Rapid identification of PS foam wastes containing HBCDD or its alternative PolyFR by X-ray fluorescence spectroscopy (XRF)

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Highlights:

- Hexabromocyclododecane (HBCDD) has been added to Annex A of the list of persistent organic pollutants (POP) of the Stockholm Convention.
- Recycling of HBCDD-containing PS foam waste will not further be allowed
- A screening method is introduced to identify HBCDD in PS foams
- HBCDD is released from PS foam by fast solvent extraction and detected by XRF analysis, using handheld XRF the method is applicable as onsite screening method to qualify PS foams in demolition waste for suitable end-of-life treatment.

Abstract:

The brominated flame retardant hexabromocyclododecane (HBCDD) was added to Annex A of the list of persistent organic pollutants (POP) of the Stockholm Convention. Thus, production and use of HBCDD will be banned, and the recycling of HBCDD-containing foam waste will be restricted. In reaction a special polymeric brominated flame retardant (PolyFR) was developed to replace HBCDD in PS foam for building and construction applications. In future, a decision has to be made whether PS foam waste is subjected to incineration (with HBCDD) or to recycling (without HBCDD). Therefore, an appropriate and rapid field method is required to distinguish between HBCDD containing and HBCDD-free foams. Here we present a screening method for identifying HBCDD containing EPS or XPS. The test principle is based on the fact that PolyFR (a brominated polymeric macromolecule) is not extractable whereas HBCDD (a low molecular substance) is. Following a rapid extraction of HBCDD the brominated flame retardant is identified and quantified via bromine analysis using a handheld XRF instrument. The method was applied successfully to 27 PS samples (foams and EPS raw materials), which were provided without any information on the applied flame retardant. The presence of HBCDD was confirmed for all HBCDDpositive samples in the test. A robustness test revealed a high correctness and a high repeatability of the test system: HBCDD equipped and HBCDD free samples were identified correctly with relative standard deviations of quantitative results below 14%. Moreover, XRF test results agree well with HBCDD determinations performed in a laboratory by GC-FID.

Keywords: PS foam, EPS, XPS, HBCDD, PolyFR, demolition waste, analysis, POP

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1 Introduction

Expanded and extruded polystyrene foams (EPS and XPS, hereinafter referred to as PS foam) for use in building and construction as insulation materials as well as EPS raw beads (expandable PS granulates) have been additivated according to the legal requirements with a flame retardant. The brominated flame retardant hexabromocyclododecane (HBCDD) has been selected and is in use for more than 50 years (Alaee et al., 2003).

In 2008 the European Union classified HBCDD as a Substance of Very High Concern (SVHC) due to its PBT properties (persistent, bioaccumulative, toxic), and it was included in Annex XIV of the REACh Regulation in 2011 (EU, 2011). After the so-called sunset date on 21st August 2015 production and application of HBCDD in PS foams in the EU is only possible if a temporary authorisation is granted by the European Chemicals Agency (ECHA) and the European Commission. An application for an authorisation was made by February 2014, however, there is no final decision on this issue yet (ECHA, 2015).

On a global level HBCDD has been added to Annex A (Elimination) of the list of persistent organic pollutants (POP) of the Stockholm Convention on 9th May 2013 (UN, 2013). The decision means that the production and use of HBCDD and HBCDD containing articles will be banned. A time limited exemption can be applied for, for production and use of PS foams for buildings.

In reaction to these legal developments alternatives for HBCDD were developed in order to replace HBCDD in PS foam for building and construction applications (EPA, 2014). The highest market potential is attributed to a special polymeric brominated flame retardant (PolyFR) (Beach et al., 2013).

However, in order to guarantee efficient end-of life treatment of future PS foam waste, an appropriate testing method is required, which is able to distinguish between HBCDD and HBCDD-free foams. Waste is considered as “HBCDD free” if HBCDD levels are below a “low POP content”, defined and agreed on by Stockholm and Basel convention. Otherwise such waste should be disposed of in such a way that the POP content is destroyed or irreversibly transformed or otherwise disposed of in an environmentally sound manner. The required limits of detection (LOD) of a testing method can be derived from typical HBCDD levels in normal insulation application, which is reported to vary in the range between 0.5 and 3.0 wt% (EXIBA, 2014). According to Stockholm and Basel Convention a low POP content of 100 ppm up to 1000 ppm is currently being discussed for HBCDD. Therefore, it may useful to reach safely an LOD below 50 ppm. These requirements are fulfilled by state-of-the-art laboratory methods. They base on GC–MS or LC-MS and reach LODs in the low ppb range (Eljarrat and Barcelo, 2004; Fromme et al., 2014; Kemmlein et al., 2009; Thuresson et al., 2012; Rani et al., 2014).

X-ray fluorescence spectroscopy (XRF) has been applied in various studies to trace sources of brominated flame retardants in indoor environments and waste plastics (Allen et al., 2008; Allen et al., 2013; Kajiwara et al., 2009; Schlummer et al., 2007). This analysing technique is fast, simple and a suitable means to detect bromine with LODs of 5 ppm (e.g. Takigami et al., 2009). However, it cannot distinguish between different brominated flame retardants.

In contrast to house dust or complex plastic wastes, PS foams exhibit only a minor variance with respect to types of brominated flame retardants. In the past, more than 95% of flame retarded PS foams were equipped with HBCDD and PolyFR is expected to reach a high market share in PS foams in future. This significantly facilitates the task of distinguishing PS foams with HBCDD from those equipped with unrestricted alternatives. HBCDD and PolyFR differ in molecular weight (642 Da versus > 100000 Da), vapour pressure and solubility. Especially the latter aspect may be used to develop a simple test method, as soon as the low solubility of PolyFR results in a significant difference in extractability of both brominated flame retardants from PS foams.

