Suitability of Portable X-Ray Fluorescence for the Quantification of Brominated Flame Retardants in Waste – A Large Scale Study in Ireland

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Introduction

Hexabromocyclododecane (HBCDD) and polybrominated diphenyl ethers (PBDEs) are additive flame retardants which have been extensively applied to a wide range of plastic items in the last few decades[1, 2]. Although suitable for the purpose intended, further research has strongly linked their chemical properties to be consistent with those of persistent organic pollutants (POPs), *i.e.* persisting in the environment for long periods of time, being readily distributed via natural processes, accumulating in fatty tissues of living organisms, and being toxic to humans and wildlife[3]. The aforementioned BFRs, being consistent with the POPs criterion, have therefore been listed in the United Nation Environment Programme (UNEP) Stockholm Convention on POPs[4, 5]. This international treaty requires member-states to create suitable legislation to restrict further environmental contamination by these hazardous compounds.

The European Union (EU), being a signatory of the treaty, have created legislation governing the concentration limits (low-POP concentration limits – LPCLs) that can be present in (i) waste goods entering the recycling stream, and (ii) newly-manufactured goods entering the market. These BFRs are sub-divided into four commercial mixtures, the name of which denoting the primary congener present in the mixture: HBCDD, containing solely HBCDD isomers; Penta-BDE, containing mostly penta-BDE congeners; Octa-BDE, containing mostly octa-BDE congeners; and Deca-BDE, containing mainly the deca-BDE congener[1]. Each of these mixtures have restrictions applied dictating how much of each can be present in a given product, entering a given stream as summarized in *Table 1* below [6-8]. Tetrabromobisphenol-A (TBBP-A) is another ubiquitous BFR used in similar applications as PBDEs and HBCDD. Though not listed as s POP, it is listed as a Class A carcinogen[9] and waste containing excess concentrations is defined as "hazardous" and requiring specialized disposal[10] (*Table 1*).

*Table 1 – List of commercial BFR mixtures listed in the UNEP Stockholm Convention, along with their relevant LPCLs as dictated by relevant EU legislation. *The sum of the Penta-, Octa-, and Deca-BDE congeners in a given product. **Subscripts with each year indicated the relevant regulation in which the concentration limit has been set-forth. ***TBBP-A not listed as a POP, but does have a concentration limit as established by EU law.*

POP Mixture(s)	UNEP Listing Year	** EU Listing Year	EU LPCL: Waste	EU LPCL: Market
Penta-BDE	2009	2010 $_{(POPs)}$	n/a	0.1 %
Octa-BDE	2009	2010 $_{(POPs)}$	n/a	0.1 %

Deca-BDE	2017	2017 (REACH)	n/a	0.1 %
HBCDD	2013	2011 (POPs)	0.1 %	0.01 %
*ΣPBDEs	2017	2010 (RoHS)	n/a	0.1 %
*** TBBP-A	n/a	2017 (WFD)	0.1 %	n/a

In order to comply with these regulations and due to the huge concentrations of plastics recycled and manufactured daily, a reliable, rapid, and cost-effective method for determining the concentrations of POP-BFRs in these products is required. Portable x-ray fluorescence (XRF) is one such method which has been evaluated recently for this application[11, 12]. Though unable to specify the species of bromine present, the technique has been reported to have varying success for the screening of items containing POP-BFRs. However, many of these studies were limited to relatively few samples and/or few types of plastics. In order to more conclusively determine the efficacy of XRF in this application, a large-scale sampling of consumer plastics from waste sites around Ireland was carried out, in which XRF-determined bromine concentrations (gathered *in-situ* at the sites) were compared to quantified concentrations of BFRs various plastic types, including: hard plastics from electrical and electronic equipment (EEE); polyurethane foams (PUFs), upholstery, and textiles from domestic and vehicular applications; and polystyrene foams from insulation foams and packaging.

Materials and Methods

A Niton XL3t XRF analyser was used to measure the concentrations of bromine in 555 waste plastics from those groups outlined above (and in *Table 2*). These measurements were carried out in triplicate and on different areas/varying orientations in order to account for inhomogeneous mixing of BFRs within the matrices of the samples. For EEE, measurements were carried out on products as presented (whole intact products) with a thickness correction applied based on estimate of material thickness using Vernier callipers. For Upholstery, textiles, and PUF, samples were removed from the parent product and folded to a thickness required for full attenuation of the device's primary x-rays. Polystyrene insulation and packaging foams were carried out as presented (similar to EEE) but also at a requisite thickness for full attenuation of x-rays (similar to PUF, upholstery and textiles).

