˚C and 200 ˚C did not efficiently vaporize the high boiler PBDEs and also produced chromatographic tailing of the OPFRs. PBDEs were observed to have Gaussian peak profiles. Chromatographic tailing was observed on all OPFRs and increased with higher volume injections and lower inlet temperature. Peak tailing is associated with chromatographically active compounds that can adsorb onto active sites (11). For OPFRs the phosphoryl functional group interacts with the silanol functional groups present on glass surfaces such as the inlet liner and GC column. To limit OPFR tailing an Agilent Technologies splitless single taper ultra inert inlet liner with proprietary surface

deactivation was used. It is believed that the surface modification involves deactivation of the silanol functional groups. Higher inlet temperatures of 275 ˚C and 300 ˚C decreased the signal intensity of OPFRs due to thermal decomposition. Therefore a final injector temperature of 250 ˚C was chosen for the vaporization of 1 to 1.5 uL of sample. A list of final GC method parameters are listed in Table 3.

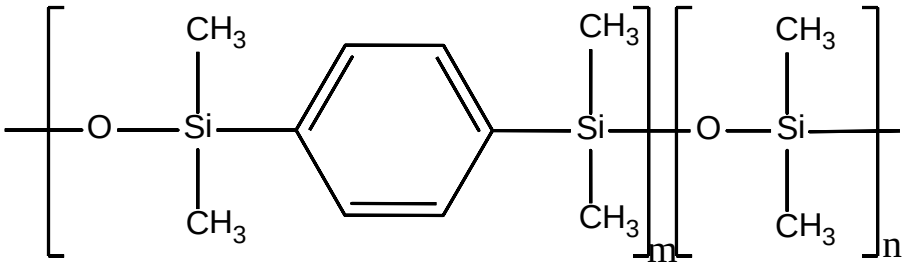

Figure 7. Structure of DB-5ms phenyl arylene polymer film (Agilent Technologies, Santa Clara, CA)**.**

Table 3. Gas Chromatography method parameters.

GC Parameter	Set Point
Analytical Column (DB-5ms)	30 m x 0.25 mm I.D. x 0.25um film
Film	Phenyl Arylene
Column Flow	1.5 mL/min
Carrier Gas	Helium (99.999%)
Oven Temperature Program	90°C (1 min) 15°C/min to 200°C (3 min 5°C/min to 250°C (0 min) 15°C/min to 300°C (8 min)
Inlet Mode	Pulsed Splitless
Injection Volume	1.2 µL
Inlet Temperature	250°C
Inlet Pressure	15.494 psi
Septum Purge Flow	3 mL/min
Gas Saver	20 mL/min after 3 min
Injection Pulse Pressure	20 psi until 1 min
Purge Flow to Split Vent	30 mL/min at 1 min
Run Time	32.667 min

Selected Reaction Monitoring

An Agilent 7000 Series Triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA) was used for analyte detection and identification. Triple quadrupole mass spectrometric detection provides several advantages over traditional detectors which solely rely on a compound's retention time or GC separation characteristics for identification. The advantages include the capacity to provide structural information, greater specificity when analyzing complex matrices, part per billion detection and operation in full scan (FS) mode, product ion scan mode and tandem mass spectrometry mode.

In the present study molecular ions are generated by an Electron Ionization (EI) source (precursor ions) and selectively filtered with quadrupole mass analyzers. Figure 8 shows a schematic of an EI-MS/MS mass spectrometer (12). Molecular ions are produced when analyte entering the ion source is exposed to a magnetically focused electron beam generated by a heated metal alloy filament. A positive voltage on a repeller plate directs positively charged molecular ions and molecular fragments into the ion optics. The ion optics lens assembly functions to electromagnetically focus the molecular ion beam and align the molecular beam with the entrance of the first quadrupole mass analyzer. The quadrupole mass analyzer selectively separates ions along its axial path length according to the molecular charge to mass ratio (m/z). Selected ions are passed to the collision cell for further molecular fragmentation. The collision cell fragmentation efficiency is set by the collision cell energy or applied voltage. Collision induced fragmentation occurs when analyte molecular ions collide with nitrogen gas molecules. When the translational energy of the precursor ions and collision gas are sufficient, the translational energy is converted into molecular vibrations that fragment the precursor ions into smaller product ions (12). The extent of collision induced fragmentation is compound specific and primarily dependent on the molecular stability of the compound. Compounds with stable molecular structures require higher applied collision cell energies and compounds with low molecular stability require low collision cell energies to produce fragmentation. In this respect it can be inferred from optimized collision cell energies, shown in Table 4, that PBDEs have higher molecular stability than OPFRs. The collision cell is not selective and therefore passes all collision

induced fragmentation products to the second quadrupole mass analyzer. The second mass analyzer then selectively separates ions along its axial path length according to specific m/z ratios. An off axis detector detects ion collisions and generates an electrical signal that is proportional to the number of collisions. The electrical signal is then plotted as a total ion chromatogram. When a single set of ions are chosen for selective monitoring the process is referred to as selected reaction monitoring (SRM). For a SRM a single transition is monitored per chemical compound. When two transitions are monitored per compound the process is referred to as multiple reaction monitoring (MRM). In this study two transitions are developed per target analyte and labeled standard. Table 5 lists the manufacture's recommended triple quadrupole mass spectrometer operating parameters that were applied in determining each MRM transitions.

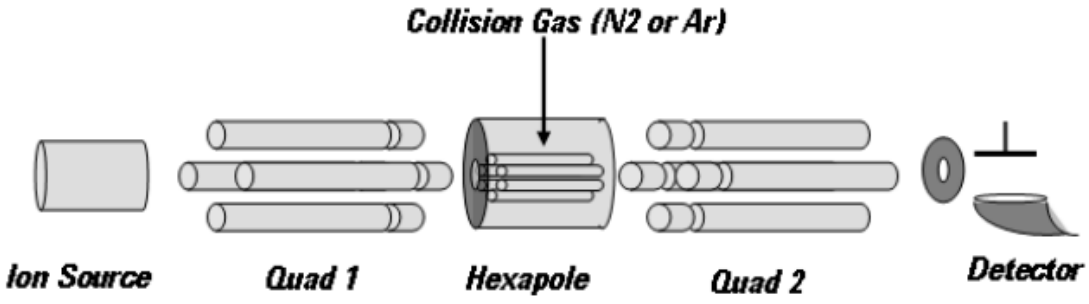

Figure 8. Triple Quadrupole mass spectrometer schematic (12).

			Quantifier			Qualifier			Dwell Time	Expected Ratio
Compound Abbreviation	**Compound Name**	**RT**	**Precursor**	**Product**	**CE**	**Precursor**	**Product**	**CE**	**(ms)**	**(%)**
dTPP	Tri-propyl phosphate-d_{21}	5.890	151.1	103.1	5	199.2	103.1	5	75	38.8
TPP	Tri-propyl phosphate	6.008	141.1	99.0	5	183.2	99.0	5	75	33.1
dTNBP	Tri-n-butyl phosphate-d_{27}	8.079	167.4	103.0	5	231.4	103.0	10	75	59.1
TNBP	Tri-n-butyl phosphate	8.222	155.3	99.0	5	211.4	99.0	5	75	38.9
dTCEP	Tris(2-chloroethyl) phosphate-d_{12}	9.095	261.3	196.1	5	261.3	131.0	10	40	90.3
TCEP	Tris(2-chloroethyl) phosphate	9.200	249.3	186.9	5	249.3	124.9	10	40	95.1
dTCIPP	Tris(2-chloroisopropyl) phosphate-d_{18}	9.382	293.3	131.0	10	295.3	131.1	10	40	69.4
TCIPP	Tris(1-chloro-2-propyl) phosphate	9.525	277.4	124.9	5	279.4	125.0	5	40	69.1
BDE-17	2,2',4-Tribromodiphenyl ether	15.853	405.7	246.0	20	407.7	248.0	20	75	97.4
BDE-28	2,4,4'-Tribromodiphenyl ether	16.529	405.7	246.0	20	407.7	248.0	20	75	96.9
^{13}C-BDE-28	2,4,4'-Tribromo[$^{13}C_{12}$]diphenyl ether	16.529	417.8	258.0	20	419.8	260.0	20	75	95.6
dTDCIPP	Tris(1,3-dichloro-2-propyl) phosphate-d_{15}	17.194	394.3	164.1	15	396.3	164.1	15	75	46.4
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate	17.455	381.2	159.0	15	383.2	159.0	15	75	47.2
dTPHP	Triphenyl phosphate-d_{15}	18.542	341.5	223.1	30	341.5	178.1	35	75	58.6
TPHP	Triphenyl phosphate	18.686	326.4	215.0	25	326.4	169.0	30	75	85.3
BDE-47	2,2',4,4'-tetrabromodiphenyl ether	20.541	485.7	325.9	20	483.7	323.9	20	75	50.9
^{13}C-BDE-47	2,2',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether	20.541	497.8	337.9	20	495.8	335.9	20	75	51.0
^{13}C-BDE-77	3,3',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether	20.068	497.8	228.0	40	497.8	230.0	40	150	92.6
BDE-100	2,2',4,4',6-pentabromodiphenyl ether	23.072	563.7	403.8	20	565.7	405.8	20	50	98.0
BDE-99	2,2',4,4',5-pentabromodiphenyl ether	23.678	563.7	403.8	20	565.7	405.8	20	50	97.7
^{13}C-BDE-99	2,2',4,4',5-pentabromo[$^{13}C_{12}$]diphenyl ether	23.678	575.7	415.9	20	577.7	417.9	20	50	96.1
EH-TBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate	23.751	421.2	392.7	17.5	419.1	390.7	20	75	81.1
BDE-85	2,2',3,4,4'-pentabromodiphenyl ether	24.550	563.7	403.8	25	565.7	405.8	25	75	98.1
^{13}C-PCB-209	**^{13}C-decachlorobiphenyl**	24.540	509.8	439.6	40	509.8	437.8	40	75	61.6
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether	24.942	643.5	483.7	25	641.5	481.7	25	75	68.6
^{13}C-BDE-154	2,2',4,4',5,6'-hexabromo[$^{13}C_{12}$]diphenyl ether	24.942	655.7	495.7	25	653.7	493.7	25	75	68.3
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether	25.652	643.5	483.7	25	641.5	481.7	25	75	69.0
^{13}C-BDE-153	2,2',4,4',5,5'-hexabromo[$^{13}C_{12}$]diphenyl ether	25.652	655.7	495.7	25	653.7	493.7	25	75	69.5
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether	28.039	563.6	455.0	37	561.6	455.0	37	150	99.5
BEH-TEBP	Bis(2-ethylhexyl) tetrabromophthalate	30.358	112.4	55.1	17.5	112.4	70.0	5	150	59.5

Table 4. MRM precursor ions, product ions, optimized collision cell energies and expected qualifier quantifier ratios.

