Identification of Brominated Flame Retardants in Leachate Samples Derived from Laboratory Tests of Waste Electronic and Electrical Equipment using a High Resolution High Accuracy Mass Spectrometer

Khanh-Hoang Nguyen[a], Mohamed Abdallah[a], Leon Isaac Peters[a], Aristide Paolo Ganci[a], Thomas Moehring[b], Stuart Harrad[a]

[a] *School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, United Kingdom.*

[b] *Life Sciences Mass Spectrometry Division, Thermo Fisher Scientific, Bremen, Germany.*

Introduction

Brominated flame retardants (BFRs) are chemicals added to consumer goods to increase their fire resistance. Restrictions and bans on the use of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) from the mid-2000s onwards has paved the way for increased use of novel brominated flame retardants (NBFRs) as alternatives. Some important examples of such NBFRs are: 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB). NBFRs have been detected in various environmental samples including foodstuffs[1], indoor dust and air[2,3], outdoor air[4] and biological samples[5]. The objective of this study is to develop a fast and efficient screening method for NBFRs through both targeted and untargeted approaches in one run and apply it to leachate samples.

Materials and Methods

Sample extraction

Samples were collected from a leachate experiment where different types of Waste Electrical and Electronic Equipment (WEEE) were leached for 24 hours in a container using deionized water. Three different groups of WEEE items were used for this experiment: 1. Mixed WEEE including small household items, computers, electrical tools, etc. in a 1000 L HDPE container; 2. Whole LCDs/CRTs in a 1000 L HDPE container, and 3. Whole fridges/freezers in a 10000 L metal container. Internal standards including ^{13}C-BDE28, ^{13}C-209 and ^{13}C-BTBPE were added to 250 mL leachate. The sample was then extracted with 50 mL of dichloromethane (DCM) by sonication for 30 min followed by mechanical shaking twice for 3 hours with 50 mL DCM. At each step, the organic layers were kept, combined and evaporated to 0.5 mL and loaded onto a SPE cartridge containing 2 g Na_2SO_4 6 g 44% acid silica, and 2 g Na_2SO_4. The cartridge was eluted with 20 mL hexane followed by 20 mL DCM. The eluent was evaporated to dryness under a gentle nitrogen stream and reconstituted in 100 µL methanol, ready for analysis.

Chemical analysis

Samples were analyzed on a UPLC-Q-Exactive Orbitrap-HRMS system. Chromatographic separation was performed on an Accucore RP-MS column (100 x 2.1 mm, 2.6 µm) with water (mobile phase A) and methanol (mobile phase B). A gradient method at 400 µL/min flow rate was applied as follows: start at 20% B; increased to 100% B over 9 min, held for 3 min; then decreased to 20% B over 0.1 min; then kept

constant for a total run time of 15 min. The injection volume was 5 µL and the column oven was set at 30 ˚C.

The APCI source was used to ionize samples in full scan negative ion mode. The parameters were set as follows: resolution 17500, AGC target 1e6, maximum injection time 100 ms, scan range 300 to 1000 m/z.

QA/QC

A field blank together with a lab blank were analyzed using the same procedures as real samples. For all data analysis in this study, two ions are considered to be the same if their mass deviation is less than ±2.5 ppm.

Data analysis

In our targeted approach, TraceFinder 3.0 (Thermo Fisher Scientific) was used for NBFRs screening with an in house mass library. The library was created by analyzing available standards with the same UPLC-Orbitrap parameters used for real samples.

For untargeted screening, the Compound Discoverer 3.0 (Thermo Fisher Scientific) software was used. Briefly, the software was configured to elucidate unknown compounds with a maximum chemical formula defined of $C_{40}H_{60}Br_{15}Cl_{10}O_{10}$. Bromine patterns with up to 12 bromines were also included for pattern matching. The program also searched for potential chemical structures for a given chemical formula using online databases such as ChemSpider.

Results and Discussion

Targeted Screening

Out of the NBFRs available in our library, only BTBPE and TBP-AE were found. TBP-AE was occasionally detected while the detection rate of BTBPE exceeded 70%. This implies a greater use of BTBPE than other NBFRs in WEEE items in this study. Another reason for this observation might be products which were treated with other NBFRs have not reached their end-of-life point yet. Besides TBP-AE and BTBPE, we also found legacy BFRs: PBDEs, HBCDs and TBBPA. While PBDEs (mainly tetra and pentaBDEs) and HBCDD were detected only at low levels in a limited number of samples, TBBP-A was ubiquitous. While TBBP-A was detected in both the lab and field blank, concentrations of TBBP-A in most samples exceeded the average blank level, by up to 570 times. Of all the 3 sample groups, mixed WEEE items tended to contain more BFRs than the other two groups. Indeed the highest levels of TBBPA, BTBPE and TBP-AE were detected in samples from this group.

Untargeted Screening

More than 10 unknown compounds with clear bromine/chlorine patterns were reported by Compound Discoverer. One of those had an ion mass of 552.76654 and showed an isotopic pattern of 4 bromine in the mass spectra. It was later elucidated as $C_{16}H_{14}Br_4O_2$ with one match from ChemSpider being 4,4'-(2,2-butanediyl)bis(2,6-dibromophenol (Figure 1). However, we note an alternative identification of a methoxylated derivative of TBBPA.

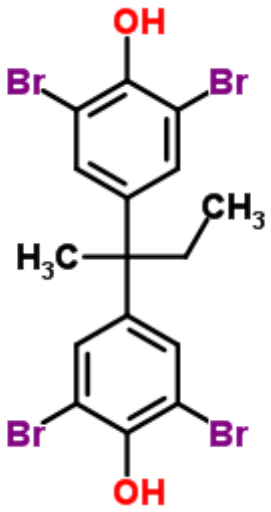

Figure 1. 4,4'-(2,2-Butanediyl)bis(2,6-dibromophenol)

Another unknown compound showed a 3 bromine pattern in its mass spectra, with a predicted formula of $C_6H_3Br_3O$. As the retention time of this unknown compound was later than that of our standards of 2,4,6-tribromophenol, 2,4,6-tribromophenyl allyl ether, 2-bromoallyl 2,4,6-tribromophenyl ether and 2,3-dibromopropyl 2,4,6-tribromophenyl ether, we therefore hypothesise this unknown to be a tribromophenol isomer.

Acknowledgement

The authors acknowledge gratefully financial support from the European Union Seventh Framework Programme (FP7-PEOPLE/2007-2013) under the ELUTE project (grant agreement no. 606857).

References

(1) Zheng, X.; Xu, F.; Luo, X.; Mai, B.; Covaci, A. *Chemosphere* **2016**, *150*, 545–550.

(2) Al-Omran, L. S.; Harrad, S. *Chemosphere* **2016**, *157*, 124–131.

(3) Tao, F.; Abdallah, M. A.; Harrad, S. *Environ. Sci. Technol.* **2016**, *50*, 13052–13061.

(4) Lee, S. C.; Sverko, E.; Harner, T.; Pozo, K.; Barresi, E.; Schachtschneider, J. A.; Zaruk, D.; DeJong, M.; Narayan, J. *Environ. Pollut.* **2016**, *217*, 62–69.

(5) Shi, Z.; Zhang, L.; Li, J.; Zhao, Y.; Sun, Z.; Zhou, X.; Wu, Y. *Environ. Int.* **2016**, *96*, 82–90.