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Portable X-ray fluorescence for the detection of POP-BFRs in waste plastics

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Keywords: Waste Plastics; LPCL Screening; POP-BFRs; PBDEs; HBCDD; XRF
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Drage, PhD; Stuart Harrad, PhD; Harald Berresheim, PhD

Abstract: The purpose of this study was to establish the efficacy of portable X-Ray Fluorescence (XRF) instrumentation as a screening tool for a variety of end of life plastics which may contain excess amounts of brominated flame retardants (BFRs), in compliance with European Union (EU) and United Nations Environment Programme (UNEP) legislative limits (low POP concentration limits - LPCLs). 555 samples of waste plastics were collected from eight waste and recycling sites in Ireland, including waste electrical and electronic equipment (WEEE), textiles, polyurethane foams (PUFs), and expanded polystyrene foams. Samples were screened for bromine content, in situ using a Niton™ XL3T GOLDD XRF analyser, the results of which were statistically compared to mass spectrometry (MS)-based measurements of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol-A (TBBP-A) concentrations in the same samples.

Regression between XRF and MS for WEEE samples show that, despite an overall favourable trend, large deviations occur for a cluster of samples indicative of other bromine-based compounds in some samples; even compensating for false-positives due to background interference from electronic components, XRF tends to over-estimate MS-determined BFR concentrations in the 100 to 10,000 mg kg⁻¹ range. Substantial deviations were additionally found between results for PUFs, textiles and polystyrene samples, with the XRF over-estimating BFR concentrations by a factor of up to 1.9; this is likely due to matrix effects influencing XRF measurements. However, expanded (EPS) and extruded polystyrene (XPS) yielded much more reliable estimations of BFR-content due to a dominance of HBCDD in these materials.

XRF proved much more reliable as a "pass/fail" screening tool for LPCL compliance (including a prospective LPCL on Deca-BDE based on REACH). Using a conservative threshold of BFR content exceeding legislative limits (710 mg kg⁻¹ bromine attributed to penta-BDE), XRF mistakenly identifies only 6 % of samples (34/555) as exceeding legislative limits.

Response to Reviewers: Please see attached file "Response to Reviewers 2"

Dear Professor Covaci,

We would like to submit the following manuscript on behalf of the authors entitled “Portable X-Ray Fluorescence for the Detection of POP-BFRs in Waste Plastics” by Martin Sharkey, Mohamed Abou-Elwafa Abdallah, Daniel S. Drage, Stuart Harrad, and Harald Berresheim, to be considered as a *Full Research Paper* for Science of the Total Environment.

This manuscript focuses primarily on human activity within the anthrosphere: the current state of technology for the screening of flame retardant POPs, the requirements for screening as pertains to current EU legislation, and refinements to the protocols of said screening through a large-scale field study. The paper’s introduction establishes hazards within the biosphere associated with these flame retardant POPs as well as their ubiquity within the environment, hence their listing as POPs and establishment of concentration limits. The results and subsequent discussion then provide a statistical overview of the efficacy of the refined screening protocols in both qualitative and quantitative instances, then evaluating its practicable efficacy in waste and recycling systems. This paper will therefore have direct implications for environmental management and policy regarding recycling systems, helping to promote the circular economy and subsequent environmental remediation.

This is an original manuscript that has been approved by all named authors and is not currently being considered for publication elsewhere.

Thank you very much for your time, and we look forward to hearing from you with regards to the manuscript’s suitability for publications in Science of the Total Environment.

Sincerely,

Martin Sharkey

PhD Candidate at Centre for Climate and Air Pollution Studies,

School of Physics, National University of Ireland Galway,

Republic of Ireland.

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Portable X-Ray Fluorescence for the Detection of POP-BFRs in Waste Plastics

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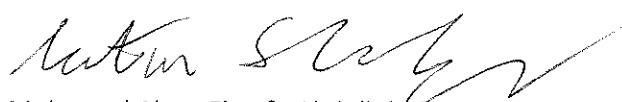
We the undersigned declare that the manuscript entitled "**Portable X-Ray Fluorescence for the Detection of POP-BFRs in Waste Plastics**" is original, has not been full or partly published before, and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by the undersigned.

We understand that the Corresponding Author is the sole contact for the editorial process. The corresponding author "**Martin Sharkey**" is responsible for communicating with the other authors about process, submissions of revisions, and final approval of proofs."

Signature of all authors:

Martin Sharkey



Mohamed Abou-Elwafa Abdallah



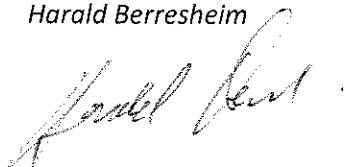
Daniel S. Drage



Stuart Harrad



Harald Berresheim



Reviewer #2:

However, Chapter 2.3: note that XRF spectroscopy is the main technique used in this paper and still technical details are missing ((K α , interferences etc etc):

The qualifier and quantifier lines, potential pitfalls like interferences and interference correction, this is really crucial and is still missing, please consider this to elaborate more on that !!

If the XRF software controls interferences than in must be adressed.

Thank you for outlining the details here which need to be expanded. A sentence has been included which states the qualifier and quantifier lines for the instrument:

“Quantification and qualification of bromine for the Niton XL3t model are achieved using the K α 1 line (11.9242 eV) and K α 2 line (11.8776 eV) respectively.”

Additional notes have also been included to expand on how and why certain interference corrections were carried out:

(i) removal of surface dust from samples – “For HIPS, ABS and insulation foam samples, the surface of the material was wiped with a clean non-fibrillating tissue prior to analysis, in order to remove sediment and dust which could interfere with the instrument’s primary x-rays or may contain traces of bromine.”;

(ii) thickness corrections for WEEE samples – “A thickness correction of 2 mm was additionally applied to the HIPS and ABS samples to help account for the finite thickness of the samples (per manufacturer guidelines); this reduces the risk of interference from substrate materials as the instrument internally estimates the density of an analyte based on Compton scattering of primary x-rays” (also outlined in section 3.2.2). Final paragraph of section 2.3 also includes a note on the additional test carried out to test the efficacy of thickness corrections, the results of which are noted in the Discussion section (lines 480-483);

(iii) thickness of samples for analysis – minimum thicknesses for analysis already outlined as that being required for full attenuation of primary x-rays, based on in-lab tests carried out by Thermo Fisher Scientific “Upholstery and other soft furnishings were manually folded, compressed to a thickness of approximately 3 cm (to achieve the thickness required for said materials for full attenuation of primary x-rays, per instrument manufacturer guidelines) and held in place by placing the instrument over the sample, in order to increase the density of the active analysis zone.”;

(iv) instrument mode of operation – “The instrument was operated in the “plastics” mode of operation, which optimises the instrument’s settings for interaction of x-rays with low density polymer materials and quantification of specific elements in their matrices.”

Reviewer #3:

The only text I would modify is that relating to scattered radiation being much less energetic than primary x-rays.

While the intensity of x-rays is reduced considerably, the energy is only modified by a few per cent.

Thank you for the correction; the sentence has been modified to reflect that the intensity of x-rays is reduced more significantly than the energy:

“As per Niton UK guidelines on the use of the device, secondary x-rays projected from the specimen deviate at angles around the device (mostly laterally) as well as at much lower intensities than primary x-rays, thus attenuating rapidly.”

1 Portable X-Ray Fluorescence for the Detection of POP-BFRs
2 in Waste Plastics

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12

13 **Abstract**

14 The purpose of this study was to establish the efficacy of portable x-ray fluorescence (XRF)
15 instrumentation as a screening tool for a variety of end of life plastics which may contain
16 excess amounts of brominated flame retardants (BFRs), in compliance with European Union
17 (EU) and United Nations Environment Programme (UNEP) legislative limits (low POP
18 concentration limits – LPCLs). 555 samples of waste plastics were collected from eight
19 waste and recycling sites in Ireland, including waste electrical and electronic equipment
20 (WEEE), textiles, polyurethane foams (PUFs), and expanded polystyrene foams. Samples
21 were screened for bromine content, *in situ* using a Niton™ XL3T GOLDD XRF analyser, the
22 results of which were statistically compared to mass spectrometry (MS)-based measurements
23 of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and
24 tetrabromobisphenol-A (TBBP-A) concentrations in the same samples.

25 Regression between XRF and MS for WEEE samples show that, despite an overall
26 favourable trend, large deviations occur for a cluster of samples indicative of other bromine-
27 based compounds in some samples; even compensating for false-positives due to background
28 interference from electronic components, XRF tends to over-estimate MS-determined BFR
29 concentrations in the 100 to 10,000 mg kg⁻¹ range. Substantial deviations were additionally
30 found between results for PUFs, textiles and polystyrene samples, with the XRF over-
31 estimating BFR concentrations by a factor of up to 1.9; this is likely due to matrix effects
32 influencing XRF measurements. However, expanded (EPS) and extruded polystyrene (XPS)
33 yielded much more reliable estimations of BFR-content due to a dominance of HBCDD in
34 these materials.

35 XRF proved much more reliable as a “pass/fail” screening tool for LPCL compliance
36 (including a prospective LPCL on Deca-BDE based on REACH). Using a conservative
37 threshold of BFR content exceeding legislative limits (710 mg kg⁻¹ bromine attributed to

38 penta-BDE), XRF mistakenly identifies only 6 % of samples (34/555) as exceeding
39 legislative limits.

40

41 **Keywords**

42 Waste Plastics; LPCL Screening; Quantification; PBDEs; HBCDD.

43

44 **1. Introduction**

45 Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two
46 groups of brominated flame retardants (BFRs) which have been extensively applied to
47 various commercial and consumer products to meet flammability standards. HBCDD has
48 been used as a flame retardant additive in expanded (EPS) and extruded (XPS) polystyrene
49 insulation foams as well as in high impact polystyrene (HIPS) for electrical housing and
50 junction boxes, as well as a textile coating agent for furniture and furnishings (Marvin et al.,
51 2011, UNEP, 2017b). Of the three commercial PBDE formulations, Penta-BDE is reportedly
52 almost exclusively used in polyurethane foams (PUFs) for domestic, office and automotive
53 applications, along with minor applications in printed circuit boards and microprocessors in
54 electrical and electronic equipment (EEE) (UNEP, 2010). Octa-BDE has been applied to
55 acrylonitrile butadiene styrene (ABS) and HIPS, largely used as casings for EEE (EC, 2011).
56 Deca-BDE was commonly used in coating agents applied to the surfaces of textiles and
57 upholstery as well as applied to HIPS for EEE as an additive compound (Weil and Levchik,
58 2009, IPCS, 1997). Over the last two decades however, concerns about their toxicity,
59 persistence and ability to bioaccumulate has led to their listing as persistent organic
60 Pollutants (POPs) under the Stockholm Convention. The commercial mixtures of Penta- and
61 Octa-BDE were listed in 2009 (UNEP, 2009), whilst HBCDD was listed in 2013 (UNEP,
62 2013), and the Deca-BDE commercial mixture listed in 2017 (UNEP, 2017a). Another
63 common legacy BFR, tetrabromobisphenol-A (TBBP-A), is also extensively used in as an
64 additive in HIPS and ABS and also reactively added to printed circuit boards for EEE (Morf
65 et al., 2003, IPCS, 1997). Though not currently under consideration for listing as a POP,
66 TBBP-A has been recently classified as H410 (very toxic to aquatic species), and listed as a
67 Class 2A carcinogen (Grosse et al., 2016, Malkoske et al., 2016). Additionally, waste articles

68 containing TBBP-A at concentrations in excess of 0.1 % is to be classified as “hazardous
69 waste” (EU, 2017b).

70 In the light of growing environmental concern, measures are being adopted in order to
71 prevent further environmental contamination from goods which were treated with POP-BFRs
72 (UNEP, 2009, EC, 2004). One such measure is the modification of recycling systems to
73 include screening procedures for goods suspected to contain high concentrations of POPs,
74 including POP-BFRs. Low POP concentration limits (LPCLs) of 1000 mg kg⁻¹ have been
75 established for each of the HBCDD, Penta-BDE and Octa-BDE commercial mixtures (EC,
76 2010, EC, 2016, EU, 2017a), in addition to a limit on Deca-BDE to come into force in 2019
77 (EU, 2017). However, a fast and cost-effective method of identifying products exceeding
78 these limits has not yet been identified, with industry standards (such as conventional
79 chromatographic-mass spectrometric techniques) being impractical for this purpose due to
80 their high running costs and low throughput.

81 Recently the use of portable x-ray fluorescence (XRF) measurements of elemental Br has
82 been suggested as a surrogate measure of POP-BFR concentrations. Several studies have
83 been performed to investigate the efficacy of portable XRF for the measurements of BFRs in
84 various plastic products, including EEE (Gallen et al., 2014, Aldrian et al., 2015, Guzzonato
85 et al., 2016) and furniture fabrics, foams and textiles (Petreas et al., 2016). Whilst these
86 studies have had varying degrees of success, they have all concluded that XRF-based
87 measurements are not capable of accurately quantifying concentrations of specific BFRs as
88 XRF measures elemental bromine only. However, Aldrian et al. (2015) and Petreas et al.
89 (2016) suggested that the use of XRF may be an effective screening tool for bromine content
90 in WEEE and furniture, as well as Schlummer et al. (2015) concluding effective screening
91 potential of HBCDD with the inclusion of an extraction process to distinguish the Br species.
92 Furthermore, Guzzonato et al. (2016) demonstrated that the accuracy of XRF measurements

93 of Br in ABS and HIPS may be improved by use of custom-made solid reference standards
94 containing Deca-BDE, and concluded that use of XRF to screen waste electrical and
95 electronic equipment (WEEE) for compliance with LPCLs was feasible. The largest recent
96 study (Sindikú et al., 2015) includes XRF screening in their methodology using varying
97 ranges of Br content, proving relatively successful in screening for BFR-content (with an
98 instrumental precision of $\pm 20\%$) but does highlight limitations in discerning the species of
99 bromine.