Thus, it was the aim of the present study to test the extractability of HBCDD and PolyFR from PS foams and related raw materials and to quantify bromine in these extracts. Combined with the assured knowledge of the type of applied flame retardants, this approach was used to develop a rapid and cost efficient screening method to identify HBCDD in PS foam and to distinguish it safely from PolyFR.

2 Materials and Methods

2.1 Materials

25 PS foam samples, 19 EPS and 6 XPS, were provided by five European producers of EPS and XPS. In addition, two raw materials (EPS raw beads) were sampled by one of these companies. Sample codes were used to name the samples for the blind test consisting of the type of material (EPS, XPS or beads) and a consecutive number.

Acetone p.A. was purchased from VWR (Darmstadt, Germany). Technical grade HBCDD was granted as reference material by a PS foam producer and used for calibration. HBCDD was dissolved in acetone and five calibration standards were produced with bromine concentrations ranging from 5 to 1000 ppm.

2.2 Methods

2.2.1 General Approach

The suggested test approach applies handheld x-ray fluorescence spectroscopy (XRF) to reveal whether the foam or bead sample contains a brominated flame retardant or not. For identification of HBCDD, the test makes use of the fact, that HBCDD is a low-molecular compound and well soluble in organic solvents, whereas PolyFR is a polymer with significantly reduced solubility. In consequence, it was assumed that HBCDD could be extracted from PS foams whereas PolyFR could not.

It is well known that PS foams shrink in acetone but the polymer does not dissolve (Wolf and Molinari, 1973). Instead, acetone treatment forms a solvent wet polymer gel and releases a polymer free supernatant of acetone. Extractable compounds like HBCDD would be dissolved in the acetone phase, whereas PolyFR would not.

2.2.2 Method to detect bromine

X-ray fluorescence: XRF was tested with a desktop instrument (Spectrolab 2000) using the routine calibration provided by the supplier of the instrument (TQK10556) for solid ground samples. Above described HBCDD standard solutions were filled into XRF sample cuvettes sealed with Prolene® films and alternatively into pre-cleaned preforms (7 ml, 40 mm height) made of polyethylene terephthalate (PET), which were closed with standard PP lids (diameter 32 mm). Both types of samples were placed on the XRF autosampler and bromine was analysed using three different targets, 150 seconds each. Thus, the overall measurement lasted 450 seconds.

In order to test, whether the method would be appropriate as a field method, a handheld XRF instrument (XL2 Air, Analyticon) was applied. The same two sets of standards subjected to desktop XRF were placed on the detector head and measured for 5-10 seconds using a XRF calibration developed for PVC samples.

Three alternative handheld detection systems were tested for their suitability for bromine detection.

Sliding spark spectroscopy (SSS) was used to analyse PS foam using an SSS2 instrument (Iosys, Germany). The SSS sensor was placed on the surface of the PS foam and the measurement was started. PS foams were further tested with a handheld Raman spectroscope (FirstDefender RM, Analyticon) and a handheld instrument for Fourier-transform infrared spectroscopy (FTIR) (TrueDefender FTX, Analyticon).

2.2.3 Bromine detection in PS foams

PS foams were cut into pieces of 4x4x2 cm and placed onto the autosampler carrousel of the desktop XRF. Bromine was measured with the XRF using the internal calibration of the XRF instrument.

2.2.4 Identification of HBCDD in PS foams and EPS beads

The following recipe turned out to be the most practical approach. 2 g of PS foam were put in a 300 ml PP container and 5 g acetone was added. The solvent caused the PS foam to shrink to a solvent wet polymer gel, releasing a supernatant of about 3 g of a clear acetone extract.

EPS beads were treated with acetone for 5 minutes allowing the beads to swell and to release HBCDD in the supernatant.

The supernatants were transferred into pre-cleaned PET preforms and these were closed with PP lids. Bromine levels of the extracts were measured by XRF and bromine levels were calculated using the calibration curve obtained from measuring HBCDD standards.

2.2.5 Robustness test of HBCDD screening method

A set of eight EPS and XPS samples was selected from the sample pool. These were analysed by the above described method using 2 g of PS foams and 5 g of acetone per sample. Extracts separated from PS gels were measured by handheld and desktop XRF. The procedure was performed by 10 different persons (7 persons recruited from the laboratory staff of our institute and 3 persons from staff without any laboratory skills) and each person analysed six of these eight PS foams.

2.2.6 Quantification of HBCDD

In order to quantify HBCDD in samples, which have been proven to contain extractable bromine, it is suggested to calculate HBCDD levels from the bromine level in the extract and the dilution factor of the extraction approach. This would be reasonable as long as the distribution coefficient, $K_{ex,gel}$, of HBCDD between both phases, extract and PS gel is equal or close to 1.

To test the validity of this assumption, $K_{ex,gel}$ was assessed in HBCDD positive samples by separating gel and extract and by measuring both phases with desktop XRF. Distribution coefficients were calculated from the ratio of HBCDD concentration in extract ($c_{HBCDD,ex}$) over HBCDD concentration in PS gel ($c_{HBCDD,gel}$), which equals the respective ratio of bromine concentrations (Equation (1)).

Equation (1) $$K_{ex,gel} = c_{HBCDD,ex} / c_{HBCDD,gel} = c_{Br,ex} / c_{Br,gel}$$

This quantitation approach was finally applied to data obtained in the above described robustness test.

2.2.7 LC-MS Screening

In extracts of two samples bromine levels were slightly increased. These extracts were screened by LC-MS (Thermo Finningan TSQ Quantum Ultra AM). Via a T-fitting extracts were directly injected into the system with 20 µl/min by a syringe pump and diluted with 300 µl/min of eluent (methanol/water; 1:1) before entering the spray chamber. The LC-MS was operated in the HESI mode (spray voltage 3000 V, vaporization temperature 350 °C) and negative ions were detected in the mass range from 200 - 1000 Dalton.

