

# A rapid method for the determination of brominated flame retardant concentrations in plastics and textiles entering the waste stream

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

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

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21 **List of non-standard abbreviations:**

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

41 **SIM:** single ion monitoring

42 **S/N:** signal to noise ratio

43 **WEEE:** waste electrical and electronic equipment

44 **XPS:** extruded polystyrene

45 **Keywords:**

46 brominated flame retardants; hexabromocyclododecane; polybrominated diphenyl ethers;

47 Stockholm Convention;

48 **Abstract**

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

67

## 68 **Introduction**

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

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

88 Currently, EU legislation is imposing “low POP concentration limit” (LPCL) values for  
89 various polymers entering the waste stream. These LPCLs are designed to prevent polymers  
90 containing restricted BFRs from being recycled and thus contaminating recycled goods and  
91 materials. The current LPCLs are 1000 mg/kg for  $\Sigma$ HBCDD and for  $\Sigma$ PBDEs (from the

92 Penta- and Octa- formulations). This means that products containing such POP-BFRs above  
93 their respective LPCLs cannot be recycled and must instead be treated to remove the BFRs  
94 from the product prior to its disposal [23]. Given the large mass of materials containing POP-  
95 BFRs at percent level concentrations that are reaching the end of their lifetime, rapid, reliable  
96 methods are required urgently to evaluate whether concentrations of BFRs in waste products  
97 comply with LPCLs (and equivalent legislative limits in other jurisdictions).

98 Currently, there are only a few studies regarding the quantitative analysis of BFRs in plastics.  
99 Allen et al. developed a method for the analysis of PBDEs in plastics, which involved stirring  
100 the polymer in 250 mL toluene for 24 hours, followed by several purification steps including  
101 liquid chromatography, silica and SPE prior to GC/MS analysis [24]. Gallen et al. performed  
102 similar methods for the analysis of PBDEs in plastics, extracting in dichloromethane (DCM)  
103 for 24 hours followed by dilution and acid silica purification [25]. Other published methods  
104 have measured PBDEs and HBCDD in plastics. These have involved crushing and  
105 pulverising plastics prior to extraction in toluene, polymer precipitation in hexane, separating  
106 into three aliquots for individual clean-up for each target compound group – multi-silica  
107 column (PBDEs), H<sub>2</sub>SO<sub>4</sub> wash and florisil column (HBCDD) [26, 27]. Similarly, there are  
108 only a handful of studies that have measured BFRs in textiles including those of Kajiwara et  
109 al. [26, 27], which involved soaking samples in DCM for 2 days, followed by dilution prior  
110 to analysis. Other studies involve a combination of vortexing and ultrasonication extraction,  
111 followed by florisil clean-up [28] and 24 hour soxhlet extraction combined with  
112 ultrasonication, followed by multi-silica column clean-up [29].

113 These pre-existing methods involve time-consuming, labour-intensive and/or high solvent  
114 consumption sample preparation and extraction, followed by multiple clean-up steps. Thus  
115 the aim of this paper was to: (a) develop a simple, sensitive, rapid and high throughput  
116 method for identification and quantification of POP-BFRs and DecaBDE in all types of waste

117 plastics and textiles; (b) validate the developed methods using certified and in-house  
118 reference materials; and (c) apply the developed method to the analysis of real waste samples.

## 119 **2. Materials and Methods**

### 120 **2.1 Chemicals and reagents**

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

124 Individual  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD standards,  $^{13}\text{C}_{12}$   $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD,  $\text{d}_{18}$ -  $\gamma$ -HBCDD,  
125 individual standards of BDEs 28, 47, 99, 100, 153, 154, 183, 209, 77 and 128,  $^{13}\text{C}_{12}$ -BDE  
126 209, PCB-129.