100 While the suitability of the XRF as a tool for predicting BFR concentrations has been
101 evaluated previously, many of the studies hitherto have been on a relatively small scale (<50
102 samples). Moreover, the range of plastics previously studied is limited to a few types and
103 applications or do not show in-depth comparisons of the accuracy and precision of XRF with
104 respect to MS analysis. In light of the introduction of LPCLs and the substantial mass of
105 waste polymers that will require screening for compliance with LPCLs (*e.g.* 42,628 tonnes of
106 WEEE collected in Ireland in 2013 (EPA, 2016)), it is vital that a rapid screening method is
107 developed to enable fast and reliable identification of waste items exceeding LPCLs.
108 Therefore the aims of this study are to (i) examine the efficacy of portable XRF
109 measurements as a predictor of BFR concentrations in a wide range of plastics in the waste
110 stream; and (ii) to determine whether portable XRF can be used as a “pass/fail” screening
111 tool for the interception of waste products exceeding LPCLs. These aims were achieved by a
112 large scale sampling campaign of recyclable plastics at waste and recycling sites in Ireland.
113 XRF measurements of bromine in a variety of waste articles (including WEEE plastics,
114 domestic and end of live vehicle (ELV) soft furnishings (PUF and upholstery fabrics) and
115 EPS/XPS insulation) were taken prior to quantitative analysis of selected BFRs via either
116 GC/MS or LC-MS/MS. To our knowledge, this is the first assessment of XRF as a tool for
117 monitoring compliance with LPCL legislation. Moreover, it represents the most

118 comprehensive assessment to date of the accuracy and suitability of hand-held XRF analysis
119 for quantification of BFR levels in waste articles.

120

121 **2. Materials and Methods**

122 ***2.1 Materials***

123 Chemical standards for native BDEs -28, -47, -77, -99, -100, -128, -153, -154, -183, -196, -
124 197, -203, -209, native α -HBCDD, β -HBCDD, γ -HBCDD, $^{13}\text{C}_{12}$ -BDE-209, $^{13}\text{C}_{12}$ - α -HBCDD,
125 $^{13}\text{C}_{12}$ - β -HBCDD, $^{13}\text{C}_{12}$ - γ -HBCDD, d_{18} - γ -HBCDD and $^{13}\text{C}_{12}$ -TBBP-A were purchased from
126 Wellington Laboratories (Guelph, ON, Canada). PCB-129 was purchased from Accustandard
127 (New Haven, CT, USA). All solvents (HPLC grade hexane, dichloromethane (DCM), iso-
128 octane and methanol) and sulfuric acid (>95 %) were purchased from Fisher Scientific
129 (Loughborough, UK).

130

131 ***2.2 Sample Collection and Field Measurement***

132 Samples were obtained from eight waste and recycling sites in Ireland and their bromine
133 concentrations measured *in situ* using a hand-held XRF device. Samples from a range of
134 different waste categories were collected: HIPS and ABS hard plastic casings from WEEE;
135 soft furnishings and textiles typical in both domestic and vehicular environments; and
136 polystyrene foams from building insulation and packaging materials. Following collection
137 and XRF analysis, destructive chemical analysis via GC-MS and LC-MS/MS was carried-out
138 on small sub-samples taken from the same parent product, within the immediate vicinity of
139 the area subjected to XRF analysis. This was performed to evaluate the accuracy with which

140 the XRF-determined bromine concentrations correlated with those of GC/MS or LC-MS/MS
141 measurements of selected BFRs.

142 In total, matched Br and BFR measurements were obtained for 555 samples; *Table 1* provides
143 an overview of the number of samples collected from each “waste type”. Following on-site
144 use of the XRF instrument, small sections of the scanned areas (~1-2 cm² for HIPS/ABS,
145 upholstery and textiles, or ~ 1-2 cm³ for polystyrene and PUF) were subsequently removed
146 and individually stored in labelled polyethylene bags. These collected samples were then
147 shipped to the University of Birmingham where concentrations of POP-BFRs and TBBP-A
148 were determined.

149

150 **2.3 XRF Analysis**

151 Each measurement involved placing the XRF instrument directly on to the measurement
152 surface, with the operator standing directly behind the instrument for the duration of the
153 measurement. As per Niton UK guidelines on the use of the device, secondary x-rays
154 projected from the specimen deviate at angles around the device (mostly laterally) **as well as**
155 **at much lower intensities** than primary x-rays, thus attenuating rapidly. Using the secondary
156 dose rates produced during plastics mode of operation, on plastic materials, and with varying
157 substrates (air, concrete, wood, etc.), the maximum dose for the user (at the device’s trigger)
158 was calculated for the sum of all measurements carried out and found to be well-below the
159 annual dose for a category B radiation worker (*i.e. <20 mSv in any single year*).

160 Determination of total bromine content in the samples was carried out *in situ* using a *Niton*
161 *XLt3-900 GOLDD X-Ray Fluorescence Analyser*. Calibration was performed by Niton UK
162 using proprietary standards containing varying concentrations of relevant inorganic
163 compounds in a polymer matrix. **Quantification and qualification of bromine for the Niton**

164 XL3t model are achieved using the K α 1 line (11.9242 eV) and K α 2 line (11.8776 eV)
165 respectively. The instrument was operated in the “plastics” mode of operation, which
166 optimises the instrument’s settings for interaction of x-rays with low density polymer
167 materials and quantification of specific elements in their matrices. Standard analyses using
168 the XRF instrument in this mode gives a 95 % confidence interval (CI = $\pm 2\sigma$) with each
169 measurement taken. The duration of analysis ranged from 30 to 105 seconds with longer
170 iterations required to improve instrumental uncertainty in samples with high bromine content
171 and for samples comprising of low density materials (Zawisza, 2012).

172 For HIPS, ABS and insulation foam samples, the surface of the material was wiped with a
173 clean non-fibrillating tissue prior to analysis, in order to remove sediment and dust which
174 could interfere with the instrument’s primary x-rays or may contain traces of bromine. A
175 thickness correction of 2 mm was additionally applied to the HIPS and ABS samples to help
176 account for the finite thickness of the samples (per manufacturer guidelines); this reduces the
177 risk of interference from substrate materials as the instrument internally estimates the density
178 of an analyte based on Compton scattering of primary x-rays. The instrument window was
179 then placed flat against the sample surface and a measurement of bromine content carried out
180 (with a minimum thickness of 10 cm for insulation samples and as presented at
181 approximately 2 mm for HIPS and ABS samples). Upholstery and other soft furnishings were
182 manually folded, compressed to a thickness of approximately 3 cm (to achieve the thickness
183 required for said materials for full attenuation of primary x-rays, per instrument manufacturer
184 guidelines) and held in place by placing the instrument over the sample, in order to increase
185 the density of the active analysis zone. Three repeat measurements were carried out on each
186 sample, several centimetres apart from each scanning point and at varying orientations. These
187 repeat measurements were required to be carried out on the same plastic panel/area and under

188 the same experimental conditions in order to detect instances of heterogeneous distribution of
189 BFRs within the body of sample.

190 Additional XRF measurements of bromine concentrations on available sub-samples of WEEE
191 HIPS and ABS samples (i.e. those aliquots removed for BFR determination) were carried out
192 in a controlled laboratory setting. These measurements were made in order to determine the
193 instances where bromine detected during field measurements were due to background
194 interference, being attributed to the presence of bromine in underlying electronic components
195 rather than from the polymeric casing itself.

196

197 ***2.4 Extraction and Clean-Up***

198 For quantitative analysis of BFRs, samples were extracted and cleaned according to methods
199 previously described (Abdallah et al., 2017). Briefly, aliquots of samples (20-100 mg) were
200 cut with a retractable blade and weighed directly into a 15 mL glass centrifuge tube and
201 spiked with 20 ng of BDEs -77 and -128, $^{13}\text{C}_{12}$ - α -, $-\beta$ -, and γ -HBCDD, $^{13}\text{C}_{12}$ -TBBP-A, and 40
202 ng $^{13}\text{C}_{12}$ -BDE-209 as internal standards. Approximately 3 mL of dichloromethane (DCM)
203 was added to the aliquot and vortexed for 2 minutes, followed by 30 minutes sonication. The
204 extraction process was repeated three times with the combined extracts collected in a separate
205 glass centrifuge tube. Crude extracts were concentrated under a gentle stream of N_2 to near-
206 dryness and reconstituted in 2 mL hexane. Extracts were washed with >95 % sulfuric acid
207 and supernatant organic layer was collected and concentrated to near-dryness under a gentle
208 N_2 stream. Samples were reconstituted in 200 μL of iso-octane containing 0.2 ng μL^{-1} PCB-
209 129 as a recovery standard. After determination of PBDEs via GC-MS, extracts were
210 reconstituted in methanol containing 0.2 ng μL^{-1} d_{18} - γ -HBCDD for determination of
211 HBCDDs and TBBP-A via LC-MS/MS analysis.

212

213 **2.5 Mass Spectrometric Analysis**

214 Quantitative analysis of PBDEs was performed in a single injection on a ThermoFisher Trace
215 1310 gas chromatograph coupled to a ThermoFisher ISQ mass spectrometer (MS). The MS
216 was operated in electron ionisation mode using selective ion monitoring (SIM). One μL of
217 the purified extract was injected for analysis using a programmable temperature vapouriser
218 (PTV) onto a Restek Rxi-5Sil MS column (15m x 0.25 mm x 0.25 μm film thickness).
219 Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1} . Full GC/MS parameters
220 have been reported previously (Abdallah et al., 2017).

221 HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid
222 chromatograph equipped with a Sil-20A auto sampler and a DGU-20A3 vacuum degasser
223 coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was
224 achieved using Agilent Pursuit XRS3 C18 column (150 mm x 2 mm, I.D., 3 μm particle size)
225 and a mobile phase of (a) 1:1 methanol/water and (b) methanol at a flow rate of $180 \mu\text{L min}^{-1}$.
226 Molecular ionisation was achieved using an electrospray ionisation (ESI) source operated in
227 negative ion mode. The MS/MS was operated in the multiple reaction monitoring (MRM)
228 mode. The MRMs transitions monitored were on m/z $640.6 \rightarrow 79$, m/z $652.4 \rightarrow 79$ and m/z
229 $657.7 \rightarrow 79$ for the native and the $^{13}\text{C}_{12}$ -labelled HBCDD diastereomers respectively and
230 $540.8 \rightarrow 79$, m/z $552.8 \rightarrow 79$ were used to monitor native and $^{13}\text{C}_{12}$ -labelled TBBP-A. Full
231 LC-MS/MS parameters have been reported previously (Abdallah et al., 2008).

232

233 **2.6 Quality Assurance/Quality Control**

234 For BFR analysis, a reagent blank consisting of 100 mg of anhydrous sodium sulfate was
235 analysed with every batch of 11 samples. "Control" samples were created using plastics and

236 textiles that contain no BFRs and were also analysed throughout the study; three Controls
237 were assessed for each matrix. None of the target compounds were found above the limits of
238 detection in the blanks. Therefore results were not corrected for blank residues and method
239 limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise
240 ratio (S/N) of 3:1 and 10:1 respectively.

241 Method accuracy and precision was assessed via repeated analysis of certified reference
242 materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to
243 textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been
244 previously measured by this laboratory and another. All values were found to be close to
245 certified or indicative levels, with a relative standard deviation of <15 % (Abdallah et al.,
246 2017).

247

248 ***2.7 Exclusion Criteria for Regression Analysis***

249 The regression analysis comprised a comparison between XRF-determined bromine, and the
250 equivalent bromine concentrations attributed to quantified BFRs (see supporting information,
251 S2). However, the accuracy of the XRF instrument must be taken into consideration for the
252 regression between its results of bromine concentrations and those from the mass
253 spectrometric analyses. The XRF instrument displays as a 95 % confidence interval or ± 2
254 standard deviations ($\pm 2\sigma$) for each analysis carried out; although this value can be altered, it
255 provides a sufficiently concise confidence interval to establish the stability of analyses.

256 During the analysis of EPS and XPS foam samples using the XRF device, a $\pm 2\sigma$ interval as
257 high as 16 mg kg⁻¹ bromine occurred with a “null” reading (i.e. the value determined by the
258 XRF instrument was 0 ± 16 mg kg⁻¹), thus a conservative 20 mg kg⁻¹ value was chosen as the
259 XRF analyser’s limit of detection (LOD_X). For the remaining polymeric materials – PUF,

260 HIPS, ABS, upholstery, textiles – a LOD_x of 10 mg kg^{-1} was chosen using the same criteria
261 as established for XPS and EPS samples (with a $\max \pm 2\sigma$ interval of 8 mg kg^{-1} for these
262 sample groups). Therefore, in instances where each of the triplicate XRF measurements
263 conducted on each sample fell below the LOD_x , that sample was not considered for the
264 regression analysis. If, however, one of the triplicate measurements was above the LOD_x
265 (and even if the average was below), the sample was included, in consideration of possible
266 non-uniform BFR distribution throughout the body of the sample.

