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Determination of Organophosphate and Brominated Flame Retardants in House Dust and Consumer Products by Gas Chromatography – Tandem Mass Spectrometry

1. SCOPE AND APPLICABILITY

This SOP describes the procedures for the analysis of house dust and consumer products (foam, batting and/or textiles) for organophosphate flame retardants (OPFRs) and polybrominated diphenyl ethers (PBDEs) using Gas Chromotography Tandem Mass Spectrometry.

2. DEFINITIONS

- BFR – Brominated Flame Retardant
- ECL – Environmental Chemistry Laboratory
- GC-MS/MS – Gas Chromatography Tandem Mass Spectrometry
- LCS – Laboratory Control Sample
- LCSD – Laboratory Control Sample Duplicate
- LIMS – Laboratory Information Management System
- MB – Method Blank
- MRM – Multiple Reaction Monitoring
- NIST SRM – National Institute of Standards and Technology Standard Reference Material
- OPFR – Organophosphate Flame Retardant
- PBDE – Polybrominated Diphenyl Ether
- PFTBA – Perfluorotributylamine
- RM – In House Reference Material
- RPD – Relative Percent Difference
- SB – Solvent Blank
- SDS – Safety Data Sheet

3. PRINCIPLE

House dust samples prepared by SOP "Sample Preparation for the Analysis of Organophosphate and Polybrominated Diphenyl Ethers in House Dust Using Sonication" and consumer product samples prepared by SOP "Sample Preparation for the Analysis of Organophosphate and Brominated Flame Retardants in Consumer Products Using Sonication" are analyzed on an Agilent

7890 series gas chromatograph coupled to an Agilent 7000 series triple quadrupole mass spectrometer.

4. INTERFERENCES

Trace-level analysis requires careful and clean preparation and analysis technique along with high-purity standards and solutions. Solvents, reagents, glassware, and other items used during sample analysis may introduce unexpected interferences or contamination to the sample. These materials are demonstrated to be free from interferences and contamination by analyzing a method blank with each sample batch.

4.1. Glassware Cleaning

4.1.1. Disposable Glassware

Glassware in this classification includes new and unused GC vials, glass tubes and Pasteur pipettes. Glassware in this classification is disposed of after use.

Disposable glassware should be cleaned prior to use by wrapping in aluminum foil and baking in muffle furnace at approximately 500°C for 3 hours.

When removing glassware from supplier box, check that no cardboard or other debris is transferred to aluminum foil. If supplies have been exposed to dust or other debris, clean glassware using method listed below for reusable glassware.

4.1.2. Reusable Glassware

Reusable glassware must be properly washed after use to prevent interference in subsequent analysis due to sample carryover.

Recommended procedures for cleaning glassware are described in SOP 02.0011.00, “Procedure for Washing Glassware for the Analysis of PCDDs/PCDFs, PCBs, OCPs, PBDEs, BFRs and Other Persistent Organic Pollutants in Environmental Samples”.

4.2. Interferences

Dust samples can contain variable amounts of matrix that can affect sample analysis. Matrix interference may cause signal suppression, enhancement and/or distorted peak shape. In addition, dirty samples will degrade the inlet, GC column and contaminate the mass spectrometer source.

Foam, batting and/or textile samples can contain high levels of target analytes that can contaminate autosampler components, inlet, GC column and the mass spectrometer source. If a high level sample is observed, subsequent samples must be checked for carryover and the analytical setup must be confirmed with a solvent blank. In addition, foam, batting and/or textile samples may contain variable amounts of matrix that will degrade the inlet, GC column and contaminate the mass spectrometer source. If contamination is suspected, solvent blank injections maybe required subsequent to each suspect sample injections.

4.3. Sample Analysis

The autosampler uses the same GC syringe to inject both standards and samples. To prevent carryover between samples, the syringe is rinsed before and after each sample injection with hexane and toluene from solvent reservoirs. The reservoirs should be rinsed three times with hexane or toluene and re-filled with fresh solvent before each analytical run. In addition, solvent blank injections are included in the run list to confirm system cleanliness. If there is evidence of carryover, it is recommended that the solvent rinse solutions, GC syringe, inlet liner and septa be replaced.

Consumer Products: Sample dilutions maybe required if high concentrations of analytes are detected. Analytes measured at or above the highest calibration point will require dilution. Diluted samples maybe added to the sequence and are injected after a Solvent Blank (SB) and are followed by a check standard. See section 8.2.3 Sequence Monitoring Criteria.

5. PRESERVATION AND HOLDING TIMES

5.1. Sample Extracts

Dust Samples: Samples are processed for OPFRs and PBDEs according to ECL SOP "Sample Preparation for the Analysis of Organophosphate Flame Retardants and Polybrominated Diphenyl Ethers in House Dust Using Sonication", DCN 05.0030.00.

