Progress report

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Projects

1. Screening for new FRs using TOF type detectors and "spectra-less" databases

2. Analysis of emerging PFRs by LC-MS/MS

3. Textile samples collection for FR analysis

4. FR leaching into saliva from toys

5. Toys analysis experiments → article submitted to EI *("Downsides of the recycling process: Harmful organic chemicals in children's toys")*

1. TOF systems & screening for FRs

- Experiments carried out at the IVM (VU, Amsterdam) during my secondment there (feb-april 2014)
- Samples for screening: dust from e-waste storage areas (Thailand) and homes (US) and in car interior samples + e-waste samples IVM (Ana)
- Ion sources used: APCI (+ and -) and AJS ESI (+ and -)
- A few slides from last time for clarity:

1. TOF systems & screening for FRs

- Interesting compounds:
  - Chlorinated unknown compound
    - APCI (-) ions: 459.875 – hexachlorinated; 316.9065 - tetrachlorinated
    - Typical APCI (-) ions for chlorinated compounds (Zhou NS et al., 2010) for which the Bruker Compound Crawler utility offered a structure: $[M-Cl+O]^-$, $[M-H]^-$ => 2-3 likely structures

Molecular Weight: 483.43

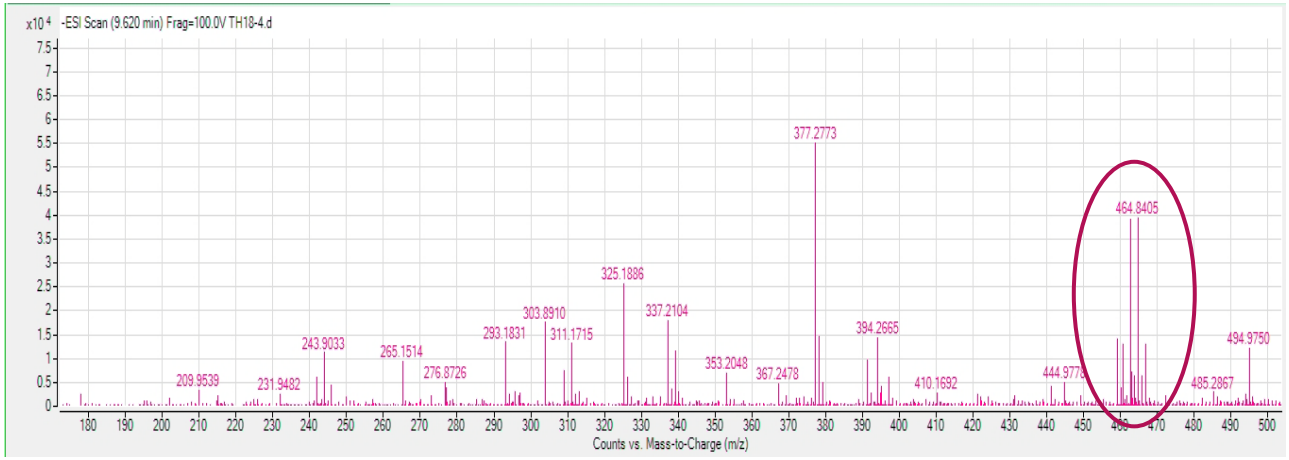
$[M-Cl+O]^-$

Molecular Weight: 463.96

$[M-H]^-$

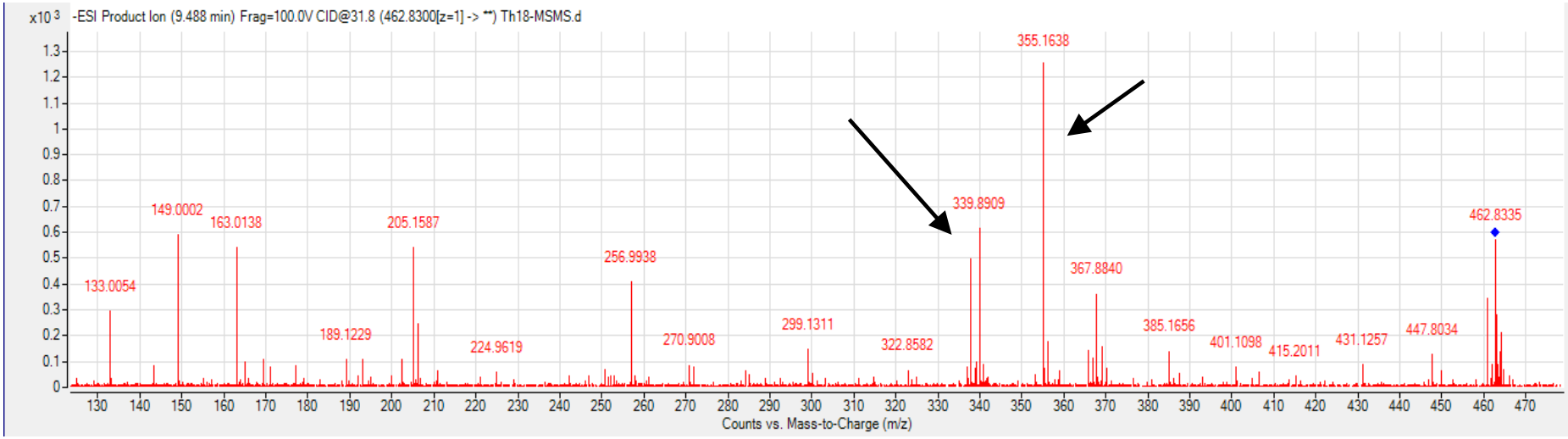
1. TOF systems & screening for FRs

- To find out which is the real compound → injected sample in LC-QToF with AJS ESI source - in ESI(-), $[M\text{-}Cl+O]^-$ are less likely than in APCI



1. TOF systems & screening for FRs

- MS/MS on ESI (-) for the unknown hexachlorinated analyte



1. TOF systems & screening for FRs

- Further web searches → patent US-8182980-B2 / 2012-05-22

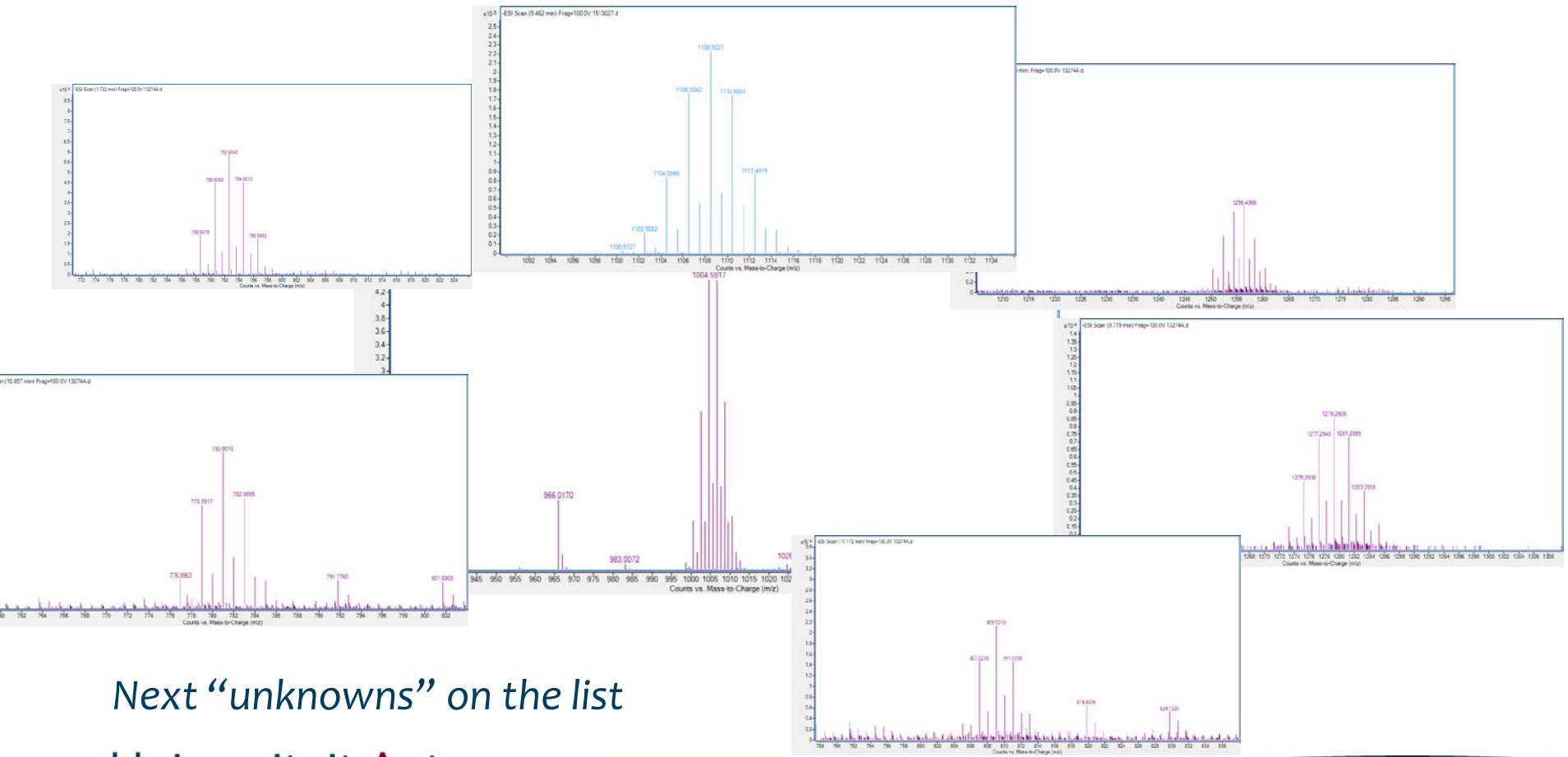
- This chemical and its derivatives are used as *initiators for polymerisation reactions* => NOT a flame retardant

