INFLAME NETWORK ASSEMBLY MEETING

15th NOVEMBER 2013, STOCKHOLM

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

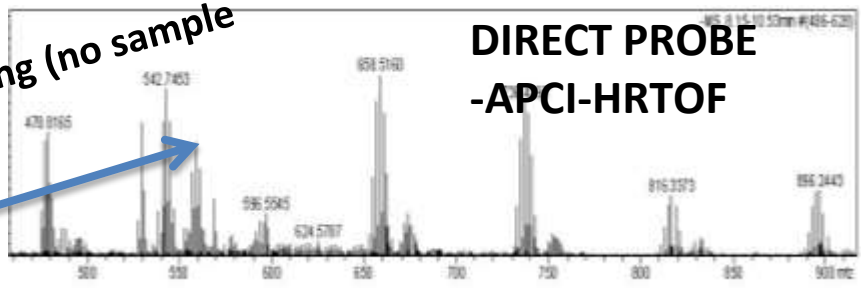
INFLAME

IVM Institute for Environmental Studies

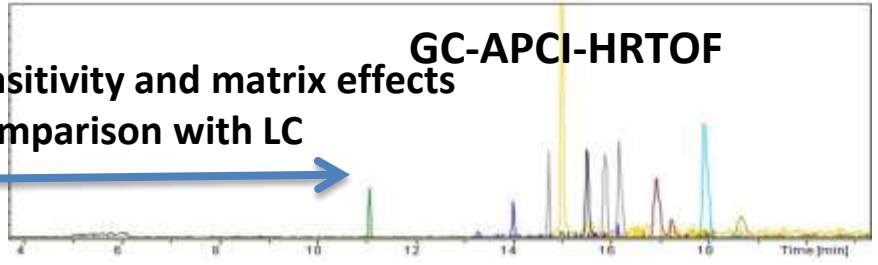
1.Novel analytical methods for flame retardants based on high resolution MS-MicroTOF II: GC-APCI, GCxGC-APCI and DIP-APCI

GC-APCI, GCxGC-APCI and DIP-APCI-RTOFMS

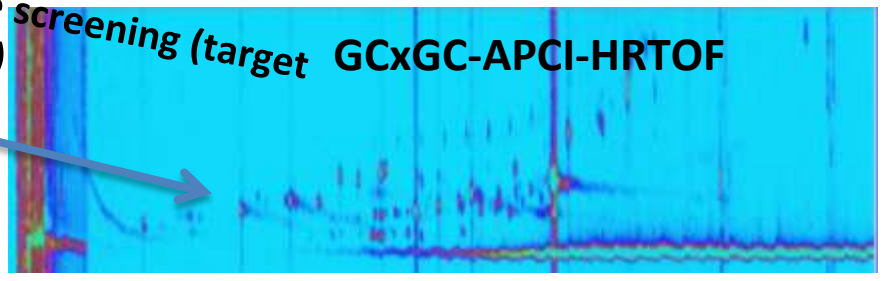
Ultra-fast screening (no sample treatment)



Separation, sensitivity and matrix effects improved in comparison with LC



Comprehensive screening (target and untargeted)



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

analytical chemistry

Article

pubs.acs.org/ac

Novel Analytical Methods for Flame Retardants and Plasticizers Based on Gas Chromatography, Comprehensive Two-Dimensional Gas Chromatography, and Direct Probe Coupled to Atmospheric Pressure Chemical Ionization-High Resolution Time-of-Flight-Mass Spectrometry

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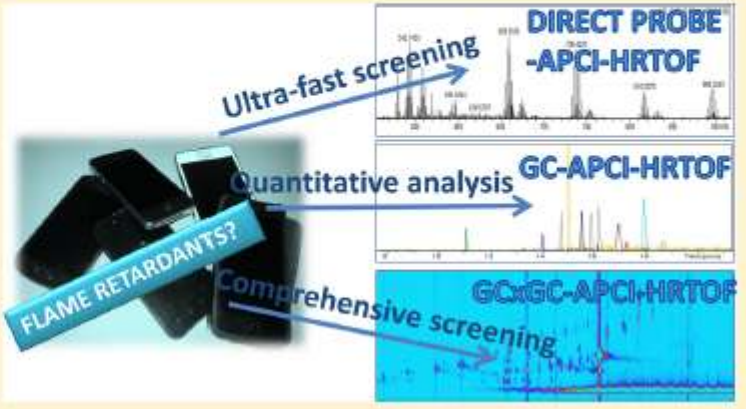
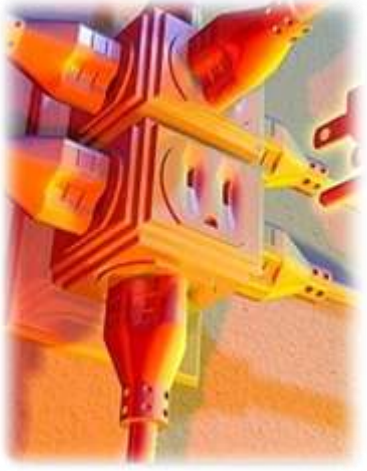
Supporting Information

