Organophosphate Flame Retardants

Method Development for the Detection of OPFRs in House Dust and Consumer Products

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Key Points

Background Information

GCMS Method Development
• OPFR Chemical Structure
• GC-MSMS
• MRM Transitions

Dust
• SRM 2585 [Organic Contaminants in House Dust]
• Extraction Process
  • Sonication assisted solvent extraction
  • Measured OPFRs in SRM 2585

Foam
• Polyurethane Foam
• Extraction Process
• BEARHFTI

• Conclusion
  • Additional Work / Method Development / Application
  • References
Replacement Flame Retardants

• Restrictions on the use of Polybrominated biphenyls (PBBs) & Polybrominated diphenyl ethers (PBDEs)
  • RoHS: Restriction of Hazardous Substances Directive (EU: PBBs & PBDE)\(^1,5\)
  • Stockholm Convention (POPs: octaBDE & pentaBDE)\(^3\)
  • California Health and Safety Code Section 108922 (penta BDE)\(^12\)
  • California Prop 65 (PBBs: cancer & development)\(^4\)

• Organophosphate Flame Retardants (OPFRs)
  • California Prop 65\(^4\)
  • Safer Consumer Products:
    – A Priority Product is a consumer product that contains one or more chemicals – known as Candidate Chemicals – that have a hazards trait that can harm people or the environment.\(^{12}\)
      - Tris(1,3-dichloro-2-proply phosphate (TDCPP) \(\rightarrow\) carcinogen
      - Tris(2-chloroethyl) phosphate (TCEP) \(\rightarrow\) carcinogen
      - Tris(2,3-dibromopropyl) phosphate \(\rightarrow\) carcinogen
Senate Bill No. 1019
Upholstered furniture: flame retardant chemicals

- Approved by Governor Brown September 30, 2014
  - Effective January 1, 2015

- bill requires labeling to indicate if the product contains flame retardant chemicals (>1000ppm or 0.1% wt/wt)
  - Fine for Violation
  - Citation will be made available to public (www.bearhfti.ca.gov)

- consumers can make an informed decision

- DTSC to assist the BEARHFTI by testing for Flame Retardant Chemicals
  - When manufacture label indicates No added Flame Retardant Chemicals
Label Requirement

- Furniture manufacture date of January 1, 2015
- SB 1019 is not retroactive

Technical Bulletin 117

- Furniture (fill materials) to be able to withstand a small open flame for at least 12 seconds
  - prevent combustion
  - delay spread of fire

The upholstery materials in this product:

- [ ] contain added flame retardant chemicals
- [ ] contain NO added flame retardant chemicals

The State of California has updated the flammability standard and determined that the fire safety requirements for this product can be met without adding flame retardant chemicals. The State has identified many flame retardant chemicals as being known to, or strongly suspected of, adversely impacting human health or development.

www.bearhfti.ca.gov

TB 117 Furniture Label from Sofa
Purchased in 2010
Compounds of Interest

Phosphate Flame Retardants (PFRs)

www.accustandard.com/phosphate-flame-retardants/
Reproduced with permission (Accustandard, Inc. New Haven, CT).
<table>
<thead>
<tr>
<th>GC-MS/MS Settings</th>
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<tbody>
<tr>
<td><strong>Injection Volume</strong></td>
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<tr>
<td><strong>GC Injector Temperature</strong></td>
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<td><strong>Source Temperature</strong></td>
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<td><strong>Collision Cell Gases</strong></td>
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<td><strong>Quadrupole Temperature</strong></td>
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Agilent 7000 Triple Quadrupole GC-MS System

- Dust and Foam Sample analysis by both GC-MS & GC-MS/MS
## GC-MS MRM Transitions Table

<table>
<thead>
<tr>
<th>Compound Abbreviation</th>
<th>Compound Name</th>
<th>RT</th>
<th>Precursor</th>
<th>Product</th>
<th>CE</th>
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<td>218.8</td>
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### MRM Transitions