267

268 **3. Results**

269 ***3.1 Total Bromine Concentrations Determined by XRF Analyses***

270 *Table 1* shows a summary of the bromine concentrations quantified using the XRF during *in*
271 *situ* analyses. Highest bromine concentrations were detected in the WEEE waste category at
272 $110,000 \text{ mg kg}^{-1}$ and $150,000 \text{ mg kg}^{-1}$ in IT & Telecoms and Display samples respectively.
273 Very high concentrations (exceeding $10,000 \text{ mg kg}^{-1}$) were also detected in the Furniture
274 Upholstery, ELV Upholstery, and ELV (other) sample groups. The Fridge/Freezer, Curtain,
275 C&D XPS, Mattress Foam and Mattress Upholstery sample groups showed very low
276 maximum Br concentrations ($< 1,000 \text{ mg kg}^{-1}$) along with low median and mean values. This
277 indicates that these sample groups underwent low levels of treatment with bromine-
278 containing compounds, and/or experienced transfer of bromine-containing compounds while
279 in use or during storage for recycling/transfer (Rauert et al., 2014). The remaining sample
280 groups showed maximum bromine content between $1,000$ and $10,000 \text{ mg kg}^{-1}$ which, along
281 with the aforementioned groups with concentrations in samples reaching roughly $150,000 \text{ mg}$
282 kg^{-1} Br, demonstrates potential from some articles in these groups to exceed LPCLs.
283 However, as is evidenced by the low median concentrations for the sample groups relative to

284 the maximum values, samples with excessively high concentrations of bromine make up a
285 minority of each remaining sample group. This indicates a relatively low proportion of waste
286 articles potentially treated with POP-BFRs in these sample groups (with the possible
287 exception of Display, Furniture Foam, Furniture Upholstery, and Vehicle Foam samples
288 groups).

289 We have additionally observed so-called “false-positives” in different waste categories. A
290 “false positive” corresponds to a situation where the XRF measurement of Br indicates the
291 LPCL for a POP-BFR to be exceeded, but the POP-BFR concentration is below the LPCL.
292 By comparison, a “false negative” would occur where the POP-BFR concentration is above
293 the LPCL, but this is not indicated by the XRF measurement of Br. These occurrences will be
294 reported by waste category in the following sections.

295

296 ***3.2 XRF – MS Total Bromine Measurement Comparison***

297 Concentrations of BFRs in the samples included in this study have been previously reported
298 by Drage et al. (2018). For comparison with XRF measurements they have been briefly
299 outlined in *Table 1*. Additionally, following MS-analysis of the collected samples, some
300 sample groups including the Mattress, Curtain, Carpet, ELV (other), Fridge/Freezer, and ELV
301 (other) sample groups showed either no excessive concentrations of BFRs or very few
302 samples with excess concentrations. These groups were therefore considered unsuitable to act
303 as comparative metrics for regressions between MS and XRF analyses.

304 ***3.2.1 – WEEE Hard Plastics***

305 In addition to the 65 WEEE samples excluded based on $Br < LOD_x$ (*Section 2.7*), a further 15
306 samples were omitted from the regression analysis due to laboratory confirmation of a
307 background interference during *in situ* measurements of the samples (*Section 2.3*). *Table 2*

308 shows the results obtained for these 15 samples, comparing the average of the on-site
309 triplicate XRF measurements to lab-based duplicate XRF measurements, the latter more
310 accurately equating to the actual concentrations of bromine in the samples.

311 Application of this additional exclusion criterion yielded a final data set of 70 ABS/HIPS
312 samples remaining for regression analysis, the result of which is shown in *Figure 1*. The
313 linear regression coefficient (slope, m) is 0.98 and the coefficient of determination (R^2) is
314 0.614. However, a notable cluster of samples ($n = 10$) show much higher concentrations of
315 bromine as determined by XRF analysis compared to the concentrations determined by
316 GC/MS / LC-MS/MS analysis (defined here as “true” Br content). *Figure 2 (a)* is a Bland-
317 Altman plot showing the variation in the Br content determined via XRF analysis as a
318 percentage of true Br content $[(XRF-MS)/MS] \times 100$, where it can be seen that these
319 outliers show at least a 4.9-fold overestimation of “true” Br content (z -test, $p < 0.001$)
320 compared to a maximum of 2.4-fold overestimation in the remainder. It is likely therefore
321 that these samples contained bromine in BFR-type chemicals other than those analysed for by
322 the MS methods used herein, such as BTBPE, tetrabromophthalic acid, and DPDPE (Al-
323 Omran and Harrad, 2016, Petty et al., 2016, IPCS, 1997).

324 *Figure 2 (b)* highlights large variations still exist between Br concentrations obtained for the
325 same samples via the two measurement techniques. Samples with similar concentrations of
326 BFRs show varying deviations between the techniques such that even employment of a
327 correction factor would have limited success in improving the regression, across all
328 concentrations shown herein. For example, samples with total Br concentrations ranging
329 between 100 and 1,000 mg kg^{-1} show deviations from -3 % to +250 % between the analysis
330 techniques for approximately 60 % of all WEEE samples therein. These variations may in
331 part be due to the presence of NBFRs alongside TBBP-A, HBCDD and PBDEs, reflecting the

332 XRF instrument's inability to specify the precise chemical form of bromine present in
333 samples.

334 3.2.2 – Furniture and Vehicle Foam

335 The XRF and MS derived concentrations of Br in 43 PUF samples are compared (*Figure 3*)
336 showing a slope of 1.70 and a R^2 value of 0.98. The high regression coefficient for these
337 samples is likely the result of interferences with primary and secondary x-rays in the high
338 thickness and low density of the PUF samples examined. Internal XRF approximations of the
339 sample's density using Compton scattering can be heavily influenced due to the presence of
340 air pockets in the samples, leading to a significant bias in the accurate quantification of
341 elemental bromine (and other elements) (Zawisza, 2012). However, assuming these biases are
342 relatively consistent throughout different PUF samples, measured results can be subsequently
343 multiplied by a correction factor derived from the inverted slope of linear regression to
344 correct this bias.

345 Although this correction factor ($\mu_{\text{puf}} = 1.70^{-1} = 0.59$) can improve the accuracy of the XRF-
346 measurements, its precision in the analysis of PUF samples remains unreliable, with relative
347 standard deviation (RSD) for individual measurements ranging from 1 % to 172 % ($\text{RSD}_{\text{avg}} =$
348 39 %). In addition, repeated XRF analyses of PUF samples on a dedicated test stand in a
349 controlled laboratory setting showed high variability in Br content depending on the
350 orientation of the sample and the surface facing the analyser window. It was observed upon
351 repeated laboratory measurements of eight furniture foam samples whose XRF results
352 deviated by >250 % from the corresponding MS-concentrations, that five of the samples had
353 shown substantial differences (z-test, $p < 0.001$) in the detected concentration of bromine on
354 surfaces which were cut away from the body of the PUF item compared to the surface
355 adjacent to the upholstery (*S1 (a), S4*). This – akin to previous observations of BFR migration

356 from fabric to dust via direct contact (Rauert et al., 2016) is consistent with migration of
357 BFRs from overlying upholstery fabric into underlying PUF, resulting in higher
358 concentrations of BFRs in PUF near contact surfaces and spatially declining concentrations
359 deeper within the material.

360 3.2.3 – Furniture and Vehicle Upholstery

361 For the regression of the 66 upholstery samples included a slope of 1.38 and a R^2 of 0.86
362 were determined (*S5 (a)*), indicating a strong correlation between the analytical techniques.
363 Similar to the PUF samples, the upholstery samples also appear to require a correction factor
364 ($\mu_{\text{upholstery}} = 1.38^{-1} = 0.72$) in order to account for the relatively low density of the material and
365 the resultant matrix effects. However, a Bland-Altman plot similar to *Figure 2 (a)*
366 demonstrated the XRF's overestimation of bromine concentrations by up to 180 % for
367 concentrations exceeding 100 mg kg^{-1} and several thousand percent for lower concentrations.
368 This phenomenon may simply be more obscured at larger concentrations due to the
369 magnitude of concentrations involved and also possibly due to a “screening-effect” within the
370 matrix of the material during XRF analysis, whereby multiple bromine atoms are in a linear
371 formation with respect to the analyser resulting in only the first and none of the subsequent
372 bromine atoms being detected (Zawisza, 2012).

373 The relative homogeneity of repeated XRF measurements and the high discrepancies between
374 Br concentrations obtained via the two measurement techniques revealed in the Bland-
375 Altman plot (*S1 (b)*), are – as for PUF materials – likely attributable to the presence of BFRs
376 not measured in this study or, in the case of some ELV samples containing green upholstery,
377 the use of green pigment containing bromine. In similar fashion to WEEE samples (*Section*
378 *3.2.1*), only 25 % of samples yielded Br concentrations derived by XRF that agreed within
379 ± 25 % of those obtained via MS (following application of the correction factor). However,

380 given the high treatment concentrations with HBCDD and Deca-BDE, the XRF could still be
381 successfully applied to the screening of upholstery for excess POP-BFRs as false-positives
382 (instances where XRF analysis indicates exceedance of an LPCL where none actually
383 occurred) at such elevated bromine concentrations were rare in this study.

384 3.2.4 –Insulation Foams - Expanded Polystyrene (EPS)

385 Of the 47 original EPS samples, 17 were excluded from the analysis due to determination of
386 Br concentrations below LOD_x . Br concentrations obtained for the remaining samples via
387 XRF and MS underwent regression analysis (*Figure 4*) showing a linear slope of 1.20 and R^2
388 of 0.98. The XRF measurements again appear to require a calibration factor in order to
389 correct the regression for offsets caused by matrix effects. Implementing this, XRF
390 measurements of 16 out of 30 samples correlate to within 25 % of MS results with 12 of these
391 16 (for which Br $>1000 \text{ mg kg}^{-1}$) agreeing to within 10 % of MS-determined bromine
392 content.

393 Despite this favourable agreement for samples containing higher Br concentrations (i.e.
394 $>1000 \text{ mg kg}^{-1}$) analysis of the data using a Bland-Altman plot (*SI (c)*) reveal potentially
395 significant outliers in this sample group most notably in the 0-10 mg kg^{-1} Br concentration
396 range (z-test, $p < 0.05$), as determined by MS analysis, despite exclusion of samples $<LOD_x$.
397 Additionally, the relative standard deviations (RSDs) of the triplicate XRF measurements
398 indicate that the samples showing poor agreement between XRF and MS have large RSDs
399 ($>25 \%$) between the individual XRF measurements, the largest RSDs (173 % each) being
400 attributed to the significant outliers highlighted in *SI (c)*. Selection criteria for more accurate
401 categorisation of Br concentrations can potentially be established from these observations;
402 specifically, omission of samples with 0-10 mg kg^{-1} Br-content (from MS analysis) and those

403 with RSDs over 25 % (from triplicate XRF analysis, results in over 80 % of samples being
404 categorised as accurate to within 10 % of the true HBCDD concentration.

405 One noteworthy EPS sample showed a much larger discrepancy between XRF-determined
406 bromine (average bromine = 3354 mg kg⁻¹; RSD = 12 %) and LC-MS/MS (total bromine =
407 1030 mg kg⁻¹) analyses. Repeat XRF measurements of the same sample in-lab yielded an
408 average for four measurements of 4275 mg kg⁻¹ bromine with a RSD of 19 % – the higher
409 RSD being attributable to the small sample size relative to the XRF measurement window,
410 such that primary x-rays are not interacting with the target sample. Such a variation between
411 XRF-determined- and LC-MS/MS-determined bromine did not occur in any other samples
412 within this group, potentially indicating another bromine-based compound in this particular
413 sample, such as tribromoallylether or PolyFR (Schlummer et al., 2015, IPCS, 1997).

414 3.2.5 –Insulation Foams - Extruded Polystyrene (XPS)

415 The linear regression for the 20 XPS samples for which XRF- and MS-derived Br
416 measurements were compared (*S5 (b)*) shows a linear slope of 1.93 with a R² of 0.97. This
417 sample group shows the largest deviation from a unity regression. Following correction, a
418 Bland-Altman plot (*SI (d)*) shows an even distribution for samples for containing >200 mg
419 kg⁻¹ bromine. However, the variation between the two Br metrics at concentrations up to 200
420 mg kg⁻¹ remains high (± 100 %).

421 This sampling, however, contained only a few with excessive concentrations of BFRs, and
422 too few overall for a more definitive linear regression. Relatively few samples have been
423 treated with BFRs and generally at much lower concentrations and other waste categories
424 based on this sampling. However, a more statistically significant sample size may reveal as
425 yet unseen nuances to this plastic.

426

427 **4. Discussion**

428 ***4.1 Utility of XRF Instrumentation as a Pass/Fail Screening Tool for LPCL Compliance***

429 In the context of portable XRF's potential use as a tool for testing compliance with POP-BFR
430 LPCL values, the incidence of "false positives" and "false negatives" is crucial. A "false
431 positive" is defined here as a specific source misclassification scenario, i.e. a situation where
432 the XRF measurement of Br indicates the LPCL for a POP-BFR to be exceeded, but the POP-
433 BFR concentration is below the LPCL. By comparison, a "false negative" occurs where the
434 POP-BFR concentration is above the LPCL, but this is not indicated by the XRF
435 measurement of Br (*Section 3*). For the purposes of discussion here, we have assumed a
436 conservative Br LPCL value based on the Br detected being due to penta-BDE. Thus, any
437 sample exceeding 710 mg Br/kg is assumed here to exceed the POP-BFR LPCL of 1,000 mg
438 POP-BFR/kg (including 1000 mg kg⁻¹ limit for Deca-BDE established by REACH).

439 Of the 555 items we tested, there were 34 false positives and no false negatives when the
440 current LPCLs for POP-BFRs are considered: 26 occurred in WEEE items (1 large household
441 appliance, 12 display items, 6 small domestic appliances, and 7 IT items); the remainder, in 2
442 vehicle fabric samples, 1 vehicle foam sample, 1 carpet sample, 1 mattress foam sample, 1
443 furniture upholstery sample, and 2 furniture foam samples. These resulted from
444 concentrations >1,000 mg kg⁻¹ of either TBBP-A alone (n=15), as yet unidentified bromine-
445 containing compounds (n=11), and in 8 instances enhancement of measured BFR
446 concentrations. However, 5 of the 11 samples with unidentified compounds are attributable to
447 false-positives due to background interference (*Section 3.2.1*) which therefore reduces the
448 number of false-positives to 29 of 555. Translating these incidences into percentages, our
449 data show that use of portable XRF to monitor compliance with current LPCLs for PBDEs
450 and HBCDD would mean that 5.2 % of articles from the waste categories studied would be

451 incorrectly identified as requiring special treatment. This compares to 47 (8.5 %) of articles
452 identified as genuinely exceeding current LPCLs and REACH limits.