ABSTRACT: In this study, we assess the applicability of different analytical techniques, namely, direct probe (DP), gas chromatography (GC), and comprehensive two-dimensional gas chromatography (GC × GC) coupled to atmospheric pressure chemical ionization (APCI) with a high resolution (HR)-time-of-flight (TOF)-mass spectrometry (MS) for the analysis of flame retardants and plasticizers in electronic waste and car interiors. APCI-HRTOFMS is a combination scarcely exploited yet with GC or with a direct probe for screening purposes and to the best of our knowledge, never with GC × GC to provide comprehensive information. Because of the increasing number of flame retardants and questions about their environmental fate, there is a need for the development

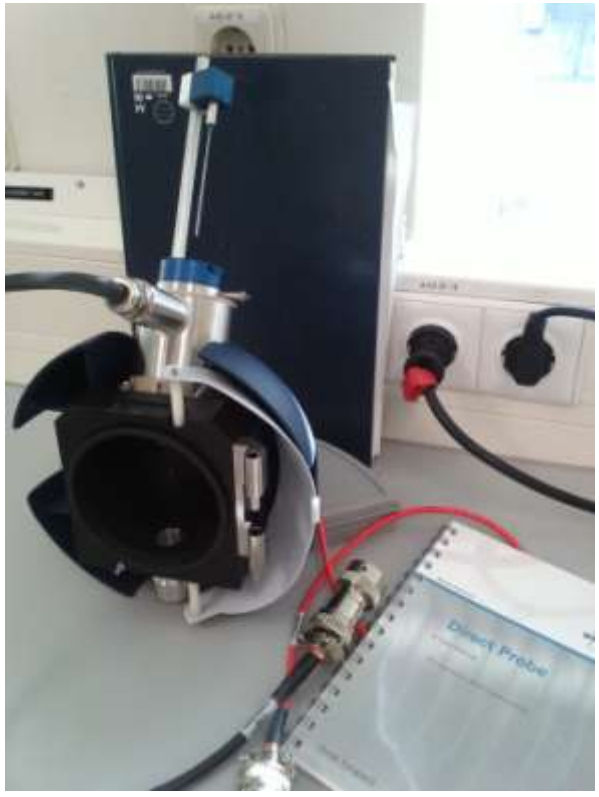


2. FAST SCREENING OF FLAME RETARDANTS AND PLASTICIZERS IN PLASTIC CONSUMER PRODUCTS AND WASTE BY DIRECT PROBE-APCI/APPI-HRTOF-MS

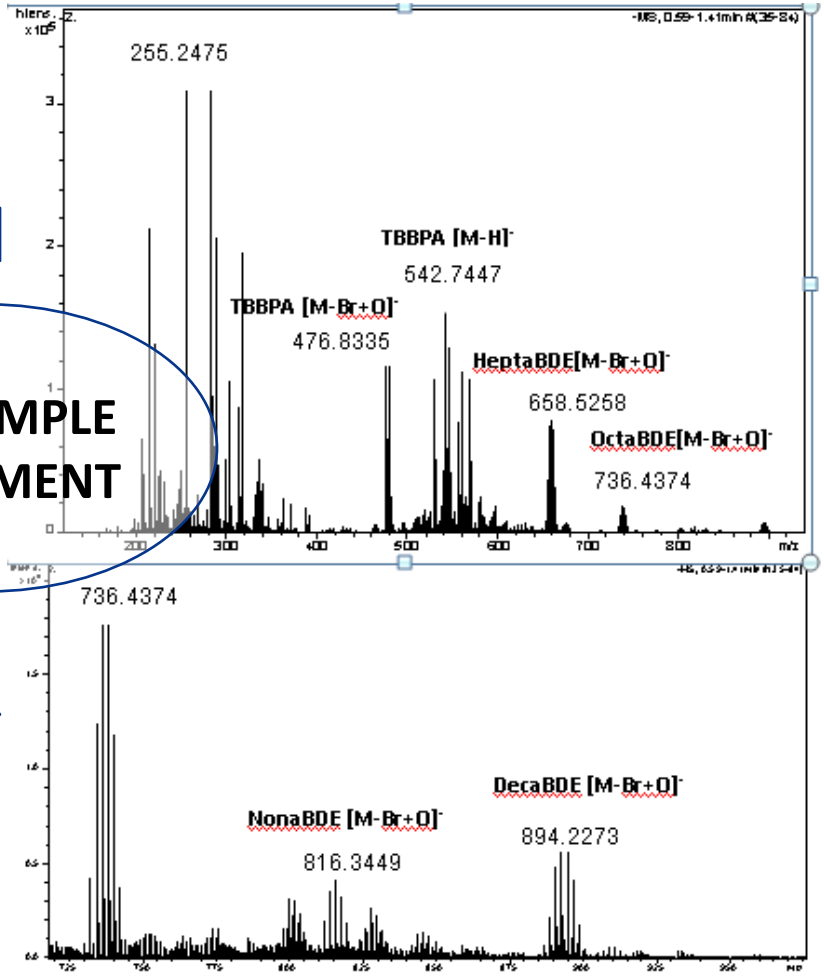
Submitted to Anal. Chim. Acta (November 2013)