- **Standards**
- **MS1 Scan → Retention Time & Precursor Ion**
- **MS2 → Product Ion Scan**
- **MSMS → CE Optimization**
  - 6 Labelled Compounds
  - 12 Native

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[Diagram: GC-MS MRM Transitions](www.agilent.com)
• 250 pg/uL alkyl, 500 pg/uL chlorinated, 1000 pg/uL TBEP & TDBPP, 2000 pg/uL TEHP
• TBEP, TDBPP and TEHP
  – Insource fragmentation w/high number of MS1 Fragments → lower abundance per fragment
  – Inlet breakdown w/multiple breakdown products, tris & bis(2-ethylhexyl) phosphate & cyclic /alkyl products
DUST SRM 2585

• Investigate the feasibility of OPFR analysis by Sonication Assisted Solvent Extraction followed by GC-MSMS

• SRM 2585 Organic Contaminants in House Dust\textsuperscript{11}
  – Dust collected from homes and commercial sources (cleaning services, motels & hotels)
    • Vacuum cleaner Bags
    • North Carolina, Maryland, Ohio, New Jersey, Montana & Wisconsin (1993-94)
  – Certified Concentration Values:
    • 33 polycyclic aromatic hydrocarbons (PAHs)
    • 30 polychlorinated biphenyls congeners (PCB)
    • 4 chlorinated pesticides
    • 15 polybrominated diphenyl ether congeners (PBDE)
      – 3 – 5000 ug/Kg (ppb) certified analyte conc. range
      – Additional 58 reference conc. values + 9 information conc.. Values

• No certification for OPFRs
SRM 2585 - Primary & Secondary Extraction

50 mg SRM → Vortex/Sonication/Centrifuge → Evaporation → Florisil Column → Evaporation → QqQ

2\textsuperscript{nd} Extraction SRM & Na\textsubscript{2}SO\textsubscript{4}

Vortex/Sonication/Centrifuge → Evaporation → Florisil Column → Evaporation → QqQ
Full Scan SRM 2585

- 50 mg SRM 2585
- MS1 Scan (80-550) of SRM 2585

- Tris (2-butoxyethyl) phosphate (TBEP) – detected in Sonication SRM dust sample
  - Retention Time 19.5
  - NIST Library probability ~ 82.4% with background subtraction

- Other analytes are difficult to detect with Scan
  - Use MRM method
• SRM 2585 matrix background is reduced
  • Native analytes and Standards detected
    • TBP, TCEP TCPP, TDCPP, TPhP, TBEP & TEHP
Other Background Sources

- **Matrix – Dust Primary Contributor**
  - Instrumentation - Extraction Secondary Contribution
  - Peaks at 16 and 19.5 minutes from Florisil
    - Wash Florisil with Hexane:Acetone and Bake at 500C, store at 150C

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**Legend:**
- SRM
- Matrix Spike
- Ref. Stnd.
- Isooctane
Background Contributions

- **TDCPP** - Lab background / equipment, difficult to eliminate
  - Blank correct final results
- **Florisil background** at 18.95 min (TBEP RT 19.16) and matching transition
  - Wash Florisil with Hexane:Acetone / bake at 500C before use → Background is reduced
    - Retention time window is different (post solvent rinse overlap is eliminated)
    - Ion Qual/Quant ratio to authenticate
      - Post solvent wash contaminate < 8% abundance of TBEP dust
      - Method Blanks
• **2nd Extraction Cycle for SRM**
  
  - **Note that all compounds not Extracted are Native** → indicating some level of binding/mass transfer process
  - Surrogate (labelled compounds) are completely transferred in primary Extraction → indicating limited/no binding/mass transfer process
2nd Extraction Cycle SRM