Table 5. Triple quadrupole mass spectrometer operating parameters.

Triple Quadrupole Parameters	**Set Point**
Ionization Source	Electron Ionization Extractor (EIEX)
Electron Energy (eV)	70
Transfer Line Temperature	280°C
Solvent Delay	5 min
Source Temperature	250°C
Quadrupole Temperature	Q_1 and Q_2 = 150°C
Gain Factor	50
MS1 Resolution	1.2 amu
MS2 Resolution	1.2 amu
Dwell Times	Variable from 40 to 150 ms
Collision Gas Flow	Nitrogen at 1.5 mL/min Helium at 2.25 mL/min

The first step in the development of compound specific MRM transitions was to acquire a total ion chromatogram (TIC) of each compound. To acquire a TIC the mass spectrometer was set to scan from 50-1000 m/z or to a minimum of 100 amu above the molecular mass of the target analyte. In full scan mode the mass spectrometer does not produce collision induced fragmentation. The collision gas and collision cell energy are turned off and the second quadrupole mass analyzer is operated as a pass through filter. In this initial step, compound retention times and EI fragmentation mass spectra (EI MS1) were determined for each compound. This was achieved by diluting certified analytical standards down to 1 ng/uL. ^{13}C-Decachlorobiphenyl (^{13}C-PCB209) was added to each solution at 100 pg/uL. ^{13}C-PCB209 serves as an injection standard ensuring proper injections by the instrument and as a reference point standard for evaluating analyte response. An injection volume of 2 uL was injected into the GC injector port (2

ng on column concentration) maintained at an isothermal temperature of 250 ˚C. The ion source temperature was set to 250 ˚C, electron energy set at 70 eV and both quadrupole temperatures set to 150 ˚C. The GC parameters were set to those listed in Table 3. Figure 9 shows the molecular structure of tris(1,3-dichloro-iso-propyl) phosphate (TDCIPP) and Figure 10 shows the TIC TDCIPP. The TIC for TDCIPP allowed for determination of a retention time and the compound's in source fragmentation mass spectrum. Compound identity was confirmed by searching the NIST MS EPA/NIH Mass Spectral Library Version 2.0. An Extracted Ion Chromatogram (EIC) was then generated by extracting 381.0 m/z from the TIC. Figure 11 shows the EIC for TDCIPP. An EIC was required to filter solvent and instrumentation background. Nonane was fist investigated as a potential solvent for standards preparation do to its low vapor pressure (0.59 kPa) however, the available grade of nonane produced a high level of background and also had questionable compatibility with the OPFR certified analytical standards and therefore was not used in final standards preparation. Toluene was instead used as the solvent. Instrument background was attributed to the inlet liner, septa and solvent reservoirs which needed to be replaced and conditioned before full scan spectra could be acquired. The EIC for TDCIPP produced a clear chromatogram with a single peak. The integrated mass spectrum of TDCIPP at 14.717-14.788 minutes is shown in Figure 12. The mass spectrum shows complete fragmentation of TDCIPP (MW 430.98 amu). Molecular fragments at 321.20, 209.20 and 99.10 m/z are produced with the sequential removal of a $C_2H_4Cl_2$ haloalkyl group of mass 110.97 amu. Molecular fragmentation also produces ions at 379.20, 381.20 and 383.20 amu with the removal of a CH_2Cl group.

The two amu step increases are a characteristic feature of chlorinated organic compounds. Figure 13 shows a detailed mass spectrum of the stable isotope distribution of TDCIPP with ^{35}Cl and ^{37}Cl at mass 381.20 amu.

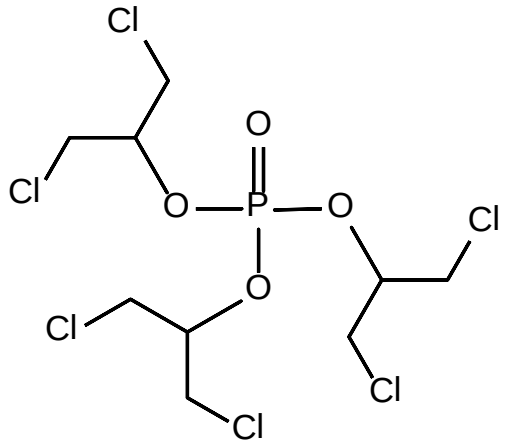

Figure 9. Molecular structure of tris(1,3-dichloro-iso-propyl) phosphate (TDCIPP).

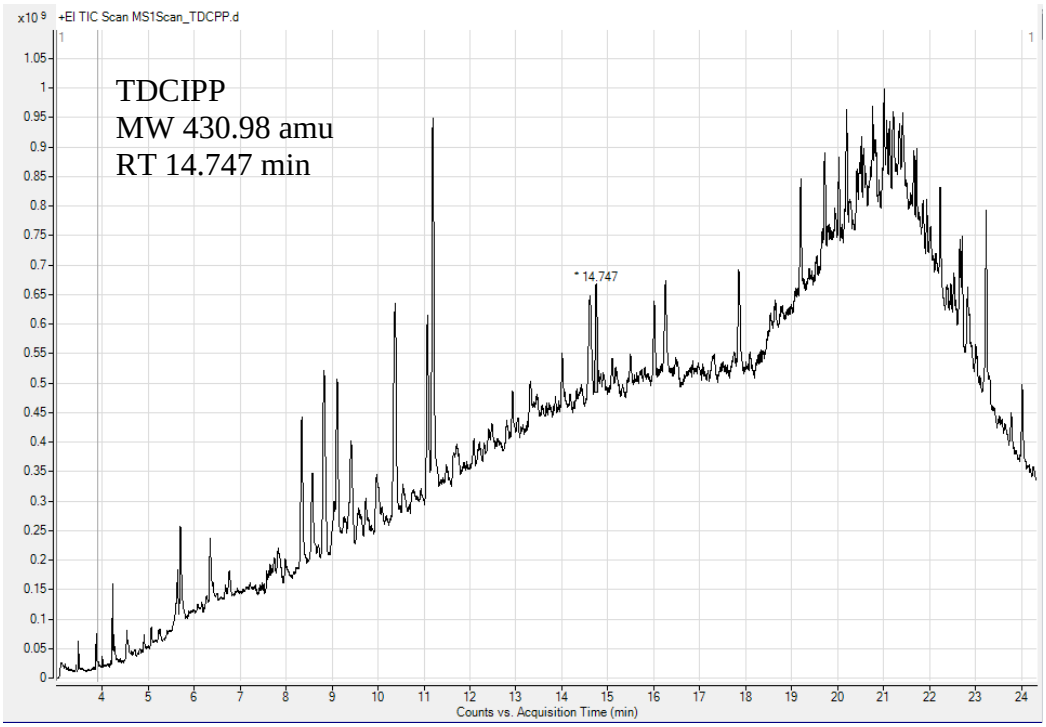

Figure 10. TDCIPP Total Ion Chromatogram (TIC) and retention time at 14.747.

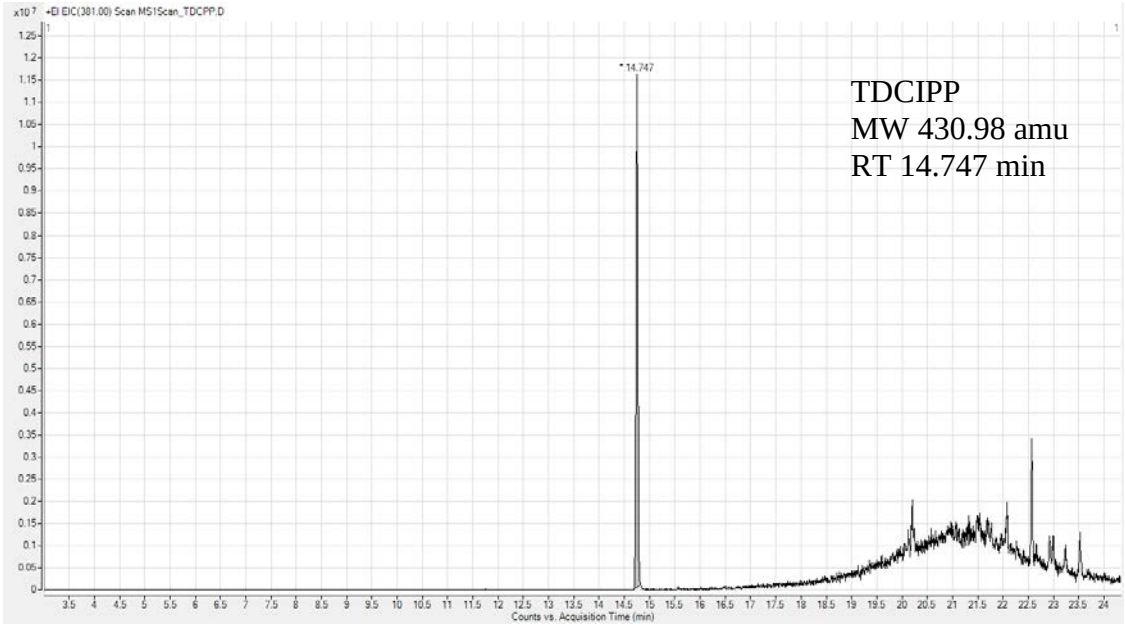

Figure 11. TDCIPP extracted ion chromatogram (381.0 m/z EIC).