DIRECT PROBE-HR-APCI-TOF (EXAMPLE PRINTED CIRCUIT SAMPLE)



NO SAMPLE TREATMENT



SAMPLE ANALYSIS AND VALIDATION. TARGETED SCREENING

Presence of flame retardants in e-waste and consumer products analyzed by direct probe-APCI/APPI(-)HRTOF-MS and concentration values obtained by a second technique[a,b]

	HexaBDE	HeptaBDE	OctaBDE	NonaBDE	DecaBDE	TBBPA	BTBPE
e-waste 1	+	+	+	+	+	+	+
	159 µg g^{-1}	1224 µg g^{-1}	675 µg g^{-1}	886 µg g^{-1}	[a]1855 µg g^{-1}	16232 µg g^{-1}	1689 µg g^{-1}
e-waste 2	_	_	_	_	_	+	n.d.
	12.9 µg g^{-1}	80 µg g^{-1}	29 µg g^{-1}	30 µg g^{-1}	71 µg g^{-1}	71 µg g^{-1}	41 µg g^{-1}
CP, double adaptor	_	+	+	+	+	+	+
	n.d.	245 µg g^{-1}	150 µg g^{-1}	n.a.	8,100 µg g^{-1}	60,000 µg g^{-1}	590 µg g^{-1}
CP, adaptor	_	+	+	+	+	+	+
	30 µg g^{-1}	2,470 µg g^{-1}	1,510 µg g^{-1}	n.a.	18,000 µg g^{-1}	68,500 µg g^{-1}	3,700 µg g^{-1}
CP, powerboard	_	_	_	_	+	+	+
	n.d.	n.d.	n.d.	n.a.	2,700 µg g^{-1}	70,200 µg g^{-1}	[b]n.d.
CP, LCD TV 1	_	+					
	30 µg g-1	110 µg g^{-1}					90 µg g^{-1}
CP, TV 1 left side	_	_					
	n.d.	n.d.					d.
CP, TV 2	_	+					
	n.d.	2,470 µg g^{-1}					700µg g^{-1}
Plastic adorn	_	+					
	n.d.	260 µg g^{-1}.	240 µg g^{-1}	n.a.	70,000 µg g^{-1}	3,700 µg g^{-1}	430 µg g^{-1}

Confirmation by mass error (< 5ppm) and isotopic pattern (below 100 mSigma)

Concentration value by a second GC-based technique

Analytical techniques used for validation of results: [a]GC-APCI(-)-HRTOF; [b]GC-NCI; n.d. non detected; n.a. non analyzed

Detectable levels of target compounds (above 0.025 w/w) in negative ionization mode were not found in car interior samples