2.2.8 GC-FID analysis

PS foams were dissolved in tetrahydrofurane (10 wt%) and precipitated by addition of the fivefold amount EtOH. Supernatants were separated from the PS gels and subjected to GC-FID analysis after passing a 0.45 µm PTFE syringe filter. GC-FID was performed on a Thermo TraceGC equipped with a 15 m GC column (ZB-5HT inferno, 0.25 mm x 0.1 µm) using a split/splittless injector at 250 °C. GC temperature started at 180 °C (4 min) and was increased to 270 °C (20 K/min, 4 min) in a first ramp and to 320 °C (20 K/min, 6 min) in a second.

3. Results and Discussion

3.1 Bromine detection

Sliding spark spectroscopy (SSS) was not effective in analysing bromine at concentrations from 0.5 - 3 wt%, most probable due to the low material density of PS foam samples. For extracts, SSS was not a suitable approach at all. Ghosal and Fang (2015) most recently described that brominated flame retardants may be identified by handheld Raman spectroscopy in rigid plastics and dense PU foams. However, testing PS foam samples with handheld Raman spectroscopy was not successful in this study. Differences between HBCDD positive and negative samples were not obtained, most likely due to high level of air which is present in the PS foam matrix. As with Raman, the tested FTIR handheld item did not detect a difference between HBCDD positive and negative samples. In contrast, desktop XRF proved to be a sensitive and linear detection tool for bromine as specified in Figure 1.

The limit of detection (LOD, calculated as lowest calibration standard) is 5 ppm.

Standard solutions were measured in standard cuvettes, sealed with a 4 µm PP film, and in PET preforms with a PP lid. As expected, the thickness of the PP lid reduced the fluorescence signal due to absorption. By comparison of 40 measurements we calculated a stable reduction by a factor of 0.64 ± 0.02 (average ± standard deviation).

As a result, bromine levels measured in PET preforms will always be an underestimation of real bromine levels. However, due to the stability of the reduction factor, real concentrations can easily be calculated. Quality assurance by daily measurements of control standards is recommended.

Handheld XRF was checked with the same set of standards in both types of containers, cuvettes and preforms. In significantly shorter time of measurement, it also proved to be a sensitive and linear detection tool for bromine as specified in Figure 2.

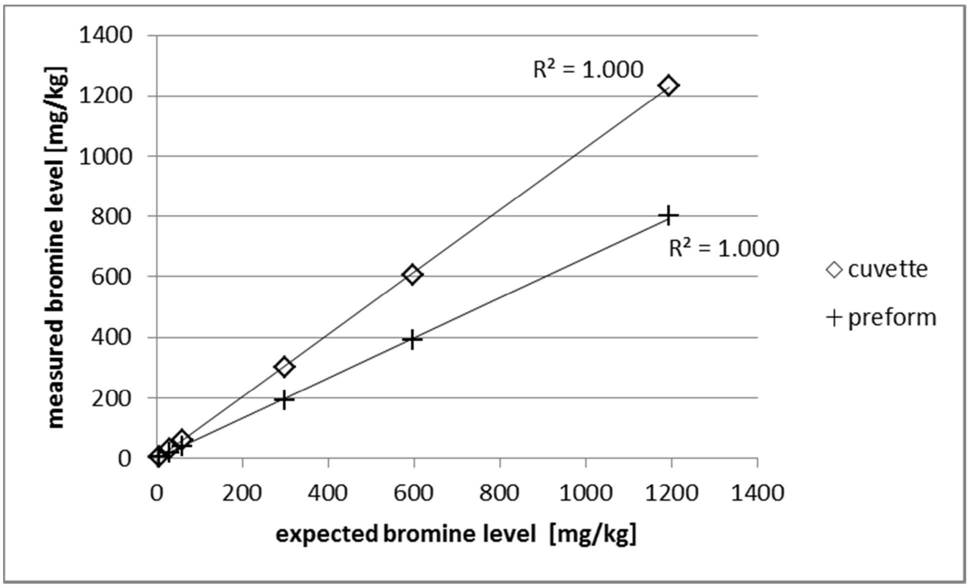

Figure 1: Calibration curves of measured versus expected bromine levels detected by desktop XRF. The upper line displays results obtained in XRF cuvettes, the lower results measured in PET preforms