453 The implications of such false positives are essentially that a small additional percentage of
454 articles will not be available for recycling and that there will be an additional unnecessary
455 economic cost incurred when such articles are subjected to special treatment. Balanced
456 against these issues, it may be argued that as the cause of the false positives are likely to be
457 either known or unidentified BFRs not targeted in our study, which may themselves become
458 subject to future legislative restriction; false positives can potentially be viewed as an
459 acceptable limitation of the use of XRF as a screening tool for LPCL compliance. By
460 comparison, false negatives would exert a more detrimental impact as they would allow
461 regulated POP-BFRs to remain in circulation. However, the absence of false negatives in our
462 study, suggests that use of hand-held XRF will only very rarely – if ever - fail to identify
463 articles that exceed LPCL values.

464 Our data on false positives indicate that portable XRF could be a viable tool for testing
465 compliance with LPCLs for EPS/XPS, as well as ELV waste and waste soft furnishings,
466 while further underlining the potential issues with the use of hand-held XRF to test for LPCL
467 compliance in WEEE due to the more frequent presence of TBBP-A and other as yet
468 unidentified compounds in such items.

469

470 ***4.2 Accuracy and Precision of XRF-Determined Bromine as a Surrogate for POP-BFRs***

471 Upon comparing the results of total Br from portable XRF analysis with compound-specific
472 mass spectrometry, the overall *accuracy* of XRF strongly depends on the type of polymer
473 under investigation. Though the regression of all sample-groups appears to follow a generally
474 linear correlation between XRF and MS results, the deviation of the slopes from unity in most

475 of the plastic types indicates that matrix effects occur prominently in low-density materials.
476 Br concentrations obtained from XRF measurements were adjusted based on subsequent
477 mass spectrometric analyses of the same samples thus allowing for a correction factor to be
478 inferred (*Section 3.2*). However, for use of this instrument as a standalone analyser for
479 accurately quantifying total bromine concentrations in the range of materials studied here,
480 suitable calibration standards unique to each type of polymer (ABS, HIPS, PUF, etc.) would
481 initially be required to ensure reliable compensation for matrix effects. Application of
482 correction factors to XRF measurements discerned following MS analysis was successful in
483 correcting the overall accuracy of the instrument for all measured concentrations, with little
484 effect on the deviations for individual measurements.

485 These corrections had little effect on the deviations for individual measurements however;
486 therefore, the estimated *precision* of the instrument still requires further refinement. In all but
487 one of the sample groups studied, the deviation of XRF analysis from the MS-determined
488 bromine content of the samples significantly exceeded a 95 % confidence interval. These
489 variations may be due to the elemental and chemical composition of individual samples
490 interfering with XRF analyses in ways unique to each sample. Additionally, as shown by the
491 occurrence of background interference in WEEE samples (*S4*), the penetration-depth of x-
492 rays is not finite as they permeate through thin plastic items to the substrate material thereby
493 skewing estimations of the sample's density by the instrument (*Section 3.2.1*).

494 As shown earlier, further uncertainties may be attributable in some cases to the presence in
495 samples of BFRs not targeted herein. The presence of these other BFRs (or other bromine-
496 based compounds) also acts as an obstacle to the more effective use of XRF an accurate
497 metric of POP-BFR concentrations (*Figure 1*). This is mainly due to the inherent lack of
498 selectivity of XRF, which renders it incapable of distinguishing between POP-BFRs and
499 other bromine-containing compounds contributing to the total Br concentration. The precise

500 detection of POP-BFRs by XRF will be exacerbated further by the presence of multiple BFRs
501 within the same sample-groups by the further-use of nBFRs.

502 Based on the present study, EPS and XPS constitute the groups which could most reliably
503 utilise XRF-quantified bromine as a surrogate for POP-BFRs *in situ* at recycling sites,
504 showing the highest number of samples with the lowest deviations from true bromine content.
505 Both groups would require specific calibration to compensate for matrix effects and improve
506 the overall accuracy of analyses. In its current state, XRF-determined bromine measurements
507 are unsuitable as a surrogate for POP-BFR determination in the remaining sample groups
508 investigated herein. Refinements to measurement protocols (*e.g.* material separation to avoid
509 background interference in WEEE) and the inclusion of reference standards specific to each
510 type of plastic could improve the accuracy of the XRF instrument. However, specific matrix
511 effects inherent in low density materials, varying chemical composition of the analyte
512 materials, and the presence of non-POP-BFRs, and the lack of specificity of XRF in
513 determining bromine species constitute substantial obstacles to the standalone use of XRF for
514 the accurate quantification of POP-BFRs in plastic media.

515

516 **5. Conclusions**

517 Our study clearly shows that portable XRF cannot be used to accurately determine absolute
518 concentrations of POP-BFRs. However, its use as a screening tool for LPCL compliance
519 appears to be viable, provided sufficient prior knowledge of typical BFR-treatment in
520 different plastics is available and the number of samples misclassified as exceeding LPCLs is
521 deemed acceptable or can be reduced. Of particular note is the applicability of XRF for
522 screening EPS and XPS materials above the proposed LPCL threshold (710 mg kg^{-1}) due to
523 the observed high precision shown for quantifying POP-BFRs in these materials. However,

524 the results obtained from the standalone use of XRF measurements as a surrogate for POP-
525 BFR determination in the other plastic types investigated agree with conclusions previously
526 reached by Gallen et al. (2014) and Petreas et al. (2016), namely that significant
527 inconsistencies between measurement techniques result in XRF alone being insufficient to
528 precisely determine BFRs, furthermore requiring MS to identify concentrations of specific
529 BFRs. Application of reference standards such as those utilized by Guzzonato et al. (2016)
530 can further enhance the accuracy of XRF as a surrogate measure of BFR concentrations.
531 Restricting screening solely to non-WEEE items further reduces the frequency of false
532 positives to 2.5 %. To ensure that waste plastics are being recycled effectively and safely, the
533 validity of XRF screening for compliance with LPCLs for POP-BFRs should remain an
534 ongoing field of investigation, in particular with respect to matrix effects and the need for
535 calibration standards, and the expected further use of NBFRs in recyclable plastics.

536 In summary, our study shows that while portable XRF may be used as a reliable (though not
537 infallible) “pass-fail” indicator of compliance with LPCLs for POP-BFRs. We also show that
538 refinements to measurement protocols (*e.g.* material separation to avoid background
539 interference in WEEE) and the inclusion of reference standards specific to each type of
540 plastic could potentially reduce the incidence of “false positives” resulting from use of
541 portable XRF, thereby diminishing the number of waste items incorrectly identified as
542 requiring special treatment.

543

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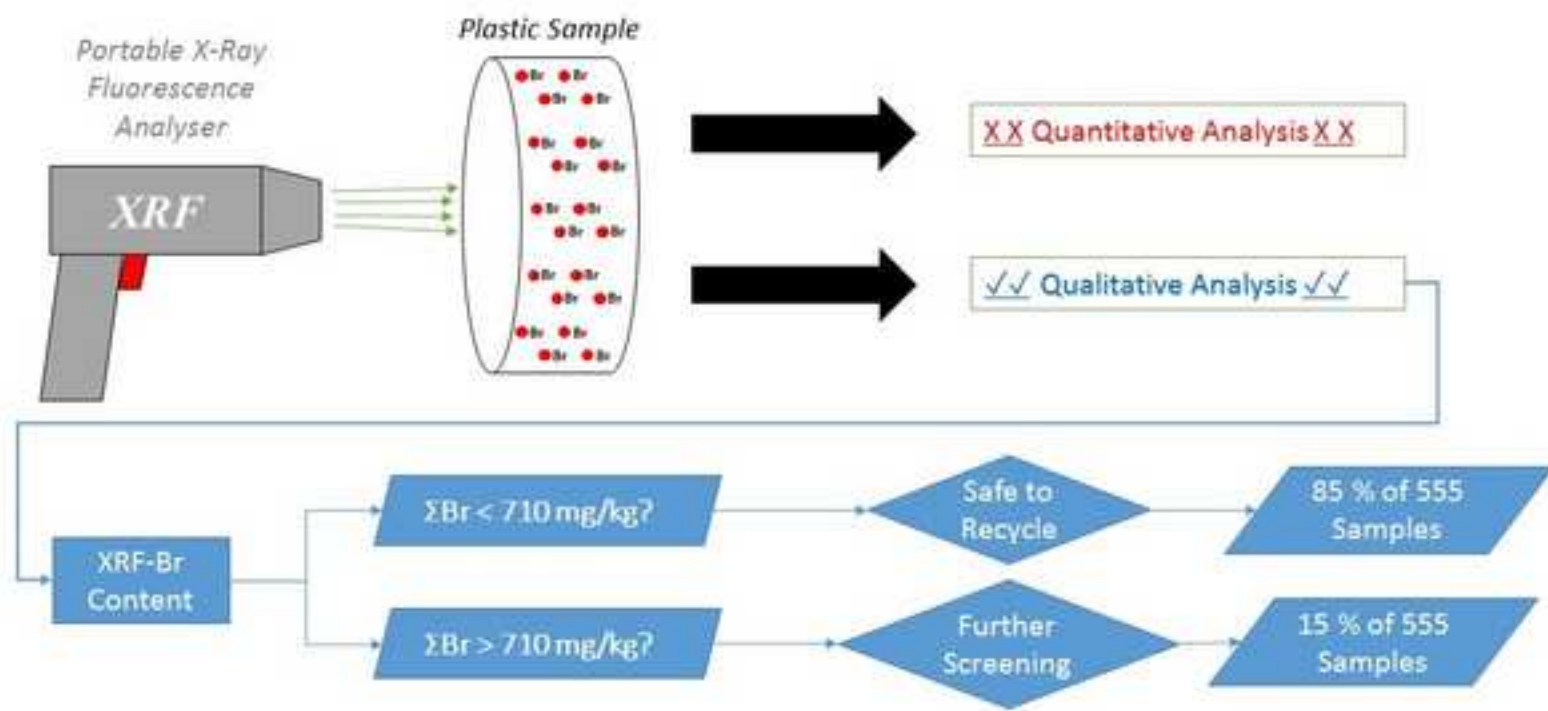
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649



Highlights

- XRF viable check of compliance of some waste categories within legislative limits
- XRF incorrectly reports legislative limits exceeded in only 6 % of samples
- Restricted to non-WEEE items, XRF incorrectly reports only 2.5 % of samples
- Accurate quantification of POP-BFRs via XRF not feasible for most waste types
- XRF quantification of POP-BFRs unreliable due to TBBP-A, NBFRs and matrix effects

1 Portable X-Ray Fluorescence for the Detection of POP-BFRs
2 in Waste Plastics

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12

13 **Abstract**

14 The purpose of this study was to establish the efficacy of portable x-ray fluorescence (XRF)
15 instrumentation as a screening tool for a variety of end of life plastics which may contain
16 excess amounts of brominated flame retardants (BFRs), in compliance with European Union
17 (EU) and United Nations Environment Programme (UNEP) legislative limits (low POP
18 concentration limits – LPCLs). 555 samples of waste plastics were collected from eight
19 waste and recycling sites in Ireland, including waste electrical and electronic equipment
20 (WEEE), textiles, polyurethane foams (PUFs), and expanded polystyrene foams. Samples
21 were screened for bromine content, *in situ* using a Niton™ XL3T GOLDD XRF analyser, the
22 results of which were statistically compared to mass spectrometry (MS)-based measurements
23 of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and
24 tetrabromobisphenol-A (TBBP-A) concentrations in the same samples.

25 Regression between XRF and MS for WEEE samples show that, despite an overall
26 favourable trend, large deviations occur for a cluster of samples indicative of other bromine-
27 based compounds in some samples; even compensating for false-positives due to background
28 interference from electronic components, XRF tends to over-estimate MS-determined BFR
29 concentrations in the 100 to 10,000 mg kg⁻¹ range. Substantial deviations were additionally
30 found between results for PUFs, textiles and polystyrene samples, with the XRF over-
31 estimating BFR concentrations by a factor of up to 1.9; this is likely due to matrix effects
32 influencing XRF measurements. However, expanded (EPS) and extruded polystyrene (XPS)
33 yielded much more reliable estimations of BFR-content due to a dominance of HBCDD in
34 these materials.

35 XRF proved much more reliable as a “pass/fail” screening tool for LPCL compliance
36 (including a prospective LPCL on Deca-BDE based on REACH). Using a conservative
37 threshold of BFR content exceeding legislative limits (710 mg kg⁻¹ bromine attributed to

38 penta-BDE), XRF mistakenly identifies only 6 % of samples (34/555) as exceeding
39 legislative limits.

