Title: A RAPID METHOD FOR THE DETERMINATION OF BROMINATED FLAME RETARDANT CONCENTRATIONS IN PLASTICS AND TEXTILES ENTERING THE WASTE STREAM

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Running Title: RAPID DETERMINATION OF BROMINATED FLAME RETARDANTS IN WASTE PRODUCTS

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List of non-standard abbreviations:
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<th>Term</th>
<th>Description</th>
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<tr>
<td>22</td>
<td>ABS</td>
<td>acrylonitrile butadiene styrene</td>
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<tr>
<td>23</td>
<td>BFRs</td>
<td>brominated flame retardants</td>
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<tr>
<td>24</td>
<td>C&amp;D</td>
<td>construction and demolition</td>
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<td>25</td>
<td>CRM</td>
<td>certified reference material</td>
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<td>26</td>
<td>ELV</td>
<td>end of life vehicles</td>
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<td>27</td>
<td>EPS</td>
<td>expanded polystyrene</td>
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<tr>
<td>28</td>
<td>HBCDD</td>
<td>hexabromocyclododecane</td>
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<tr>
<td>29</td>
<td>LOD</td>
<td>limit of detection</td>
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<td>30</td>
<td>LOQ</td>
<td>limit of quantification</td>
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<tr>
<td>31</td>
<td>LPCL</td>
<td>low POP concentration limit</td>
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<td>32</td>
<td>MRM</td>
<td>multiple reaction monitoring</td>
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<tr>
<td>33</td>
<td>PBDEs</td>
<td>polybrominated diphenyl ethers</td>
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<td>34</td>
<td>PLE</td>
<td>pressurized liquid extraction</td>
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<td>35</td>
<td>POPs</td>
<td>persistent organic pollutants</td>
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<tr>
<td>36</td>
<td>PTV</td>
<td>programmable temperature vaporiser</td>
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<tr>
<td>37</td>
<td>PUF</td>
<td>polyurethane foam</td>
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<tr>
<td>38</td>
<td>RFs</td>
<td>response factors</td>
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<tr>
<td>39</td>
<td>RRT</td>
<td>relative retention time</td>
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<tr>
<td>40</td>
<td>RSD</td>
<td>relative standard deviation</td>
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SIM: single ion monitoring

S/N: signal to noise ratio

WEEE: waste electrical and electronic equipment

XPS: extruded polystyrene

Keywords:

brominated flame retardants; hexabromocyclododecane; polybrominated diphenyl ethers;

Stockholm Convention;
Abstract

Due to new European legislation, products going to waste are subject to “low persistent organic pollutant concentration limits”. Concentrations of restricted brominated flame retardants in waste products must be determined. A rapid extraction and clean-up method was developed for determination of brominated flame retardants in various plastics and textiles. The optimised method used vortexing and ultrasonication in dichloromethane followed by sulfuric acid clean-up to determine target compounds. Polybrominated diphenyl ethers were determined via GC/MS and hexabromocyclododecane via LC-MS/MS. Good recoveries of target analytes were obtained after 3 extraction cycles. The method was validated using polypropylene and polyethylene certified reference materials as well as previously characterised textiles, expanded and extruded polystyrene samples. Measured concentrations of target compounds showed good agreement with the certified values indicating good accuracy and precision. Clean extracts provided low noise levels resulting in low limits of quantification (0.8-1.5 ng/g for polybrominated diphenyl ethers and 0.3 ng/g for α-, β- and γ-hexabromocyclododecane). The developed method was applied successfully to real consumer products entering the waste stream and it provided various advantages over traditional methods including reduced analysis time, solvent consumption, minimal sample contamination and high sample throughput which is crucial to comply with the implemented legislation.
Introduction

Brominated flame retardants (BFRs) are a wide group of chemicals that have been used to impart flame retardancy in a variety of applications. Two of the most widely used BFRs since the 1980s are polybrominated diphenyl ethers (PBDEs – used in plastics, textiles, electronic casings, circuitry) and hexabromocyclododecane (HBCDD – primarily used in expanded polystyrene (EPS) and extruded polystyrene (XPS) for use in thermal building insulation) [1]. Concerns regarding their environmental impacts have led to the listing of HBCDD as well as the commercial PBDE formulations, Penta- and Octa-BDE, under the Stockholm Convention on persistent organic pollutants (POPs) [2, 3]. Moreover, the Deca-BDE formulation is currently under consideration to be listed as a POP [4] and has already been subject to significant restriction within Europe since the expiry of the European Union restriction of hazardous substances exemption on 1st July 2008 [5].