<table>
<thead>
<tr>
<th>Analyte</th>
<th>2nd Extraction Relative Abund./Total Relative Abund. (%)</th>
</tr>
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<tbody>
<tr>
<td>TBP</td>
<td>9.7</td>
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<td>TCEP</td>
<td>17.5</td>
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<td>TCPP</td>
<td>14.5</td>
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<tr>
<td>TDCPP</td>
<td>9.3</td>
</tr>
<tr>
<td>TPhP</td>
<td>3.8</td>
</tr>
<tr>
<td>TBEP</td>
<td>5.8</td>
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</table>
Additional Method Development Experiments

- ASE Comparison
- Florisil Background
  - 500C bake, solvent rinse & MF
- Extraction Tubes
  - 500C bake, solvent rinse & MF
- Solvent miscibility of standards
- Test for Extraction Efficiency based on 3 cycles
  - Increase sonication time/additional cycle
- Recovery of low boilers
  - Eliminate evaporation to dryness steps
    - High volatility of low boilers (TBP, TPP, TCEP, TCPP)
- Test for loss of analytes during fractionation
  - Hexane fraction was tested and no lose of analytes observed
- Retention of analytes on Florisil
  - Additional ethyl acetate eluent added to Florisil column, showed no retention
- Investigation of low responding compounds
  - TDBPP for break down (single RT & multiple fragments in MS1 scan)
  - TEHP for break down (multiple RT (cyclization of alkyl groups, BEHP & TEHP and multiple fragments in MS1 scan)
  - TBEP for break down (single RT and multiple fragments in MS1 scan)
    - Checked different Transitions pairs for increased detection
## Surrogate Recovery

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method Blank Average % Surrogate Recovery</th>
<th>MB Standard Deviation</th>
<th>Matrix Spike Average % Surrogate Recover</th>
<th>MS Standard Deviation</th>
<th>SRM (DUST) Average % Surrogate Recovery</th>
<th>SRM Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>dTBP</td>
<td>34.99</td>
<td>5.81</td>
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<td>106.7</td>
<td>18.04</td>
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<td>dTCEP</td>
<td>50.78</td>
<td>5.26</td>
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<td>10.3</td>
<td>92.6</td>
<td>3.65</td>
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<td>dTCPP</td>
<td>54.80</td>
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<td>116.6</td>
<td>2.0</td>
<td>149.0</td>
<td>6.92</td>
</tr>
</tbody>
</table>

- Higher recovery for SRM
- Lower Recovery for Na$_2$SO$_4$ Spiked MB and MS
  - SRM acts as keeper
  - Evaporation to 100uL rather than dryness
    - **Showed 30-40% increase in recovery**

%recovery = [(MB/PCB209L)/(Ref.Stnd./PCB209L)]*100
%average recovery is over three replicates for each of MB, MS and SRM
## Mean value (Standard Deviation) of OPFRs Measured in Matrix Spike

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Matrix Spike ng/g Na$_2$SO$_4$</th>
<th>Calculated Value ng/g Na$_2$SO$_4$</th>
<th>Accuracy</th>
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<td>TEP</td>
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<tr>
<td>TBP</td>
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<tr>
<td>TCPP</td>
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<td>TPhP</td>
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<td>TBEP</td>
<td>1858 (83)</td>
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<td>4608 (504)</td>
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\[
\frac{TPhP_{RefSD}}{dTPhP_{RefSD}} = \frac{TPhP_{SRM}}{dTPhP_{SRM}}
\]

\[
\frac{TEHP_{RefSD}}{dTEHP_{RefSD}} = \frac{TEHP_{SRM}}{dTEHP_{SRM}}
\]
# Mean value (Stdev) of OPFRs Measured in SRM 2585

Comparison to Reference Literature

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<tr>
<th>Analyte</th>
<th>Avg (ug/g)</th>
<th>Stdev (ug/g)</th>
<th>Avg (ug/g)</th>
<th>Stdev (ug/g)</th>
<th>Avg (ug/g)</th>
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<th>Stdev (ug/g)</th>
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*Includes Ortho, Para and Meta Isomers