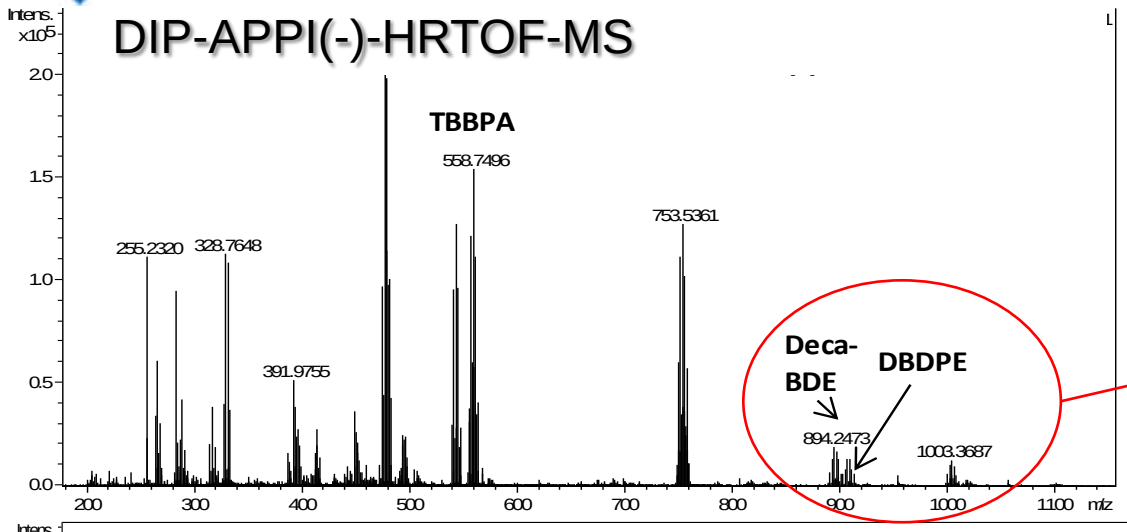
INFLAME

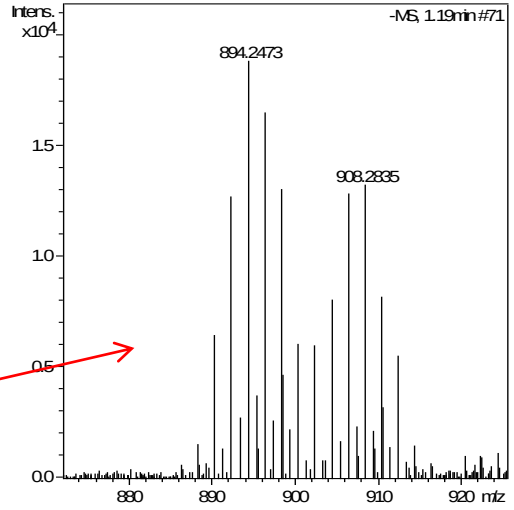
SAMPLE ANALYSIS AND VALIDATION. UNTARGETED SCREENING

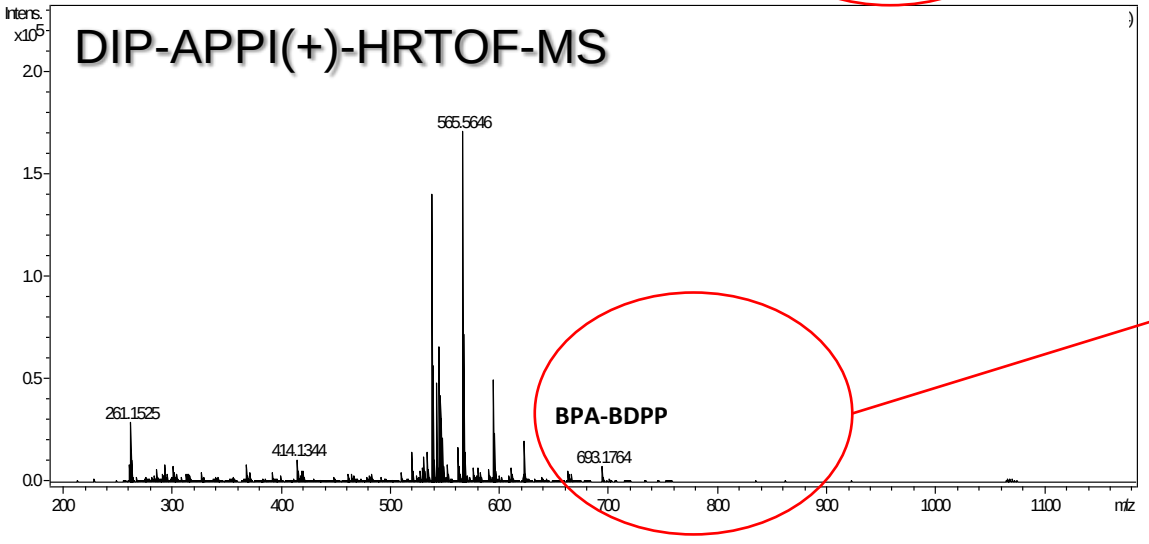
Identification of flame retardants and plasticizers in untargeted screening by direct probe-APCI(+)HRTOF-MS