Legislative action has meant that waste products containing BFRs listed as POPs are subject to severe restrictions regarding the method of disposal. Furthermore, common methods of disposal such as landfilling, recycling or incineration run the risk of releasing BFRs into the environment [6-10]. Furthermore, BFRs have already been measured in various components of the waste stream, including landfill leachate [11-13], sewage based samples [11, 14-18], electronic waste treatment centres and waste incinerator emissions and residues, leading to substantially elevated BFR concentrations in environmental and biological samples impacted by such activities and matrices [8-10, 16, 19-22].

Currently, EU legislation is imposing “low POP concentration limit” (LPCL) values for various polymers entering the waste stream. These LPCLs are designed to prevent polymers containing restricted BFRs from being recycled and thus contaminating recycled goods and materials. The current LPCLs are 1000 mg/kg for ΣHBCDD and for ΣPBDEs (from the
Penta- and Octa-formulations). This means that products containing such POP-BFRs above their respective LPCLs cannot be recycled and must instead be treated to remove the BFRs from the product prior to its disposal [23]. Given the large mass of materials containing POP-BFRs at percent level concentrations that are reaching the end of their lifetime, rapid, reliable methods are required urgently to evaluate whether concentrations of BFRs in waste products comply with LPCLs (and equivalent legislative limits in other jurisdictions).

Currently, there are only a few studies regarding the quantitative analysis of BFRs in plastics. Allen et al. developed a method for the analysis of PBDEs in plastics, which involved stirring the polymer in 250 mL toluene for 24 hours, followed by several purification steps including liquid chromatography, silica and SPE prior to GC/MS analysis [24]. Gallen et al. performed similar methods for the analysis of PBDEs in plastics, extracting in dichloromethane (DCM) for 24 hours followed by dilution and acid silica purification [25]. Other published methods have measured PBDEs and HBCDD in plastics. These have involved crushing and pulverising plastics prior to extraction in toluene, polymer precipitation in hexane, separating into three aliquots for individual clean-up for each target compound group – multi-silica column (PBDEs), H$_2$SO$_4$ wash and florisil column (HBCDD) [26, 27]. Similarly, there are only a handful of studies that have measured BFRs in textiles including those of Kajiwara et al. [26, 27], which involved soaking samples in DCM for 2 days, followed by dilution prior to analysis. Other studies involve a combination of vortexing and ultrasonication extraction, followed by florisil clean-up [28] and 24 hour soxhlet extraction combined with ultrasonication, followed by multi-silica column clean-up [29].

These pre-existing methods involve time-consuming, labour-intensive and/or high solvent consumption sample preparation and extraction, followed by multiple clean-up steps. Thus the aim of this paper was to: (a) develop a simple, sensitive, rapid and high throughput method for identification and quantification of POP-BFRs and DecaBDE in all types of waste
plastics and textiles; (b) validate the developed methods using certified and in-house reference materials; and (c) apply the developed method to the analysis of real waste samples.

2. Materials and Methods

2.1 Chemicals and reagents

All solvents used for extraction and LC-MS/MS analysis were of HPLC grade (Fisher Scientific, Loughborough, UK). Silica (70-130 mesh), and concentrated sulfuric acid were purchased from Sigma-Aldrich (St Louis, MA, USA).

Individual α-, β- and γ-HBCDD standards, \(^{13}\text{C}_{12}\) α-, β- and γ-HBCDD, d$_{18}$-γ-HBCDD, individual standards of BDEs 28, 47, 99, 100, 153, 154, 183, 209, 77 and 128, \(^{13}\text{C}_{12}\)-BDE 209, PCB-129.

Certified reference materials for polyethylene (ERM-EC590) and polypropylene (ERM-EC591) were purchased from IRMM (Brussels, Belgium). In-house laboratory reference material for textiles, EPS and XPS were obtained from the National Institute for Environmental Studies (NIES, Tsukuba City, Ibaraki, Japan).