Consumer Products: Samples are processed for OPFRs and BFRs according to ECL SOP "Sample Preparation for the Analysis of Organophosphate and Brominated Flame Retardants in Consumer Products Using Sonication", DCN 05.0031.00.

Sample extracts shall be stored in sealed glass vials in the dark at ≤6°C when not in use. Septa on autosampler vials containing sample extracts should be replaced as soon as possible after puncture, and the vials returned promptly to dark storage at ≤6°C.

5.2. Holding Times

Due to the stability of these analytes, there is no holding time limit for dust or consumer product samples that are stored in the dark at ≤6°C. Foam, batting and textiles samples shall be stored in sealed glass containers or sealed plastic bags with the sample fully enclosed in aluminum foil at ≤6°C .

6. EQUIPMENT AND SETUP

For details on the recommended consumables and equipment, see Table 1.

6.1. Description

The instrument used for sample analysis is an Agilent 7890 series gas chromatograph coupled to an Agilent 7000 series triple quadrupole mass spectrometer (GC-MS/MS).

6.2. Operating Conditions

Sample data are acquired using the Agilent Technologies MassHunter GC/MS Acquisition program (Version B.07.00 or higher). Suggested settings for the GC and mass spectrometer are listed in Table 2. Samples are analyzed using electron ionization and multiple ion monitoring. A list of analytes, including example retention times, transitions and collision cell energies, can be found in Table 3.

6.3. Instrument Consumables

For details on the recommended instrument consumables, see Table 4.

7. STANDARDS AND REAGENTS

7.1. Solvents

For details on the recommended solvents, see Table 5.

7.2. Standards

7.2.1. Standards

For details on the recommended standards used (concentration, part number and supplier), see Table 6.

All standards shall be certified. When available, it is recommended to use certified analyte concentrations corrected for purity.

7.2.2. Calibration Standard

Example calibration standard concentrations are listed in Table 7. The calibration standard shall be prepared using certified standards and calibrated pipettors. Standard preparation details shall be recorded in the laboratory notebook.

7.2.3. Surrogate Standard, Laboratory Control Standard and Injection Standard

Information regarding standards, including suppliers, part numbers, and concentrations; are included in ECL SOP 05.0030.00: “Sample Preparation for the Analysis of Organophosphate Flame Retardants and Polybrominated Diphenyl Ethers in House Dust Using Sonication” for dust preparation, or ECL SOP 05.0031.00: “Sample Preparation for the Analysis of Organophosphate and Brominated Flame Retardants in Consumer Products Using Sonication” for consumer products.

8. METHOD PROCEDURE

8.1. Batch QC Requirements

Dust: The following Quality Control (QC) analyses must be performed for each sample batch: Method Blank (MB), Laboratory Control Sample (LCS), Standard Reference

Material (SRM), Standard Reference Material (SRM) Duplicate and Sample Duplicate. A sample batch is defined as up to 15 samples, including QC samples prepared together.

Consumer Products: The following Quality Control (QC) analyses must be performed for each sample batch: Method Blank (MB), Laboratory Control Sample (LCS), Laboratory Control Sample Duplicate (LCSD), Reference Material and Sample Duplicate. A sample batch is defined as up to 24 samples, including QC samples prepared together.

8.1.1. Method Blank

The MB is analyzed at a minimum frequency of one per sample preparation batch and is subjected to the entire analytical process. The MB is prepared as follows; 50 mg (±10 mg) of sodium sulfate (Dust) or 50 mg (±5 mg) analyte-free foam (Consumer Products) are weighed and spiked with the appropriate surrogate standard (see Dust or Consumer Products Sample Preparation SOP for composition and concentration).

The MB demonstrates that the analytical process itself does not introduce contamination and is within defined limits. Small amounts of analytes may be detected in blanks. If the amount measured is greater than the LOQ, the source of contamination should be located and corrected.

8.1.2. Laboratory Control Sample

Each LCS is processed with 50 mg (±10 mg**)** of sodium sulfate (Dust) or 50 mg (±5 mg) of analyte-free foam (Consumer Products) spiked with the appropriate LCS standard and surrogate standard and subjected to the entire analytical process (See Dust or Consumer Products Sample Preparation SOP for composition and concentration). The LCS is used to test inter-batch precision and to determine expected analyte recoveries. The percent recovery of the target analytes in the LCS standard must be within 50-150%.

Consumer Products: The LCS and LCSD must have a relative percent difference (RPD) of ≤30% for each target analyte.

8.1.3. Standard Reference Material (SRM)/Reference Material (RM)

Dust: The SRM and SRM duplicate are analyzed at a minimum frequency of one set per sample preparation batch and are subjected to the entire analytical process. The SRM is prepared as follows: 50 mg (±10 mg) of NIST SRM 2585 is weighed and spiked with Surrogate Standard. It is analyzed to test the method accuracy. NIST SRM 2585 provides certified values for select PBDEs and reference values for select OPFRs. Certified and reference values are shown in the NIST Certificate of Analysis (see reference 7). PBDE results must be within 70-130% of certified values. The SRM and SRM duplicate must have a relative percent difference (RPD) of ≤30% for each target analyte.

