ER1: Ana M. Ballesteros Gómez
IVM-VU University Amsterdam
(01-04-2012/30-3-2014)
Supervision: Pim E.G. Leonards
MAIN RESEARCH RESULTS

IVM-VU
- 1. Development/comparison of different analysis techniques for FRs (BFRs and PFRs)
- 2. Analysis of RDP and BDP in plastics of electronic products
- 3. Identification and analysis of a novel BFR (TTBP-TAZ) in plastics and dust

COLLABORATIONS:
- University of Antwerp, Toxicological Centre:
  - A. Ionas (ESR1), A. Covaci: identification and use of alternative analysis methods for novel FR and plasticizers
  - (Secondment Oct-Nov 2013) C.Erratico, N. van de Eede, A. Ionas, A. Covaci: Metabolism studies with microsomes incubations with EHDPHP
- University of Amsterdam (VU), Department of Analytical Chemistry
  - W. Jonker, J. Kool. LC microfractionation/toxicity of electronic products leachate (ongoing)
GC-APCI, GCxGC-APCI and DIP-APCI-RTOFMS

Ultra-fast screening (no sample treatment)

Separation, sensitivity and matrix effects improved in comparison with LC

Comprehensive screening (target and untargeted)

First time of coupling GCxGC with HRTOF
GC or LC (APCI-HRTOF)?

**GC-APCI**

- PBDEs (tri- till octa-)
- New BFRs except DBDPE
- PFRs

- Better sensitivity
- Less matrix effects
- Separation of isomers of TBP, TMPP

**LC-APCI**

- Nona- and Deca BDE
- HBCD
- RDP, BDP, TTBP-TAZ

- Better sensitivity, prevent thermal degradation or peak widening in transfer line
- Separation of isomers of HBCD
1. Solvent extraction (50mg with 20mL DCM, 24 h shaking+10 min sonicating) validated with ENFIRO PAC polymers
2. Ultracentrifugation (10,000 rpm, 5 min)
3. Dilution with methanol 10-1000 times
4. Analysis by LC-APCI(+) - HRTOF
<table>
<thead>
<tr>
<th>PRODUCTS 2012</th>
<th>RBDPP w/w</th>
<th>BPA-BDPP w/w</th>
<th>Other PFRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>powerboard 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>powerboard 2</td>
<td>0.002</td>
<td>0.01</td>
<td>TPHP</td>
</tr>
<tr>
<td>adaptor 1</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>adaptor 2</td>
<td>0.3</td>
<td>0.06</td>
<td>TPHP</td>
</tr>
<tr>
<td>Television</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>LCD television</td>
<td>0.06</td>
<td>0.07</td>
<td>TPHP, TCEP, TMP</td>
</tr>
<tr>
<td>Children toy 1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>TBOEP</td>
</tr>
<tr>
<td>Children toy 2</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Children toy 3</td>
<td>0.003</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Power button of a vacuum cleaner</td>
<td>0.3</td>
<td>0.2</td>
<td>TPHP, TMPP</td>
</tr>
<tr>
<td>Plastic adorn</td>
<td>0.05</td>
<td>0.15</td>
<td>TPHP, TMPP</td>
</tr>
<tr>
<td>Heat sealer</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRODUCTS BEFORE 2005</th>
<th>RBDPP w/w</th>
<th>BPA-BDPP w/w</th>
<th>Other PFRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scanner 1</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Scanner 2</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Scanner 3</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Television 1</td>
<td>5.7</td>
<td>n.d.</td>
<td>TPHP</td>
</tr>
<tr>
<td>Television 2</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Television 3</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Television 4</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>PC monitor</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Television monitor</td>
<td>0.007</td>
<td>n.d.</td>
<td>TPHP</td>
</tr>
<tr>
<td>Flatscreen TV monitor</td>
<td>n.d.</td>
<td>n.d.</td>
<td>TPHP</td>
</tr>
<tr>
<td>Printer 1</td>
<td>7.8</td>
<td>n.d.</td>
<td>TPHP</td>
</tr>
<tr>
<td>Printer 2</td>
<td>0.005</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Printer 3</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
</tbody>
</table>
Novel Triazine-based Flame Retardant (TTBP-TAZ) in Plastic Consumer Products and Dust

- TTBP-TAZ is first time reported in samples in this study
- There are no analytical method reported for this compound
- Solvent extraction without clean-up
- Analysis by LC-APCI(+)-HRTOF-MS
Identification by DP(+)-HRTOFMS

*DP-APCI(+)-HRTOF-MS spectra of the power board sample 1 containing TTBP-TAZ*
Presence of TTBP-TAZ in products and dust

<table>
<thead>
<tr>
<th>Product</th>
<th>Number of samples containing TTBP-TAZ</th>
<th>Concentration range (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical power boards and adaptors (n=4)</td>
<td>4</td>
<td>(0.01-0.8)</td>
</tr>
<tr>
<td>Children toys (n=4)</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Televisions (n=2)</td>
<td>2</td>
<td>(0.06, 1.9)</td>
</tr>
<tr>
<td>Other household appliances (n=3)</td>
<td>2</td>
<td>(0.3, 0.6)</td>
</tr>
</tbody>
</table>

