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BROMINATED FLAME RETARDANTS IN IRISH WASTE STREAMS – XRF SCREENING SUITABILITY AND FIRST RESULTS

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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]. Although suitable for the purpose intended, further research has strongly indicated that these flame retardants have very high bioaccumulation potentials [2] and are liable to cause adverse effects to human health and to the environment at large [3]. These findings prompted the United Nations Environment Programme to prohibit the further use of HBCDD and both the Penta- and Octa-BDE commercial formulations in the majority of commercial applications under the Stockholm Convention on persistent organic pollutants [4]. Consequently, both HBCDD and those PBDE congeners found in the Penta- and Octa-BDE formulations are now known as POP-BFRs.

Despite this legislation, there exists a large volume of consumer items still in use which have been treated with these POP-BFRs, items which may remain in circulation unless removed and treated separately to conventional recyclables. The European Commission have set limits on the allowable concentrations of HBCDD (<100ppm) and PBDEs (<1000ppm) in recyclable goods [5] in order to maximize the quantity of plastics that can be recycled while minimizing environmental contamination. However, methods to determine which goods contain POP-BFRs in excess of low POP concentration limits (LPCLs) are not widely available to waste and recycling sites and are, although accurate, costly, time-consuming and difficult to use.

To that end, a reliable, quick and cost-effective method of screening waste plastics for POP-BFRs exceeding LPCLs is needed, one which can be conveniently applied at as many waste and recycling sites as possible. This research involves the determination of the typical concentrations of BFRs used in a range of waste plastic items from recycling sites in Ireland, as well as the evaluation of the suitability of portable x-ray fluorescence (XRF) in screening said waste plastics for POP-BFRs. Additionally, options available for enhancing the performance of XRF for this screening process are being explored including the utilization of correction algorithms to improve elemental quantification.

Materials and Methods

A Niton XL3t XRF analyser is being used to measure the concentration of bromine in the plastics of various consumer items from recycling sites in Ireland: the hard plastic casings of waste electrical and electronic equipment (WEEE); the polyurethane upholstery and foams from soft furnishings and textiles; and the polystyrene foams from building insulation and packaging materials. Measurements of thirty to sixty seconds duration are taken in triplicate on the surface of the product, followed by the removal of a small section of the measured surface for conventional chromatographic-mass spectrometric analysis for PBDEs and HBCDDs, specifically targeting those congeners and diastereomers most abundant in the relevant commercial formulations [6]. In the case of items of waste electrical and electronic equipment (WEEE), this protocol is repeated twice more over different areas on the surface of the test item in order to establish any discrepancies which may occur due to underlying electronics, cooling units, or from different plastics. The XRF-determined total bromine and the MS-determined BFR concentrations are then compared in order to establish how accurately the XRF can measure bromine (and by extension BFR) concentrations and whether the presence of other bromine-containing compounds may interfere with the efficacy of the XRF in screening for POP-BFRs.

Results and Discussion

High concentrations of POP-BFRs have been established in the samples analysed thus far, some exceeding the LPCLs by very large margins, most notably in polyurethane foams from furniture (Figure 1). However, many sample groups contain predominantly BDE-209 (Figures 1, 2), the major congener present in the currently non-regulated Deca-BDE commercial mixture. This overlap between regulated POP-BFRs and non-regulated BFRs could prove particularly problematic for this screening

process; however, recent recommendations for the listing of Deca-BDE in the Stockholm Convention, if actualised, will nullify this issue [7].
Initial comparisons between XRF and MS analyses reveal high correlations across several of the analysed sample groups; however, there is a tendency for the XRF to over-estimate the concentrations of bromine compared to actual BFR concentrations (Figure 3). Due to this trend being present across several sample groups and various materials, the discrepancy is likely a result of the limitations of the instrument itself rather than interference from other bromine-containing compounds. Correction factors for the XRF are currently being developed and tested which, once deployed, should overcome this issue.
Issues also arise in the analysis of finitely thick samples, such as for the hard plastic casings from WEEE items. Preliminary result have shown that XRF analysis of WEEE on-site can be affected by underlying substrates such as circuit boards and electronics if the measurement site is of too low a thickness; further analysis of these results are currently underway. Adjustments to the measurement protocol are being investigated which focus on the use of less-penetrative x-rays in order to compensate for thinner hard plastic samples without the need for dismantling of the WEEE item.