Consumer Products: The RM is analyzed at a minimum frequency of one per sample preparation batch and is subjected to the entire analytical process. The RM is prepared as follows: 50 mg (±5 mg) of RM foam is weighed

and spiked with Surrogate Standard. RM results must be within 70-130% of defined value for cryomilled RM and 50-150% for unmilled RM.

8.1.4. Sample Duplicate

Dust: A duplicate sample is analyzed at a minimum frequency of one per batch. The Sample Duplicate is prepared as follows; 50 mg (± 10 mg) of dust is weighed and spiked with the appropriate surrogate standard and subjected to the entire analytical process (see Dust Sample Preparation SOP for composition and concentration). A duplicate sample is used to determine the intra batch precision of the analysis. The Sample Duplicate must have a relative percent difference (RPD) of ≤ 30% for each target analyte. Failure to meet the acceptance criteria due to an unavoidable lack of sample homogeneity must be noted in the case narrative of the final report.

Consumer Products: A duplicate sample is analyzed at a minimum frequency of one per batch. The Sample Duplicate is prepared as follows; 50 mg (± 5mg) of foam and or textile is weighed and spiked with the appropriate surrogate standard and subjected to the entire analytical process (see Consumer Products Sample Preparation SOP for composition and concentration). A duplicate sample is used to determine the intra batch precision of the analysis.

Cryomilled duplicate samples must have a relative percent difference (RPD) of ≤30% for each target analyte. Failure to meet the acceptance criteria, due to the inability of cryomilling to completely homogenize the sample must be noted in the case narrative of the final report.

Un-milled duplicate samples must have a relative percent difference (RPD) of ≤50%. Failure to meet the acceptance criteria due to an unavoidable lack of sample homogeneity must be noted in the case narrative of the final report.

8.2. Instrument QC Requirements

8.2.1. Tuning of Mass Spectrometer

The Agilent GC-MS/MS is auto-calibrated using PFTBA anytime instrument maintenance is performed (such as changing the column, source cleaning or any maintenance procedure requiring instrument venting and or power shutdown).

Before each analytical sequence, an instrument check tune is performed. If the system passes check tune, the sequence can be run. If check tune fails, auto-calibration should be performed again. Example check tune values are shown in Figure 1.

8.2.2. Calibration Curves

Calibration curves, consisting of seven standards with concentrations ranging from 25 to 1050 pg/µL, are generated by MassHunter Quantitative Analysis software (Version B.08.00 or higher) using the ratio of the peak area of the analyte to the assigned labeled standard plotted against concentration. MassHunter Workstation calculated calibration curve concentrations must be within 80-120% percent of the method defined values. Calibration curves must be continuous and have an R-

squared value equal to or greater than 0.990. A minimum of five points must be used to build the calibration curves and a minimum of five calibration standards are used to calculate the average qualifier response ratios for both native and labelled compounds. Qualifier/Quantifier relative response ratios must be within 80-120% of the expected value for both native and labelled compounds that have an expected relative response ratio greater than 50. Qualifier/Quantifier relative response ratios must be within 70-130% of the expected value for both native and labelled compounds that have an expected relative response ratio less than 50. Surrogate concentration are calculated by MassHunter Quantitative Analysis software using the average response factors of a minimum of five points. If the aforementioned conditions are not met, check instrument performance.

For consumer products, the range of reportable values is determined by the lowest and highest calibration curve concentrations. For dust, the range of reportable values is determined by the peak area of the lowest and highest calibration curve standards. Reportable values must be bracketed.

A new calibration curve is generated for each sample batch.

8.2.3. Sequence Monitoring Criteria

A calibration check standard (concentrations equivalent to calibration standard 4) is analyzed at the end of each batch of samples and is injected after one or more Solvent Blank (SB) injection. The calibration check standard is quantified with the calibration curve and must be within 70-130% of the expected value. If the calibration check standard does not meet acceptance criteria it canbe rerun one time.

8.3. Sample Analysis

8.3.1. Data Acquisition

The sample data are acquired using the Agilent Technologies MassHunter GC/MS Acquisition software (Version B.07.00 or higher). A sequence table shall contain the following columns; Vial, Name, Data File, Method File, Method Path, Type, Dilution, Amount, Total Amount and Data Path. A sequence table is prepared with the following recommended sample order:

1) Solvent Blank
2) Calibration Standards
3) Solvent Blank
4) Method Blank
5) Laboratory Control Sample
6) Laboratory Control Sample Duplicate (Consumer Products)
7) SRM/RM Sample
8) SRM Duplicate (Dust)
9) Batch Samples
10) Solvent Blank
11) Calibration Check Standard

One or more solvent blank injections maybe required subsequent to sample injections with high level of target analytes and/or matrix to confirm no carry over is observed. See section 4.2 Interferences.