40

41 **Keywords**

42 Waste Plastics; LPCL Screening; Quantification; PBDEs; HBCDD.

43

44 **1. Introduction**

45 Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two
46 groups of brominated flame retardants (BFRs) which have been extensively applied to
47 various commercial and consumer products to meet flammability standards. HBCDD has
48 been used as a flame retardant additive in expanded (EPS) and extruded (XPS) polystyrene
49 insulation foams as well as in high impact polystyrene (HIPS) for electrical housing and
50 junction boxes, as well as a textile coating agent for furniture and furnishings (Marvin et al.,
51 2011, UNEP, 2017b). Of the three commercial PBDE formulations, Penta-BDE is reportedly
52 almost exclusively used in polyurethane foams (PUFs) for domestic, office and automotive
53 applications, along with minor applications in printed circuit boards and microprocessors in
54 electrical and electronic equipment (EEE) (UNEP, 2010). Octa-BDE has been applied to
55 acrylonitrile butadiene styrene (ABS) and HIPS, largely used as casings for EEE (EC, 2011).
56 Deca-BDE was commonly used in coating agents applied to the surfaces of textiles and
57 upholstery as well as applied to HIPS for EEE as an additive compound (Weil and Levchik,
58 2009, IPCS, 1997). Over the last two decades however, concerns about their toxicity,
59 persistence and ability to bioaccumulate has led to their listing as persistent organic
60 Pollutants (POPs) under the Stockholm Convention. The commercial mixtures of Penta- and
61 Octa-BDE were listed in 2009 (UNEP, 2009), whilst HBCDD was listed in 2013 (UNEP,
62 2013), and the Deca-BDE commercial mixture listed in 2017 (UNEP, 2017a). Another
63 common legacy BFR, tetrabromobisphenol-A (TBBP-A), is also extensively used in as an
64 additive in HIPS and ABS and also reactively added to printed circuit boards for EEE (Morf
65 et al., 2003, IPCS, 1997). Though not currently under consideration for listing as a POP,
66 TBBP-A has been recently classified as H410 (very toxic to aquatic species), and listed as a
67 Class 2A carcinogen (Grosse et al., 2016, Malkoske et al., 2016). Additionally, waste articles

68 containing TBBP-A at concentrations in excess of 0.1 % is to be classified as “hazardous
69 waste” (EU, 2017b).

70 In the light of growing environmental concern, measures are being adopted in order to
71 prevent further environmental contamination from goods which were treated with POP-BFRs
72 (UNEP, 2009, EC, 2004). One such measure is the modification of recycling systems to
73 include screening procedures for goods suspected to contain high concentrations of POPs,
74 including POP-BFRs. Low POP concentration limits (LPCLs) of 1000 mg kg⁻¹ have been
75 established for each of the HBCDD, Penta-BDE and Octa-BDE commercial mixtures (EC,
76 2010, EC, 2016, EU, 2017a), in addition to a limit on Deca-BDE to come into force in 2019
77 (EU, 2017). However, a fast and cost-effective method of identifying products exceeding
78 these limits has not yet been identified, with industry standards (such as conventional
79 chromatographic-mass spectrometric techniques) being impractical for this purpose due to
80 their high running costs and low throughput.

81 Recently the use of portable x-ray fluorescence (XRF) measurements of elemental Br has
82 been suggested as a surrogate measure of POP-BFR concentrations. Several studies have
83 been performed to investigate the efficacy of portable XRF for the measurements of BFRs in
84 various plastic products, including EEE (Gallen et al., 2014, Aldrian et al., 2015, Guzzonato
85 et al., 2016) and furniture fabrics, foams and textiles (Petreas et al., 2016). Whilst these
86 studies have had varying degrees of success, they have all concluded that XRF-based
87 measurements are not capable of accurately quantifying concentrations of specific BFRs as
88 XRF measures elemental bromine only. However, Aldrian et al. (2015) and Petreas et al.
89 (2016) suggested that the use of XRF may be an effective screening tool for bromine content
90 in WEEE and furniture, as well as Schlummer et al. (2015) concluding effective screening
91 potential of HBCDD with the inclusion of an extraction process to distinguish the Br species.
92 Furthermore, Guzzonato et al. (2016) demonstrated that the accuracy of XRF measurements

93 of Br in ABS and HIPS may be improved by use of custom-made solid reference standards
94 containing Deca-BDE, and concluded that use of XRF to screen waste electrical and
95 electronic equipment (WEEE) for compliance with LPCLs was feasible. The largest recent
96 study (Sindikú et al., 2015) includes XRF screening in their methodology using varying
97 ranges of Br content, proving relatively successful in screening for BFR-content (with an
98 instrumental precision of $\pm 20\%$) but does highlight limitations in discerning the species of
99 bromine.

100 While the suitability of the XRF as a tool for predicting BFR concentrations has been
101 evaluated previously, many of the studies hitherto have been on a relatively small scale (<50
102 samples). Moreover, the range of plastics previously studied is limited to a few types and
103 applications or do not show in-depth comparisons of the accuracy and precision of XRF with
104 respect to MS analysis. In light of the introduction of LPCLs and the substantial mass of
105 waste polymers that will require screening for compliance with LPCLs (*e.g.* 42,628 tonnes of
106 WEEE collected in Ireland in 2013 (EPA, 2016)), it is vital that a rapid screening method is
107 developed to enable fast and reliable identification of waste items exceeding LPCLs.
108 Therefore the aims of this study are to (i) examine the efficacy of portable XRF
109 measurements as a predictor of BFR concentrations in a wide range of plastics in the waste
110 stream; and (ii) to determine whether portable XRF can be used as a “pass/fail” screening
111 tool for the interception of waste products exceeding LPCLs. These aims were achieved by a
112 large scale sampling campaign of recyclable plastics at waste and recycling sites in Ireland.
113 XRF measurements of bromine in a variety of waste articles (including WEEE plastics,
114 domestic and end of live vehicle (ELV) soft furnishings (PUF and upholstery fabrics) and
115 EPS/XPS insulation) were taken prior to quantitative analysis of selected BFRs via either
116 GC/MS or LC-MS/MS. To our knowledge, this is the first assessment of XRF as a tool for
117 monitoring compliance with LPCL legislation. Moreover, it represents the most

118 comprehensive assessment to date of the accuracy and suitability of hand-held XRF analysis
119 for quantification of BFR levels in waste articles.

120

121 **2. Materials and Methods**

122 ***2.1 Materials***

123 Chemical standards for native BDEs -28, -47, -77, -99, -100, -128, -153, -154, -183, -196, -
124 197, -203, -209, native α -HBCDD, β -HBCDD, γ -HBCDD, $^{13}\text{C}_{12}$ -BDE-209, $^{13}\text{C}_{12}$ - α -HBCDD,
125 $^{13}\text{C}_{12}$ - β -HBCDD, $^{13}\text{C}_{12}$ - γ -HBCDD, d_{18} - γ -HBCDD and $^{13}\text{C}_{12}$ -TBBP-A were purchased from
126 Wellington Laboratories (Guelph, ON, Canada). PCB-129 was purchased from Accustandard
127 (New Haven, CT, USA). All solvents (HPLC grade hexane, dichloromethane (DCM), iso-
128 octane and methanol) and sulfuric acid (>95 %) were purchased from Fisher Scientific
129 (Loughborough, UK).

130

131 ***2.2 Sample Collection and Field Measurement***

132 Samples were obtained from eight waste and recycling sites in Ireland and their bromine
133 concentrations measured *in situ* using a hand-held XRF device. Samples from a range of
134 different waste categories were collected: HIPS and ABS hard plastic casings from WEEE;
135 soft furnishings and textiles typical in both domestic and vehicular environments; and
136 polystyrene foams from building insulation and packaging materials. Following collection
137 and XRF analysis, destructive chemical analysis via GC-MS and LC-MS/MS was carried-out
138 on small sub-samples taken from the same parent product, within the immediate vicinity of
139 the area subjected to XRF analysis. This was performed to evaluate the accuracy with which

140 the XRF-determined bromine concentrations correlated with those of GC/MS or LC-MS/MS
141 measurements of selected BFRs.

142 In total, matched Br and BFR measurements were obtained for 555 samples; *Table 1* provides
143 an overview of the number of samples collected from each “waste type”. Following on-site
144 use of the XRF instrument, small sections of the scanned areas (~1-2 cm² for HIPS/ABS,
145 upholstery and textiles, or ~ 1-2 cm³ for polystyrene and PUF) were subsequently removed
146 and individually stored in labelled polyethylene bags. These collected samples were then
147 shipped to the University of Birmingham where concentrations of POP-BFRs and TBBP-A
148 were determined.

149

150 **2.3 XRF Analysis**

151 Each measurement involved placing the XRF instrument directly on to the measurement
152 surface, with the operator standing directly behind the instrument for the duration of the
153 measurement. As per Niton UK guidelines on the use of the device, secondary x-rays
154 projected from the specimen deviate at angles around the device (mostly laterally) as well as
155 at much lower intensities than primary x-rays, thus attenuating rapidly. Using the secondary
156 dose rates produced during plastics mode of operation, on plastic materials, and with varying
157 substrates (air, concrete, wood, etc.), the maximum dose for the user (at the device’s trigger)
158 was calculated for the sum of all measurements carried out and found to be well-below the
159 annual dose for a category B radiation worker (*i.e.* <20 mSv in any single year).

160 Determination of total bromine content in the samples was carried out *in situ* using a *Niton*
161 *XLt3-900 GOLDD X-Ray Fluorescence Analyser*. Calibration was performed by Niton UK
162 using proprietary standards containing varying concentrations of relevant inorganic
163 compounds in a polymer matrix. Quantification and qualification of bromine for the Niton

164 XL3t model are achieved using the K α_1 line (11.9242 eV) and K α_2 line (11.8776 eV)
165 respectively. The instrument was operated in the “plastics” mode of operation, which
166 optimises the instrument’s settings for interaction of x-rays with low density polymer
167 materials and quantification of specific elements in their matrices. Standard analyses using
168 the XRF instrument in this mode gives a 95 % confidence interval ($CI = \pm 2\sigma$) with each
169 measurement taken. The duration of analysis ranged from 30 to 105 seconds with longer
170 iterations required to improve instrumental uncertainty in samples with high bromine content
171 and for samples comprising of low density materials (Zawisza, 2012).

172 For HIPS, ABS and insulation foam samples, the surface of the material was wiped with a
173 clean non-fibrillating tissue prior to analysis, in order to remove sediment and dust which
174 could interfere with the instrument’s primary x-rays or may contain traces of bromine. A
175 thickness correction of 2 mm was additionally applied to the HIPS and ABS samples to help
176 account for the finite thickness of the samples (per manufacturer guidelines); this reduces the
177 risk of interference from substrate materials as the instrument internally estimates the density
178 of an analyte based on Compton scattering of primary x-rays. The instrument window was
179 then placed flat against the sample surface and a measurement of bromine content carried out
180 (with a minimum thickness of 10 cm for insulation samples and as presented at
181 approximately 2 mm for HIPS and ABS samples). Upholstery and other soft furnishings were
182 manually folded, compressed to a thickness of approximately 3 cm (to achieve the thickness
183 required for said materials for full attenuation of primary x-rays, per instrument manufacturer
184 guidelines) and held in place by placing the instrument over the sample, in order to increase
185 the density of the active analysis zone. Three repeat measurements were carried out on each
186 sample, several centimetres apart from each scanning point and at varying orientations. These
187 repeat measurements were required to be carried out on the same plastic panel/area and under

188 the same experimental conditions in order to detect instances of heterogeneous distribution of
189 BFRs within the body of sample.

190 Additional XRF measurements of bromine concentrations on available sub-samples of WEEE
191 HIPS and ABS samples (i.e. those aliquots removed for BFR determination) were carried out
192 in a controlled laboratory setting. These measurements were made in order to determine the
193 instances where bromine detected during field measurements were due to background
194 interference, being attributed to the presence of bromine in underlying electronic components
195 rather than from the polymeric casing itself.

196

197 ***2.4 Extraction and Clean-Up***

198 For quantitative analysis of BFRs, samples were extracted and cleaned according to methods
199 previously described (Abdallah et al., 2017). Briefly, aliquots of samples (20-100 mg) were
200 cut with a retractable blade and weighed directly into a 15 mL glass centrifuge tube and
201 spiked with 20 ng of BDEs -77 and -128, $^{13}\text{C}_{12}$ - α -, $-\beta$ -, and γ -HBCDD, $^{13}\text{C}_{12}$ -TBBP-A, and 40
202 ng $^{13}\text{C}_{12}$ -BDE-209 as internal standards. Approximately 3 mL of dichloromethane (DCM)
203 was added to the aliquot and vortexed for 2 minutes, followed by 30 minutes sonication. The
204 extraction process was repeated three times with the combined extracts collected in a separate
205 glass centrifuge tube. Crude extracts were concentrated under a gentle stream of N_2 to near-
206 dryness and reconstituted in 2 mL hexane. Extracts were washed with >95 % sulfuric acid
207 and supernatant organic layer was collected and concentrated to near-dryness under a gentle
208 N_2 stream. Samples were reconstituted in 200 μL of iso-octane containing 0.2 ng μL^{-1} PCB-
209 129 as a recovery standard. After determination of PBDEs via GC-MS, extracts were
210 reconstituted in methanol containing 0.2 ng μL^{-1} d_{18} - γ -HBCDD for determination of
211 HBCDDs and TBBP-A via LC-MS/MS analysis.

212

213 **2.5 Mass Spectrometric Analysis**

214 Quantitative analysis of PBDEs was performed in a single injection on a ThermoFisher Trace
215 1310 gas chromatograph coupled to a ThermoFisher ISQ mass spectrometer (MS). The MS
216 was operated in electron ionisation mode using selective ion monitoring (SIM). One μL of
217 the purified extract was injected for analysis using a programmable temperature vapouriser
218 (PTV) onto a Restek Rxi-5Sil MS column (15m x 0.25 mm x 0.25 μm film thickness).
219 Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1} . Full GC/MS parameters
220 have been reported previously (Abdallah et al., 2017).

221 HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid
222 chromatograph equipped with a Sil-20A auto sampler and a DGU-20A3 vacuum degasser
223 coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was
224 achieved using Agilent Pursuit XRS3 C18 column (150 mm x 2 mm, I.D., 3 μm particle size)
225 and a mobile phase of (a) 1:1 methanol/water and (b) methanol at a flow rate of $180 \mu\text{L min}^{-1}$.
226 Molecular ionisation was achieved using an electrospray ionisation (ESI) source operated in
227 negative ion mode. The MS/MS was operated in the multiple reaction monitoring (MRM)
228 mode. The MRMs transitions monitored were on m/z $640.6 \rightarrow 79$, m/z $652.4 \rightarrow 79$ and m/z
229 $657.7 \rightarrow 79$ for the native and the $^{13}\text{C}_{12}$ -labelled HBCDD diastereomers respectively and
230 $540.8 \rightarrow 79$, m/z $552.8 \rightarrow 79$ were used to monitor native and $^{13}\text{C}_{12}$ -labelled TBBP-A. Full
231 LC-MS/MS parameters have been reported previously (Abdallah et al., 2008).