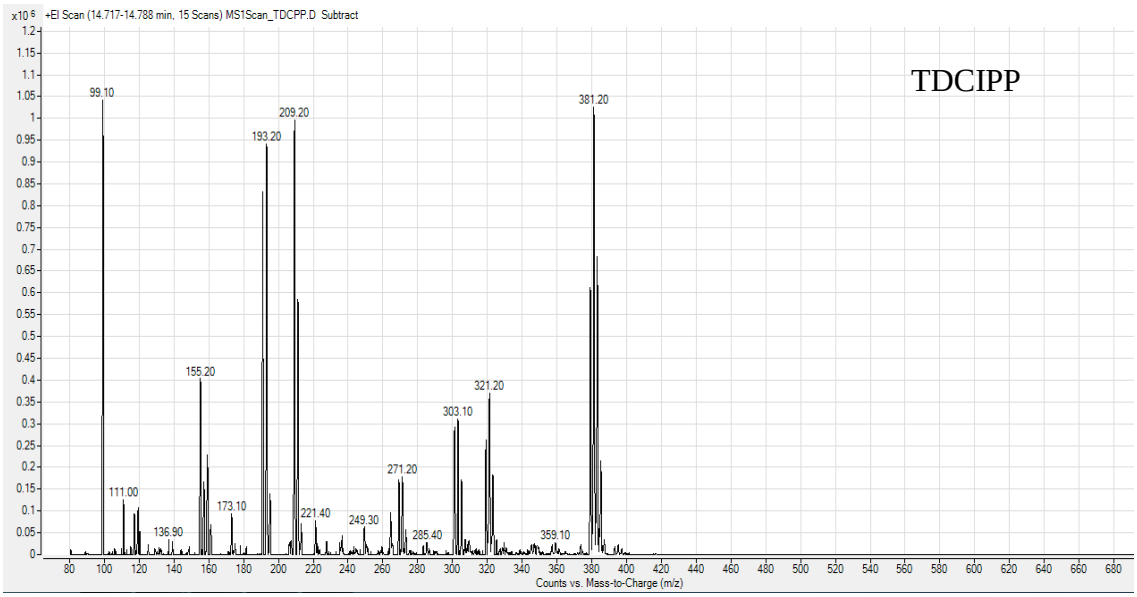

Figure 12. TDCIPP EI mass spectrum shows complete fragmentation of the molecule.

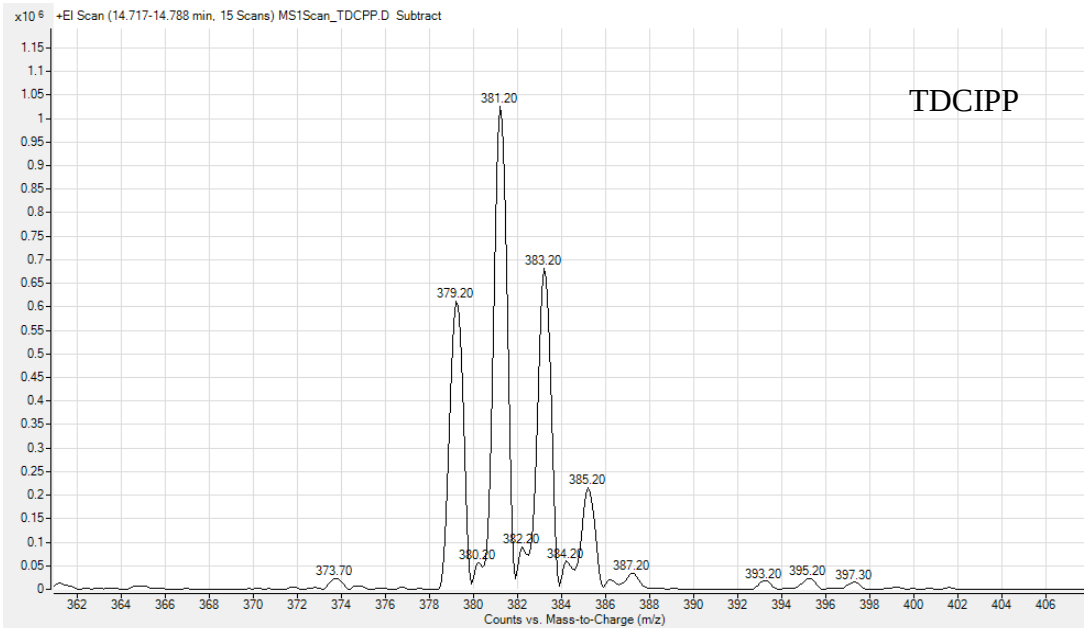

Figure 13. TDCIPP isotope distribution for naturally occurring ^{35}Cl and ^{37}Cl.

The second step in the development of MRM transitions is the selection of precursor ions. This was accomplished by selecting molecular fragments from the EI source fragmentation mass spectrum. Precursor ions were selected based on signal intensity and on the capacity to further fragment within the collision cell. For TDCIPP, 381.20 and 383.20 m/z were selected for collision cell energy (CE) optimization. For CE optimization and determination of product ions, the mass spectrometer was operated in product ion scan mode. In product ion scan mode the first quadrupole selectively monitors the precursor ion and the second quadrupole scans over a selected mass range. The scan range was specified to span from a low end and high end that would be able to monitor the precursor ion's molecular mass and its response. The collision cell energy was increased from 5 – 40 volts in increments of 5 volts. Product ion intensity was monitored relative to the quantitation SRM transition of ^{13}C-PCB209. Normalization to ^{13}C-PCB209 compensated for injection volume differences. TDCIPP was found to have an optimal collision cell energy of 15 volts and a product ion of 159.00 m/z for both precursor ions. Figure 14 shows the product ion scan for precursor ions 381.20 and 383.20 m/z at a collision energy of 15 volts. Higher collision cell energies were found to completely fragment the precursor ions while lower collision cell energies were found to be ineffective at fragmentation. A collision cell energy of zero volts produced negligible fragmentation as was expected.

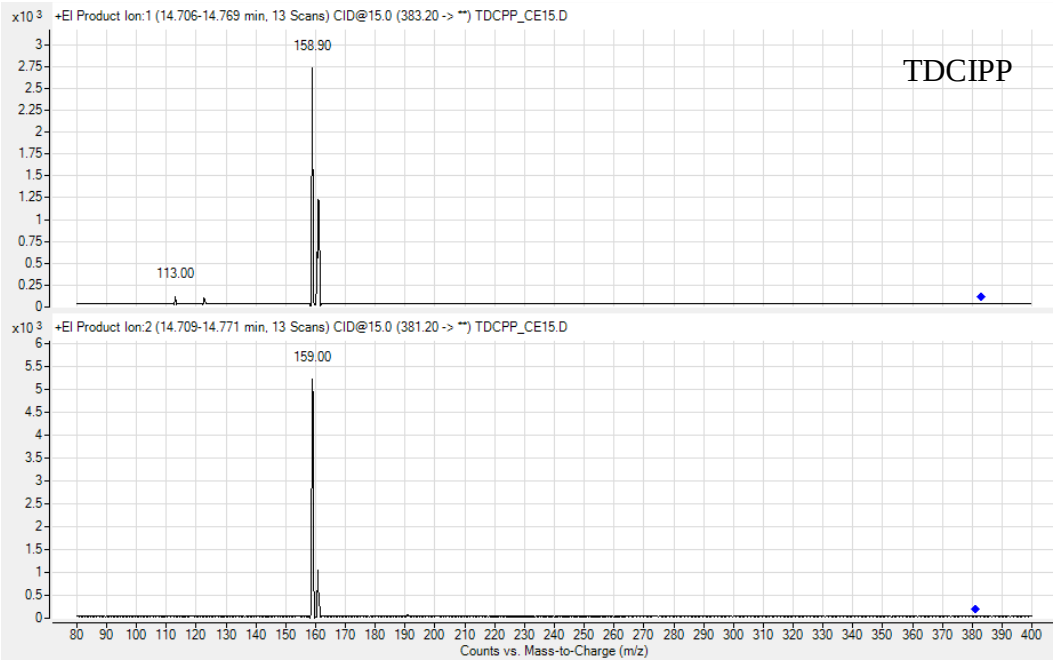

Figure 14. TDCIPP product ion scans for precursor ions 381.20 and 383.20 m/z at collision energy of 15 volts.

Legacy PBDE flame retardants were also subjected to the aforementioned MRM transition development steps. PBDE mass spectra are unlike those generated by OPFRs due to the differences in chemical structural and chemical stability between the two compound classes. Figure 15 shows the molecular structure of BDE-47 and Figure 16 shows the EI MS1 mass spectrum of BDE-47 at 20.931 minutes. The mass spectrum does not exhibit complete fragmentation of the molecular species (MW 485.71 amu). The decreased fragmentation can be attributed to the peripheral bromine atoms which are able to absorb electrons and create Br^- ions. This corresponds with studies that monitor Br^- ions for PBDE analysis rather than the molecular ions. Molecular fragments at 486.00 M^+, 406.00 $[M\text{-}Br]^+$ and 246 $[M\text{-}2Br]^+$ m/z are produced with the removal of an

electron, single bromine and two bromine atoms respectively. Figure 17 shows a detailed mass spectrum of the natural isotope distribution of BDE-47 at 486.0 amu. The distribution profile is due to the expected distribution of ^{79}Br and ^{81}Br and is a general characteristic of all brominated organics. Precursor ions were selected based on signal intensity and on the ability to undergo further fragmentation. For BDE-47, M^+ molecular ions 486.00 and 484.00 m/z were selected for collision cell energy optimization. For CE optimization and determination of product ions the mass spectrometer was operated in product ion scan mode, as is described above. BDE-47 was found to have an optimal collision cell energy of 20 volts with product ions 325.90 and 323.90 m/z. Figure 18 shows the product ion scans for BDE-47 with precursor ions 486.00 and 484.00 m/z at a collision energy of 20 volts. PBDEs respond similarly to OPFRs with respect to the general correlation that higher collision cell energy produces increased molecular fragmentation and lower collision cell energy produces decreased molecular fragmentation.