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### Ref. Lit. Comparison

![Bar chart comparing OPFR concentrations in different studies](chart.png)
Mean value (Stdev) of OPFRs Measured in SRM 2585 Comparison to Reference Literature

Ref. Lit. Comparison (w/o TBEP)

- TCEP & TCPP are higher than Ref. Lit. values
- TCP is lower than Ref. Lit. values
  - Method Changes tighten up results
• Five Samples from (BEARHFTI)
  – Visual inspection for color, adhesive, mixture of different types of foam (homogeneity)

• Sample Screening
  – Extract 50 mg foam with 10 mL DCM
  – Vortex 1 minute & Sonication for 10 minutes
    • Remove liquid layer with pasteur pipette
  – Add 100 uL of DCM Foam Extract to 9.9 mL DCM and vortex
    • 100x dilution
      – Further dilutions maybe needed if high concentration is found
      – No dilution of extract (if 100x shows no Flame Retardant)
  – Transfer 80 uL of 100x Dilution to GC vial
    – (aliquot 80 uL 100x Extract, add 10 uL IS Surrogate and 10uL PCB209L)

• Analyze on GCMS
  – Scan & MRM
Physical Appearance

Sample A

Sample B

Sample C

Sample D

Sample E
Sample Screening

Sample A

Extract 50 mg foam with 10 mL DCM
- Vortex/Sonication
- Further Testing Required to Test Extraction Efficiency

Remove liquid phase with pasteur pipette

100 uL of DCM Foam Extract to 9.9 mL DCM (100x)

Final GC Vial Dilution 125x

80 uL 100x Extract + 10 uL IS Surrogate + 10uL PCB209L
Sample C, D, & E Duplicate Extracts

Sample E

- multi component foam/compressed together or adhesive?
  - Cloth, Fibers, plastic mesh, different color foam
    - Possibly recycled material
- Difficulty in sampling heterogeneous foam sample
  - Extract for Sample and Duplicate have different color
  - Increased sample size to 200 mg
    - Increasing sample size may decrease sample variability
MRM - Foam Samples A & B

MRM & Scan of Foam Samples A & B show no evidence for select OPFRs
- 125x (n=2), 1.25x (n=1)
- Overlaid with Na₂SO₄ method blank (n=2)
Foam Sample C – unknown analysis

- TPhP Full Scan NIST Library - TPhP 91.6% Probability
- PBDE (Tetra and Penta also detected, NIST Probability)
  - 76.0% PBDE (Tetra Bromo), 54.4% & 66.7% PBDE (Penta Bromo)
Sample C – Unknown NIST Data

- 91.6% TPhP
- 76.0% PBDE (Tetra Bromo)
- 55% PBDE (Penta Bromo)
- 66.7% PBDE (Penta Bromo)
Foam Sample C

- TPhP detected
- MRM - 125x dilution of Foam DCM Extract (n=2)
  - 10965 ug/g foam (1.1% TPhP)
POPs QqQ PBDE Method – Sample C

- BDE-47, BDE-100, BDE-99
  - Compares well with composition of commercial technical mixture
- PBDE MRM Method - 125x dilution of Foam DCM Extract
  - 67705 ug/g foam (6.7% PBDE)
Foam Sample D

- TCEP detected (dwarfs IS peaks)
  - Full Scan NIST Library Match 90.1%
- MRM - 125x dilution of Foam DCM Extract
  → 500x Dilution 81054 ug/g foam (8.1% TCEP)
Sample D – NIST Match

TCEP Full Scan NIST Library Match 90.1 %
Foam Sample E

- TPhP & TCPP detected, Full Scan Library Match TCPP 62.9% & TDCPP 75.5%
- MRM - 125x dilution of Foam DCM Extract
  → 500x dilution 23481 ug/g foam & 31545 ug/g foam (E1 2.35 % & E2 3.16%)
  - 200 mg Foam Sample to decrease sample variability
Sample E – NIST Library Match TCPP