Small cut-outs were then taken from the body of the parent product with a pre-cleaned retractable blade (~ 1 cm^2 for EEE, 2-3 cm^3 for other materials), stored in polyethylene containers, and transported for a laboratory for determination of POP-BFR concentrations. Extraction of target compounds, extract clean-up, and analysis of compounds using GC-MS and LC-MS/MS were carried out via methods described previously[13].

Statistical comparisons were carried out between XRF-determined total bromine concentrations and MS-quantified BFRs using: regression analysis, to determine the overall accuracy of Br concentrations compared to actual BFR-content; Bland-Altman plots, to determine the precision of analyses in similar concentration ranges; and z-tests, to evaluate the level of significance of any correlations found.

Results and Discussion

Comparing XRF-determined bromine concentrations with quantified BFRs, the accuracy of the instrument in screening for BFRs depends acutely on the type of material being analysed. As shown in *Table 2* below, the slopes

of all sample-groups deviate from a unity regression, even accounting (where possible) for instances of false-positives (detection of bromine via XRF with no congruent BFR concentrations via MS). This indicates that, despite advancements in XRF for the analysis of polymers, matrix effects substantially alter the accuracy of the device for this application. There is, however, potential to rectify these accuracy issues through the application of matrix-matched calibration standards, which have been previously tested for common EEE plastic materials[14].

Table 2 – Overview of results from regression analyses for each waste/sample group, showing regression and correlation coefficients for XRF-Br and MS-BFRs (PBDEs, HBCDD, and TBBP-A).
PUF = polyurethane foam; IT & Tele. = internet technology and telecommunications device; SDA = small domestic appliance; LHA = large household appliance; ELV = end-of-life vehicle; ELV other = vehicle floor mats and interior trim; Furn. = furniture; Matt. = mattresses; Up. = upholstery; C&D = construction and demolition; Pack. = packaging.

Sample-Group	# of samples, n	Slope, m	r^2 (r)	Sample-Group	n # of samples, n	Slope, m	r^2 (r)
IT & Tele.	*78*	*0.60*	*0.99 (0.99)*	*Furn. Up*	*22*	*0.59*	*0.80 (0.89)*
SDA	*26*	*0.52*	*0.97 (0.98)*	*Matt. Up*	*17*	*0.08*	*0.13 (0.36)*
Display	*43*	*0.63*	*0.57 (0.75)*	*ELV Up.*	*50*	*0.78*	*0.99 (0.99)*
LHA	*57*	*0.58*	*1.0 (1.0)*	*C&D EPS*	*40*	*0.81*	*0.99 (0.99)*
Fridge	*30*	*0.16*	*0.37 (0.61)*	*C&D XPS*	*20*	*0.43*	*0.68 (0.82)*
Furn. PUF	*20*	*0.58*	*0.98 (0.99)*	*Pack. EPS*	*7*	*0.78*	*0.99 (0.99)*
Matt. PUF	*17*	*0.49*	*0.47 (0.69)*	*Pack. XPS*	*14*	*0.81*	*0.98 (0.99)*
ELV PUF	*38*	*0.60*	*0.86 (0.93)*	*Curtain*	*15*	*0.52*	*0.96 (0.98)*
ELV other	*30*	*0.71*	*1.0 (1.0)*	*Carpet*	*31*	*0.57*	*0.36 (0.60)*

Though some sample-groups show very favourable regression coefficients indicative of a correlation between the measurement techniques, more in-depth analysis using Bland-Altman plots show that the precision of the XRF still requires refinement. EEE hard plastic and upholstery sample-groups are particularly noteworthy in this regard: despite having otherwise favourable regression coefficients, Bland-Altman plots show very large variances (on the order of several hundred percent) between the measurement techniques in the 100-10,000 mg/kg concentration range – a range of particular interest given that the legislative limits are mainly at 1,000 mg/kg (or 0.1 %). This shows that, despite a mechanism for correcting overall accuracy of XRF analyses, large deviations in the precision of measurements remains a substantial issue for the quantification of BFRs using this device, even before taking into account its inability to discern the species of bromine detected.

There remains potential for this device to be suitable for the large-scale screening of waste with excess concentrations of POP-BFRs using a suitably refined methodology[15]. However, the limitations of portable XRF for this application must also be acknowledged, therefore any such methodology would require an acceptable margin for error due to it limited precision.

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