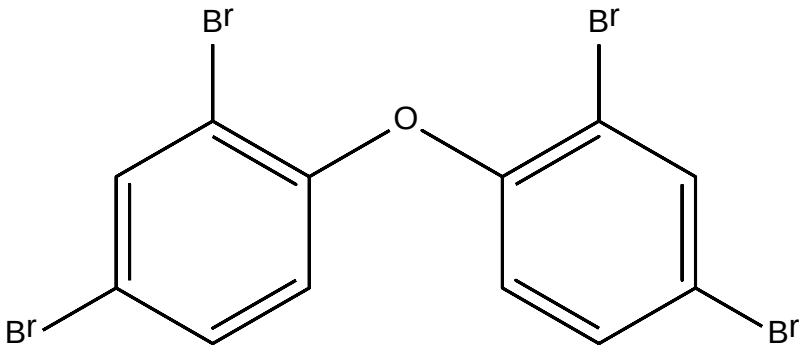

Figure 15. Molecular structure of 2,2',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether (BDE-47).

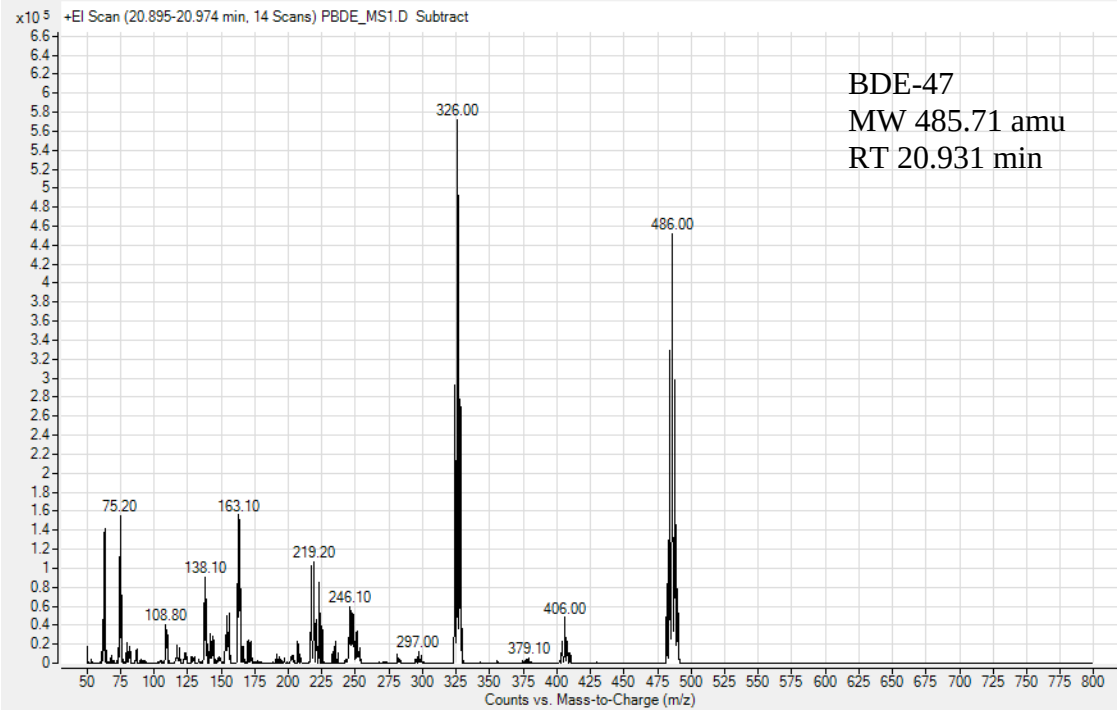

Figure 16. BDE-47 EI mass spectrum shows partial fragmentation of the molecular ion.

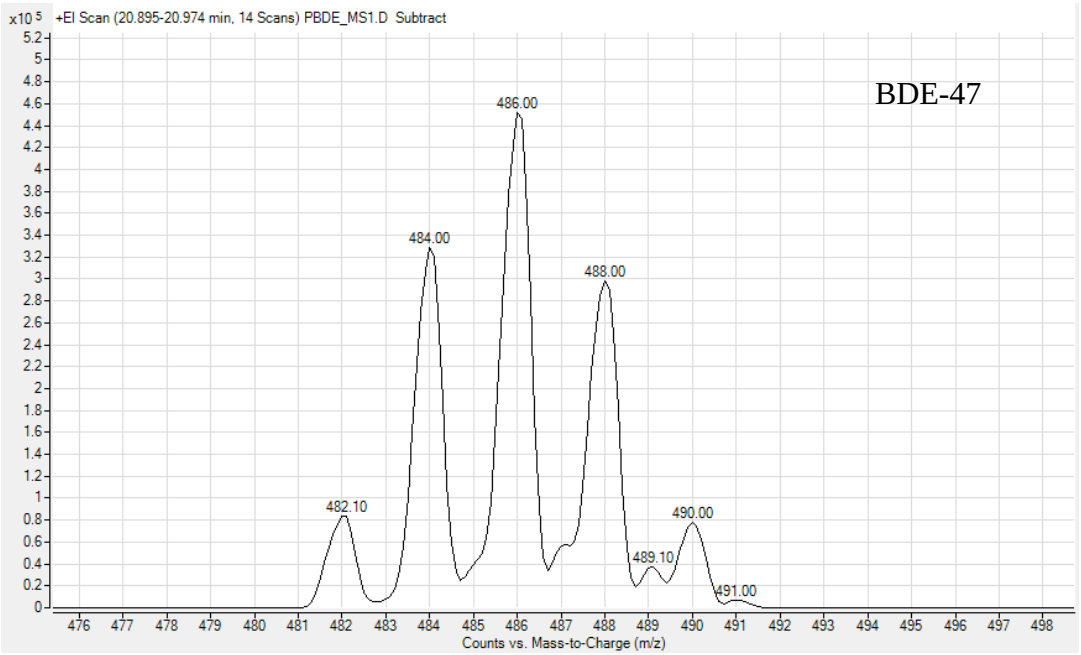

Figure 17. BDE-47 isotope distribution mass spectrum for ^{79}Br and ^{81}Br.

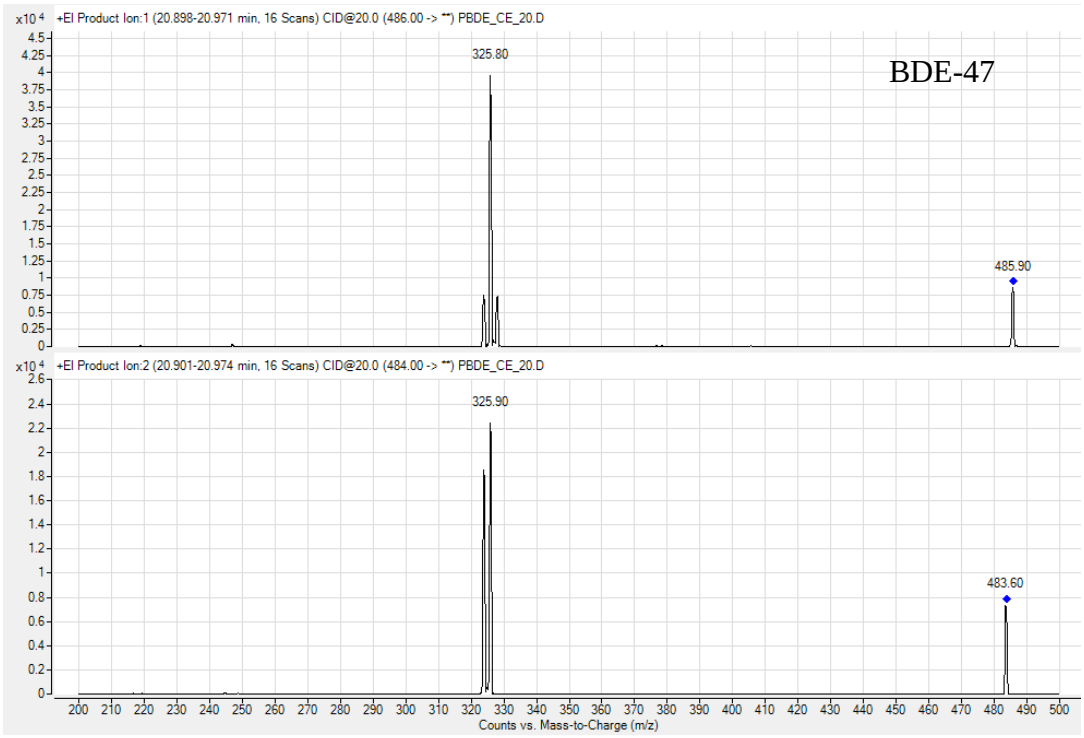

Figure 18. BDE-47 product ion scans for precursor ions 486.00 and 484.00 m/z at a collision energy of 20 volts.