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

### 131 **2.2 Sample collection**

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

### 135 **2.3 Sample preparation, extraction and clean-up**

136 In the optimised method, samples were cut into small pieces ( $< 1 \text{ cm}^2$ ) **using a retractable**  
137 **knife blade** and aliquots (ca. 200 mg) were accurately weighed, transferred into 15 mL glass

138 centrifuge tubes and spiked with 30 ng of all internal standards ( $^{13}\text{C}_{12}$   $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD,  
139  $^{13}\text{C}_{12}$ -BDEs 77 and 128), except for  $^{13}\text{C}_{12}$ -BDE-209, of which 120 ng was spiked.

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

157 Several parameters were considered to enhance the efficiency of extraction including size-  
158 reduction, solvent type and extraction temperature. Size-reduction of hard plastic samples  
159 was sought to increase the surface area of contact with the extraction solvents. This was  
160 performed using a Fritsch Pulverisette 0 cryo-vibratory micro mill (Idar-Oberstein,  
161 Germany). Plastic chips (~ 2 mm  $\times$  5 mm  $\times$  5 mm) were added to the stainless steel grinding  
162 mortar (50 mL volume) along with a stainless steel ball (25 mm diameter) and submerged in

163 liquid nitrogen ( $-196\text{ }^{\circ}\text{C}$ ) to aid the pulverisation process. The sample was then ground at a  
164 vibrational frequency of 30 Hz for 5 min and repeated 3 times resulting in plastic particles  
165 that passed through a 250  $\mu\text{m}$  mesh aluminium sieve. Aliquots (typically 50 mg) of the  
166 pulverised plastics were then used for further testing [30].

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

## 172 **2.4 Sample Analysis**

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

182 HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid  
183 chromatograph, equipped with a SIL-20A autosampler, a DGU-20A3 vacuum degasser  
184 coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was  
185 achieved using Agilent Pursuit XRS3  $\text{C}_{18}$  column (150 mm  $\times$  2 mm I.D., 3  $\mu\text{m}$  particle size)  
186 and a mobile phase of (a) 1:1 methanol/water with 2 mM ammonium acetate and (b)

187 methanol at a flow rate of 180  $\mu\text{L min}^{-1}$ . Molecular ionisation was achieved using an  
188 electrospray ionisation (ESI) source operated in negative ion mode. MS/MS detection  
189 operated in the multiple reaction monitoring (MRM) mode was used for quantitative  
190 determination of HBCDD isomers based on  $m/z$  640.6 $\rightarrow$ 79,  $m/z$  652.4 $\rightarrow$ 79 and  $m/z$  657.7 $\rightarrow$   
191 79 for the native,  $^{13}\text{C}_{12}$ -labelled and  $\text{d}_{18}$ -labelled diastereomers, respectively. Full LC-MS/MS  
192 parameters have been reported previously [32].

### 193 **2.5 Quality Assurance / Quality Control**

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

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

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

## 209 **3. Results and Discussion**

## 210 **3.1 Optimisation of method parameters**

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

### 215 **3.1.1 Optimisation of extraction**

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

222 Our results showed higher extraction efficiencies for PBDEs from two types of plastic  
223 polymers (i.e. polypropylene and polyethylene) when using DCM compared to toluene. This  
224 was also evident even when toluene extractions were performed at higher temperatures (60  
225 °C) than DCM extractions (30 °C) (Figure 1). No significant differences (t-test,  $p > 0.05$ ) in  
226 the extraction efficiencies of HBCDD isomers from textiles, EPS and XPS were observed  
227 upon using DCM or toluene as extraction solvent (Table SI-1).

228 Optimum extraction times were also investigated. Results showed a marked improvement in  
229 recoveries upon increasing the initial mixing time (by vortex) from 30 sec to 2 min for both  
230 types of polymers investigated (Figure 2). A study of the percent recovery of target  
231 compounds as a function of ultrasonication time revealed 5 min and 30 min as the optimum  
232 for plastic and textile samples, respectively (Figure 3). EPS samples were completely soluble

233 after 2 min of vortexing in DCM, hence the ultrasonication time was not a determinant factor  
234 in their extraction. However, XPS samples showed a slightly different behaviour and slight  
235 increase in HBCDD recovery was observed upon increasing the ultrasonication time from 2  
236 to 5 mins (Figure 3). In our quest to minimise variations in method parameters, we opted to  
237 use 5 min ultrasonication time for all PS samples.