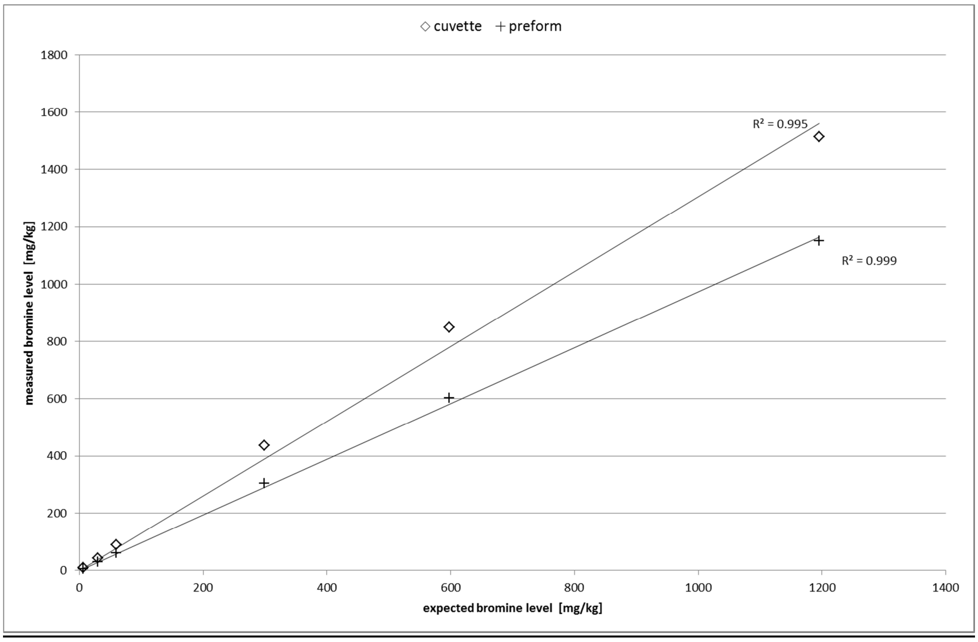

Figure 2: Measured versus expected bromine levels detected by handheld XRF

The limit of detection, however, was 2 to 3 times higher compared to the desktop instrument, when allowing a maximum measurement time of 10 sec. Again, a stable but slightly higher reduction by a factor of 0.71 ± 0.03 (average ± standard deviation) was calculated for fluorescence signals, enabling a calculation of real bromine levels. As for desktop XRF, a quality assurance by daily measurements of control standards is recommended to assure this factor.

3.2 XRF result of PS foam samples and extracts

Bromine levels were measured by desktop XRF in PS foam samples and related extracts.

Bromine levels of extracts were calculated from the calibration curve obtained for standards in preforms in order to correct measured data for the above described reduction of XRF signals. Table 1 gives an overview of exact bromine levels detected in PS foam samples and related extracts as well as the result of the screening test.

As given in Table 1 most PS foams provide bromine levels above 1000 ppm, with one exception (sample EPS-9), which does not contain significant amounts of bromine. Bromine levels of related extracts, however, can be grouped into two clusters. One group of samples contains levels above 700 mg/kg and indicate the presence of significant amounts of extractable brominated compounds, most probably HBCDD. The other group of samples contains only minor bromine levels (max. 50 ppm). These low levels are interpreted as extractable amounts of oligomers of PolyFR, whereas the major part of the brominated additive remains in the polymer matrix.

In order to distinguish extracts levels of bromine caused by HBCDD safely from those caused by PolyFR oligomers a threshold bromine level was defined. As a pragmatic approach, it was decided that for detection of HBCDD an extract bromine level must be twice as high as the highest measured bromine concentration detected in PolyFR containing PS foams, i.e. 100 ppm. If bromine levels of extracts exceeded 100 ppm, the investigated PS samples were expected to contain HBCDD as an extractable brominated compound and marked as HBCDD positive (compare Table 1).

In sample XPS-4 a bromine level of 305 mg/kg was measured in the extract, whereas the level in the PS foam was among the highest. This level is high compared to samples with PolyFR but low compared to clear HBCDD positive samples. Therefore, the presence of both flame retardant additives, PolyFR and HBCDD, in the sample is most likely.

The test approach has also been applied to expandable EPS raw beads, which require more time to form a polymer gel. Table 1 reports bromine levels in EPS beads and related extracts separated from the polymer gel 5 minutes after addition of acetone. Bromine levels in extracts of beads seem to be lower than those of PS foams most probably due to a low rate of diffusion of HBCDD from a bead into an extract. As a result, one has to expect lower extract levels in HBCDD positive beads samples compared to foam tests. However, extracts from HBCDD positive beads still reached a level of 518 mg/kg.

3.3 Comparison of results with additive declaration by sample providers

Results were compared with additive information given by sample providers after testing (Table 1). Test results stated the information in all cases. For sample EPS-9, the absence of any brominated additive was indicated. Low levels analysed seem to be an analytical artefact or indicate the base line (limit of detection) of the detector.

For sample EPS-8, the absence of HBCDD was stated by the supplier. However, our test identified a high level of extractable bromine. An LC-MS analysis of the extract verified the presence of HBCDD.

As discussed above, sample XPS-4 seems to contain both PolyFR and an extractable brominated compound. LC-MS analysis of the extract clearly revealed the presence of HBCDD, however, at significantly lower level compared to sample EPS-8 (Supplementary information). It is suggested that these low levels of HBCDD origin recycled PS from aged PS foams, which may have been applied in the production of this XPS sample.

Table 1: Bromine levels measured in PS foams and EPS beads and in their respective extracts (n.d.: not determined).

Sample Code	PS foam [mg Br/kg foam]	Extract [mg Br/kg extract]	Test result	Test result matches with suppliers information	Remarks
EPS-1	8727	2372	HBCDD	Yes	
EPS-2	5245	1235	HBCDD	Yes	
EPS-3	6619	5	No HBCDD	Yes	
EPS-4	8491	24	No HBCDD	Yes	
EPS-5	3350	2528	HBCDD	Yes	
EPS-6	4747	42	No HBCDD	Yes	
EPS-7	1501	734	HBCDD	Yes	
EPS-8	2562	1108	HBCDD	No	Presence of HBCDD confirmed by LC-MS
EPS-9	3	n.d.	No FR	Yes	
EPS-10	2786	1967	HBCDD	Yes	
EPS-11	3354	34	No HBCDD	Yes	
EPS-12	1960	970	HBCDD	Yes	
EPS-13	2121	8	No HBCDD	Yes	
EPS-14	4304	1745	HBCDD	Yes	
EPS-15	3814	25	No HBCDD	Yes	
EPS-16	3697	1437	HBCDD	Yes	
EPS-17	2717	20	No HBCDD	Yes	
EPS-18	1062	885	HBCDD	Yes	
EPS-19	3245	20	No HBCDD	Yes	
XPS-1	6599	1595	HBCDD	Yes	
XPS-2	14070	41	No HBCDD	Yes	
XPS-3	6217	2631	HBCDD	Yes	
XPS-4	10300	305	Small amounts of HBCDD	No	Presence of small amounts of HBCDD confirmed by LC-MS, possibly from a recyclate
XPS-5	9122	4495	HBCDD	Yes	
XPS-6	8778	48	No HBCDD	Yes	
Beads-1	6030	5	No HBCDD	Yes	
Beads-2	5192	518	HBCDD	Yes	