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References
1. Ipcs. Flame retardants (EHC 192, 1997). 1997 [cited 2016 March 14]; Available from: http://www.inchem.org/documents/ehc/ehc/ehc192.htm.

2. Nyholm, J.R., Persistence, bioaccumulation and toxicity assessment of selected brominated flame retardants, in Department of Chemistry. 2009, Umea University: Umeá, Sweden. p. 67.

3. Eljarrat, E. and D. Barceló, Handbook of Environmental Chemistry - Brominated Flame Retardants. Handbook of Environmental Chemistry, ed. Damiá Barceló and A.G. Kostianoy. Vol. 16. 2011, Verlag Berlin Heidelberg: Springer Verlag. 305.

4 UNEP. Stockholm Convention on Persistent Organic Pollutants: Amendment to Annex A. United Nations Environment Programme. 2013 [cited 2016 March 12]; available from: http://chm.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx

5 EU. Regulation No 2016/293 Amending Regulation (EC) No 850/2004 on Persistent Organic Pollutants. 2010 [cited 2016 May 27]; available from: http://eur-lex.europa.eu/legal- content/EN/TXT/PDF/?uri=CELEX:32016R0293&from=EN

6 La Guardia, M.J., R.C. Hale, and E. Harvey, Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. Environmental Science & Technology, 2006. 40(20): p. 6247-6254.

7 UNEP. POPRC-11/1: Decabromodiphenyl ether (commercial mixture, c-deca-BDE). United Nations Environment Programme. 2015 [cited 2016 March 13]; available from: http://chm.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/33 09/Default.aspx

Figure 1

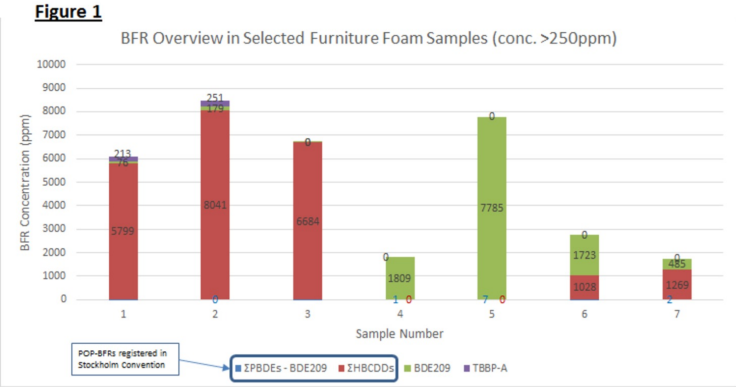

Figure 2

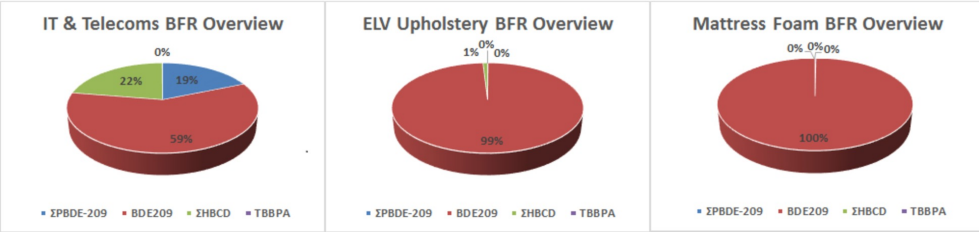

Figure 3