MRM development was completed for all native and isotopically labeled compounds listed in Tables 1 and 2. Figures 18 and 19 show the EI MS1 mass spectrum of tris(1,3-dichloro-2-propyl) phosphate-d_{15} (dTDCIPP) and 2,2',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether (^{13}C-PBDE-47) in contrast to the unlabeled species. Chemical shifts are observed for both dTDCIPP and ^{13}C-PBDE-47 corresponding to their respective mass difference as compared to the ^{1}H and ^{12}C unlabeled compounds. The mass spectrum of dTDCIPP shows a mass shift of 13 amu for the peak at 381.20 m/z. The shift corresponds to the 13 deuterium atoms remaining on the labelled compound after the loss of a CD_2CL fragment. The mass spectrum for ^{13}C-BDE-47 shows a

chemical shift of 12 amu for the M^+, $[M-Br]^+$ and $[M-2Br]^+$ peaks, corresponding to the twelve ^{13}C phenyl carbons. All deuterated and ^{13}C compounds investigated had an analogous mass spectra profile as compared to their respective unlabeled equivalent. Table 4 summarizes the MRM precursor ions, product ions, optimized collision cell energy and qualifier quantifier response ratio. The qualifier quantifier response ratio is an additional specificity criterion for GC-MS/MS analysis. The response ratio is unique for each chemical compound and is specified at specific GC-MS/MS instrument operating parameters. The response ratios were established by selecting two MS/MS transitions for each chemical compound as is described above. It establishes a specific response ratio between the qualifier and quantifier transitions that must be met to establish positive identification of a target analyte. The qualifier quantifier response ratio was established for each analyte by using neat standards and a percent error of +/- 20% was established under defined mass spectrometer method analysis conditioned. It is for this reason that multiple transitions (MRM) were developed for each analyte rather than a single transition (SRM). The qualifier quantifier response ratio, analyte retention time and m/z establish three unique identifiers for each target analyte.

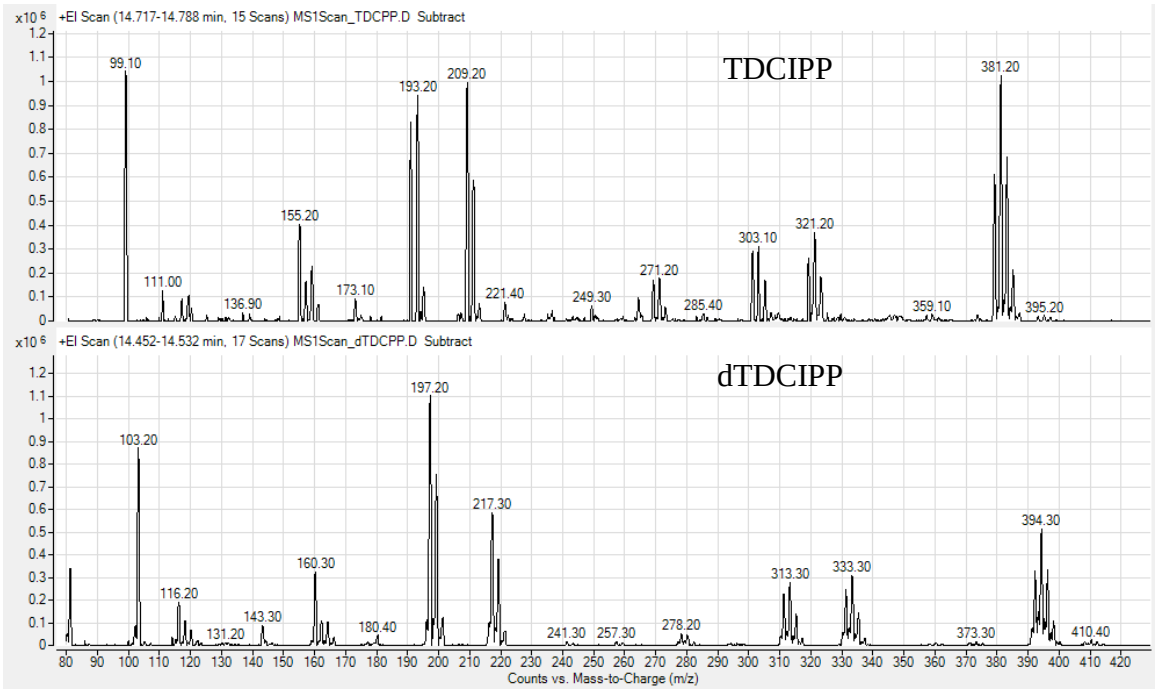

Figure 18. TDCIPP and dTDCIPP EI MS1 mass spectra shift.

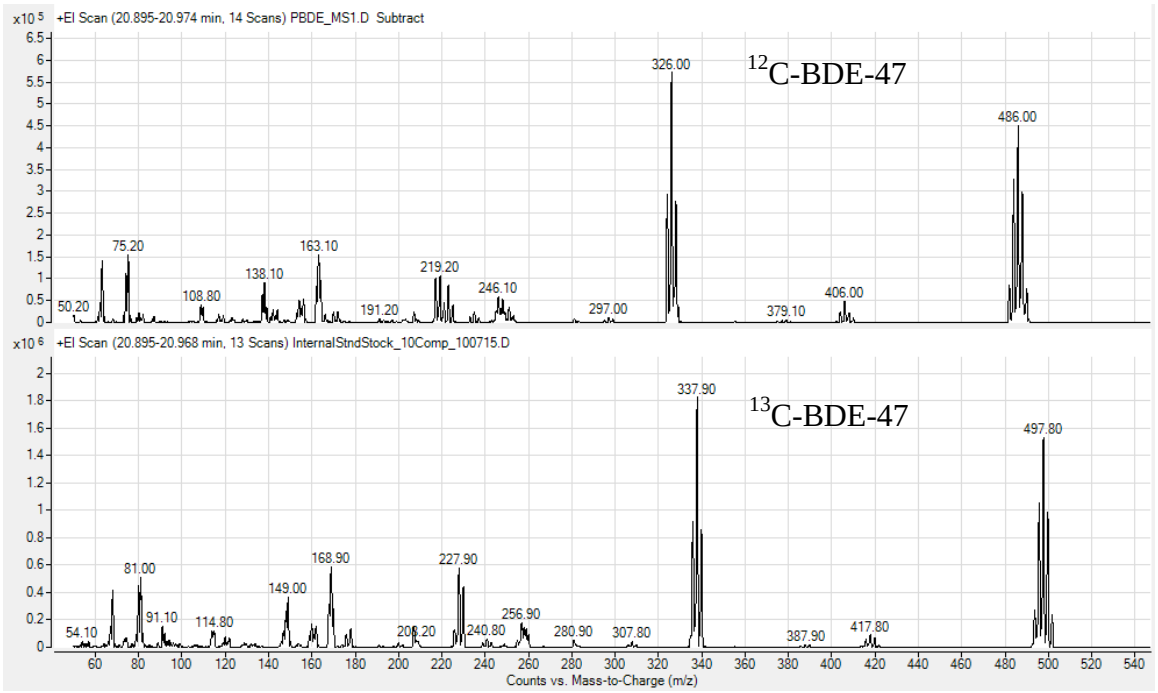

Figure 19. ^{12}C-BDE-47 and ^{13}C-BDE-47 EI MS1 mass spectra shift.

Sample Extraction – Consumer Products

The consumer product sample extraction procedure was in part adopted from Stapleton et. al. with modifications (10). First, a 50 mg (+/- 5) foam or textile sample is weighed using an analytical balance. The foam or textile sample is cut from the bulk material, using a surgical grade razor blade. The 50 mg sample is subsequently transferred to a 10 mL glass tube prebaked at 500 °C for 3 hours. Once the sample is completely transferred, the tube is capped with a solvent rinsed phenolic screw cap. The sampling procedure is repeated for all subsequent samples. It is important to note that laboratory gloves, razor blades, plastic weighing dishes and aluminum were replaced after each sample weighing to prevent cross contamination from samples with potentially high level of flame retardants. In this respect, contact surface transfer to aluminum foil was tested by wiping 100 cm^2 of aluminum foil with a foam sample containing TCEP. The aluminum foil contact surface was subsequently extracted and tested for TCEP. TCEP was detected and confirmed to transfer via surface to surface contact.

To extract the additive flame retardants 5 mL of dichloromethane (DCM) is added to the sample tube. The sample tube is then agitated by vortexing the submerged sample for 1 minute at 3000 rotations per minute followed by sonication for 10 minutes at room temperature. The liquid extract is then removed with a pasteur pipette and transferred to a 3 mL bond elute cartridge fitted with two 20 um pore size frits to remove any large particulate matter. The liquid extract is collected in a pre-weighed extract collection tube. Once the extract is removed, 5 mL of additional fresh DCM is added to the sample tube and the vortex and sonication steps are repeated. The second aliquot of DCM is then

transferred to the cartridge and filtered as described above. The sample is then centrifuged for 2 minutes to collect any remaining DCM adsorbed to the sample and subsequently transferred to the 3 mL cartridge. The primary and secondary extracts are pooled and the extract collection tube capped and weighed. The final extract volume is then normalized to 10.0 mL by calculating the volume of the extract using the density of DCM (1.325 g/mL at 25 °C) and adding a makeup aliquot of DCM to bring the final extract volume to 10 mL. The makeup DCM accounts for the DCM lost to evaporation during the sample preparation steps. A schematic of the extraction process is shown in Figure 20.

As part of method development process the extraction efficiency of DCM coupled with vortex and sonication was tested by performing a three cycle extraction and monitoring the instrument response post each 5 mL extraction cycle. Test results showed that two 5 mL DCM extraction cycles were sufficient at removing an average of 99.93 percent of the additive flame retardants in a test set of four samples with high concentration of additive flame retardants. Table 6 shows the area counts for three foam samples and one cover fabric sample. The primary extraction cycle was determined to have an average extraction efficiency of 93.72 percent, the secondary extraction cycle having an extraction efficiency of 6.21 percent and the third extraction cycle having an extraction efficiency of 0.07 percent. It was therefore concluded that two 5 mL DCM extraction cycles were adequate at removing 99.9 percent of all additive flame retardants. The sonication extraction procedure was found to be simple and effective.