3.4 Semi-quantitative analysis of HBCDD

Bromine levels measured in PS foam extracts may be used to assess the amount of HBCDD present in the PS foams themselves. Therefore, two things are required: a) the knowledge of the distribution coefficient of HBCDD between extract and PS gel phase, $K_{ex,gel}$, and b) the assumption that all extractable bromine is caused by HBCDD must be valid. The latter assumption is assumed to be reasonable when keeping in mind that almost all past EPS and XPS products were equipped with HBCDD. The distribution coefficient, however, is not available from literature and was assessed experimentally. Eight HBCDD positive samples were investigated and the calculated distribution coefficients are displayed in Table 2.

As most calculated distribution coefficients were close to 1.0 (average 0.96, RSD 21 %) it was decided to use a value of 1.0 to semi-quantify HBCDD. In this case, HBCDD levels in PS foams (c(HBCDD, PS foam)) can simply be calculated by multiplying the bromine concentration of extracts by the total mass ($m_T = m_{acetone} + m_{foam}$) and dividing the results by the mass of PS foam subjected to analysis and by the bromine share of HBCDD (i.e. 75 wt%) (equation (2)).

Semi-quantification has been performed with ten samples with high extract levels of bromine. Calculated HBCDD levels are presented in Figure 3 and compared to HBCDD levels calculated from direct bromine determinations of PS foams (bromine levels were divided by 0.75, the bromine share of HBCDD). Similar HBCDD levels were obtained for three out of ten samples, only. In the other seven cases, HBCDD levels re-calculated from extracts are significantly higher than those from direct XRF measurements. Direct measurements of foam levels, however, are unexpectedly low and out of the normal range of HBCDD levels reported by producers. This is reasonable as the XRF sampling depth for bromine in polymeric matrices is in the low mm range. When measuring PS foams, x-rays pass both, PS matrix and air incorporated into foam samples, and thus a number of phase interfaces. This may result in multilateral reflections of fluorescent X-rays, which do not reach the detector cell of the X-ray instrument in total.

Equation (2) $$c(\text{HBCDD, PS foam}) = c(\text{Br, ex.}) * m_T \, / \, (0.75 * m_{foam})$$

Table 2: Experimentally determined distribution coefficients of HBCDD between extract and PS gel phase, $K_{ex,gel}$

Sample code	Concentration of bromine in PS gel [mg/kg]	Concentration of bromine in extract [mg/kg]	Distribution coefficient
EPS-1	2729	3020	1.11
EPS-5	3198	2325	0.73
EPS-10	2966	1820	0.61
EPS-12	1180	1101	0.93
EPS-14	2662	2496	0.94
EPS-16	1361	1593	1.17
XPS-3	3128	3557	1.14
XPS-5	5385	5745	1.07
		Average	0.96
		RSD (%)	21%

Samples EPS-1, EPS-5 and EPS-10 and EPS-16 have similar levels, whereas the calculated HBCDD concentration of sample EPS-2 is close to that of sample EPS-12. Compared to EPS, samples XPS-3 and XPS-5 contain higher HBCDD levels. This was expected, because XPS is known to contain higher HBCDD levels compared to EPS. However, HBCDD containing XPS-1 showed a HBCDD concentration below 10000 mg/kg HBCDD. This seems to be reasonable when considering the low bromine level obtained for this sample by direct XRF measurement of the PS foams.

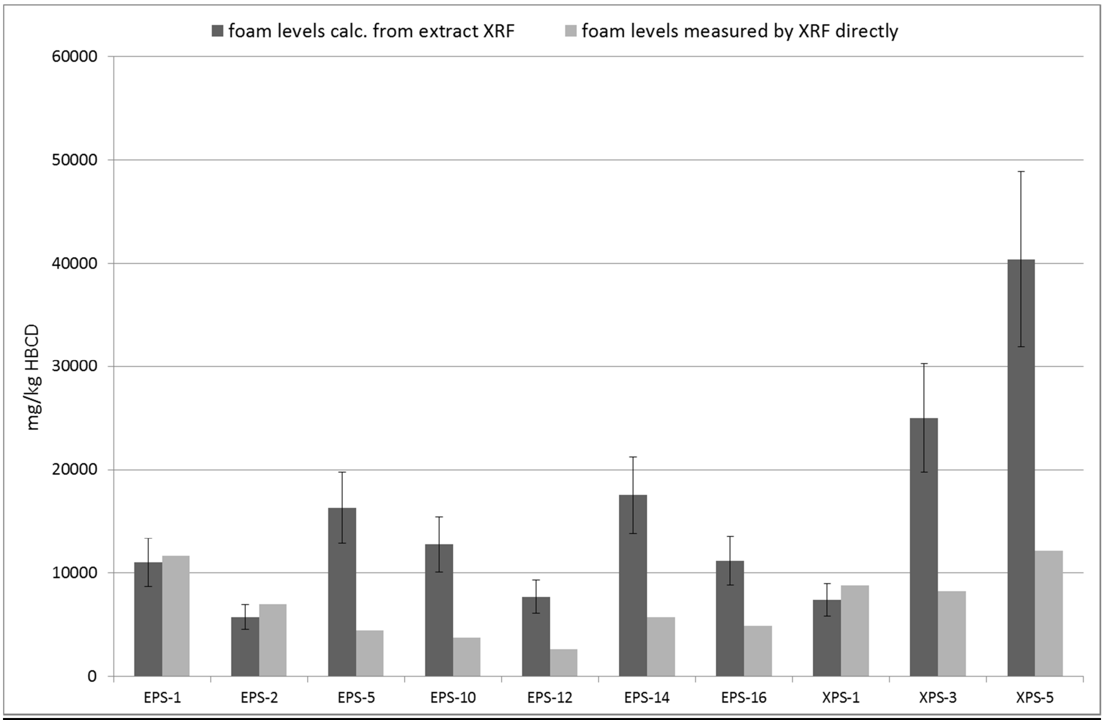

Figure 3: HBCDD levels of ten PS foam samples calculated from XRF measurements of extracts (dark bars) and determined by XRF in PS foams directly (light bars)