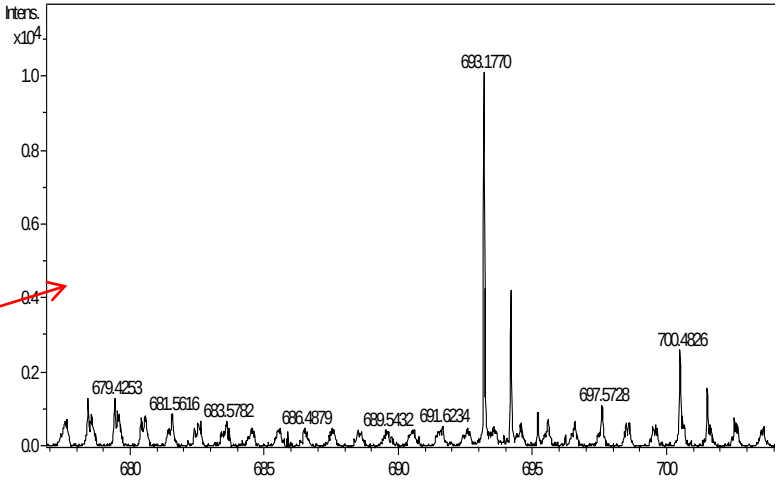
	PBDPP (RDP)	BPA-BDPP (BDP)
e-waste 1	-	-
e-waste 2	-	-
CP, double adaptor	+	+
CP, adaptor	-	-
CP, heat sealer	+	+
CP, powerboard	+	+
CP, LCD TV 1	+	+
CP, LCD TV 2	+	+
CP, TV 1, rigth side	-	-
CP, TV 1 left side	-	-
CP, TV 2	-	-
Christmas ornament	+	+

Power board sample









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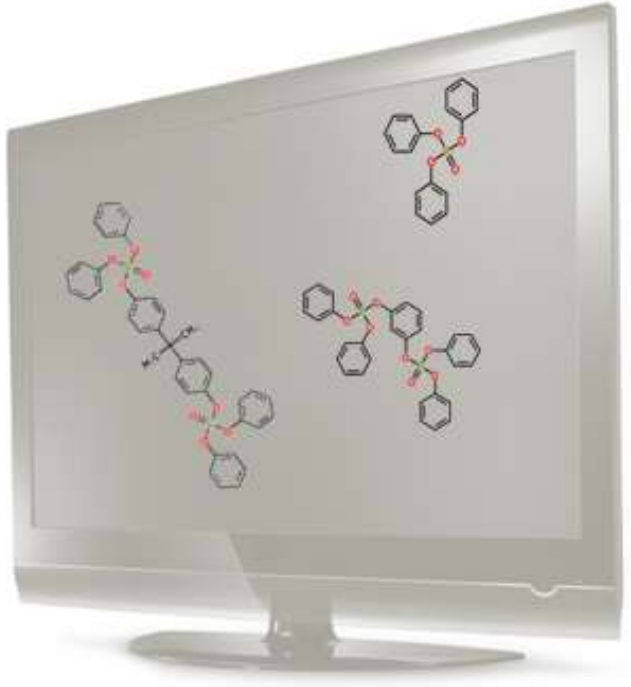
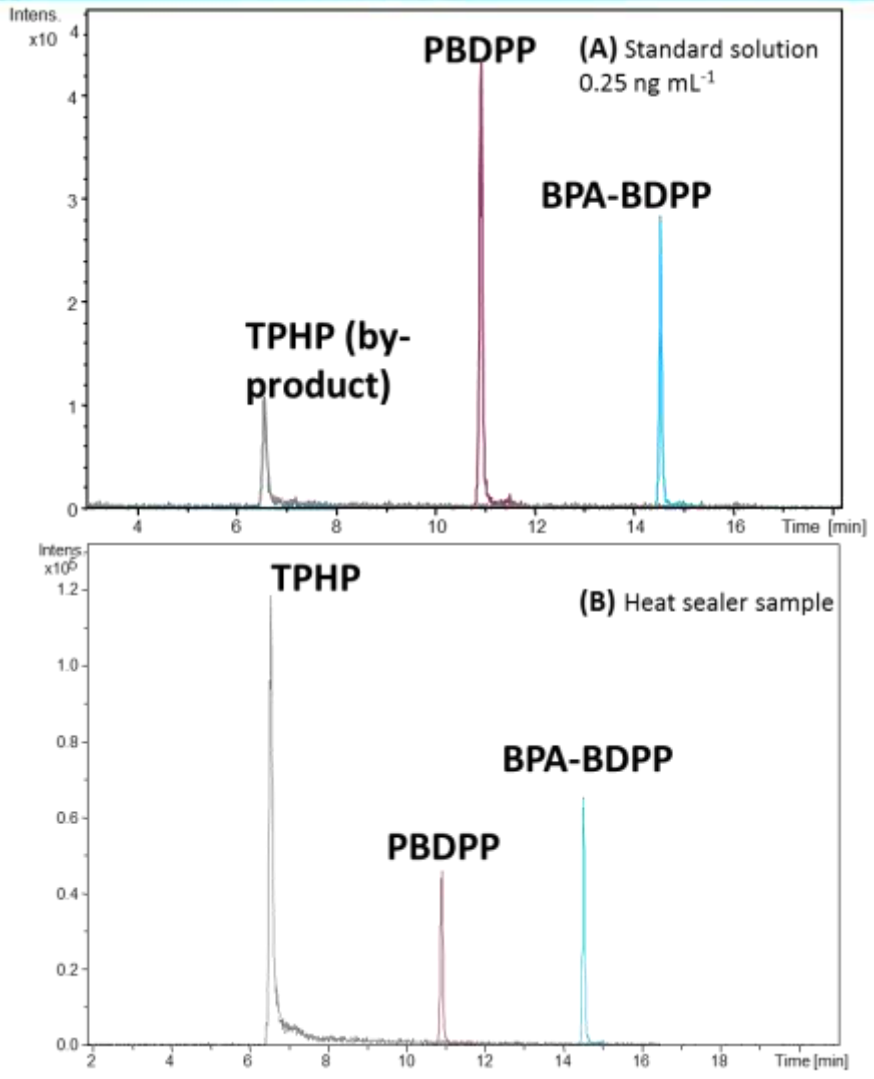
3. Analysis of two alternative organophosphorus flame retardants in electronic and plastic consumer products: resorcinol bis-(diphenylphosphate) (RBDPP) and bisphenol A bis (diphenylphosphate) (BPA-BDPP)