Table 6. Extraction cycle efficiency of DCM coupled with vortex and sonication.

Sample	Analyte	Cycle 1 Area Counts	Cycle 2 Area Counts	Cycle 3 Area Counts
Chair 1 Foam	TCEP	5,952	481	-
	TCIPP	40,445,220	4,020,853	16,694
FM600	TCIPP	840	189	-
	TDCIPP	592	-	-
	TPHP	5,162,185	164,156	2,004
Chair 1 Fabric	TCEP	2,597,713	25,676	835
	TCIPP	284,050	2,914	129
	TDCIPP	21,539	285	51
Foam C	TCEP	55	-	-
	TCIPP	588	-	-
	TDCIPP	356	-	-
	TPHP	7,092,833	176,753	984
	BDE-17	37,210	1,387	33
	BDE-28	117,683	3,774	67
	BDE-47	8,694,701	305,442	1,960
	BDE-100	1,145,970	28,188	289
	BDE-99	4,882,947	178,166	854
	BDE-85	176,318	3,846	-
	BDE-154	129,919	2,682	-
	BDE-153	110,726	2,034	-
	BDE-183	618	13	-

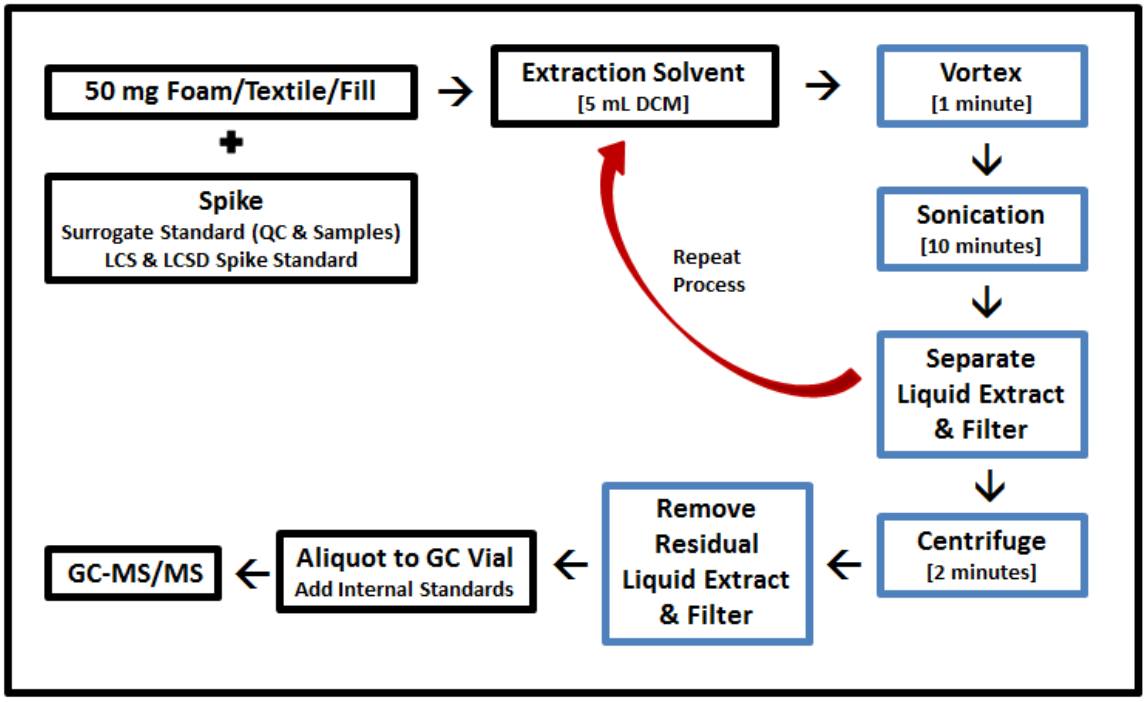

Figure 20. Extraction schematic for sonication assisted solvent extraction of consumer products.

Sample Extraction – House Dust

The house dust sample extraction procedure was in part adopted from Van dee Eede et. al. with modifications (13). Sieved house dust is separated by mechanical shaking through a series of sieves to separate larger particulate matter and debris collected by household vacuum cleaners from the fine dust fraction used for analysis. First, 50 mg (+/- 10) of sieved SRM 2585 dust or house dust sample, collected in vacuum cleaner bags, is weighed using an analytical balance. For quality control samples (method blank and laboratory control spikes) 50 mg of sodium sulfate was used. The 50 mg sample is subsequently transferred to a 10 mL glass tube and capped. The sampling procedure is repeated for all subsequent samples. SRM 2585 dust is then extracted with a 2 mL aliquot of Hexane:Acetone (3:1 v/v) mixture by vortex agitation for 1 minute followed by sonication for 7 minutes. The sample is then centrifuged for 3 minutes at maximum speed or until the fine dust fraction settles at bottom of tube, being careful not to disturb the settled dust. The supernatant is removed with a Pasteur pipette and transferred to a clean glass tube. The aforementioned steps are repeated two additional times to yield a final pooled extract volume of 6 mL per sample. The 6 mL of dust extract is then evaporated to 100 uL under direct flow of ultra high purity nitrogen gas at 5 psi. The sample extract is then solvent exchanged by the addition of 6 mL hexane and mixed thoroughly by vortex. The hexane is then evaporated to 1 mL under direct flow of nitrogen gas at 5 psi. Fractionation of polar and non-polar flame retardants is then performed by solid phase extraction (SPE) on 500 mg of preconditioned florisil. The florisil is preconditioned by washing in Hexane:Acetone (1:1 v/v) for 5 minutes and

repeating for a total of three time. The florisil was subsequently dried in a ventilated hood and baked in a furnace oven at 500 °C for 3 hours. Conditioned florisil is stored at 150 °C until ready to use. The 500 mg of conditioned florisil is packed into each 3 mL cartridges and held in place by capping both open ends with 20 um frits. The florisil SPE columns are prewashed with 6 mL of hexane prior to use. Waste collection vessels are exchanged with sample PBDE eluent collection vessels. The 1 mL sample extract is then loaded onto the florisil column followed by three 200 uL sample tube rinses. When the receding level of the extract reaches the top of the florisil, 8 mL of hexane is added to the column. A continues flow of hexane is maintained and the eluate, containing PBDEs, is collected as fraction 1. Once the SPE column stops dripping, the eluate collection vessels are changed to OPFRs, fraction 2. OPFRs are then eluted with 10 mL of ethyl acetate. The PBDE and OPFR fractions are both solvent exchanged to isooctane under direct flow of nitrogen gas at 5 psi. A schematic of the extraction process is shown in Figure 21.

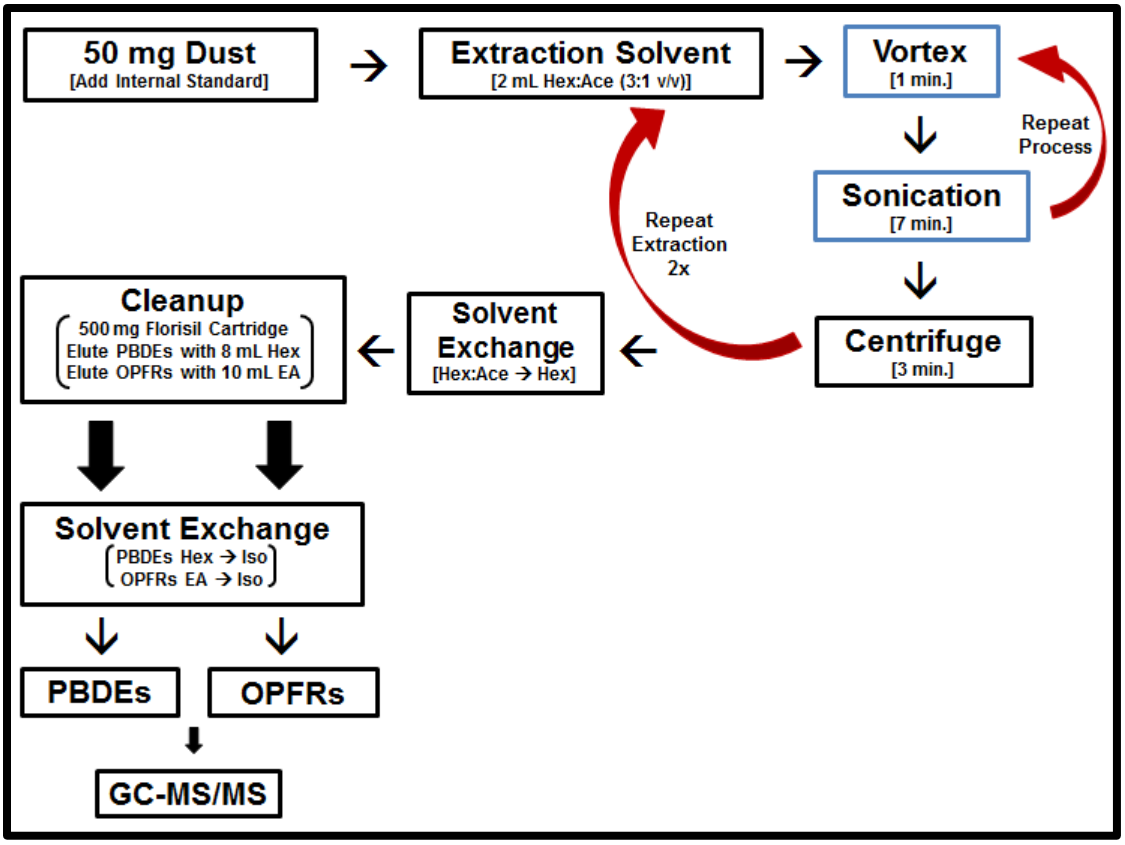

Figure 21. Extraction schematic for sonication assisted solvent extraction of house dust.