Full Scan NIST Library Match TCPP 62.9%
Sample E – NIST Library Match TDCPP

Full Scan NIST Library Match TDCPP 75.5%
% Flame Retardant in BEARHFTI Foam Samples

<table>
<thead>
<tr>
<th>BEARHFTI</th>
<th>% OPFR (wt/wt)</th>
<th>% PBDE (wt/wt)</th>
<th>% Phosphorus (wt/wt)</th>
<th>ppm (mg P/kg Foam)</th>
<th>XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - AY01618 - 1</td>
<td>-</td>
<td>-</td>
<td>- [-]</td>
<td>- [-]</td>
<td>-</td>
</tr>
<tr>
<td>B - AY01619 - 1</td>
<td>-</td>
<td>-</td>
<td>- [-]</td>
<td>- [-]</td>
<td>-</td>
</tr>
<tr>
<td>C - AY01620 - 1</td>
<td>1.1 % (TPhP)</td>
<td>6.74 %[2.8 % BDE-47 + 0.54 % BDE-100 + 3.4 % BDE-99]</td>
<td>0.104 [0.15]</td>
<td>1040 [1446]</td>
<td>Phosphorus Bromine</td>
</tr>
<tr>
<td>D - AY01621 - 1</td>
<td>8.1 % (TCEP)</td>
<td>-</td>
<td>0.88 [0.98]</td>
<td>8800 [9772]</td>
<td>Phosphorus Chlorine</td>
</tr>
<tr>
<td>E - AY01622 - 1</td>
<td>2.36 % [0.66 % (TCPP) + 1.7 % (TDCPP)]</td>
<td>-</td>
<td>0.184 [0.14]</td>
<td>1840 [1426]</td>
<td>Phosphorus Chlorine</td>
</tr>
<tr>
<td>E - AY01622 - 2</td>
<td>3.16 % [0.66 % (TCPP) + 2.5 % (TDCPP)]</td>
<td>-</td>
<td>0.242 [0.20]</td>
<td>2420 [1969]</td>
<td>Phosphorus Chlorine</td>
</tr>
</tbody>
</table>

XRF Results Agree
• Screening for the presences of Phosphorus, Chlorine & Bromine
GCMS & ICP [P] Screening Results Agree

**GC-MS/MS & ICP Independent Screening**

Additional Work

- Test Multiple Sampling Locations for Variability
  - Homogenous and Heterogeneous Samples
- Standard Blank Foam and SRM Foam
- Extraction Efficiency
  - Add additional extraction steps to increase extraction efficiency
Additional Method Development

• Foam - Further Development of Method QC
  – Foam Blank & Foam SRM
  – Test extraction efficiency & Sample Variability
  – Integrate additional OPFRs & PBDEs

• Dust – Finalize Method Changes

• Method Application Goals
  – Fire Fighter Occupational Exposure
  – California Residential Dust
  – Consumer Products
    • SB 1019
      – Screening Method
      – OPFRs & PBDEs
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- Dr. Sabrina Crispo Smith
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  - Standards Preparation

- Dr. Miaomiao Wang & Dr. Emily Parry
  - TOF

Dr. Myrto Petreas
Dr. John Quinn
Dr. June-Soo Park
References

References:
4. Proposition 65 List of Chemicals; Office of Environmental Health Hazard Assessment: Sacramento, CA, 2014
Questions
Questions Asked

• Foam
  • Year, Density, Source (furniture), does it correspond with expected use?
  • Does foam dissolve in DCM?
  • Any additional compounds detected in the foam samples?
  • Is the plan to add additional OPFRs and PBDEs to method?
  • Why were standards added at end of process.

• Dust
  • Comparison with most recent studies, how is it compare?
  • Evaporation to dryness and loss of low boilers.