3.5 Accuracy and reproducibility

Finally, the test approach was performed by ten co-workers of the Fraunhofer Institute, seven people from the laboratory staff and three people without any analytical or chemical skills. Each tester analysed six out of eight samples and produced extracts of 2 g PS foam samples in PET preforms. This resulted in a data set of 60 handheld XRF data and re-calculated PS-foam levels. In addition, extracts were measured by desktop XRF. Both data sets are presented in Figure 4 and unequivocally identify EPS-1, EPS-2, EPS-5, EPS-10 and XPS-1 as HBCDD positive samples and EPS-11, EPS 15 and XPS-2 as HBCDD negative. XRF results compare well to GC-FID data and – if available – producer information on HBCDD levels. All foam tests were performed as blind test and thus, the 100 % agreement of measured data with producer data (compare Table 1) points to a high accuracy of the rapid test procedure suggested in this paper.

Furthermore, XRF data in Figure 4 indicate a low relative standard deviation (RSD) of data of individual PS foam samples with 7-14 % RSD with handheld XRF and 7-16 % RSD with desktop XRF. Considering that the data were obtained by 10 different people and included 60 independent sample preparations and XRF measurements, the suggested method shows a high reproducibility and robustness.

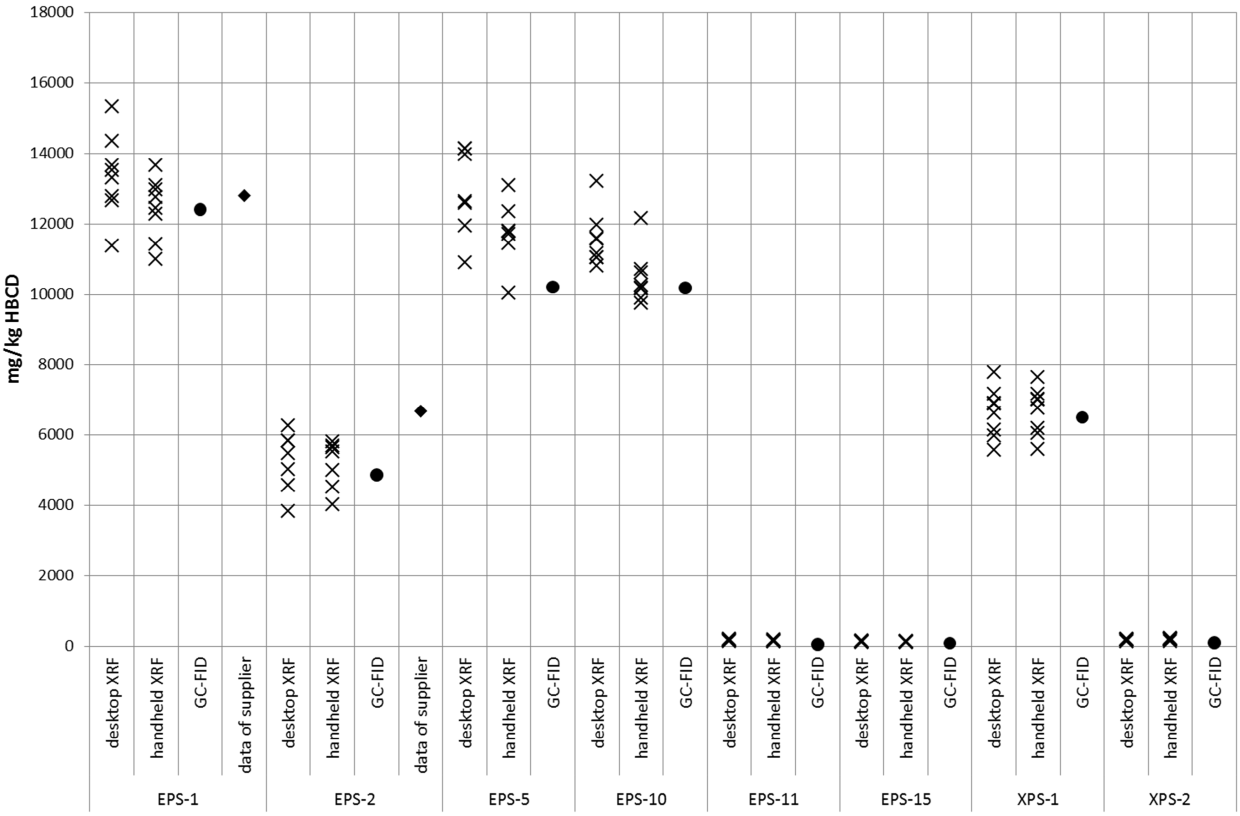

Figure 4: HBCDD data of 8 selected PS foam samples computed from handheld XRF and desktop XRF of extracts (X, 6-8 data point per sample) compared to HBCDD levels determined by GC-FID (●) and producer data of samples EPS 1 and EPS 2 (◆).

4 Conclusions

4.1 Applicability of an extractive method as an on-site test

For commercialisation of the method, a simple handling and suitable containers have to be identified, which may not consist of a material that dissolves in acetone. Final measurement of extracts can easily be performed in PET-preforms with PP lid. Extraction itself can be performed in any container with a minimum volume of 250 ml.