Method Validation – NIST SRM 2585

Sonication extraction coupled with GC-MS/MS analysis was validated against NIST SRM 2585, Organic Contaminants in House Dust. SRM 2585 is composed of sieved dust collected over a two year time period (1993-94) from homes and commercial vacuum cleaner bags from six US states including North Carolina, Maryland, Ohio, New Jersey, Montana and Wisconsin (14). NIST provides certified values for 33 Polycyclic Aromatic Hydrocarbons (PAHs), 30 Polychlorinated Biphenyls (PCBs), 4 Chlorinated Pesticides and 15 PBDEs. NIST also provides 58 reference concentration values and 9 information concentration values for additional compounds in the aforementioned chemical classes (14). NIST however does not provide certified or reference values for OPFRs in SRM 2585. OPFR results were therefore compared with the literature.

Figure 22 shows a bar graph comparing initial method validation results for nine PBDE congeners against NIST certified values. PBDE values compared well with NIST certified values with a percent difference range of 3.6 to 22.8. Relative standard deviation ranged from 0.1 to 15.4 percent indicating good repeatability. The initial method validation data for PBDEs showed good agreement between experimental results and certified values, therefore sample extraction and GC-MS/MS analysis was concluded to have good accuracy for measurement of PBDEs. Table 7 summarizes the initial method validation findings for four replicates samples of SRM 2585.

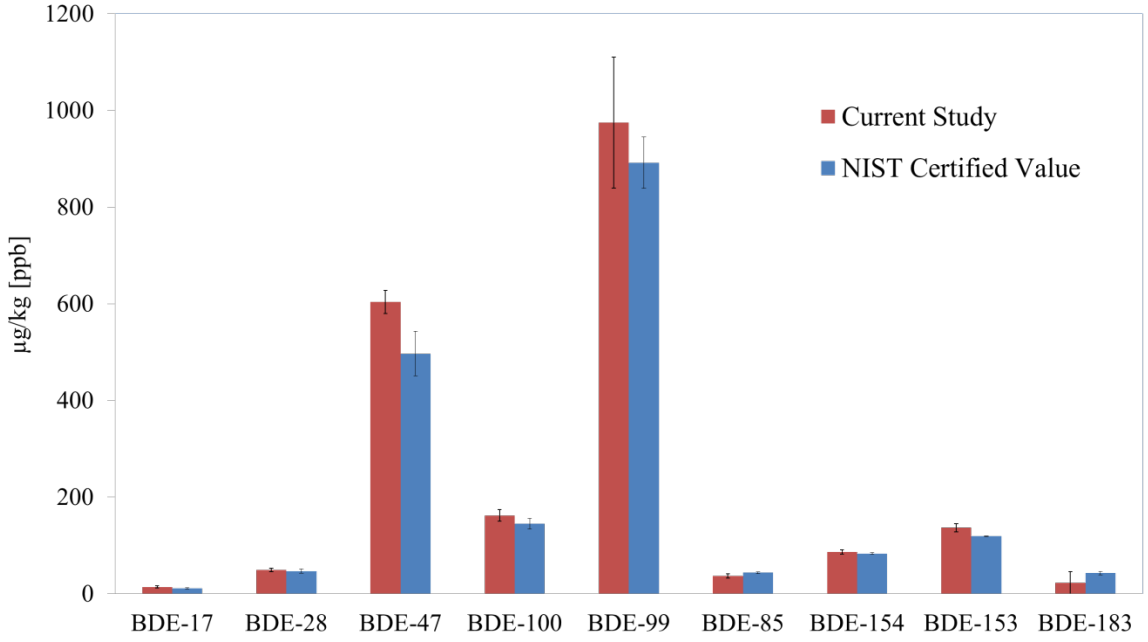

Figure 22. PBDE levels measured in NIST SRM 2585.

Table 7. PBDE experimental data and NIST certified values for SRM 2585.

	Current Study				NIST Certified Value	
	Average	**STDV**	**RSD**	**% Difference**	**ug/kg**	**STDV**
BDE-17	14.1	2.2	15.4	22.8	11.5	1.2
BDE-28	49.2	3.4	6.9	4.9	46.9	4.4
BDE-47	603.9	23.6	3.9	21.5	497.0	46.0
BDE-100	162.2	12.1	7.4	11.8	145.0	11.0
BDE-99	975.2	135.5	13.9	9.3	892.0	53.0
BDE-85	37.0	4.5	12.1	15.6	43.8	1.6
BDE-154	86.5	4.6	5.3	3.6	83.5	2.0
BDE-153	136.9	8.3	6.1	15.0	119.0	1.0
BDE-183	45.5	0.0	0.1	5.7	43.0	3.5

The analytical method was evaluated for OPFRs in SRM 2585 by comparing measured analyte concentrations to values reported in the literature. TPP was not included in the comparison as it was not detected in this study or reported in the referenced studies. Figure 23 shows a bar graph comparing initial method validation results for five OPFRs against values reported in the literature. OPFR values with a percent difference range of 1.2 to 54.7. Relative standard deviation ranged from 2.8 to 12.0 percent indicating good repeatability. The current study estimated OPFR levels relatively higher than the values reported in the literature. This may be attributed to the fact that the sonication extraction time was extended. The initial method validation data for OPFRs shows that sonication coupled with GC-MS/MS can selectively detect and quantify OPFRs in dust. Table 8 summarizes the initial method validation findings.

In addition to comparing final analyte calculated concentration to NIST and the literature, method quality control parameters were also established. Method quality control included a method blank, laboratory control spike and laboratory control spike duplicate, internal standard (deuterated and carbon-13) recovery, retention time monitoring and qualifier quantifier response ratio for compound identification.

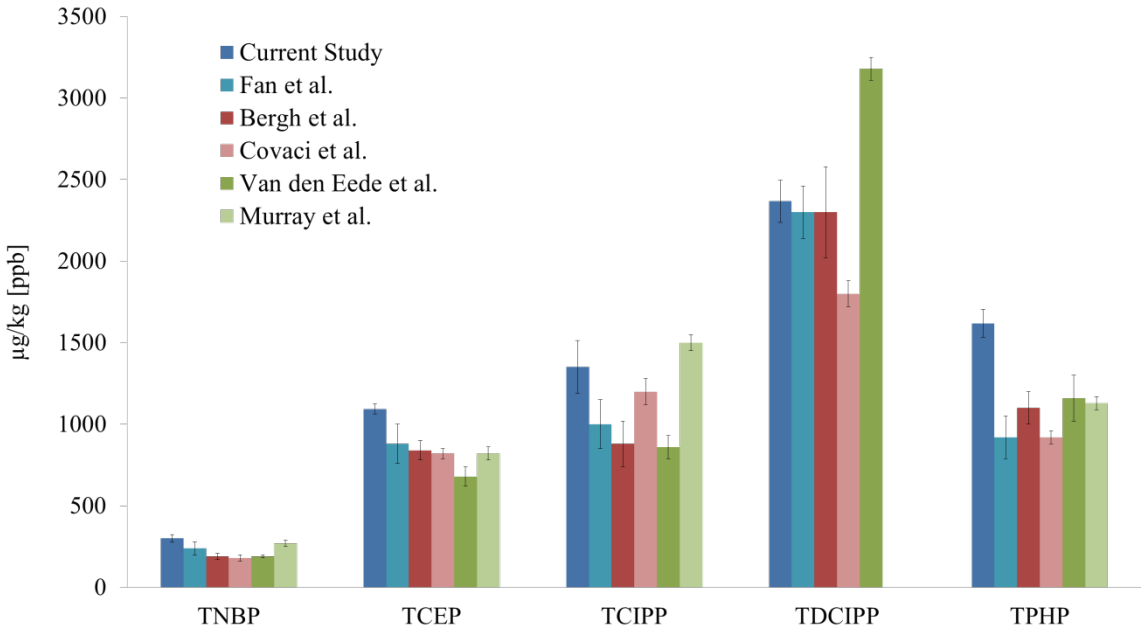

Figure 23. OPFR levels measured in NIST SRM 2585 compared to Fan et al. (15), Bergh et al. (16), Covaci et al. (17), Van den Eede et al. (18) and Murray et al. (19).

Table 8. OPFR experimental and reference literature data for SRM 2585.

	Current Study				Reference Literature	
	Average	**STDV**	**RSD**	**% Difference**	**ug/kg**	**STDV**
TNBP	300.3	23.1	7.7	40.3	214.0	35.0
TCEP	1093.5	30.6	2.8	35.3	808.0	67.6
TCIPP	1351.0	161.5	12.0	24.2	1088.0	238.9
TDCIPP	2367.0	129.0	5.4	1.2	2395.0	497.1
TPHP	1618.1	85.1	5.3	54.7	1046.0	104.6

Method Validation – Consumer Products

Consumer product results were validated by an inter laboratory collaboration with Duke University (Nicholas School of the Environment, Durham, NC) and with an in house evaluation with Liquid Chromatography Time of Flight Mass Spectrometry (Agilent Technologies 6550 iFunnel LC-QTOF) and Inductively Coupled Plasma Optical Emission Spectroscopy (PerkinElmer Optima 7300 DV ICP-OES).

The LC-QTOF was primarily used for unknown determination and more importantly for validation of GC-MS/MS compound identification results. For the ten samples listed in Figure 24 LC-QTOF and GC-MS/MS results were identical for all OPFRs and BFRs that are ionizable and chromatographically separable by both techniques. Two compound classes, PBDEs and higher order OPFR derivatives such as tetrakis(2-Chloroethyl) dichloroisopentyl diphosphate (V6) cannot be analyzed by both analytical techniques. See Figure 25 for chemical structure of V6. PBDEs are GC specific, due to their nonpolar structure and molecular stability. V6 is LC specific, due to its multiple oxygen atoms that render it highly hydrophilic. Sample Chair 1 Fabric was found to contain V6 and sample Foam C was found to contain PBDEs. These results were aligned with Duke University results for PBDEs and the relative high concentration of phosphorus found by ICP-OES for Chair 1 Fabric.

