Analysis of Polybrominated Dibenzodioxins and Dibenzofurans in House Dust

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Acknowledgements and Disclaimers

- Acknowledgements – Roshni Sarala, Ranjit Gill
- Disclaimers:
  - The views expressed herein are those of the authors and do not necessarily reflect those of the California Department of Toxic Substances Control
  - Use of product names does not constitute endorsement
Outline

• Introduction
• Analytical Method (Modified 1613)
• Analysis (GC/MS)
• Compare/contrast sample prep technologies
• Establish Accuracy/Precision of Method- (Low/Mid/High concentrations)
• Preliminary Results – House Dust
• Conclusions
Introduction

Importance - Why Do we Care?

• highly toxic
• PBDD/F created from other toxins (BFR’s, PBDE’s) found in consumer products.
  • Thermal Decomposition / Manufacturing byproduct of BFR’s
  • PBDE Photolytic Decomposition produces PBDF’s
• Human are exposed to PBDD/F – health concern
  – Airborne particles from BFR waste incineration (TV casings, Electronic circuit boards) or household/industrial fires
  – Other sources: food (fish, seafood), sediment, house dust, water
FRB8  dont say formulate!!!!!!!

is "byproduct" the right word?
Brown, FReber@DTSC, 3/20/2015

D7  this is how I modified it. Hopefully it's oK.
Change anything you wish, so that you are confortable with it.
Darcy, 3/24/2015
Modified 1613 Analytical Method

Sample Prep / ASE Extraction

Roto - Evaporation

Supelco Cleanup*

Roto + N₂ Evaporation

Analysis – Hi-Res GC/MS

* Supelco® Multi-layered Silica Column &
* Supelco® Dual-layer Carbon Reversible Tube
DT1  OK - Fixed.
Tarrant, Darcy@DTSC, 3/18/2015

DT4  My thoughts, feel free to disagree. And yes, this is different from how I initially envisioned the presentation unfolding.

I am thinking we should take out references to the Rocket Evaporator right here at the beginning.

Under future work, we introduce the Rocket -- we will repeat the low/mid/high validation, but using the Rocket to concentrate the samples. We can then show a picture of two of hte Rocket and you can briefly discuss how it works.
Tarrant, Darcy@DTSC, 3/20/2015
Sample Preparation

Sample wt = 0.5 g (dust), 2g (soils, sand)   Hydromatrix used as bulking agent

20 µL Internal Standards = $^{13}$C$_{12}$ labeled
10 µL Natives – non Labeled (method validation):

**Dioxins**

- 2,3,7,8- TBDD
- 1,2,3,7,8 - PeBDD
- 1,2,3,4,7,8-HxBDD
- 1,2,3,6,7,8 -HxBDD
- 1,2,3,4,6,7,8-HpBDD
- 1,2,3,4,6,7,8,9-OBDD

**Furans**

- 2,3,7,8 TBDF
- 2,3,4,7,8-PeBDF
- 1,2,3,4,7,8-HxBDF
- 1,2,3,4,6,7,8-HxBDF
- 1,2,3,4,6,7,8,9-OBDF

10 µL Recovery Standards = $^{13}$C$_{12}$ labeled

- 1,2,3,7,8 PeBDF
- 1,2,3,7,8,9 HxBDD
Fixed 2468 tbdf
Darcy, 3/24/2015
ASE Extraction

ASE Conditions:

– 22 mL Cells
– Conditions:
  • Preheat 0 min; P=1500 psi, Heat: 5 min @ 100°C;
  • Static 5 min, Flush 60% Vol, purge 60s,
  • 3 Cycles (100% Toluene)
Old Style Cleanup Method

- Silica/Carbon Cleanup (16 hrs)
- Al Cleanup (overnight Al Kiln + 4 hrs)
- 4 rotovap steps = 16 hrs; eliminates 2 steps (8 hrs)
- Total Time saved = min 28 hrs = 3.5 days
day and a half to prep

keep it simple and brief

Brown, FReber@DTSC, 3/20/2015
Supelco Column Conditioning

10% AgNO₃ Si (3g, -S)
22% H₂SO₄ Si (6g, - bases)
44% H₂SO₄ Si (4.5g, hyd fats)
2% KOH Si (3g, -H⁺)

200 mL Hexane

40 mL Toluene
100 mL Hexane

Carboxan 1016 (100 mg, 75m²/g)
Carboxan 1000 (100 mg, 1200m²/g)

Multi-Layer Silica Gel Dioxin Column

Dual-Layer Reversible Carbon Column
Conditioning of columns
- removes trapped air
- establishes consistent flow
- removes background contamination

For Carbon column
- wet carbon surface allows analytes to achieve maximum contact w/ the surface of the packing material.

Q: does Supelco need a Trademark symbol?