2.2 Sample collection

Waste plastic, polystyrene and textile samples were collected from landfills across Ireland during 2015 and 2016 as part of a separate study. Thirteen samples (2 x C&D, 4 x WEEE, 2 ELV, 5 Soft Furnishing) were selected at random for the purposes of this study.

2.3 Sample preparation, extraction and clean-up

In the optimised method, samples were cut into small pieces (< 1 cm$^2$) using a retractable knife blade and aliquots (ca. 200 mg) were accurately weighed, transferred into 15 mL glass
centrifuge tubes and spiked with 30 ng of all internal standards ($^{13}$C$_{12}$ α-, β- and γ-HBCDD, $^{13}$C$_{12}$-BDEs 77 and 128), except for $^{13}$C$_{12}$-BDE-209, of which 120 ng was spiked.

Samples were extracted by adding approximately 3 mL of DCM to samples before vortexing for 2 mins. Plastic samples were sonicated for 5 minutes, whilst textile samples were sonicated for 30 minutes. The extract was collected in a separate centrifuge tube and the process was repeated twice, collecting all DCM extracts in the same centrifuge tube. Samples were then evaporated to approximately 2 mL at 40 °C under a gentle stream of nitrogen. Two mL of hexane was added to the sample to precipitate any dissolved plastics. The sample was evaporated to < 1 mL and reconstituted to 2 mL in hexane (to ensure removal of DCM) and vortexed for 2 minutes. About 2 mL of >98% concentrated sulfuric acid was added to the sample prior to vortexing for 30 s. Samples were left for at least 1 hour followed by centrifugation at 3000 g for 5 minutes to separate the aqueous and organic layers. The clean supernatant hexane layer was collected in a glass tube and concentrated to near-dryness. The sample was reconstituted in 100 µL hexane/isoctane containing 0.2 ng/µL PCB-129 as recovery determination standard and transferred to a glass-inserted autosampler vial for quantitative analysis of PBDEs and screening for HBCDDs by GC/MS. Samples that were positive for HBCDD were then solvent exchanged into 100 µL methanol (containing 0.2 ng/µL d$_{18}$-γ-HBCDD as a recovery determination or syringe standard) for quantitative determination of HBCDDs via LC-MS/MS.

Several parameters were considered to enhance the efficiency of extraction including size-reduction, solvent type and extraction temperature. Size-reduction of hard plastic samples was sought to increase the surface area of contact with the extraction solvents. This was performed using a Fritsch Pulverisette 0 cryo-vibratory micro mill (Idar-Oberstein, Germany). Plastic chips (~ 2 mm × 5 mm × 5 mm) were added to the stainless steel grinding mortar (50 mL volume) along with a stainless steel ball (25 mm diameter) and submerged in
liquid nitrogen (−196 °C) to aid the pulverisation process. The sample was then ground at a vibrational frequency of 30 Hz for 5 min and repeated 3 times resulting in plastic particles that passed through a 250 μm mesh aluminium sieve. Aliquots (typically 50 mg) of the pulverised plastics were then used for further testing [30].

For pressurised liquid extraction (PLE), an ASE 350 (Dionex, Sunnyvale, CA, USA) was used. Extraction was carried out using DCM at 90 °C and 1500 psi. The heating time was 5 minutes, static time 4 min, purge time 90 s, flush volume 60%, with three static cycles required to achieve maximum recovery of all target compounds. Further details of the SPE method parameters with in-cell cleanup can be found elsewhere [31].

2.4 Sample Analysis

Quantitative analysis of PBDEs and screening of HBCDDs was performed in a single injection on a ThermoFisher Trace 1310 gas chromatograph coupled to a ThermoFisher ISQ mass spectrometer (MS). The MS was operated in electron ionisation mode using selective ion monitoring (SIM). 1 μL of the purified extract was injected for analysis using a programmable temperature vaporiser (PTV) onto a Restek Rxi-5Sil MS column (15 m x 0.25 mm x 0.25 μm film thickness). Helium was used as the carrier gas at a flow rate of 1.5 mL/min with methane as the reagent gas. Further details of GC/MS conditions including the GC temperature programme and ions monitored are provided in the supporting information (SI).

HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid chromatograph, equipped with a SIL-20A autosampler, a DGU-20A3 vacuum degasser coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was achieved using Agilent Pursuit XRS3 C18 column (150 mm x 2 mm I.D., 3 μm particle size) and a mobile phase of (a) 1:1 methanol/water with 2 mM ammonium acetate and (b)
methanol at a flow rate of 180 µL min⁻¹. Molecular ionisation was achieved using an electrospray ionisation (ESI) source operated in negative ion mode. MS/MS detection operated in the multiple reaction monitoring (MRM) mode was used for quantitative determination of HBCDD isomers based on m/z 640.6→79, m/z 652.4→79 and m/z 657.7→79 for the native, ¹³C₁₂-labelled and d₁₈-labelled diastereomers, respectively. Full LC-MS/MS parameters have been reported previously [32].

2.5 Quality Assurance / Quality Control

A reagent blank consisting of 200 mg of anhydrous sodium sulfate was analysed with every 5 samples. “Control” samples were created using plastics and textiles that contain no BFRs and were also analysed throughout the study. Three control samples were assessed for each matrix. None of the target compounds were found above the limits of detection in the blanks. Therefore results were not corrected for blank residues and method limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise ratio (S/N) of 3:1 and 10:1 respectively.

For a given peak to be identified as a target pollutant in a sample, the following criteria needed to be met:

1. The S/N must exceed 3:1
2. The isotope ratios (for bromine) must be within ±15% of the average for the 2 calibration sets run before and after that sample batch.
3. The relative retention time (RRT) of the peak in the sample must be within ±0.2% of the average value determined for the same congener in the 2 calibration sets run before and after that sample batch

3. Results and Discussion
3.1 Optimisation of method parameters

Several initial experiments were conducted during method development designed to optimise sample preparation parameters with the aim of improving extraction efficiency for all target compounds, whilst minimising sample preparation time and chromatographic interferences. These experiments were classified into two main categories:

3.1.1 Optimisation of extraction

Previous analyses of consumer goods, especially plastics, have involved the pulverisation of samples prior to extraction to improve recoveries [24-29, 33]. This study investigated pulverisation as a necessary step in extraction. Furthermore, the study also opted to test aggressive solvents including DCM and toluene in order to achieve maximum possible recoveries within the shortest possible extraction time. Extraction efficiencies were compared to PLE as a benchmark exhaustive extraction technique.

Our results showed higher extraction efficiencies for PBDEs from two types of plastic polymers (i.e. polypropylene and polyethylene) when using DCM compared to toluene. This was also evident even when toluene extractions were performed at higher temperatures (60 °C) than DCM extractions (30 °C) (Figure 1). No significant differences (t-test, p > 0.05) in the extraction efficiencies of HBCDD isomers from textiles, EPS and XPS were observed upon using DCM or toluene as extraction solvent (Table SI-1).

Optimum extraction times were also investigated. Results showed a marked improvement in recoveries upon increasing the initial mixing time (by vortex) from 30 sec to 2 min for both types of polymers investigated (Figure 2). A study of the percent recovery of target compounds as a function of ultrasonication time revealed 5 min and 30 min as the optimum for plastic and textile samples, respectively (Figure 3). EPS samples were completely soluble
after 2 min of vortexing in DCM, hence the ultrasonication time was not a determinant factor in their extraction. However, XPS samples showed a slightly different behaviour and slight increase in HBCDD recovery was observed upon increasing the ultrasonication time from 2 to 5 mins (Figure 3). In our quest to minimise variations in method parameters, we opted to use 5 min ultrasonication time for all PS samples.

The effect of pulverisation on the recoveries of PBDEs from plastic samples was investigated. Extraction of PBDEs from the studied polypropylene and polyethylene polymers using ultrasonication with DCM achieved recoveries of 77-83 % (without pulverisation) and 79-84 % (with pulverisation). Extraction with toluene achieved 26-35 % (without pulverisation), 56-63 % (with pulverisation at 30 °C) and 68-76 % (with pulverisation at 60 °C) (Figure 4). Extraction by PLE using DCM as the extraction solvent exhibited marginally higher recoveries of 79-85 % (without pulverisation) and 82-88 % (with pulverisation) than ultrasonication with DCM. However, this difference was not statistically significant.