Preferably, the container has a wide mouth to facilitate the filling of PS foam and a lid with a spout to decant the extract safely from the polymer gel. Containers like these are accessible from providers of laboratory equipment.

In the final test kit, PS foams will be filled into the container and acetone will be provided in PET preforms and poured over PS foam. After dissolution the extract is decanted and poured back into the PET preform. After closure with the PP lid, the extract is ready for measurement by handheld XRF.

Basing on the assumptions, that a) the limit of detection (LOD) of bromine is 10 ± 2 ppm for handheld XRF tools and b) that the proposed extraction (2 g foam and 5 g acetone) dilutes the bromine by a factor of 3.5, the LOD of the method can be calculated as 35 ± 7 ppm bromine, which corresponds to 47 ± 9 ppm HBCDD.

4.2 Managing PS foam waste by application of the proposed HBCDD screening test

The screening test may be applied to PS foam waste gained during demolition, dismantling or refurbishment of old buildings. Taking for granted that the PS foam insulation is normally supplied by one manufacturer only, the HBCDD content of the waste of a specific building can be analysed with one simple on-site test, as proposed in Chapter 4.1. To improve the validity of such a test approach, it is recommended to perform a test for each building floor. If HBCDD free, the waste can be used for recycling, in case of HBCDD detection destruction in a municipal solid waste incineration plant with energy recovery is the treatment option of choice (Mark et al. 2015). Alternatively, the CreaSolv® technology may be applicable, which has been shown to separate brominated flame retardants from styrenic polymers (Schlummer et al., 2006). However, it is not available in industrial scale and therefore not yet accepted by the Basel Convention as a method for the destruction of HBCDD or for the recovery of bromine.

For disposal of the test kit, both, the container containing swollen PS gel and the PET preform (containing the acetone extract) can be discarded as household waste.

4.3 Input control for recycling centres or EPS foam production sites

The test might also be applicable as input control in recycling centres or at PS foam production sites. In both cases, PS foam material might be much denser than normal PS foam. At recycling centres, PS foam is often compressed for transportation to reduce costs, for production of EPS foam EPS raw beads are applied. Nevertheless, compressed PS foam or EPS beads can be subjected to the extraction process; however dissolution takes longer (> 5 minutes).

For recycling centres, the use of a handheld XRF is recommendable anyway, as it can be used as a fast tool to distinguish between the samples with and without brominated additives. Only bromine positive samples require the specific extraction HBCDD test.

4.4 PolyFR detection

Last but not least, the proposed test scheme might perform as an identification method for PolyFR. Thus, it may become an important analytical tool in input control and quality assurance of raw materials EPS beads at EPS foam production sites.

Alternative quantitative approaches for a specific analysis for a polymeric additive are rather complicated. They might include size exclusion chromatography and subsequent mass spectrometric detection approaches (LC-MS). However, PolyFR is not a single compound, but a polymer consisting of different chain lengths. Minimum molecular sizes, suitable detectors and mass ranges need to be confirmed and to be agreed on in order to develop and harmonize a high performance analysis of PolyFR. The proposed approach is much easier, faster and does not require all these specific information.

5 Acknowledgments

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7 Supplementary information

LC-(ESI)-MS analysis of extracts from samples EPS-8 and XPS-4 indicate clearly a brominated compound with the isotope pattern of HBCDD (636.6, 638.6, 640.6, 642.6). The amount of HBCDD in sample EPS-8 is at least four times higher than in sample XPS-4 (compare ratio 640/592).