232

233 **2.6 Quality Assurance/Quality Control**

234 For BFR analysis, a reagent blank consisting of 100 mg of anhydrous sodium sulfate was
235 analysed with every batch of 11 samples. "Control" samples were created using plastics and

236 textiles that contain no BFRs and were also analysed throughout the study; three Controls
237 were assessed for each matrix. None of the target compounds were found above the limits of
238 detection in the blanks. Therefore results were not corrected for blank residues and method
239 limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise
240 ratio (S/N) of 3:1 and 10:1 respectively.

241 Method accuracy and precision was assessed via repeated analysis of certified reference
242 materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to
243 textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been
244 previously measured by this laboratory and another. All values were found to be close to
245 certified or indicative levels, with a relative standard deviation of <15 % (Abdallah et al.,
246 2017).

247

248 ***2.7 Exclusion Criteria for Regression Analysis***

249 The regression analysis comprised a comparison between XRF-determined bromine, and the
250 equivalent bromine concentrations attributed to quantified BFRs (see supporting information,
251 S2). However, the accuracy of the XRF instrument must be taken into consideration for the
252 regression between its results of bromine concentrations and those from the mass
253 spectrometric analyses. The XRF instrument displays as a 95 % confidence interval or ± 2
254 standard deviations ($\pm 2\sigma$) for each analysis carried out; although this value can be altered, it
255 provides a sufficiently concise confidence interval to establish the stability of analyses.

256 During the analysis of EPS and XPS foam samples using the XRF device, a $\pm 2\sigma$ interval as
257 high as 16 mg kg^{-1} bromine occurred with a “null” reading (i.e. the value determined by the
258 XRF instrument was $0 \pm 16 \text{ mg kg}^{-1}$), thus a conservative 20 mg kg^{-1} value was chosen as the
259 XRF analyser’s limit of detection (LOD_X). For the remaining polymeric materials – PUF,

260 HIPS, ABS, upholstery, textiles – a LOD_x of 10 mg kg^{-1} was chosen using the same criteria
261 as established for XPS and EPS samples (with a $\max \pm 2\sigma$ interval of 8 mg kg^{-1} for these
262 sample groups). Therefore, in instances where each of the triplicate XRF measurements
263 conducted on each sample fell below the LOD_x , that sample was not considered for the
264 regression analysis. If, however, one of the triplicate measurements was above the LOD_x
265 (and even if the average was below), the sample was included, in consideration of possible
266 non-uniform BFR distribution throughout the body of the sample.

267

268 **3. Results**

269 ***3.1 Total Bromine Concentrations Determined by XRF Analyses***

270 *Table 1* shows a summary of the bromine concentrations quantified using the XRF during *in*
271 *situ* analyses. Highest bromine concentrations were detected in the WEEE waste category at
272 $110,000 \text{ mg kg}^{-1}$ and $150,000 \text{ mg kg}^{-1}$ in IT & Telecoms and Display samples respectively.
273 Very high concentrations (exceeding $10,000 \text{ mg kg}^{-1}$) were also detected in the Furniture
274 Upholstery, ELV Upholstery, and ELV (other) sample groups. The Fridge/Freezer, Curtain,
275 C&D XPS, Mattress Foam and Mattress Upholstery sample groups showed very low
276 maximum Br concentrations ($< 1,000 \text{ mg kg}^{-1}$) along with low median and mean values. This
277 indicates that these sample groups underwent low levels of treatment with bromine-
278 containing compounds, and/or experienced transfer of bromine-containing compounds while
279 in use or during storage for recycling/transfer (Rauert et al., 2014). The remaining sample
280 groups showed maximum bromine content between $1,000$ and $10,000 \text{ mg kg}^{-1}$ which, along
281 with the aforementioned groups with concentrations in samples reaching roughly $150,000 \text{ mg}$
282 kg^{-1} Br, demonstrates potential from some articles in these groups to exceed LPCLs.
283 However, as is evidenced by the low median concentrations for the sample groups relative to

284 the maximum values, samples with excessively high concentrations of bromine make up a
285 minority of each remaining sample group. This indicates a relatively low proportion of waste
286 articles potentially treated with POP-BFRs in these sample groups (with the possible
287 exception of Display, Furniture Foam, Furniture Upholstery, and Vehicle Foam samples
288 groups).

289 We have additionally observed so-called “false-positives” in different waste categories. A
290 “false positive” corresponds to a situation where the XRF measurement of Br indicates the
291 LPCL for a POP-BFR to be exceeded, but the POP-BFR concentration is below the LPCL.
292 By comparison, a “false negative” would occur where the POP-BFR concentration is above
293 the LPCL, but this is not indicated by the XRF measurement of Br. These occurrences will be
294 reported by waste category in the following sections.

295

296 ***3.2 XRF – MS Total Bromine Measurement Comparison***

297 Concentrations of BFRs in the samples included in this study have been previously reported
298 by Drage et al. (2018). For comparison with XRF measurements they have been briefly
299 outlined in *Table 1*. Additionally, following MS-analysis of the collected samples, some
300 sample groups including the Mattress, Curtain, Carpet, ELV (other), Fridge/Freezer, and ELV
301 (other) sample groups showed either no excessive concentrations of BFRs or very few
302 samples with excess concentrations. These groups were therefore considered unsuitable to act
303 as comparative metrics for regressions between MS and XRF analyses.

304 ***3.2.1 – WEEE Hard Plastics***

305 In addition to the 65 WEEE samples excluded based on $Br < LOD_x$ (*Section 2.7*), a further 15
306 samples were omitted from the regression analysis due to laboratory confirmation of a
307 background interference during *in situ* measurements of the samples (*Section 2.3*). *Table 2*

308 shows the results obtained for these 15 samples, comparing the average of the on-site
309 triplicate XRF measurements to lab-based duplicate XRF measurements, the latter more
310 accurately equating to the actual concentrations of bromine in the samples.

311 Application of this additional exclusion criterion yielded a final data set of 70 ABS/HIPS
312 samples remaining for regression analysis, the result of which is shown in *Figure 1*. The
313 linear regression coefficient (slope, m) is 0.98 and the coefficient of determination (R^2) is
314 0.614. However, a notable cluster of samples ($n = 10$) show much higher concentrations of
315 bromine as determined by XRF analysis compared to the concentrations determined by
316 GC/MS / LC-MS/MS analysis (defined here as “true” Br content). *Figure 2 (a)* is a Bland-
317 Altman plot showing the variation in the Br content determined via XRF analysis as a
318 percentage of true Br content $[(XRF-MS)/MS] \times 100$, where it can be seen that these
319 outliers show at least a 4.9-fold overestimation of “true” Br content (z -test, $p < 0.001$)
320 compared to a maximum of 2.4-fold overestimation in the remainder. It is likely therefore
321 that these samples contained bromine in BFR-type chemicals other than those analysed for by
322 the MS methods used herein, such as BTBPE, tetrabromophthalic acid, and DPDPE (Al-
323 Omran and Harrad, 2016, Petty et al., 2016, IPCS, 1997).

324 *Figure 2 (b)* highlights large variations still exist between Br concentrations obtained for the
325 same samples via the two measurement techniques. Samples with similar concentrations of
326 BFRs show varying deviations between the techniques such that even employment of a
327 correction factor would have limited success in improving the regression, across all
328 concentrations shown herein. For example, samples with total Br concentrations ranging
329 between 100 and 1,000 mg kg^{-1} show deviations from -3 % to +250 % between the analysis
330 techniques for approximately 60 % of all WEEE samples therein. These variations may in
331 part be due to the presence of NBFRs alongside TBBP-A, HBCDD and PBDEs, reflecting the

332 XRF instrument's inability to specify the precise chemical form of bromine present in
333 samples.

334 3.2.2 – Furniture and Vehicle Foam

335 The XRF and MS derived concentrations of Br in 43 PUF samples are compared (*Figure 3*)
336 showing a slope of 1.70 and a R^2 value of 0.98. The high regression coefficient for these
337 samples is likely the result of interferences with primary and secondary x-rays in the high
338 thickness and low density of the PUF samples examined. Internal XRF approximations of the
339 sample's density using Compton scattering can be heavily influenced due to the presence of
340 air pockets in the samples, leading to a significant bias in the accurate quantification of
341 elemental bromine (and other elements) (Zawisza, 2012). However, assuming these biases are
342 relatively consistent throughout different PUF samples, measured results can be subsequently
343 multiplied by a correction factor derived from the inverted slope of linear regression to
344 correct this bias.

345 Although this correction factor ($\mu_{\text{puf}} = 1.70^{-1} = 0.59$) can improve the accuracy of the XRF-
346 measurements, its precision in the analysis of PUF samples remains unreliable, with relative
347 standard deviation (RSD) for individual measurements ranging from 1 % to 172 % ($\text{RSD}_{\text{avg}} =$
348 39 %). In addition, repeated XRF analyses of PUF samples on a dedicated test stand in a
349 controlled laboratory setting showed high variability in Br content depending on the
350 orientation of the sample and the surface facing the analyser window. It was observed upon
351 repeated laboratory measurements of eight furniture foam samples whose XRF results
352 deviated by >250 % from the corresponding MS-concentrations, that five of the samples had
353 shown substantial differences (z-test, $p < 0.001$) in the detected concentration of bromine on
354 surfaces which were cut away from the body of the PUF item compared to the surface
355 adjacent to the upholstery (*S1 (a), S4*). This – akin to previous observations of BFR migration

356 from fabric to dust via direct contact (Rauert et al., 2016) is consistent with migration of
357 BFRs from overlying upholstery fabric into underlying PUF, resulting in higher
358 concentrations of BFRs in PUF near contact surfaces and spatially declining concentrations
359 deeper within the material.

360 3.2.3 – Furniture and Vehicle Upholstery

361 For the regression of the 66 upholstery samples included a slope of 1.38 and a R^2 of 0.86
362 were determined (*S5 (a)*), indicating a strong correlation between the analytical techniques.
363 Similar to the PUF samples, the upholstery samples also appear to require a correction factor
364 ($\mu_{\text{upholstery}} = 1.38^{-1} = 0.72$) in order to account for the relatively low density of the material and
365 the resultant matrix effects. However, a Bland-Altman plot similar to *Figure 2 (a)*
366 demonstrated the XRF's overestimation of bromine concentrations by up to 180 % for
367 concentrations exceeding 100 mg kg^{-1} and several thousand percent for lower concentrations.
368 This phenomenon may simply be more obscured at larger concentrations due to the
369 magnitude of concentrations involved and also possibly due to a “screening-effect” within the
370 matrix of the material during XRF analysis, whereby multiple bromine atoms are in a linear
371 formation with respect to the analyser resulting in only the first and none of the subsequent
372 bromine atoms being detected (Zawisza, 2012).

373 The relative homogeneity of repeated XRF measurements and the high discrepancies between
374 Br concentrations obtained via the two measurement techniques revealed in the Bland-
375 Altman plot (*S1 (b)*), are – as for PUF materials – likely attributable to the presence of BFRs
376 not measured in this study or, in the case of some ELV samples containing green upholstery,
377 the use of green pigment containing bromine. In similar fashion to WEEE samples (*Section*
378 *3.2.1*), only 25 % of samples yielded Br concentrations derived by XRF that agreed within
379 ± 25 % of those obtained via MS (following application of the correction factor). However,

380 given the high treatment concentrations with HBCDD and Deca-BDE, the XRF could still be
381 successfully applied to the screening of upholstery for excess POP-BFRs as false-positives
382 (instances where XRF analysis indicates exceedance of an LPCL where none actually
383 occurred) at such elevated bromine concentrations were rare in this study.

384 3.2.4 –Insulation Foams - Expanded Polystyrene (EPS)

385 Of the 47 original EPS samples, 17 were excluded from the analysis due to determination of
386 Br concentrations below LOD_x . Br concentrations obtained for the remaining samples via
387 XRF and MS underwent regression analysis (*Figure 4*) showing a linear slope of 1.20 and R^2
388 of 0.98. The XRF measurements again appear to require a calibration factor in order to
389 correct the regression for offsets caused by matrix effects. Implementing this, XRF
390 measurements of 16 out of 30 samples correlate to within 25 % of MS results with 12 of these
391 16 (for which Br $>1000 \text{ mg kg}^{-1}$) agreeing to within 10 % of MS-determined bromine
392 content.

393 Despite this favourable agreement for samples containing higher Br concentrations (i.e.
394 $>1000 \text{ mg kg}^{-1}$) analysis of the data using a Bland-Altman plot (*SI (c)*) reveal potentially
395 significant outliers in this sample group most notably in the 0-10 mg kg^{-1} Br concentration
396 range (z-test, $p < 0.05$), as determined by MS analysis, despite exclusion of samples $<LOD_x$.
397 Additionally, the relative standard deviations (RSDs) of the triplicate XRF measurements
398 indicate that the samples showing poor agreement between XRF and MS have large RSDs
399 ($>25 \%$) between the individual XRF measurements, the largest RSDs (173 % each) being
400 attributed to the significant outliers highlighted in *SI (c)*. Selection criteria for more accurate
401 categorisation of Br concentrations can potentially be established from these observations;
402 specifically, omission of samples with 0-10 mg kg^{-1} Br-content (from MS analysis) and those

403 with RSDs over 25 % (from triplicate XRF analysis, results in over 80 % of samples being
404 categorised as accurate to within 10 % of the true HBCDD concentration.