TTBP-TAZ concentration ranges in weight percentage (% w/w) in plastic consumer products purchased in 2012

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Number of samples containing TTBP-TAZ</th>
<th>Median</th>
<th>Range (ng g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On electronics (n=8)</td>
<td>4</td>
<td>535</td>
<td>(1070-22150)</td>
</tr>
<tr>
<td>Around electronics (n=7)</td>
<td>4</td>
<td>220</td>
<td>(220-3950)</td>
</tr>
<tr>
<td>In floor dust (n=2)</td>
<td>1</td>
<td>-</td>
<td>(&lt;20-160)</td>
</tr>
</tbody>
</table>

TTBP-TAZ average concentrations and ranges in ng g⁻¹ in dust

*aQuantitation limit 60 ng g⁻¹
Percentage by weight of material

- Television 1
- Power board 1
- Heat sealer
- Adorn
- Adaptor 1
- Television 2
- Power board 2
- Adaptor 2

**Correlation Analysis**

- 2,4,6-TBP
- TTBP-TAZ

**Correlation Details**

- $r=0.557$, $P$-value $=0.001$, $n=7$
- $r=0.551$, $P$-value $=0.001$, $n=8$
METABOLISM STUDIES ON EHDPP

 ✓ Incubation with human liver microsomes or cytosol
 ✓ Analysis by QTOF (and QQQ) for identification based on accurate mass and fragmentation patterns (due to lack of standards)
 ✓ Targeted screening (Meteor software, in silico model) and untargeted screening (Agilent software)
EHDPHP

Monohydroxilated metabolites with –OH in the alkyl chain (OH1-8)

Monohydroxilated metabolites with –OH in the phenyl group (OH9)

Dihydroxilated metabolites (OH2 1-10)

Phase-II glucuronide-conjugates (GLUC1-8)

Metabolites with one ketone group (O1 and O2)

Metabolites with one OH- and one ketone group (OOH1-OOH5)

Phase-II glucuronide-conjugates (GLUCb1)

Hydrolysis metabolite (DPHP)

38 metabolites
RELATIVE ABUNDANCE OF METABOLITES

Ion signal

[M+H]+ or [M-H]-
[M+58]+
…OVERVIEW MAIN RESEARCH RESULTS


3. **Ballesteros Gómez, Ana; Brandsma, S.H.; de Boer, Jacob; Leonards, Pim E.G. Direct probe atmospheric pressure photoionization/atmospheric pressure chemical ionization high-resolution mass spectrometry for fast screening of flame retardants and plasticizers in products and waste. 2014 Analytical and Bionalytical Chemistry. DOI 10.1007/s00216-014-7636-8**


Manuscript DOI: 10.1021/es4057032

Contribution to conferences

INVITED ORAL PRESENTATIONS

1. Novel analytical methods for flame retardants based on high resolution MS-MicroTOF II: GC-APCI, GCxGC-APCI and DP-APCI/APPI.

ORAL CONTRIBUTIONS

1. New screening tools for flame retardants in e-waste based on GC, GCxGC and direct probe coupled to APCI-HRTOF.
   Authors: Ballesteros-Gomez A (presenting author), de Boer, Jacob.; Leonards, Pim
   Conference: BFR2013, San Francisco (California).2013
2. New screening tools for flame retardants in e-waste based on GC, GCxGC and direct probe coupled to APCI-HRTOF.
   Authors: Ballesteros-Gomez, Ana (presenting author), de Boer, Jacob; Leonards, Pim
   Conference: Dioxin2013, Daegu (South Korea).2013

CO-AUTHOR

   Authors: Ionas, Alin (presenting author); Ballesteros-Gomez, Ana; Leonards, Pim; Covaci, Adrian
   Conference: Dioxin2013, Daegu (South Korea).2013
2. Poster. Identification strategies for flame retardants employing spectra-less databases.
   Authors: Ionas, Alin; Ballesteros-Gomez, Ana; Leonards, Pim; Covaci, Adrian
   Conference: Dioxin2013, Daegu (South Korea).2013
1. Chemical & Engineering News, 4 April 2014, ISSN 0009-2347, American Chemical Society.  
: http://cen.acs.org/articles/92/web/2014/04/Scientists-Uncover-New-Brominated-Flame.html

2. C2W (Chemisch2Weekblad). VU betrapt kunststofindustrie op geheim ingrediënt, 14 April 2014,  
http://www.c2w.nl/vage-vlamvertrager.366677.lynkx
NWO (Netherlands, IVM-VU University) 3 year Junior Researcher (July 2014)
FWO (Belgium, University of Antwerpt) 1 year postdoc (June 2014)

After INFLAME: postdoctoral researcher at University of Antwerp, A. Covaci
Thank you for your attention 😊!

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