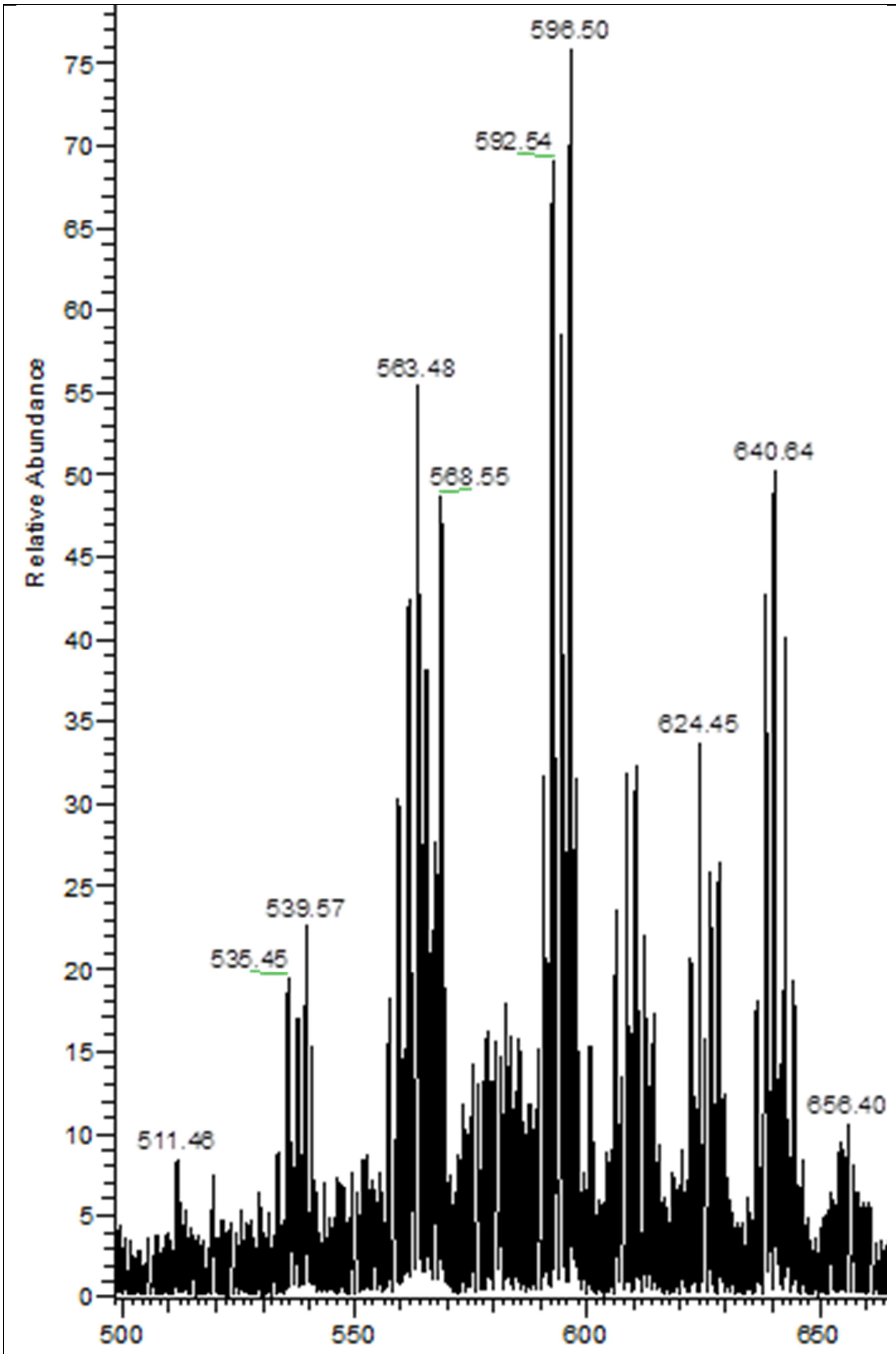

Fig. A1: ESI-MS spectrum of sample XPS-4

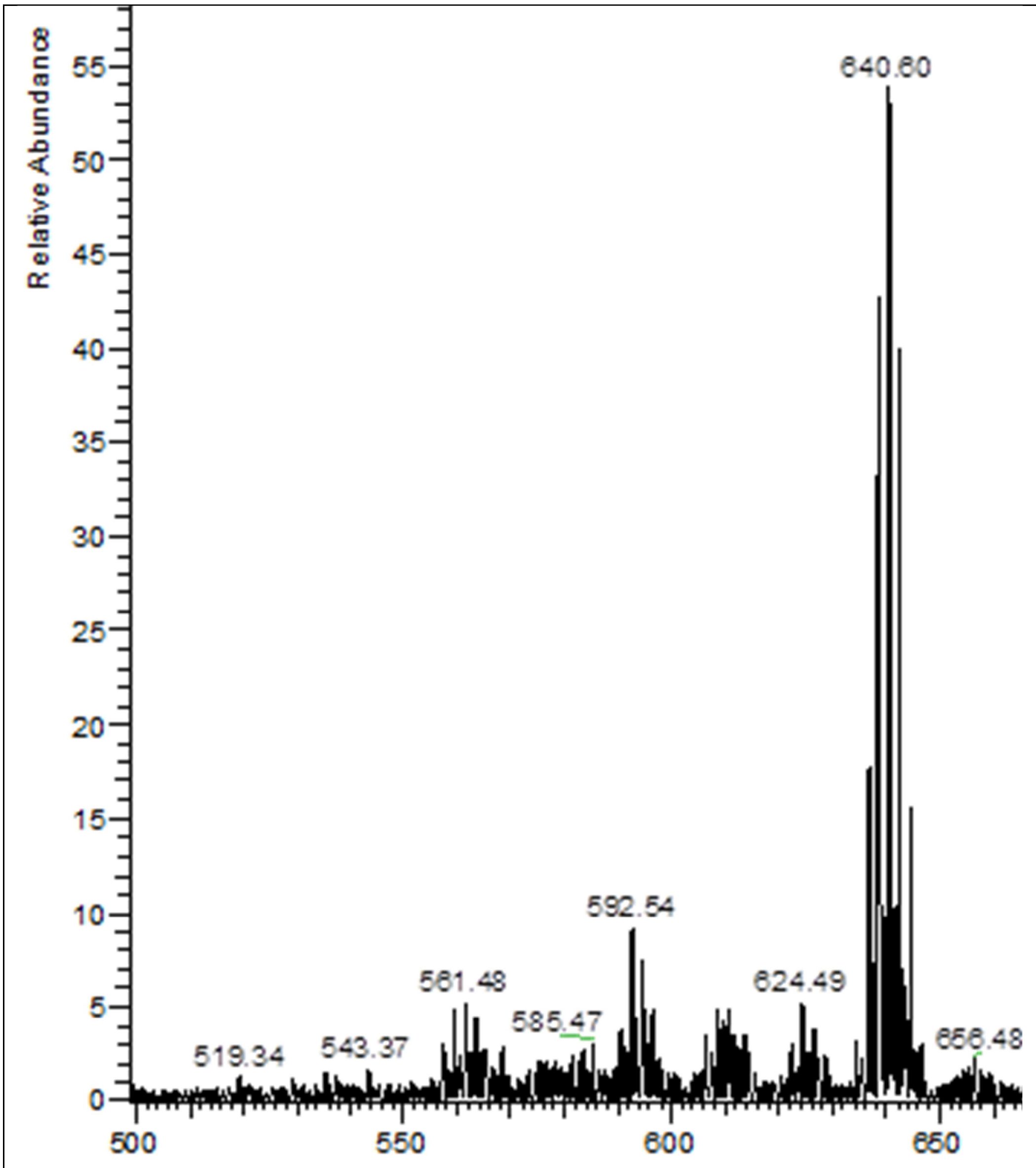

Fig. A2: ESI-MS spectrum of sample EPS-8