8.3.2. Integration of Chromatograms

Chromatograms are processed using Agilent Technologies MassHunter Workstation software Quantitative Analysis for QqQ (Version B.08.00 or higher). The data are processed in batches which include the calibration curve standards, QC, samples and calibration check standard. Each analyte peak should be checked for correct integration, Qualifier/Quantifier peak ratio and retention time.

8.3.3. Data Processing

Once the integration check is complete, a summary report is generated for each batch. Analyte concentrations are calculated in ug/kg dust or mg/kg consumer product.

8.4. Data Reporting

8.4.1. Data Files

A log file is created for each run and is located in the data folder. After run completion, the log file shall be printed and placed into the GC sample log book. Additionally, the run information should be transferred to the electronic sample log file (Sample Counts.xlsx) stored on the GC-MS/MS computer.

Data files are stored on the GC-MS/MS computer by creating a subdirectory named according to the ECL Authorization Number and or other unique identifiers. The subdirectory shall contain all relavent data, including the sequence log, MRM data results, check tune report, and other relavent data. Data backups will be created according to ECL procedures.

8.4.2. Final Data Submission

Once all sample processing and analysis for the sample batch or project are complete, the analyst shall review and confirm the data are correct. Failed samples shall be re-extracted and analyzed, if sample material is available. Once data are confirmed by analyst, the batch or project data shall be peer reviewed. If suspect data are found, the peer review analyst will ask sample analyst for confirmation. Once the data are confirmed by peer review analyst, the data and or report shall be submitted to supervisor for final approval.

9. MAINTENACE AND TROUBLE SHOOTING

9.1. Agilent GC Triple Quadrupole Mass Spectrometer

9.1.1. Maintenance

Prior to sample analysis, rinse autosampler vials with hexane or toluene and fill to capacity or replace when deemed necessary. Run instrument check tune and verify criteria shown in Figure 1 are met.

Weekly: Recommend replacement of septa, glass inlet liner, and o-ring weekly or when deemed necessary. After replacement, check the system for leaks by running an Air and Water Check or by running an instrument check tune. If a leak is found, the inlet and or column connections should be checked.

Six Months: Foreline pump oil is recommended to be changed every 6 months. The tune solution vial volume should be checked and more added, if necessary.

As needed: Recommend replacement of the analytical column and source cleaning be performed when sample injections reach 1000 or when deemed necessary by analyst. Instrument consumables and parts (e.g. filaments, electron multipliers, etc.) and carrier gas traps should be replaced when needed. Sample syringe is recommended to be replaced when sample injections reach 500 or when deemed necessary by analyst.

The system is maintained by analyst, unless a system failure occurs (low sensitivity, electronic faults, etc.). In the case of system failures, it is recommended to contact an Agilent service technician. After maintenance requiring a system vent or power off, an auto-tune shall be performed to verify the analytical system is calibrated and operating within normal parameters.

9.1.2. Standards Check

Before using a new standard, it is recommended to verify that the new standard meets the method performance QC limits. A Reference Standard is prepared to check the Internal Standard and LCS Standard by spiking appropriate amounts of each into toluene and quantifying the new standard using the aforementioned data acquisition and quantitation methods.

9.1.3. Trouble Shooting

For trouble-shooting help, refer to the Agilent 7000 Triple Quadrupole GC/MS System Troubleshooting and Maintenance Manual (Second Edition, 2009).

10. REFERENCES

1. Agilent 7000 Triple Quadrupole GC/MS System Troubleshooting and Maintenance Manual. Second Edition, 2009 (P/N G7000-90037).
2. ECL SOP 02.0011.00: “Procedure for Washing Glassware for the Analysis of PCDDs/PCDFs, PCBs, OCPs, PBDEs, BFRs and Other Persistent Organic Pollutants in Environmental Samples.”

3. ECL SOP 05.0030.00: “Sample Preparation for the Analysis of Organophosphate Flame Retardants and Polybrominated Diphenyl Ethers in House Dust Using Sonication.”
4. ECL SOP 05.0031.00: “Sample Preparation for the Analysis of Organophosphate and Brominated Flame Retardants in Consumer Products Using Sonication.”
5. Van den Eede, N., A. C. Dirtu, et al. (2012). "Multi-residue method for the determination of brominated and organophosphate flame retardants in indoor dust." Talanta 89: 292-300.
6. Bergh, C., G. Luongo, et al. (2012). "Organophosphate and phthalate esters in standard reference material 2585 organic contaminants in house dust." Analytical and Bioanalytical Chemistry 402(1): 51-59.
7. Certificate of Analysis, Standard Reference Material 2585; National Institute of Standards and Technology: Gaithersburg, MD, January 12, 2018.