405 One noteworthy EPS sample showed a much larger discrepancy between XRF-determined
406 bromine (average bromine = 3354 mg kg⁻¹; RSD = 12 %) and LC-MS/MS (total bromine =
407 1030 mg kg⁻¹) analyses. Repeat XRF measurements of the same sample in-lab yielded an
408 average for four measurements of 4275 mg kg⁻¹ bromine with a RSD of 19 % – the higher
409 RSD being attributable to the small sample size relative to the XRF measurement window,
410 such that primary x-rays are not interacting with the target sample. Such a variation between
411 XRF-determined- and LC-MS/MS-determined bromine did not occur in any other samples
412 within this group, potentially indicating another bromine-based compound in this particular
413 sample, such as tribromoallylether or PolyFR (Schlummer et al., 2015, IPCS, 1997).

414 3.2.5 –Insulation Foams - Extruded Polystyrene (XPS)

415 The linear regression for the 20 XPS samples for which XRF- and MS-derived Br
416 measurements were compared (*S5 (b)*) shows a linear slope of 1.93 with a R² of 0.97. This
417 sample group shows the largest deviation from a unity regression. Following correction, a
418 Bland-Altman plot (*SI (d)*) shows an even distribution for samples for containing >200 mg
419 kg⁻¹ bromine. However, the variation between the two Br metrics at concentrations up to 200
420 mg kg⁻¹ remains high (± 100 %).

421 This sampling, however, contained only a few with excessive concentrations of BFRs, and
422 too few overall for a more definitive linear regression. Relatively few samples have been
423 treated with BFRs and generally at much lower concentrations and other waste categories
424 based on this sampling. However, a more statistically significant sample size may reveal as
425 yet unseen nuances to this plastic.

426

427 **4. Discussion**

428 ***4.1 Utility of XRF Instrumentation as a Pass/Fail Screening Tool for LPCL Compliance***

429 In the context of portable XRF's potential use as a tool for testing compliance with POP-BFR
430 LPCL values, the incidence of "false positives" and "false negatives" is crucial. A "false
431 positive" is defined here as a specific source misclassification scenario, i.e. a situation where
432 the XRF measurement of Br indicates the LPCL for a POP-BFR to be exceeded, but the POP-
433 BFR concentration is below the LPCL. By comparison, a "false negative" occurs where the
434 POP-BFR concentration is above the LPCL, but this is not indicated by the XRF
435 measurement of Br (*Section 3*). For the purposes of discussion here, we have assumed a
436 conservative Br LPCL value based on the Br detected being due to penta-BDE. Thus, any
437 sample exceeding 710 mg Br/kg is assumed here to exceed the POP-BFR LPCL of 1,000 mg
438 POP-BFR/kg (including 1000 mg kg⁻¹ limit for Deca-BDE established by REACH).

439 Of the 555 items we tested, there were 34 false positives and no false negatives when the
440 current LPCLs for POP-BFRs are considered: 26 occurred in WEEE items (1 large household
441 appliance, 12 display items, 6 small domestic appliances, and 7 IT items); the remainder, in 2
442 vehicle fabric samples, 1 vehicle foam sample, 1 carpet sample, 1 mattress foam sample, 1
443 furniture upholstery sample, and 2 furniture foam samples. These resulted from
444 concentrations >1,000 mg kg⁻¹ of either TBBP-A alone (n=15), as yet unidentified bromine-
445 containing compounds (n=11), and in 8 instances enhancement of measured BFR
446 concentrations. However, 5 of the 11 samples with unidentified compounds are attributable to
447 false-positives due to background interference (*Section 3.2.1*) which therefore reduces the
448 number of false-positives to 29 of 555. Translating these incidences into percentages, our
449 data show that use of portable XRF to monitor compliance with current LPCLs for PBDEs
450 and HBCDD would mean that 5.2 % of articles from the waste categories studied would be

451 incorrectly identified as requiring special treatment. This compares to 47 (8.5 %) of articles
452 identified as genuinely exceeding current LPCLs and REACH limits.

453 The implications of such false positives are essentially that a small additional percentage of
454 articles will not be available for recycling and that there will be an additional unnecessary
455 economic cost incurred when such articles are subjected to special treatment. Balanced
456 against these issues, it may be argued that as the cause of the false positives are likely to be
457 either known or unidentified BFRs not targeted in our study, which may themselves become
458 subject to future legislative restriction; false positives can potentially be viewed as an
459 acceptable limitation of the use of XRF as a screening tool for LPCL compliance. By
460 comparison, false negatives would exert a more detrimental impact as they would allow
461 regulated POP-BFRs to remain in circulation. However, the absence of false negatives in our
462 study, suggests that use of hand-held XRF will only very rarely – if ever - fail to identify
463 articles that exceed LPCL values.

464 Our data on false positives indicate that portable XRF could be a viable tool for testing
465 compliance with LPCLs for EPS/XPS, as well as ELV waste and waste soft furnishings,
466 while further underlining the potential issues with the use of hand-held XRF to test for LPCL
467 compliance in WEEE due to the more frequent presence of TBBP-A and other as yet
468 unidentified compounds in such items.

469

470 ***4.2 Accuracy and Precision of XRF-Determined Bromine as a Surrogate for POP-BFRs***

471 Upon comparing the results of total Br from portable XRF analysis with compound-specific
472 mass spectrometry, the overall *accuracy* of XRF strongly depends on the type of polymer
473 under investigation. Though the regression of all sample-groups appears to follow a generally
474 linear correlation between XRF and MS results, the deviation of the slopes from unity in most

475 of the plastic types indicates that matrix effects occur prominently in low-density materials.
476 Br concentrations obtained from XRF measurements were adjusted based on subsequent
477 mass spectrometric analyses of the same samples thus allowing for a correction factor to be
478 inferred (*Section 3.2*). However, for use of this instrument as a standalone analyser for
479 accurately quantifying total bromine concentrations in the range of materials studied here,
480 suitable calibration standards unique to each type of polymer (ABS, HIPS, PUF, etc.) would
481 initially be required to ensure reliable compensation for matrix effects. Application of
482 correction factors to XRF measurements discerned following MS analysis was successful in
483 correcting the overall accuracy of the instrument for all measured concentrations, with little
484 effect on the deviations for individual measurements.

485 These corrections had little effect on the deviations for individual measurements however;
486 therefore, the estimated *precision* of the instrument still requires further refinement. In all but
487 one of the sample groups studied, the deviation of XRF analysis from the MS-determined
488 bromine content of the samples significantly exceeded a 95 % confidence interval. These
489 variations may be due to the elemental and chemical composition of individual samples
490 interfering with XRF analyses in ways unique to each sample. Additionally, as shown by the
491 occurrence of background interference in WEEE samples (*S4*), the penetration-depth of x-
492 rays is not finite as they permeate through thin plastic items to the substrate material thereby
493 skewing estimations of the sample's density by the instrument (*Section 3.2.1*).

494 As shown earlier, further uncertainties may be attributable in some cases to the presence in
495 samples of BFRs not targeted herein. The presence of these other BFRs (or other bromine-
496 based compounds) also acts as an obstacle to the more effective use of XRF an accurate
497 metric of POP-BFR concentrations (*Figure 1*). This is mainly due to the inherent lack of
498 selectivity of XRF, which renders it incapable of distinguishing between POP-BFRs and
499 other bromine-containing compounds contributing to the total Br concentration. The precise

500 detection of POP-BFRs by XRF will be exacerbated further by the presence of multiple BFRs
501 within the same sample-groups by the further-use of nBFRs.

502 Based on the present study, EPS and XPS constitute the groups which could most reliably
503 utilise XRF-quantified bromine as a surrogate for POP-BFRs *in situ* at recycling sites,
504 showing the highest number of samples with the lowest deviations from true bromine content.
505 Both groups would require specific calibration to compensate for matrix effects and improve
506 the overall accuracy of analyses. In its current state, XRF-determined bromine measurements
507 are unsuitable as a surrogate for POP-BFR determination in the remaining sample groups
508 investigated herein. Refinements to measurement protocols (*e.g.* material separation to avoid
509 background interference in WEEE) and the inclusion of reference standards specific to each
510 type of plastic could improve the accuracy of the XRF instrument. However, specific matrix
511 effects inherent in low density materials, varying chemical composition of the analyte
512 materials, and the presence of non-POP-BFRs, and the lack of specificity of XRF in
513 determining bromine species constitute substantial obstacles to the standalone use of XRF for
514 the accurate quantification of POP-BFRs in plastic media.

515

516 **5. Conclusions**

517 Our study clearly shows that portable XRF cannot be used to accurately determine absolute
518 concentrations of POP-BFRs. However, its use as a screening tool for LPCL compliance
519 appears to be viable, provided sufficient prior knowledge of typical BFR-treatment in
520 different plastics is available and the number of samples misclassified as exceeding LPCLs is
521 deemed acceptable or can be reduced. Of particular note is the applicability of XRF for
522 screening EPS and XPS materials above the proposed LPCL threshold (710 mg kg^{-1}) due to
523 the observed high precision shown for quantifying POP-BFRs in these materials. However,

524 the results obtained from the standalone use of XRF measurements as a surrogate for POP-
525 BFR determination in the other plastic types investigated agree with conclusions previously
526 reached by Gallen et al. (2014) and Petreas et al. (2016), namely that significant
527 inconsistencies between measurement techniques result in XRF alone being insufficient to
528 precisely determine BFRs, furthermore requiring MS to identify concentrations of specific
529 BFRs. Application of reference standards such as those utilized by Guzzonato et al. (2016)
530 can further enhance the accuracy of XRF as a surrogate measure of BFR concentrations.
531 Restricting screening solely to non-WEEE items further reduces the frequency of false
532 positives to 2.5 %. To ensure that waste plastics are being recycled effectively and safely, the
533 validity of XRF screening for compliance with LPCLs for POP-BFRs should remain an
534 ongoing field of investigation, in particular with respect to matrix effects and the need for
535 calibration standards, and the expected further use of NBFRs in recyclable plastics.

536 In summary, our study shows that while portable XRF may be used as a reliable (though not
537 infallible) “pass-fail” indicator of compliance with LPCLs for POP-BFRs. We also show that
538 refinements to measurement protocols (*e.g.* material separation to avoid background
539 interference in WEEE) and the inclusion of reference standards specific to each type of
540 plastic could potentially reduce the incidence of “false positives” resulting from use of
541 portable XRF, thereby diminishing the number of waste items incorrectly identified as
542 requiring special treatment.

543

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649

TABLES*Table 1 – Statistical summary of total XRF-Br and MS-BFR concentrations categorized by Waste Type.*

Waste Type	Sample Group	Total No. of Samples (N)	XRF-Br Range (mg kg⁻¹)	XRF-Br Median (mg kg⁻¹)	MS-ΣBFRs Range (mg kg⁻¹)	MS-ΣBFRs Median (mg kg⁻¹)	Number of Samples for Regression
<i>Waste Electrical and Electronic Equipment (WEEE)</i>	<i>IT & Telecoms *</i>	78	0 – 110,000	18	0 – 110,000	0.5	36
	<i>Small Domestic Appliances *</i>	26	0 – 1,900	1	0 – 10,000	0.1	7
	<i>Display *</i>	43	0 – 150,000	320	0 – 270,000	58	27
	<i>Large Household Appliances</i>	57	0 – 2,100	0	0 – 2,000	0.04	0
	<i>Fridge/Freezer</i>	30	0 – 14	0	0 – 3.6	0	0
<i>Expanded Polyurethane Foams</i>	<i>Furniture Foam *</i>	20	0 – 12,000	110	0 – 8,500	100	17
	<i>Mattress Foam</i>	17	0 – 880	59	0 – 870	8.4	0
	<i>ELV Foam *</i>	38	0 – 780	14	0 – 740	1.6	26
<i>Fabrics & Upholstery</i>	<i>Furniture Upholstery *</i>	22	0 – 87,000	320	0 – 73,000	112	17
	<i>Mattress Upholstery</i>	17	0 – 240	10	0 – 58	8.7	0
	<i>ELV Upholstery *</i>	50	0 – 35,000	72	0 – 31,000	17	49
<i>Construction & Demolition</i>	<i>C&D EPS *</i>	40	9,200	45	0 – 10,000	83	27
	<i>C&D XPS *</i>	20	160	23	0 – 94	20	16
<i>Packaging</i>	<i>Pack EPS *</i>	7	0 – 5,600	18	0 – 5,900	1.1	3
	<i>Pack XPS *</i>	14	0 – 1,300	2	0 – 370	0.2	4
<i>Other Textiles & Plastics</i>	<i>ELV (other)**</i>	30	0 – 28,000	12	0 – 23,000	3.8	0
	<i>Curtain</i>	15	0 – 88	3	0 – 58	0	0
	<i>Carpet</i>	31	0 – 9,600	8	0 – 7,000	0.1	0

* *Sample-groups included for regression analysis (see Section 3.2).*

** *Sample-group consists of plastics from roof trim, floor mats, under seat EPS padding, etc. thus making it unsuitable for regression of similar materials.*

1 **Figure Captions**

2 *Figure 1* Regression between total Br concentrations (mg kg^{-1}) measured by XRF and
3 GC/MS / LC-MS/MS for 70 WEEE samples (slope $m = 0.98$, $R = 0.78$, $R^2 =$
4 0.61). Data represented by “x” symbols (inset outlined portion) show samples
5 suspected of having NBFs or other bromine-containing compounds. Omitting
6 those data yields $m = 0.91$, $R = 0.96$, $R^2 = 0.93$.

7 *Figure 2 (a)* Bland-Altman plot for WEEE samples showing the deviation of XRF-
8 determined Br from MS-quantified Br (%), with the latter assumed to
9 represent true Br values (mg kg^{-1}).

10 *Figure 2 (b)* Exploded view of data from Figure 2 (a) highlighting samples in lower
11 deviation bracket and omitting those outliers attributed to NBF presence as
12 outlined in Figure 1.