Submitted to Chemosphere, November 2013



Analysis of RBDPP and BPA-BDPP in products

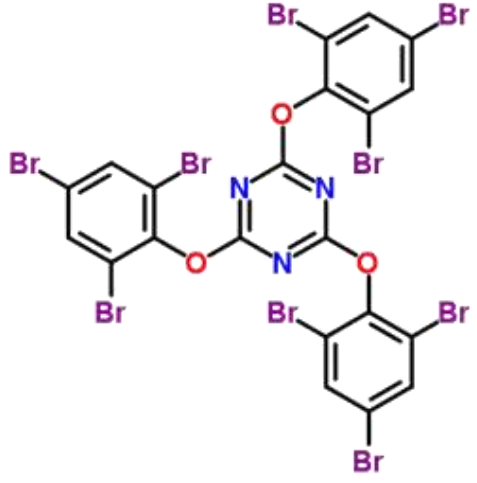
1. Solvent extraction (50mg with 20mL DCM, 24 h shaking+10 min sonicating) validated with ENFIRO PAC polymers
2. Ultracentrifugation (10.000 rpm, 5 min)
3. Dilution with methanol 10-1000 times
4. Analysis by LC-APCI(+)-HRTOF



PRODUCTS 2012			
	RBDPP w/w	BPA-BDPP w/w	Other PFRs
powerboard 1	0.002	0.01	TPHP
powerboard 2	n.d.	n.d.	-
adaptor 1	0.3	0.06	TPHP
adaptor 2	0.02	0.05	TPHP
Television	n.d.	n.d.	-
LCD television	0.06	0.07	TPHP, TCEP,TMPP
Children toy 1	n.d.	n.d.	TBOEP
Children toy 2	n.d.	n.d.	-
Children toy 3	0.003	0.005	-
Power button of a vacuum cleaner	n.d.	n.d.	-
Plastic adorn	0.3	0.2	TPHP, TMPP
Heat sealer	0.05	0.15	TPHP, TMPP

PRODUCTS BEFORE 2005			
	RBDPP w/w	BPA-BDPP w/w	Other PFRs
Scanner 1	n.d.	n.d.	-
Scanner 2	n.d.	n.d.	-
Scanner 3	n.d.	n.d.	-
Television 1	5.7	n.d.	TPHP
Television 2	n.d.	n.d.	-
Television 3	n.d.	n.d.	-
Television 4	n.d.	n.d.	-
PC monitor	n.d.	n.d.	-
Television monitor	0.007	n.d.	TPHP
Flatscreen TV monitor	n.d.	n.d.	TPHP
Printer 1	7.8	n.d.	TPHP
Printer 2	0.005	n.d.	-
Printer 3	n.d.	n.d.	-

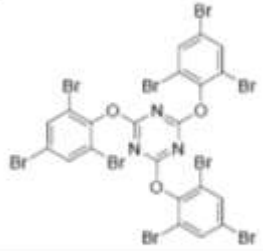
4.- A Novel Triazine-based Flame Retardant (TTBP-TAZ) in Plastic Consumer Products and Dust



To be sent in December to ES&T

Novel Triazine-based Flame Retardant (TTBP-TAZ) in Plastic Consumer Products and Dust

Table 28: Chemical structure of 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine and some basic information on this novel BFR.