11. TABLES

Table 1: Recommended Consumables and Supplies

Item	Description	Supplier	Part/Model #
Glassware			
GC vial 300 µL	300 µL amber vial with insert and writing patch	Wheaton[1]	225328
GC vial 1.5 mL	Micro-V Vial Amber, 1.5mL, 12x32MM	VWR[2]	66064-914
Pasteur pipettes	Borosilicate glass, overall length 22.9 cm (9")	VWR	14673-043
Volumetric flask – 3 mL	Volumetric Cylindrical Flask, ±0.015 mL	VWR	14209-628
Volumetric flask – 5 mL	Volumetric Cylindrical Flask, ±0.02 mL	VWR	14204-538
Volumetric flask – 10 mL	Volumetric Cylindrical Flask, ±0.02 mL	VWR	14203-258
Plastics			
Pipette bulbs	Small-volume, natural rubber latex, 2 mL	VWR	82024-554
20 µL pipette tips	ART Barrier, Low Retention 20 µL Barrier (2749-05-HR)	VWR	89031-352
200 µL pipet tips	ART Barrier, Low Retention 200 µL Barrier (2769-05-HR)	VWR	89031-374
300 µL pipet tips	ART Barrier, Low Retention 300 µL Barrier (2739-05-HR)	VWR	89031-394
1000 µL pipet tips	LTS 1 ml Tips, RT-LTS-A-L1000µL-/F	Mettler-Toledo[3]	30389212
5000 µL pipet tips	LTS 5 mL Tips, RT-LTS-A-5000µL-192/8	Mettler-Toledo	30389256
GC vial caps	ABC cap with PTFE/ Silicone Septum	Wheaton	W225332-0204
Other			
20 µL pipette	Electronic Pipette, LTS E4-20XLS+ 2-20 µL	Mettler-Toledo	17014487
100 µL pipette	Electronic Pipette, LTS E4-100XLS+ 10-100 µL	Mettler-Toledo	17014483
300 µL pipette	Electronic Pipette, LTS E4-300XLS+ 20-300 µL	Mettler-Toledo	17014488
1 mL pipette	Electronic Pipette, LTS E4-1000XLS+ 100-1000 µL	Mettler-Toledo	17014482
5 mL pipette	Electronic Pipette, LTS E4-5000XLS 500-5000 µL	Mettler-Toledo	17012312

[1]wheaton.com, [2]us.vwr.com, [3]us.mt.com

Table 2: Recommended Instrumentation and Analytical Conditions for GC-MS/MS

GC	Agilent 7890A or 7890B Series
Autosampler	Agilent 7000 Series
Analytical column	DB-5ms 30 m x 0.25 mm I.D. x 0.25µm film thickness (P/N 122-5532UI)
Initial column flow rate	1.5 mL/min (constant flow)
Carrier gas	Helium
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)
Run time	32.667 min
Front Inlet Split/Splitless Parameters	
Mode	Pulsed Splitless
Injection volume	1.5 µL
Inlet liner	Agilent Ultra Inert Liner, splitless, single taper, glass wool (P/N 5190-3163)
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
Triple Quadrupole Mass Parameters	
Spectrometer	Agilent 7000 Series
Source	Electron Impact Extractor (EIEX)
Electron Energy (eV)	70
Tune file	atune_250.eiex.tune.xml
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
MRM Mode Conditions	
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
Software	
Data acquisition	Agilent MassHunter Data Acquisition Software (Ver. B.07.00. or higher)
Qualitative analysis	MassHunter Workstation Software for Qualitative Analysis (Ver. B.06.00 or higher)
Quantitative analysis	MassHunter Workstation Software for Quantitative Analysis (Ver. B.08.00 or higher)