As a quantitative comparison between three different analytical techniques, phosphorus content was measured by ICP-OES and phosphorus content was calculated based on the molecular mass fraction of phosphorus and concentration of OPFR found by GC-MS/MS and Duke University (GC-MS). Briefly, ICP-OES analysis included

complete digestion of 750 mg of sample (polyurethane foam/cover fabric) in analytical grade concentrated nitric acid (70%). Phosphorus optical emission, at a wavelength of 214.914 nm, was monitored. Duke University extracted foam and or cover fabric samples by sonication in 10 mL dichloromethane (DCM) and analyzed samples on an Agilent GC-MS system (10). Figure 24 shows that the phosphorus results to be comparable between the different analytical techniques (Chair 1 Foam and Chair 2 Foam were not analyzed by ICP-OES due to limited sample material). Foam A and Foam B was not analyzed by Duke as LC-QTOF, GC/MS/MS and ICP-OES determined that no additive flame were detectable. Chair 1 Fabric was the sample which did not have comparable results. It was concluded that this sample contained high levels of V6 which is not detectable by GC-MS methods, as was noted above. The relatively small amount of TCEP detected by GC methodology is possibly a byproduct of incomplete synthesis of V6 in the technical product. Table 9 shows a direct comparison of six foam samples and 2 cover fabric samples analyzed in duplicate. Results indicate good agreement between the current method development study and Duke University for all OPFRs, PBDEs and BFRs measured. The results also indicate that the current study has slightly higher results. This may be attributed to the current study having a series of two 5 mL DCM extraction cycles rather than a single 10 mL DCM extraction used by Duke University.

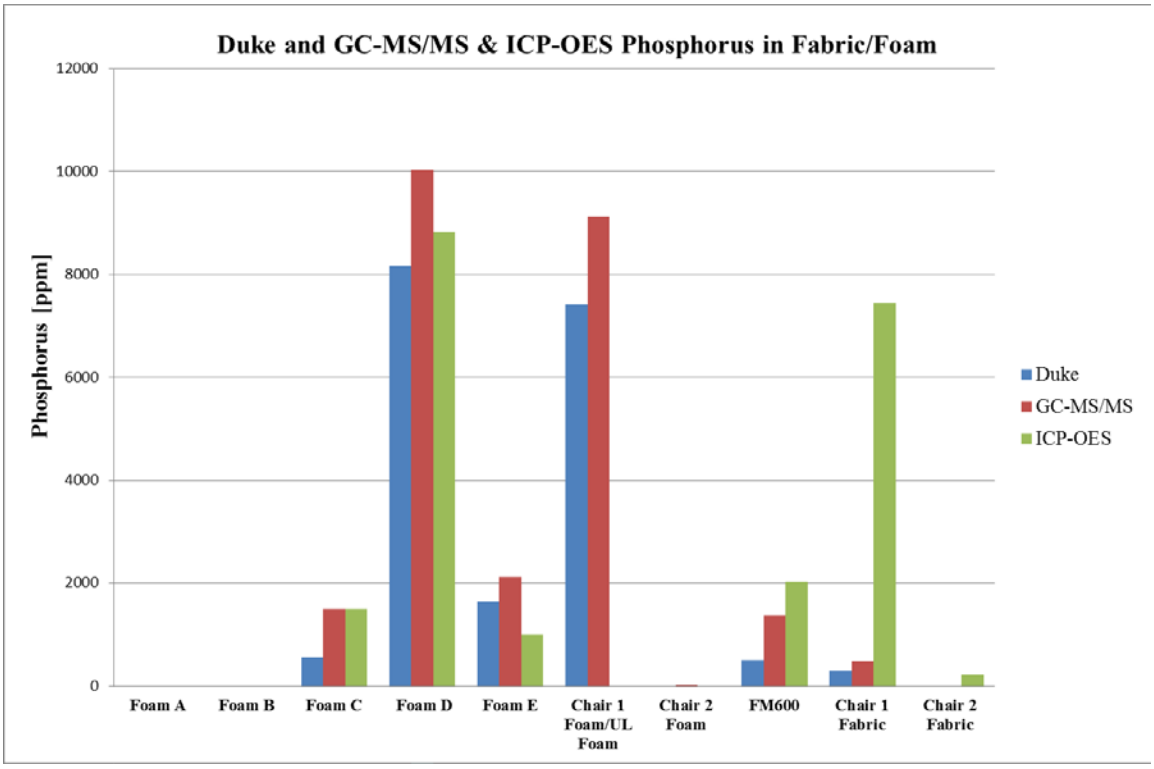

Figure 24. Phosphorus content in fabric/foam consumer product samples determined by Duke University (GC-MS), GC-MS/MS and ICP-OES.

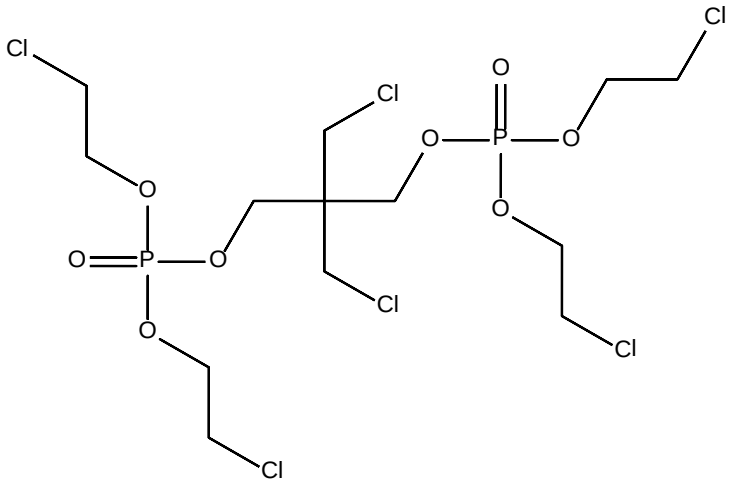

Figure 25. Chemical Structure tetrakis(2-Chloroethyl) dichloroisopentyl diphosphate (V6).

Table 9. Sample analysis by Duke University (GC-MS) and current study (GC-MS/MS).

Sample	Analyte	Duke [mg/g]	GC-MSMS [mg/g]
Foam C	TPHP	6.00	7.67
	BDE-47	12.00	13.67
	BDE-100	4.05	5.38
	BDE-99	20.70	19.20
	BDE-154	1.56	1.60
	BDE-153	1.82	1.95
Foam D	TCEP	75.00	92.46
	TCIPP	0.24	0.00
Foam E1	TCIPP	5.90	6.54
	TDCIPP	15.00	20.97
Chair 1 foam/UL Foam	TCEP	0.08	0.02
	TCIPP	78.30	96.40
Chair 2 foam	TCIPP	0.00	0.01
FM600	TPHP	5.20	14.46
	EH-TBB	10.45	19.14
	BEH-TEBP	17.02	17.26
Chair 1 Fabric	TCEP	2.70	3.86
	TCIPP	0.00	0.65
	TDCIPP	0.00	0.13
Chair 2 Fabric		0.00	0.00

Conclusion

A Gas Chromatography Tandem Mass Spectrometry (GC-MS/MS) method was developed for the simultaneous measurement of six OPFR, eleven PBDE and two novel brominated flame retardants. Sonication assisted solvent extraction was applied for two different sample matrices, consumer products and house dust. Sonication extraction was found to be an effective extraction method that was simple, accurate and reproducible for both consumer product and dust. As part of the GC-MS/MS method development procedure, discrete molecular transitions were developed for each analyte and its respective deuterated or carbon-13 labeled standard. Target compound identification was confirmed by empirically established retention times and by compound specific qualifier quantifier response ratios. For secondary conformation, the NIST MS EPA/NIH Mass Spectral Library or neat standard mass spectra were checked. The method was validated for consumer products by an inter laboratory collaboration with Duke University and by comparison of phosphorus content with ICP-OES. PBDE dust results were evaluated against NIST Standard Reference Material 2585, Organic Contaminants in House Dust (SRM 2585) and OPFR results were evaluated against reference literature. For product screening the method was shown to demonstrate high selectivity and sensitivity. For product samples, with positive test results, the sample extract would require a several fold dilution. The relative high concentration of additive flame retardants can therefore be easily detected with little background or matrix interferences which is diluted out or of limited nature due to the samples being synthetic. Dust, however, can be a challenging matrix, due to the number of compounds found in an average house dust sample and the

relative concentration of each. Dust matrix interference was experienced for detection of EH-TBB and BEH-TBP. The challenge here originates from the relative high extent of in source fragmentation of both EH-TBB and BEH-TBP. Smaller fragmentation ions generally have a larger number of interfering species originating from the matrix. For consumer products, the synthetic material is less complex and both EH-TBB and BEH-TBP were easily detected and measured. EH-TBB and BEH-TBP both require further development for analysis in house dust.

The GC-MS/MS method is limited with respect to the targeted detection of a small number of prominent flame retardants. Decabromodiphenyl ether (PBDE-209), a regulated legacy flame retardant, is difficult to measure with GC-MS/MS. The compound can be screened in consumer products but quantification is challenging. In addition, flame retardants such as melamine and tetrakis (2-chloroethyl) dichloroisopentyl diphosphate (V6), are difficult to measure using gas chromatography. Polar and thermally labile compounds such as melamine and V6 can only be accurately quantified by liquid chromatography methodologies. Further method development is needed for the inclusion of PBDE-209 and additional novel flame retardants introduced by chemical manufactures that may have a toxicological end point.

Measurement of chemicals in consumer products and house dust plays an important role in understanding environmental contamination and assessing exposure sources and routes. In the current study an analytical tool was developed for measuring flame retardant levels in household upholstered furniture, the exposure source and dust, the primary exposure route.

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