Ethyl 4-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)benzoate

CAS 125989-27-7

1. TOF systems & screening for FRs

Halogenated “unknowns” – IVM e-waste samples



Next “unknowns” on the list

2. Analysis of emerging PFRs by LC-MS/MS

- We've reported V6 from 32 samples of soil and 8 of sediment collected near e-waste dumping sites *(experiments within the INTERFLAME, in collaboration with dr. Masayuki Someya, NIES, Japan – on secondment to the UA)*

- GC-ECNI/MS: not the most adequate technique for analysing V6 *(if liner gets dirty → substantial drop in sensitivity)*

- New organophosphorus FRs have been set in use after the PBDE phase-out (e.g. RDP and BDP)

2. Analysis of emerging PFRs by LC-MS/MS

- Instrument used: Agilent 1290 LC coupled to a 6460 triple quadropole mass spectrometer
- Ion source: AJS (Agilent JetStream) ESI in positive mode
- Column used: Grace VisionHT C18 Classic, 2.1 x 100 mm, 3 µm
- Mobile phases: Water / Methanol, both with 5 mM ammonium formate

2. Analysis of emerging PFRs by LC-MS/MS

Common and trade names	Abbreviation	MW	
Tris(chloroethyl) phosphate	TCEP	285.49	TCEP-d12
Tris(chloropropyl) phosphate	TCIPP	327.56	
Tris(1,3-dichloropropyl) phosphate	TDCPP	430.90	TDCPP-d15
2,2-Bis(chloromethyl)-1,3-propanediol bis[bis(2-chloroethyl) phosphate]	V6	582.99	
Tris(phenyl) phosphate	TPHP	326.29	TPHP-d15
Tris(methylphenyl) phosphate	iDPP	390.45	
2-Ethylhexyl diphenyl phosphate	EHDPP	362.41	
Trixylenyl Phosphate	TXP	410.48	
Resorcinol bis(diphenyl phosphate)	RDP	574.46	
Bisphenol A bis(diphenyl phosphate)	BDP	692.63	
tris(2-chloroethyl-1,1,2,2-d4) phosphate	*TCEP-d12*	*297.55*	
tris(2,3-dichloropropyl-1,1,2,3,3-d5) phosphate	*TDCPP-d15*	*445.98*	
tris(phenyl-d5) phosphate	*TPHP-d15*	*341.38*	

2. Analysis of emerging PFRs by LC-MS/MS

- Instrumental parameters were optimised for all of the analytes *(by directly infusing them into the source)*
- The LC program was optimised so that analytes similar would elute in the same time segment *(with the same parameters)*
- The transitions were optimised using the Optimiser software for Agilent

2. Analysis of emerging PFRs by LC-MS/MS

- Matrix: dust *(to begin with)*

- Still to-do:
  - SPE optimisation
  - Check the robustness and matrix effects
  - Validate the method

3. Textile samples collection for FR analysis

- 2 type of samples collected so far:
  - Curtains (50-60 samples, from 3 stores)
  - Carpets (9 samples, from 1 store) → need to collect a few more
  - Any other ideas ?

- Analysis:
  - Direct probe-TOF (IVM, second part of the secondment) as a screening tool
  - GC-MS (EI and ECNI)
  - LC-QqQ

4. FR leaching into saliva from toys

- In the planning stages: during the second part of secondment @ IVM (feb-april 2014)

- Extraction
  - Artificial saliva (mixture of carboxymethylcellulose, sorbitol, sodium, and potassium chloride) → need to add enzymes also: α-amylase and maybe also: lysozyme, salivary lactoperoxidase, lactoferrin, Immunoglobulin A
  - Try collecting some real human saliva ?
- Efficiency assessment: using CRMs (EC-590, 591) for PBDEs

- Matrices: mainly hard plastic, maybe also textile

Other future work

- Try to identify some of the Br compounds in the consumer product samples
- Prepare abstract for the Setac Europe 2014
- Start compiling the information about identification of unknowns into a publication
- Gather a few more textile samples *(carpets, others ?)*

Thank you for your attention