Darcy, 3/24/2015
Supelco Column Cleanup

Fraction 1a: RH, o-PCB
- 80 mL Hexane
- 30 mL 3% MeCl₂/Hex

Fraction 1b: Non-planar interferences
- 80 mL Hexane
- 30 mL 3% MeCl₂/Hex
- 100% Toluene

Fraction 2: PBDD/F, non o-PCBs
- Vacuum Manifold

FRB4
D7
D4
D6
D5
FRB4

Say "reverse elute", not "reverse phas"

Supelco process saves us approx XXX number of hours of prep time over old school method
Brown, FReber@DTSC, 3/20/2015

D2
28 hrs or 3.5 days min save (not including overnight kiln of Alumina - this is stated on the next slide)
Darcy, 3/24/2015

D4
Regarding 3% mecl2 / hexane
Step recommended by supelco
= removes possible interferences
allows additional removal of non-planar interferences.
Darcy, 3/24/2015

D5

D6
FYI - supelco's nomenclature for PCB's
- see MS word document attached
has explanation of ortho meta ana para pcb's
Darcy, 3/24/2015
Analytical Method

• Instrumentation
  – Thermo DFS high resolution mass spectrometer
  – Dual Trace Ultra GCs
    • SSL/PTV injectors
    • Electronic flow control
  – TriPlus Extended Rail autosampler
Analytical Method

- **MS operating conditions**
  - MID mode
  - 10,000 resolution using PFK as mass reference
- **GC operating conditions**
  - DB5-MS (15 m x 0.25 mm id x 0.1 μm film)
  - He as carrier gas using programmed flow mode
Analytical Method

– 2 µL injection
– PTV injector using programmed temperature
  • 75 °C initial temperature
  • 200 °C transfer temperature
  • 1 min pressure surge
  • 300 °C cleaning temperature

– GC Temperature program
  • 140 °C initial temperature (2 min)
  • 270 °C at 5 °C/min
  • 300 °C at 10 °C/min (9 min hold time)
TIC Chromatogram
PBDF Calibration Curves

![Graph showing calibration curves for different structures with R² values of 1 and 0.9999. The x-axis represents Mass Ratio, and the y-axis represents Area Ratio. The graph includes data for various structures labeled as 2,3,7,8-TeBDF, 2,4,6,8-TBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF, and OBDF.](image-url)
PBDD Calibration Curves

R² = 0.9997

R² = 0.9995

R² = 0.9991

R² = 1

Area Ratio

Mass Ratio

2,3,7,8-TeBDD
1,2,3,7,8-PeBDD
1,2,3,(4,7,8 & 6,7,8)-HxBDD
1,2,3,7,8,9-HxBDD
1,2,3,4,6,7,8-HpBDD
OBDD
Low/Mid/High Level Accuracy/Precision

- **Low level concentration accuracy/precision**
  - Spike clean matrix at between CS1/CS2
- **Middle level concentration accuracy/precision**
  - Spike clean matrix at concentration equivalent of CS3 from calibration curve
- **High level concentration accuracy/precision**
  - Spike clean matrix at concentration equivalent of CS5 from calibration curve
### Low Concentration

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Spiked (pg/g)</th>
<th>Measured (pg/g)</th>
<th>RSD</th>
<th>RPD</th>
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# High-Level Concentration

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<th>Compound Name</th>
<th>Spiked (pg/g)</th>
<th>Measured (pg/g)</th>
<th>RSD</th>
<th>RPD</th>
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</tbody>
</table>
House Dust

Bromofurans

Bromodioxins
Results

• PBDFs

• PBDDs
Conclusions

- PBDFs >> PBDDs
  - Possibly due to rearrangement/breakdown of PBDEs
- Few 2,3,7,8-substituted PBDD/F congeners observed
  - 3,3′,4,4′ substituted PBDE gives a 2,3,7,8-substituted PBDF
  - Most 3,3′,4,4′ BDEs are not major BDE congeners
- Other mechanisms
Future Directions

• Repeat accuracy/precision study
  – Using new sample concentration technology
• Assess potential interference of PBDEs
• Examine larger subset of house dust samples
Rocket Evaporator

- Inner chamber
  - Holds sample vials/flasks
  - Under vacuum
  - Centrifuge
  - Heated by mild steam

- Outer chamber
  - Steam bath
  - Vacuum pump
  - Chiller (external)
RotoVap vs Rocket Evaporator

- **Rotovap**
  - 1 ASE cell extract in 20 min
  - 6 carbon column eluates to 1 mL in 2 hr
  - 1-2 days of N₂ reduction to 20 µL in GC vial

- **Rocket Evaporator**
  - 18 ASE cell extracts simultaneously in 20 min
  - 6 carbon column eluates to 20 µL in GC vial in 2 hr
  - No dry ice, no N₂
Rotovap vs Rocket

Rocket-Rotovap Comparison
average of 3 samples each
error bars = ± std error ( s/sqrt(n) )

Concentration (pg/g)

Rocket Results
Rotovap Results
Conclusions

• Supelco cleanup process faster and uses less solvent than previous dioxin/furan cleanup method
• Analytical method detects tetra-octa
  – Octa congeners subject to breakdown, not reliable
• Use of Rocket Evaporator can potentially save 2-3 days time over rotovaping individual samples
  – Allows for unattended operation
Parting Thought

• “The bearing of a child takes nine months, no matter how many women are assigned.”

— Frederick P. Brooks Jr. Author of “Mythical Man-Month: Essays on Software Engineering”