HBCDD in Expanded and Extruded Polystyrene – Screening for Compliance with Low POP Concentration Limits using X-Ray Fluorescence

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Introduction

Since the invention of mass-production methods in the mid-twentieth century, expanded polystyrene has become a hugely popular plastic for various applications such as food containers, packaging materials and insulation panels for buildings (Thompson et al., 2009). It became apparent, however, that the lattermost application in particular had associated fire safety hazards due to the high flammability of the polymer (Junod, 1976). Therefore, to preserve the use of expanded polystyrene (EPS) and extruded polystyrene (XPS) as highly effective insulation materials, it became necessary to counteract the associated fire hazards via addition of flame retarding chemicals.

Hexabromocyclododecane (HBCDD) has, in the last few decades, been extensively used worldwide in EPS and XPS building insulation foams (Marvin et al., 2011, Eljarrat and Barceló, 2011). However, subsequent scientific studies have highlighted adverse effects of HBCDD on the environment, as HBCDD displays environmental persistence, toxicity, and capacity for bioaccumulation (Eljarrat and Barceló, 2011); the decision was therefore made to list the commercially-used mixtures of HBCDD in the Stockholm Convention on persistent organic pollutants (POPs) (UNEP, 2013). Following the introduction of this policy, European Union legislation was established determining a "low POP concentration limit" (LPCL) of 0.1% weight HBCDD content (equivalent total bromine content of approximately 0.074%) in EPS and XPS foams (EC, 2016); an exception to this rule was allowed which gives treaty-signatories a moratorium of 5 years before a suitable replacement chemical must be incorporated into the manufacture of polystyrene insulation foams.

Approaching this deadline, a rapid and cost-effective way of determining the HBCDD content of treated insulation foams is required. To that end, we investigate here the use of a portable X-ray fluorescence (XRF) device to determine the accuracy to which the XRF can quantify HBCDD content in EPS and XPS building insulation materials and to identify possible limitations to its use as a screening tool. Additionally, given concerns about the presence of restricted BFRs in goods not subject to flame retardancy regulations (e.g. as a result of HBCDD-treated PS being recycled into new applications), we also tested a number of EPS and XPS packaging material samples for HBCDD content.

Materials and Methods

Samples of expanded polystyrene (EPS) and extruded polystyrene XPS were collected from four waste site categories: firstly, from recently demolished buildings (directly from the source of waste); secondly, from a demolition company which stockpiles re-usable waste insulation for future construction operations; thirdly, from a waste site handling material from demolished buildings as well as waste furniture and furnishings, scrap metals and WEEE; and finally, from offices in the Galway area of Ireland and a local recycling site (the lattermost representing the majority of packaging material samples).

Samples were analysed for total bromine content using a Niton XL3t-900 GOLDD XRF analyser and these results compared to conventional LC-MS/MS analysis for accurate HBCDD quantification. Samples were analysed for total Br content by scanning with the XRF for 60 to 105 seconds on a minimum sample thickness of 50 mm, and in 4 locations (several centimetres apart) on the surface of the sample.

Following screening for Br content via XRF, samples were subjected to quantitative analysis for HBCDD via LC-MS/MS using a methodology previously reported by Harrad et al, 2009.

Results and Discussion

Table 1 – Overview of samples gathered and analysed, including information on exceedances of LPCLs and regressions between XRF and MS analyses of samples.

Sample Group	# of Samples	# w/ HBCDD > 1000ppm	HBCDD Range	XRF vs. MS Regression (R^2)	XRF[a] vs. MS Regression Slope	# false positives[b]	# false negatives[c]
C&D EPS	40	19	0 – 10,200	0.985 (p<0.001)	0.807	0	0
C&D XPS	20	0	0 – 94	0.683 (<0.001)	0.423	0	0
Packaging EPS	7	2	0 – 5,900	0.994 (p<0.001))	0.769	0	0
Packaging XPS	14	2	0 – 1,070	0.976 (p<0.001)	0.503	0	0

[a] *note that XRF measurements of Br were converted to equivalent HBCDD values by multiplying by 1.34*
[b] *false positive means XRF identified a sample as exceeding the LPCL but this was not confirmed by the LC-MS/MS measurement of HBCDD*
[c] *false negative means XRF identified a sample as not exceeding the LPCL when the LC-MS/MS measurement of HBCDD revealed the LPCL to be exceeded*

Comparison of XRF and LC-MS/MS measurements of HBCDD in XPS and EPS

Statistically significant positive linear correlations were observed between the XRF and the LC-MS/MS measurements of HBCDD (Table 1); high R^2 values were found for the C&D EPS and both packaging categories (>0.95), while the lowest R^2 value was for C&D XPS, likely due to the fact that the bromine/BFR concentrations within these samples were close to or below the instrumental limits of detection (LOD).

Matrix effects resulting from the physical characteristics of the PS material can alter the bromine quantification via mechanisms such as inaccurate estimation of sample density or loss of energy of primary x-rays due to propagation through the medium. This results in the slopes of the regressions between XRF and LC-MS/MS measurements deviating significantly from unity (Table 1) and highlights that XRF is not a direct substitute for LC-MS/MS. We do note however, that under-estimations caused by such matrix effects (regression slopes <1) can be at least partially corrected via the use of suitable matrix-matched calibration standards for EPS and XPS (Guzzonato et al., 2016).

Presence of HBCDD in Packaging EPS and XPS

The largest fraction of waste materials here exceeding LPCLs due to POP-BFR content was the C&D EPS samples, with ~48% of samples containing HBCDD at concentrations exceeding 1,000 ppm HBCDD, or 740 ppm Br, while the C&D XPS samples showed none exceeding. Samples of both EPS

and XPS Packaging showed HBCDD concentrations exceeding its LPCL. This indicates that PS products not originally intended to have been treated with flame retardants, can also contain HBCDD (likely as a result of incorporation of recycled HBCDD-treated PS, among other mechanisms) and may therefore also require screening for compliance with LPCLs.

XRF screening for LPCL Compliance

Construction and demolition (C&D) EPS showed the highest fraction of samples exceeding LPCLs at 48 %, while C&D XPS conversely showed no exceedances, and packaging EPS and XPS showed exceedances of 29 % and 14 % respectively; however, the relatively small sample sizes should be noted and extrapolation to larger sample sizes should be carried out with caution. Table 1 also shows no false positives or false negatives in the context of LPCL compliance. Thus, the abovementioned issues related to the correlation between XRF and LC-MS/MS measurements notwithstanding, portable XRF appears a viable option for checking compliance of EPS and XPS materials with POP LPCLs.

It should be noted however, that EPS and XPS is likely a "special case" particularly suited to XRF screening as – consistent with the literature on FR-use in EPS and XPS – non-POP-BFRs were not detected in any of our samples (the presence of which could lead to false positives). Work presented elsewhere at this conference shows this not to the case for other BFR-containing waste streams such as soft furnishings, electrical and electronic equipment etc.

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