Table 3: Analyte List and Recommended Multiple Reaction Monitoring Settings

Compound Abbreviation	Compound Name	RT (min)	Quantifier		CE (V)	Qualifier		CE (V)	Dwell Time (ms)	Qual/Quant (%)
			Precursor	Product		Precursor	Product			
dTPP	Tri-n-propyl phosphate-d_{21}	5.930	151.1	103.1	5	199.2	103.1	5	75	41.7
TPP	Tri-n-propyl phosphate	6.050	141.1	99.0	5	183.2	99.0	5	75	34.1
dTNBP	Tri-n-butyl phosphate-d_{27}	8.120	167.4	103.0	5	231.4	103.0	10	75	68.3
TNBP	Tri-n-butyl phosphate	8.255	155.3	99.0	5	211.4	99.0	5	75	42.4
dTCEP	Tris(2-chloroethyl) phosphate-d_{12}	9.145	261.3	196.1	5	261.3	131.0	10	40	90.5
TCEP	Tris(2-chloroethyl) phosphate	9.245	249.3	124.9	10	249.3	186.9	5	40	94.6
dTCIPP	Tris(2-chloroisopropyl) phosphate-d_{18}	9.425	293.3	131.0	10	295.3	131.1	10	40	67.6
TCIPP	Tris(1-chloro-2-propyl) phosphate	9.575	277.4	124.9	5	279.4	125.0	5	40	69.8
BDE-17	2,2',4-Tribromodiphenyl ether	15.950	405.7	246.0	20	407.7	248.0	20	75	97.5
BDE-28	2,4,4'-Tribromodiphenyl ether	16.665	405.7	246.0	20	407.7	248.0	20	75	97.2
^{13}C-BDE-28	2,4,4'-Tribromo[$^{13}C_{12}$]diphenyl ether	16.665	417.8	258.0	20	419.8	260.0	20	75	95.4
dTDCIPP	Tris(1,3-dichloro-2-propyl) phosphate-d_{15}	17.300	394.3	164.1	15	396.3	164.1	15	75	46.3
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate	17.550	381.2	159.0	15	383.2	159.0	15	75	47.8
dTPHP	Triphenyl phosphate-d_{15}	18.650	341.5	223.1	30	341.5	178.1	35	75	55.1
TPHP	Triphenyl phosphate	18.755	326.4	215.0	25	326.4	169.0	30	75	82.9
^{13}C-BDE-47	2,2',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether	20.655	497.8	337.9	20	495.8	335.9	20	75	50.4
BDE-47	2,2',4,4'-tetrabromodiphenyl ether	20.655	485.7	325.9	20	483.7	323.9	20	75	50.4
^{13}C-BDE-79	3,3',4,5'-tetrabromo[$^{13}C_{12}$]diphenyl ether	21.125	497.8	337.9	20	495.8	335.9	20	75	49.5
^{13}C-BDE-77	3,3',4,4'-tetrabromo[$^{13}C_{12}$]diphenyl ether	22.250	497.8	228.0	40	497.8	230.0	40	150	91.8
BDE-100	2,2',4,4',6-pentabromodiphenyl ether	23.158	563.7	403.7	20	565.7	405.8	20	150	97.8
^{13}C-BDE-99	2,2',4,4',5-pentabromo[$^{13}C_{12}$]diphenyl ether	23.751	575.7	415.9	20	577.7	417.9	20	40	97.0
BDE-99	2,2',4,4',5-pentabromodiphenyl ether	23.751	563.7	403.8	20	565.7	405.8	20	40	98.1
^{13}C-dEH-TBB	2-ethylhexyl-d_{17}-2,3,4,5-tetrabromo[$^{13}C_6$]benzoate	23.685	426.9	398.8	20	428.9	400.8	20	40	63.0
EH-TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate	23.815	421.2	392.7	17.5	419.1	390.7	20	40	79.9
BDE-85	2,2',3,4,4'-pentabromodiphenyl ether	24.622	563.7	403.7	25	565.7	405.8	25	75	97.9
^{13}C-BDE-154	2,2',4,4',5,6'-hexabromo[$^{13}C_{12}$]diphenyl ether	25.015	655.7	495.7	25	653.7	493.7	25	75	69.1
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether	25.015	643.5	483.7	25	641.5	481.7	25	75	68.2
^{13}C-BDE-153	2,2',4,4',5,5'-hexabromo[$^{13}C_{12}$]diphenyl ether	25.739	655.7	495.7	25	653.7	493.7	25	75	69.3
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether	25.739	643.5	483.7	25	641.5	481.7	25	75	68.2
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether	28.183	561.6	455.0	37	563.6	455.0	37	150	98.2
^{13}C-dBEH-TEBP	Bis(2-ethylhexyl-d_{17})-tetrabromo[$^{13}C_6$]phthalate	30.104	128.3	62.1	15	128.3	80.1	5	75	68.0
BEH-TEBP	Bis(2-ethylhexyl) tetrabromophthalate	30.531	112.4	55.1	17.5	112.4	70.0	5	75	59.4