Chemical structure	
PRAB sTAB Previous abbreviations	TTBP-TAZ (T3BPhO-Taz BrPhTriaz
IUPAC name	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine
Common names	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine Tris(2,4,6-tribromophenoxy)-s-triazine Tris(tribromophenoxy)-s-triazine s-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy)- (SCI) Tris(tribromophenyl) cyanurate
Trade names	FR 245; FR 368; GX 6145; Pyroguard SR 245; SR 245; TBPC; XZ-2500
CAS No	25713-60-4
MW	1067.43
Log K_{ow}	12.97
K_{ow}	1.00×10^{7}
Vapour pressure (Torr)	2.02×10^{-29}

4.10.2. Methods of analysis

No information could be identified on methods of analysis of TTBP-TAZ in environmental or food samples.

4.10.3. Sources and use

TTBP-TAZ is sold under a number of trade names and available through several commercial sources on the Internet. It is used in HIPS and ABS polymers (Weil and Levchuck, 2009).

TTBP-TAZ is listed in ELINCS (European List of Notified Chemical Substances). It is not classified in Annex VI of Regulation (EC) No 1272/2008.[28]

4.10.4. Environmental fate

No information could be identified.

4.10.5. Hazard identification

No information could be identified.

- ✓ **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**

Presence of TTBP-TAZ in products and dust

TTBP-TAZ concentration range in weight percentage (% w/w) in plastic consumer products		
Product	Number of samples containing TTBP-TAZ	[a]Concentration range w/w
Electrical powerboards and adaptors (n=4)	4	(0.01-0.8)
Children toys (n=4)	0	-
Televisions (n=2)	2	(0.06, 1.9)
Houseware (n=3)	2	(<0.0002-0.6)

Median TTBP-TAZ concentrations and ranges in ng g^{-1} in dust			
Sampling site	Number of samples containing TTBP-TAZ	Average	[a]Concentration range (ng g^{-1})
On electronics (n=5)	3	5500	(430-15100)
Around electronics (n=5)	3	660	(220-1300)
On floor (n=2)	1	160	-

Looking for unknown FRs

-Better to analyse products than dust (high concentration)

-Full scan MS detector

-Alternative techniques like DP, and LC better than GC

-Alternative sources APCI, APPI

-Still a high number of unknown halogenated compounds....

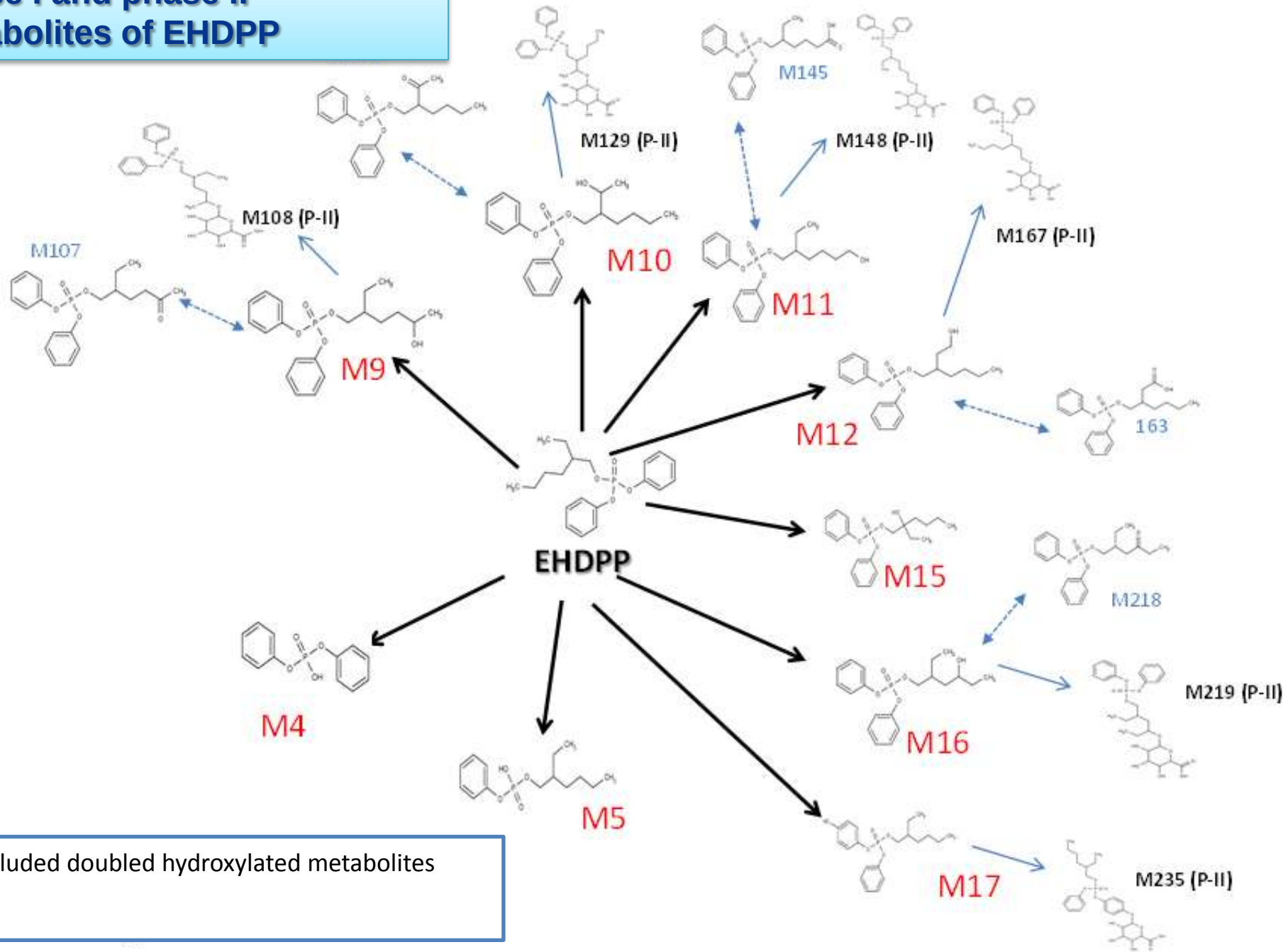
5.- SECONDENT AT UNIVERSITY OF ANTWERPT (OCTOBER-NOVEMBER 2013)