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

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

### 252 **3.1.2 Optimisation of clean-up**

253 Due to the nature of the matrices examined here, an aggressive clean-up procedure was  
254 required prior to injection of extracts for analysis on GC-MS and LC-MS/MS. All sample  
255 matrices were tested in triplicate using two different clean-up steps. Test (i) involved loading  
256 concentrated extracts onto pre-conditioned sulfuric acid impregnated (44 %) silica columns.

257 The target BFRs were eluted with 12 mL hexane:DCM (1:1, v/v). Test (ii) involved washing  
258 the concentrated extracts (ca. 2 mL hexane) with >98% concentrated sulfuric acid, prior to  
259 centrifugation and collection of the target BFRs in the supernatant organic layer.

260 Visual inspection of extracts demonstrated that test (i) was suitable for polypropylene and  
261 textile based samples. However, EPS, XPS and polyethylene based samples produced turbid  
262 extracts, which drastically reduced the S/N ratio of analyte peaks in the corresponding  
263 chromatograms (Figure SI-1), therefore increasing the LOQ. Thus it was decided that test (i)  
264 was unsuitable as a universal method.

265 Test (ii) produced clean extracts for all matrices, whilst taking overall less time and using less  
266 solvent. Therefore it was decided that test (ii) was the appropriate clean-up step for all sample  
267 matrices investigated in the current study.

## 268 **3.2 Method Validation**

### 269 *3.2.1 Linearity and range*

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

### 275 *3.2.2 Method accuracy and precision*

276 Method accuracy and precision was assessed via repeated analysis of certified reference  
277 materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to  
278 textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been  
279 previously measured by our research group and another laboratory. The method was

280 validated for PBDEs by replicate analysis (n=5) of two different certified reference materials  
281 ERM-EC591 and ERM-EC590 (Table 1).

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

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

### 295 *3.2.3 Sensitivity, limits of detection and quantification*

296 The method achieved consistently high recoveries of target compounds and internal standards  
297 (80-90 %) at the lower limits of the calibration range for each of the studied compounds. No  
298 interference was observed in the method or field blanks analysed alongside the samples. This  
299 combined with a low baseline (Figure SI-2) meant that the method achieved high sensitivity  
300 and low detection limits. Instrumental method LODs were estimated based on a 3:1 S/N ratio  
301 (Table SI-2). The LOQ was determined by a concentration equivalent to a S/N ratio of 10:1  
302 in the samples (0.8 ng/g for BDEs -28, -47, -99 and -100; 1.0 ng/g for BDEs -153, -154 and -  
303 183; 1.5 ng/g for BDE-209; 0.3 ng/g for  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD). These were considered

304 satisfactory given that it is believed that consumer products have been treated at considerable  
305 concentrations, whilst the current LPCL (1000 mg/kg) is more than  $10^6$  higher than our  
306 highest LOQ.

### 307 **3.3. Application to real samples**

308 The developed extraction and clean-up method was applied to the analysis of real samples  
309 entering the waste stream. These comprised 13 samples (2 x EPS cavity wall insulation foam  
310 (from construction and demolition (C&D) waste), 4 x waste electrical and electronic  
311 equipment (WEEE, all comprised of ABS/HIPS housing), 2 x end of life vehicle waste (ELV)  
312 (1 x polyurethane foam (PUF), 1 x upholstery textile), and 5 x soft furnishings (1 x carpet, 2  
313 x PUF, 2 x upholstery textile)) collected from waste treatment sites in Ireland. Our analytical  
314 method displayed good performance evidenced by high recoveries of all internal standards as  
315 well as providing clean extracts with low base line in the mass chromatograms (Figure SI-3).