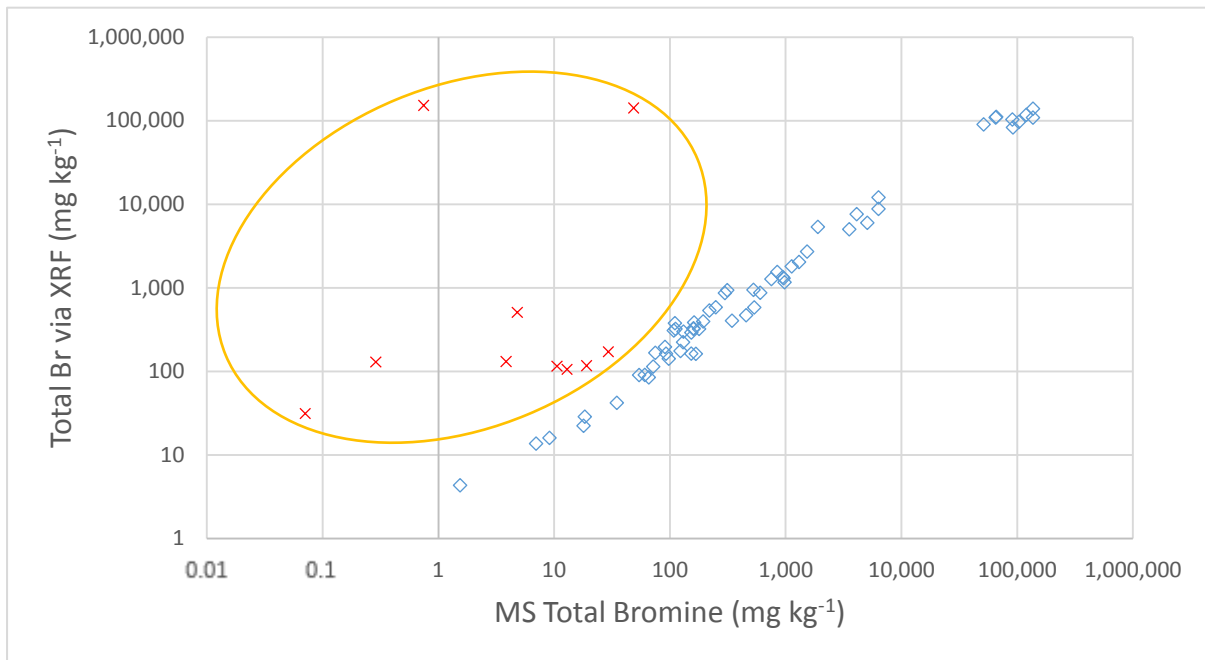
13 *Figure 3* Regression between total Br concentrations (mg kg^{-1}) measure by XRF and
14 GC/MS / LC-MS/MS for 43 PUF samples (slope $m = 1.70$, $R = 0.99$, $R^2 =$
15 0.98).

16 *Figure 4* Regression between total Br concentrations (mg kg^{-1}) measure by XRF and
17 GC/MS / LC-MS/MS for 30 EPS samples ($m = 1.20$, $R = 0.99$, $R^2 = 0.98$).

18

19 **FIGURES**

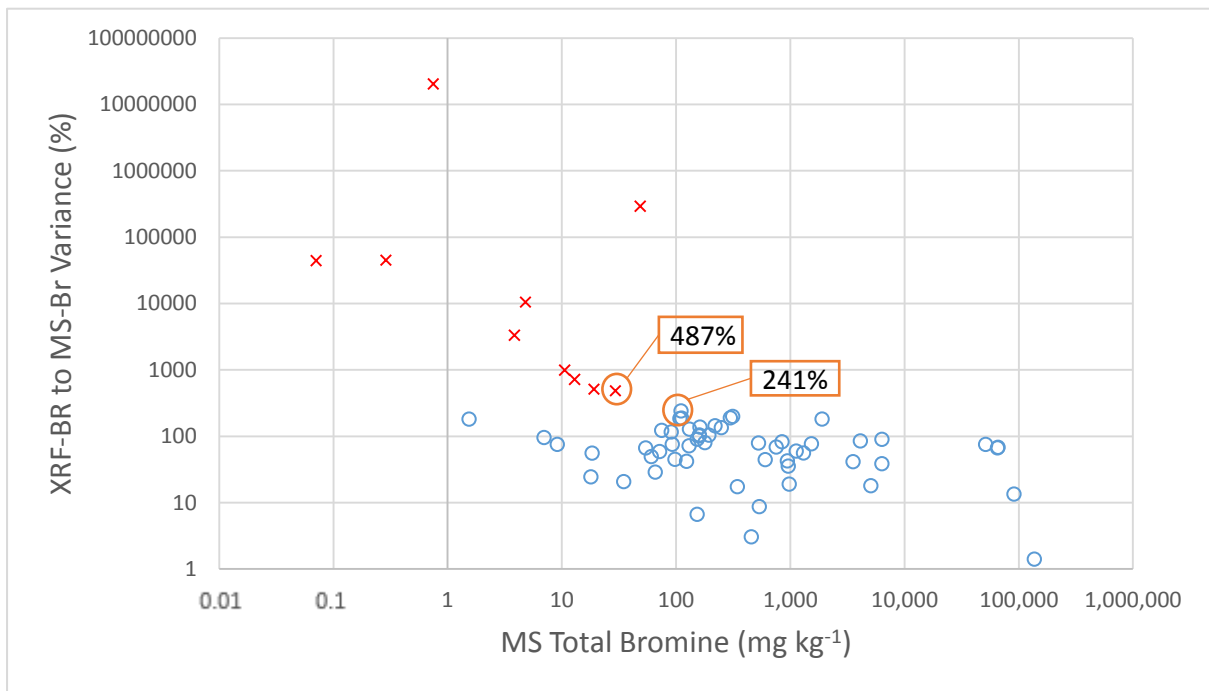
20 *Figure 1*



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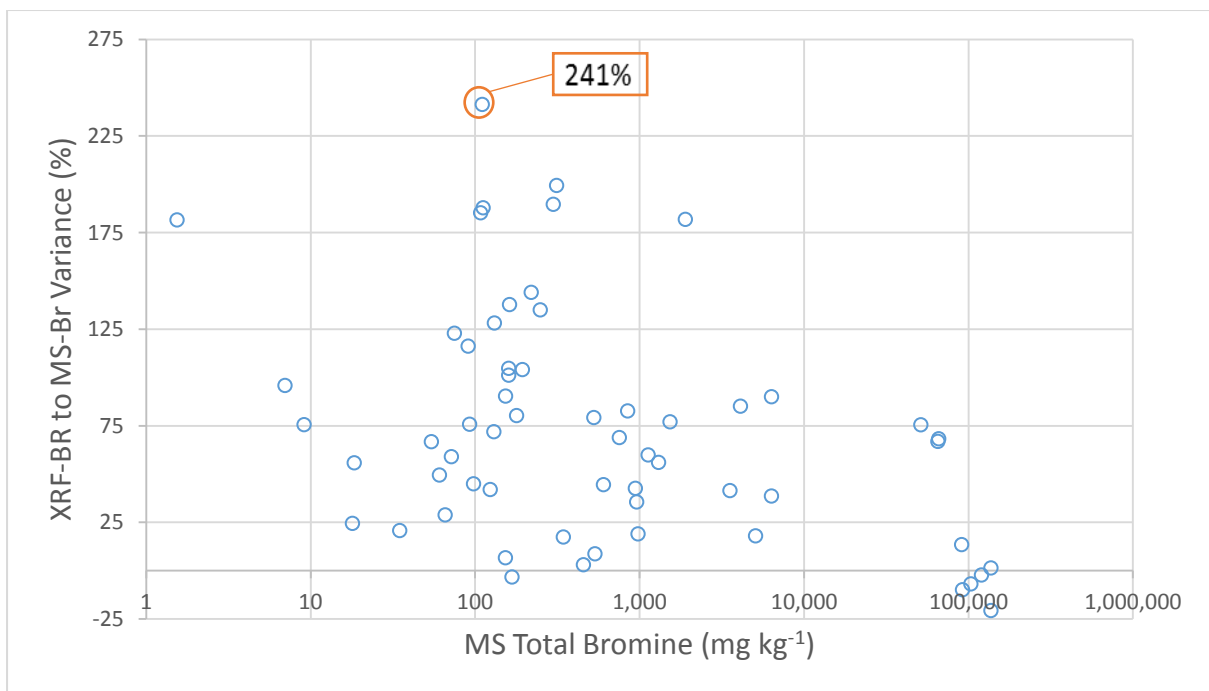
23 *Figure 2 (a)*



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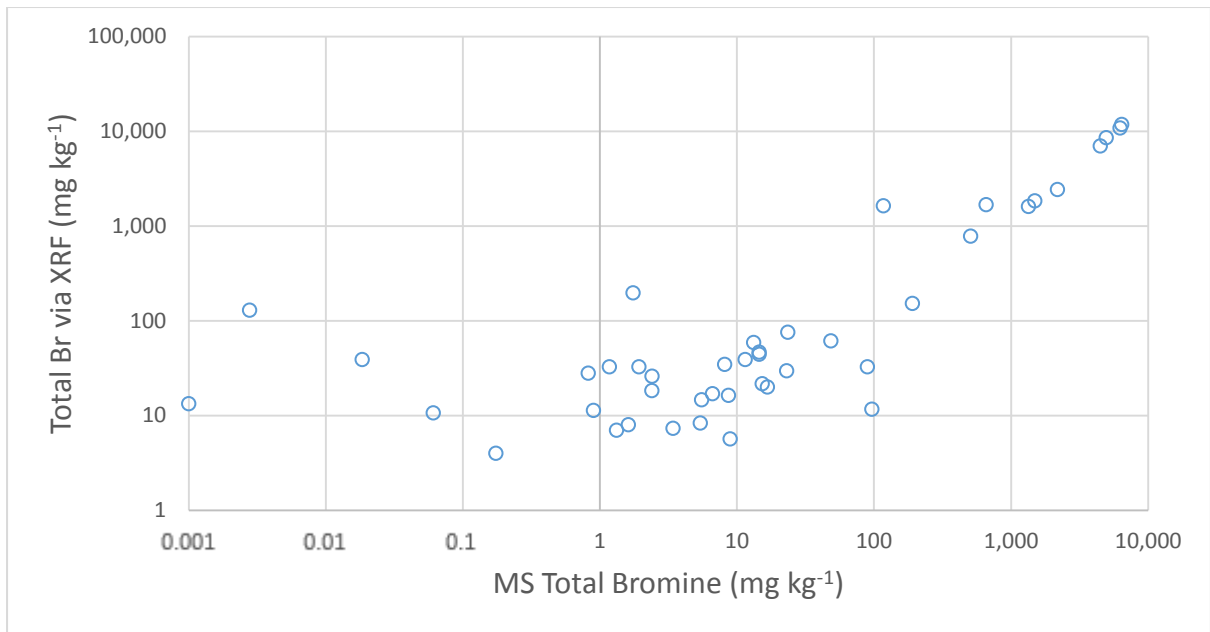
26 *Figure 2 (b)*



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29 *Figure 3*

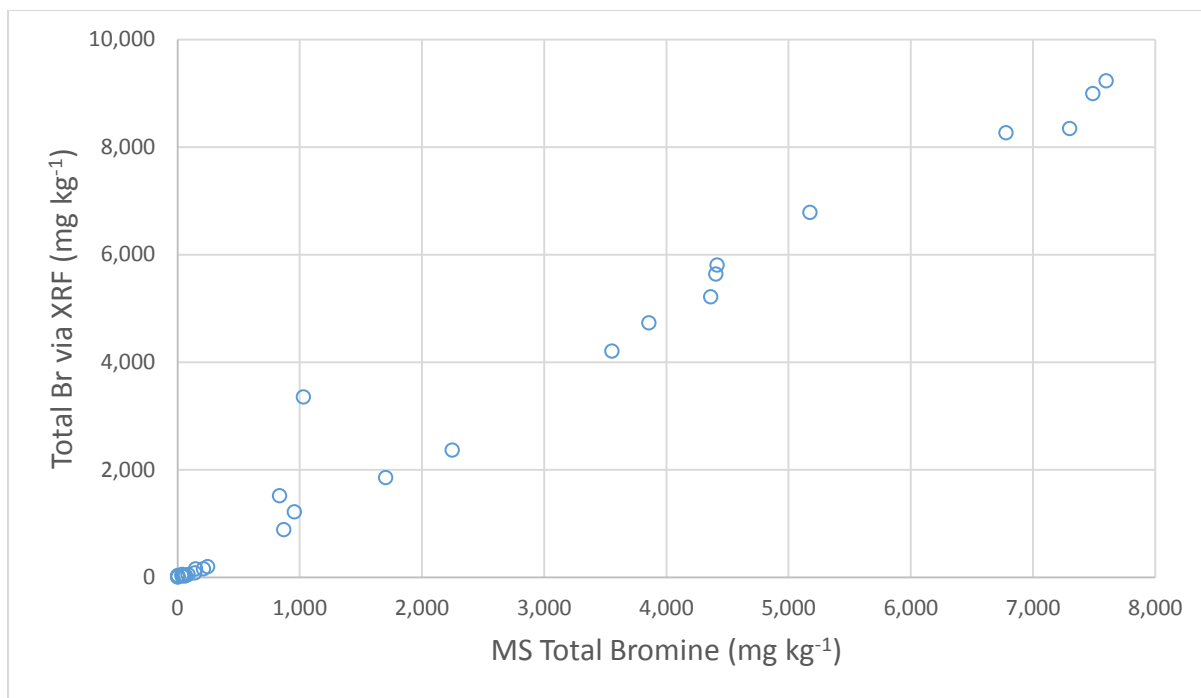


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33 *Figure 4*



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