A. Ballesteros, C. Erratico, N. van de Eede, A. Ionas, A. Covaci

METABOLISM STUDIES ON EHDPP AND TTBP-TAZ

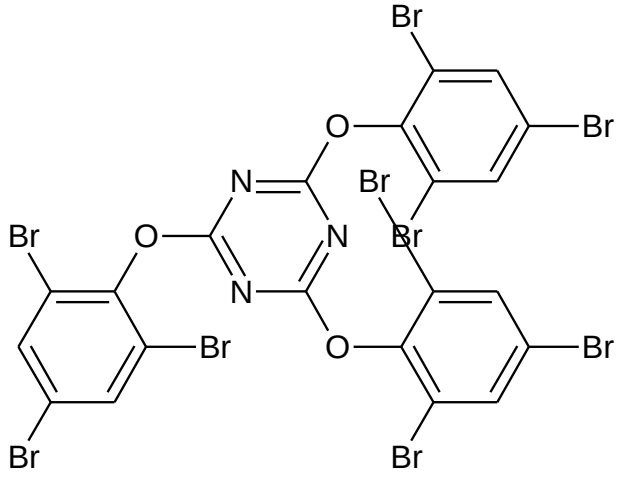
- ✓ Incubation with HLM (Phase I) or liver S9 fraction (Phase II)
- ✓ LLE for TTBP-TAZ
- ✓ Analysis by QTOF (and QQQ) for identification based on accurate mass and fragmentation patterns (due to lack of standards)

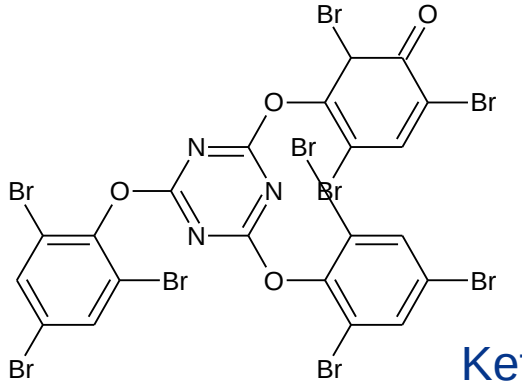
Phase I and phase II metabolites of EHDPP



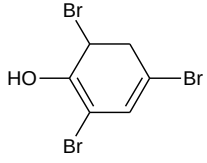
Not included doubled hydroxylated metabolites

PHASE I METABOLITES OF TTBP-TAZ





Ketone-metabolite



Tribromophenol

PROPOSALS WRITTING

- VENI, NWO (NL), 3-year project for young scientist. Host institution IVM-VU.
- FWO (Belgium) 1 or 3 year postdoct. Host institution: UA
- Deadline (both) January 2014, starting date September-October (both) 2014

Thank you for your attention ☺!

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