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

321 Whilst the two ELV foam samples contained only negligible levels of BFRs (<10 ng/g)  
322 currently listed under the Stockholm Convention, BDE-209 was present in both foam and  
323 upholstery at extremely high concentrations – if a similar LPCL of 1000 mg/kg was imposed  
324 for DecaBDE, then these two samples would exceed it by up to 30 times. These high  
325 concentrations of BDE-209 are consistent with previous dust measurements of BDE-209  
326 from UK cars where median concentrations were 100 mg/kg (there is currently no data from  
327 within Ireland) [34].

328 With respect to soft furnishings, much lower concentrations were detected in the carpet  
329 sample with only BDE-209 found at 150 mg/kg. In our sofa samples, BDE-209 and HBCDD  
330 were found in high concentrations in both foam and upholstery. HBCDD was detected in  
331 both foam samples at or above the current LPCL (in one upholstery sample it exceeded it by  
332 a factor of 42. BDE-209 was also found in both samples at concentrations above 1000 mg/kg.  
333 Interestingly, upholstery samples contained considerably higher concentrations than foam  
334 samples for HBCDD and BDE-209. Both HBCDD and DecaBDE have had known  
335 applications as backcoating of fabrics used as furniture upholstery [35]. This suggests that  
336 concentrations found in foam samples could be the result of BFR migration from flame-  
337 retarded upholstery. This backed up by a previous study that demonstrated migration of BFRs  
338 from source to dust through direct contact [36]. These high levels of BDE-209 and HBCDD  
339 in domestic furniture are consistent with previous dust measurements in UK homes (there is  
340 currently no data from within Ireland) – BDE-209 was found in concentrations as high as  
341 2200 mg/kg [37] whilst HBCDD has been found at levels as high as 140 mg/kg [38].

342 Concentrations of BFRs in our samples of WEEE were more variable than in the other waste  
343 streams examined here, with HBCDDs, PBDEs and BDE-209 detected. In all but one WEEE  
344 sample, multiple BFRs were found in the same samples. This suggests that either different  
345 components of the same product were treated with different flame retardants; or that a  
346 mixture of raw polymer material (potentially comprising recycled materials treated with  
347 different BFRs) was used in its manufacture. However, in the TV sample, the presence of  
348 congeners comprising the Penta- and Octa-BDE formulations at levels only 2% of the BDE-  
349 209 concentration (60,000 mg/kg), is likely a result of impurities in the commercial mixture  
350 or debromination of BDE-209 during the process of incorporating the flame retardant  
351 formulation into the polymer [39].

#### 352 4. Summary

353 A rapid, simple and sensitive method was developed for the extraction and clean-up of POP-  
354 BFRs (PBDEs and HBCDD) from consumer products prior to analysis by GC-MS and LC-  
355 MS/MS. The method involved a combination of vortexing, ultrasonication followed by  
356 H<sub>2</sub>SO<sub>4</sub> clean up to remove polymers and other co-extracted compounds from the extracts.  
357 The method was validated using certified reference materials and displayed good accuracy  
358 and precision. Application of the validated method to a limited number of real samples of  
359 consumer products entering the waste stream revealed some interesting results. The BFR  
360 concentrations determined in such products highlights the need for a rapid determination for  
361 these compounds in plastics; in all 6 of the 13 samples studied, the concentration of HBCDD  
362 exceeded the LPCL, with a further 5 samples containing BDE-209 at concentrations >1000  
363 mg/kg, pertinent given the likely future introduction of an LPCL for Deca-BDE. Items  
364 containing concentrations of POP-BFRs exceeding LPCLs cannot be recycled. The  
365 developed method provided advantages over previous methods including reduced solvent  
366 consumption, shorter analysis time and enhanced recovery of target analytes, allowing for  
367 high sample throughput that will expedite future monitoring of compliance with LPCLs.

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373 samples used as in-house reference materials.

374

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