Since PLE involves a lower sample throughput, along with a substantially higher volume of solvent used, we opted to use ultrasonication with DCM at 30 °C as the chosen extraction method. Pulverisation of plastic samples prior to extraction did not produce any significant increase in recovery of target PBDEs. Therefore, a sample pulverisation step was deemed unnecessary.

### 3.1.2 Optimisation of clean-up

Due to the nature of the matrices examined here, an aggressive clean-up procedure was required prior to injection of extracts for analysis on GC-MS and LC-MS/MS. All sample matrices were tested in triplicate using two different clean-up steps. Test (i) involved loading concentrated extracts onto pre-conditioned sulfuric acid impregnated (44 %) silica columns.
The target BFRs were eluted with 12 mL hexane:DCM (1:1, v/v). Test (ii) involved washing the concentrated extracts (ca. 2 mL hexane) with >98% concentrated sulfuric acid, prior to centrifugation and collection of the target BFRs in the supernatant organic layer. Visual inspection of extracts demonstrated that test (i) was suitable for polypropylene and textile based samples. However, EPS, XPS and polyethylene based samples produced turbid extracts, which drastically reduced the S/N ratio of analyte peaks in the corresponding chromatograms (Figure SI-1), therefore increasing the LOQ. Thus it was decided that test (i) was unsuitable as a universal method. Test (ii) produced clean extracts for all matrices, whilst taking overall less time and using less solvent. Therefore it was decided that test (ii) was the appropriate clean-up step for all sample matrices investigated in the current study.

### 3.2 Method Validation

#### 3.2.1 Linearity and range

A linear ($R^2 > 0.99$) five point calibration curve was constructed successfully for each target compound (with at least 3 measurements at each concentration level) over a wide concentration range (20pg/µL – 5ng/µL) using the assigned internal standards. Relative response factors (RFs) were estimated for each target compound. The relative standard deviation (RSD) of RFs for each target compound did not exceed 5%.

#### 3.2.2 Method accuracy and precision

Method accuracy and precision was assessed via repeated analysis of certified reference materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been previously measured by our research group and another laboratory. The method was
validated for PBDEs by replicate analysis (n=5) of two different certified reference materials ERM-EC591 and ERM-EC590 (Table 1).

In the absence of a CRM for HBCDD, replicate analysis (n=5) of four different materials (1 x XPS, 1 x EPS, 2 x polyester fabrics) were analysed. These materials have previously been measured for HBCDDs by our research group and another laboratory, the results of which were used as indicative values (Table 2).

There were no significant differences between our measured concentrations of reference materials compared to certified/indicative measurements (t-test, p<0.05). This combined with a low RSD between measurements (<15 %, except for BDE-28, which is <20% due to its proximity to the LOQ in ERM-EC591) demonstrates that this is an accurate, precise and robust method for determination of BFRs in various plastic and textile samples. The results have demonstrated that there is no requirement for a pulverization step prior to extraction, whilst only one clean-up step is required, regardless of the matrix tested. This confirms the simplicity (i.e. minimal number of steps) of the developed method and fulfils the need for rapid and high throughput analysis.

3.2.3 Sensitivity, limits of detection and quantification

The method achieved consistently high recoveries of target compounds and internal standards (80-90 %) at the lower limits of the calibration range for each of the studied compounds. No interference was observed in the method or field blanks analysed alongside the samples. This combined with a low baseline (Figure SI-2) meant that the method achieved high sensitivity and low detection limits. Instrumental method LODs were estimated based on a 3:1 S/N ratio (Table SI-2). The LOQ was determined by a concentration equivalent to a S/N ratio of 10:1 in the samples (0.8 ng/g for BDEs -28, -47, -99 and -100; 1.0 ng/g for BDEs -153, -154 and -183; 1.5 ng/g for BDE-209; 0.3 ng/g for α-, β- and γ-HBCDD). These were considered
satisfactory given that it is believed that consumer products have been treated at considerable
concentrations, whilst the current LPCL (1000 mg/kg) is more than $10^6$ higher than our
highest LOQ.