Table 4: Recommended GC-MS/MS Consumables and Supplies

Item	Description	Supplier	Part/Model #
GC Supplies			
Helium	Helium, Ultra High Purity (UHP) 99.999%	Airgas[5]	He UHP300
Nitrogen	Nitrogen, Ultra High Purity (UHP) 99.999%	Airgas	NI UHP300
Helium Gas Trap	Big Universal Trap, helium, 1/8" fittings	Agilent[6]	RMSH-2
N_2 Gas Trap	Big Universal Trap, 1/8" fittings, Nitrogen	Agilent	RMSN-2
Syringe	ALS syringe, 10 µL, Fixed Needle, FN 23/42/cone	Agilent	9301-0713
Septum	Non-stick bleed and temperature optimized (BTO) septa, 11 mm	Agilent	5183-4757
Inlet Liner	Inlet Liner, Ultra Inert, splitless,single taper, glass wool (5pk)	Agilent	5190-3163
Column	DB-5ms (30m, 0.25mm I.D, 0.25µm film thickness)	Agilent	122-5532UI
Inlet Ferrule	Ferrule, 0.4 mm id, 15% graphite/85%Vespel, 0.1 to 0.25 mm column, short	Agilent	5181-3323
Wash Vial	4ml wash/waste vial 25/PK	Agilent	5182-0551
MS Interface Ferrule	Ferrule, 0.4 mm id, preconditioned for MSD interface, 15% graphite/ 85% Vespel, 0.25 mm column, long	Agilent	5062-3508
MS Supplies			
Source Filament	Filament, high temperature EI ion source, for GC/MS	Agilent	G7005-60061
MS Tune Solution	Perfluorotributylamine (PFTBA), MS Grade CAS # 311-89-7	Agilent	8500-0656
Pump Oil	Inland Vacumm Pump Fluid 45, 1 Liter	Agilent	6040-0834
Microgrit	Alumina Oxide Powder	Agilent	8660-0791
Cotton Swabs	Swabs for cleaning GC/MS Source, 100/pk	Agilent	5080-5400
Electron Multiplier	Triple Axis Electron Multiplier	Agilent	G3170-80103

[5]airgas.com, [6]agilent.com

Table 5: Recommended Solvents

Solvent	Description	Supplier	Catalog Number
Hexane	JT Baker, Ultra Resi-Analyzed, (Avantor[7] 9262-02)	VWR	JT9262-2
Toluene	JT Baker, Ultra Resi-Analyzed, (Avantor 9336-02)	VWR	JT9336-2

[7]avantormaterials.com

Table 6: Recommended Native and Labelled Standards

Standard Type	Component	Concentration (ng/µL)	Supplier	Part Number
Native Standards	BDE-17	50	Wellington[8]	BDE-17
	BDE-28	50	Wellington	BDE-28
	BDE-47	50	Cambridge Isotope Labs[9]	BDE-47-CS
	BDE-85	50	Wellington	BDE-85
	BDE-99	50	Cambridge Isotope Labs	BDE-99-CS
	BDE-100	50	Cambridge Isotope Labs	BDE-100-CS
	BDE-153	50	Cambridge Isotope Labs	BDE-153-CS
	BDE-154	50	Cambridge Isotope Labs	BDE-154-CS
	BDE-183	50	Cambridge Isotope Labs	BDE-183-CS
	TPP	100	AccuStandard[10]	PFRS-021S
	TNBP	100	AccuStandard	PFRS-009S
	TCEP	100	AccuStandard	PFRS-024S
	TCIPP	100	AccuStandard	PFRS-025S
	TDCIPP	100	AccuStandard	PFRS-027S
	TPHP	100	AccuStandard	PFRS-020S
	EH-TBB	100	AccuStandard	FRS-041S
	BEH-TEBP	100	AccuStandard	FRS-040S
Labelled Standards	^{13}C-BDE-28	50	Wellington	MBDE-28
	^{13}C-BDE-47	50	Wellington	MBDE-47
	^{13}C-BDE-77	50	Wellington	MBDE-77
	^{13}C-BDE-79	50	Wellington	MBDE-79
	^{13}C-BDE-99	50	Wellington	MBDE-99
	^{13}C-BDE-153	50	Wellington	MBDE-153
	^{13}C-BDE-154	50	Wellington	MBDE-183
	dTPP	1000	Cambridge Isotope Labs	DLM-8901-1.2
	dTNBP	50	Wellington	dTBP
	dTCEP	50	Wellington	dTCEP
	dTCIPP	100	Cambridge Isotope Labs	DLM-9317-1.2
	dTDCIPP	50	Wellington	dTDCPP
	dTPHP	50	Wellington	dTPP
	^{13}C-dEH-TBB	50	Wellington	MEHTBB
	^{13}C-dBEH-TEBP	50	Wellington	MBEHTBP