3.3. Application to real samples

The developed extraction and clean-up method was applied to the analysis of real samples
entering the waste stream. These comprised 13 samples (2 x EPS cavity wall insulation foam
(from construction and demolition (C&D) waste), 4 x waste electrical and electronic
equipment (WEEE, all comprised of ABS/HIPS housing), 2 x end of life vehicle waste (ELV)
(1 x polyurethane foam (PUF), 1 x upholstery textile), and 5 x soft furnishings (1 x carpet, 2
x PUF, 2 x upholstery textile)) collected from waste treatment sites in Ireland. Our analytical
method displayed good performance evidenced by high recoveries of all internal standards as
well as providing clean extracts with low base line in the mass chromatograms (Figure SI-3).

Levels of different BFRs varied depending on the type of waste measured (Table 3). Two
samples of EPS used as cavity wall insulation were found to contain HBCDD at more than
five times the corresponding LPCL (5800 and 5200 mg/kg). No other BFRs were detected in
the two EPS samples. This is consistent with the fact that cavity wall insulation has
historically been treated with commercial HBCDD.

Whilst the two ELV foam samples contained only negligible levels of BFRs (<10 ng/g)
currently listed under the Stockholm Convention, BDE-209 was present in both foam and
upholstery at extremely high concentrations – if a similar LPCL of 1000 mg/kg was imposed
for DecaBDE, then these two samples would exceed it by up to 30 times. These high
concentrations of BDE-209 are consistent with previous dust measurements of BDE-209
from UK cars where median concentrations were 100 mg/kg (there is currently no data from
within Ireland) [34].
With respect to soft furnishings, much lower concentrations were detected in the carpet sample with only BDE-209 found at 150 mg/kg. In our sofa samples, BDE-209 and HBCDD were found in high concentrations in both foam and upholstery. HBCDD was detected in both foam samples at or above the current LPCL (in one upholstery sample it exceeded it by a factor of 42. BDE-209 was also found in both samples at concentrations above 1000 mg/kg. Interestingly, upholstery samples contained considerably higher concentrations than foam samples for HBCDD and BDE-209. Both HBCDD and DecaBDE have had known applications as backcoating of fabrics used as furniture upholstery [35]. This suggests that concentrations found in foam samples could be the result of BFR migration from flame-retarded upholstery. This backed up by a previous study that demonstrated migration of BFRs from source to dust through direct contact [36]. These high levels of BDE-209 and HBCDD in domestic furniture are consistent with previous dust measurements in UK homes (there is currently no data from within Ireland) – BDE-209 was found in concentrations as high as 2200 mg/kg [37] whilst HBCDD has been found at levels as high as 140 mg/kg [38].

Concentrations of BFRs in our samples of WEEE were more variable than in the other waste streams examined here, with HBCDDs, PBDEs and BDE-209 detected. In all but one WEEE sample, multiple BFRs were found in the same samples. This suggests that either different components of the same product were treated with different flame retardants; or that a mixture of raw polymer material (potentially comprising recycled materials treated with different BFRs) was used in its manufacture. However, in the TV sample, the presence of congeners comprising the Penta- and Octa-BDE formulations at levels only 2% of the BDE-209 concentration (60,000 mg/kg), is likely a result of impurities in the commercial mixture or debromination of BDE-209 during the process of incorporating the flame retardant formulation into the polymer [39].

4. Summary
A rapid, simple and sensitive method was developed for the extraction and clean-up of POP-BFRs (PBDEs and HBCDD) from consumer products prior to analysis by GC-MS and LC-MS/MS. The method involved a combination of vortexing, ultrasonication followed by H$_2$SO$_4$ clean up to remove polymers and other co-extracted compounds from the extracts. The method was validated using certified reference materials and displayed good accuracy and precision. Application of the validated method to a limited number of real samples of consumer products entering the waste stream revealed some interesting results. The BFR concentrations determined in such products highlights the need for a rapid determination for these compounds in plastics; in all 6 of the 13 samples studied, the concentration of HBCDD exceeded the LPCL, with a further 5 samples containing BDE-209 at concentrations >1000 mg/kg, pertinent given the likely future introduction of an LPCL for Deca-BDE. Items containing concentrations of POP-BFRs exceeding LPCLs cannot be recycled. The developed method provided advantages over previous methods including reduced solvent consumption, shorter analysis time and enhanced recovery of target analytes, allowing for high sample throughput that will expedite future monitoring of compliance with LPCLs.

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dibenzofurans (PBDD/Fs) in municipal solid waste incinerators, *Environ Pollut.* 2010, 158, 1595-1602.


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