[8]well-labs.com, [9]isotope.com, [10]accustandard.com

Table 7: Recommended Calibration Standard Concentrations

Calibration Standard [pg/µL]								
Analyte		**Cal. 1**	**Cal. 2**	**Cal. 3**	**Cal. 4**	**Cal. 5**	**Cal. 6**	**Cal. 7**
Native	BDE-17	25	50	100	200	400	700	1050
	BDE-28	25	50	100	200	400	700	1050
	BDE-47	25	50	100	200	400	700	1050
	BDE-85	25	50	100	200	400	700	1050
	BDE-99	25	50	100	200	400	700	1050
	BDE-100	25	50	100	200	400	700	1050
	BDE-153	25	50	100	200	400	700	1050
	BDE-154	25	50	100	200	400	700	1050
	BDE-183	25	50	100	200	400	700	1050
	TPP	25	50	100	200	400	700	1050
	TNBP	25	50	100	200	400	700	1050
	TCEP	25	50	100	200	400	700	1050
	TCIPP	25	50	100	200	400	700	1050
	TDCIPP	25	50	100	200	400	700	1050
	TPHP	25	50	100	200	400	700	1050
	EH-TBB*	25	50	100	200	400	700	1050
	BEH-TEBP*	25	50	100	200	400	700	1050
Labelled	^{13}C-BDE-28	50	50	50	50	50	50	50
	^{13}C-BDE-47	50	50	50	50	50	50	50
	^{13}C-BDE-77	200	200	200	200	200	200	200
	^{13}C-BDE-79	100	100	100	100	100	100	100
	^{13}C-BDE-99	50	50	50	50	50	50	50
	^{13}C-BDE-153	100	100	100	100	100	100	100
	^{13}C-BDE-154	100	100	100	100	100	100	100
	dTPP	100	100	100	100	100	100	100
	dTNBP	125	125	125	125	125	125	125
	dTCEP	250	250	250	250	250	250	250
	dTCIPP	250	250	250	250	250	250	250
	dTDCIPP	250	250	250	250	250	250	250
	dTPHP	250	250	250	250	250	250	250
	^{13}C-dEH-TBB*	250	250	250	250	250	250	250
	^{13}C-dBEH-TEBP*	250	250	250	250	250	250	250

*EH-TBB, BEH-TEBP and corresponding labelled standards are not included in dust analysis.

12. FIGURES

Figure 1. Example GC-MS/MS System Check Tune

Triple Quadrupole GC/MS System Verification - Tune

Instrument Name	GCMSQQQ-2 / US13156A01	**MS Model**	7000
Tune Date & Time	10/10/2015 1:37:06 PM		
Tune File	D:\MassHunter\GCMS\1\7000\autotune_250.elex.tune.xml		

Instrument Actuals

Ionization mode	EI+	Rough Vacuum	1.47E+2 mTorr
Source Temperature	251 °C	High Vacuum	7.43E-5 Torr
Quad. 1 Temperature	150 °C	Turbo Speed	100.0 %
Quad. 2 Temperature	150 °C	Turbo Power	21.568 W
Emission Current	35 uA		

MS1 Checktune Results	Value	Limit	Result
Low mass assignment (target 69.00, actual 69.00)	0.00	<= 0.20	OK
Mid mass assignment (target 264.00, actual 264.00)	0.00	<= 0.20	OK
High mass assignment (target 502.00, actual 502.00)	0.00	<= 0.20	OK
Low mass isotope position (target 70.00, actual 70.00)	0.00	<= 0.20	OK
Mid mass isotope position (target 265.00, actual 265.00)	0.00	<= 0.20	OK
High mass isotope position (target 503.00, actual 503.00)	0.00	<= 0.20	OK
Low mass isotope ratio	1.10%	>= 0.5% and <= 1.6%	OK
Mid mass isotope ratio	5.72%	>= 4.2% and <= 6.9%	OK
High mass isotope ratio	9.99%	>= 7.9% and <= 12.3%	OK
Ratio of mid mass to low mass	18.65%	>= 5.0%	OK
Ratio of high mass to low mass	5.52%	>= 0.8%	OK
Low mass precursor ratio	0.08%	<= 3.00%	OK
Mid mass precursor ratio	0.31%	<= 6.00%	OK
High mass precursor ratio	0.17%	<= 12.00%	OK

MS2 Checktune Results			
Low mass assignment (target 69.00, actual 69.00)	0.00	<= 0.20	OK
Mid mass assignment (target 264.00, actual 264.00)	0.00	<= 0.20	OK
High mass assignment (target 502.00, actual 502.00)	0.00	<= 0.20	OK
Low mass isotope position (target 70.00, actual 70.00)	0.00	<= 0.20	OK
Mid mass isotope position (target 265.00, actual 265.00)	0.00	<= 0.20	OK
High mass isotope position (target 503.00, actual 503.00)	0.00	<= 0.20	OK
Low mass isotope ratio	1.08%	>= 0.5% and <= 1.6%	OK
Mid mass isotope ratio	5.67%	>= 4.2% and <= 6.9%	OK
High mass isotope ratio	10.03%	>= 7.9% and <= 12.3%	OK
Low mass precursor ratio	0.45%	<= 3.00%	OK
Mid mass precursor ratio	0.00%	<= 6.00%	OK
High mass precursor ratio	0.10%	<= 12.00%	OK

Detector			
EMV	1652	<= 2900	OK
Maximum gain factor	1059	>= 100	OK

Air and Water Check	Abundance	Relative Abundance	Limit	Result
PFTBA (69.00)	1533003			
Water	24007	1.57%	<= 20.00%	OK
Oxygen	4399	0.29%	<= 2.50%	OK
Nitrogen	16393	1.07%	<= 10.00%	OK

* Nitrogen values are calculated from oxygen abundance

13. REVIEW

Signatures	Date