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**Open-ended Working Group of the Basel Convention  
on the Control of Transboundary Movements of  
Hazardous Wastes and Their Disposal  
Tenth meeting**

Nairobi, 30 May–2 June 2016

Item 3 (b) (i) a. of the provisional agenda\*

**Matters related to the work programme of the****Open-ended Working Group for 2016–2017:****scientific and technical matters: technical guidelines:****technical guidelines on the environmentally sound****management of wastes consisting of, containing or****contaminated with persistent organic pollutants**

## **Compilation of comments on low persistent organic pollutant contents**

### **Note by the Secretariat**

1. As referred to in document UNEP/CHW/OEWG.10/5, the work programme of the Open-ended Working Group for the biennium 2016–2017 included the work towards a review of all provisional low persistent organic pollutant content values in the technical guidelines referred to in paragraph 2 of decision BC-12/3.
2. In paragraphs 9 and 10 of decision BC-12/3, the Conference of the Parties invited parties and others to submit to the Secretariat, comments and related information on the low persistent organic pollutant content values and requested the Secretariat to compile them for consideration by the Open-ended Working Group at its tenth meeting.
3. As of 25 April 2016, comments were received from Canada, the European Union and its member States, and the European HBCD Industry Group, as compiled in the annex to the present note. The present note, including its annex, has not been formally edited.

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\* UNEP/CHW/OEWG.10/1.

## Annex

### Compilation of comments on low persistent organic pollutant contents

Country/Organization	General Comments
<b>Canada</b>	<p>Canada continues to follow closely the issue of POPs found in products and wastes. We recognize the low POP content of the Stockholm Convention as an important concept to ensure that POPs are not released into the environment when disposed. As reported under the Stockholm Convention in 2006 and 2012 through its National Implementation Plan, Canada takes significant measures through legislation, regulations, programs, policies, and other actions to manage and eliminate POPs from the environment.</p> <p>Several POPs have been managed and controlled in Canada for many years through the actions of various levels of government. As a result:</p> <ul style="list-style-type: none"> <li>- Canada has no stockpiles of the original POP pesticides. These were never manufactured in Canada and their use has been discontinued for many years. The sale or use of POP pesticides listed under the Stockholm Convention is prohibited through the Pest Control Products Act.</li> <li>- The by-products dioxins and furans were declared toxic under the Canadian Environmental Protection Act in 1990. Canada-wide Standards focusing on atmospheric releases were developed in 2001 and 2003 and have been successful in reducing releases in five sectors: waste incineration; burning salt laden wood in coastal pulp and paper boilers; iron sintering; electric arc furnace steel manufacturing; and conical municipal waste combustion.</li> <li>- Under the federal PCB Regulations, PCBs at a concentration of 50 mg/kg or more must be destroyed at authorized facilities. Below that concentration, PCBs must be managed in an environmentally sound manner.</li> </ul> <p>While several POPs have been effectively controlled, some of the more recent ones listed under the Stockholm Convention bring new challenges in the environmentally sound management of waste containing these substances. This is the case for flame retardants such as PBDEs (hexa-BDE, hepta-BDE, tetra-BDE, and penta-BDE) and the industrial chemical PFOS, which are found in many consumer products. The manufacture, sale, offer for sale, and import of these substances are already prohibited under federal regulations.</p> <p>Nonetheless, we have undertaken work, e.g. studies to determine concentrations in landfill leachate to better understand the risk of releases of these substances through waste management activities in Canada. There remain gaps in our knowledge, and we continue to seek information on the presence and concentration of these POPs in different waste streams and their potential for releases through disposal and recycling operations.</p> <p>This will give us a strong baseline to explore best options for reducing and preventing the release of POPs into the environment.</p> <p>Looking ahead, Canada will continue to investigate POPs listed under the Stockholm Convention to find effective measures and take steps necessary to prevent their releases into the environment as waste. This will be especially important for those POPs that are found in everyday consumer products, and where different solutions may be needed to meet both chemicals management objectives and circular economy goals.</p> <p>We look forward to sharing the findings of our work with Parties when completed.</p>
<b>European Union and its member States</b>	<p>The EU and its Member States are satisfied with the Technical Guidelines on POPs adopted during COP-12. In particular, the low POP content values included in the Technical Guidelines coincide with the limit values contained in EU legislation, whereby a value of 1000 mg/kg as a sum has been laid down for the POP-BDEs (hexabromodiphenyl ether and heptabromodiphenyl ether and tetrabromodiphenyl ether and pentabromodiphenyl ether). As regards hexabromocyclododecane (HBCD), the EU and its Member States expect that a low POP content value of 1000 mg/kg will be adopted in an amendment of Regulation (EC) 850/2004 which should be published in the Official Journal before the summer. Therefore, as regards the POP-BDEs and HBCD, the EU and its Member States support low POP content values of 1000 mg/kg as a sum and 1000 mg/kg, respectively.</p> <p>Ireland recently conducted a study "Analysis of Automotive Shredder Residue from the Composition, Recycling and Recovery Trial for End of Life Vehicles in the Republic of Ireland" which contains the chemical analyses on two Automotive Shredder Residue samples. The EU and its Member States are not aware of other new studies regarding the low POP content in comparison to the studies referred to in the General technical guidelines adopted at COP-12.</p>
<b>European HBCD Industry</b>	Submitted the document entitled "Determination of HBCD in Polystyrene Foams with the GC-FID Technique", which is reproduced hereafter.



## Determination of HBCD in Polystyrene Foams with the GC-FID Technique

25<sup>th</sup> September 2015

### Rationale and Method Development

#### General Introduction and Regulatory Context

Within the EU, Hexabromocyclododecane (HBCD) has been identified as a Substance of Very High Concern (SVHC), is listed in Annex XIV of REACH<sup>i</sup> and is therefore subject to authorisation. The sunset date for HBCD under Annex XIV of REACH has been the 21<sup>st</sup> August 2015, which means that the substance HBCD cannot be placed on the market or used after the 21<sup>st</sup> August 2015, unless an authorisation is granted for its specific use or the use is exempted from authorisation.

HBCD has also been listed in Annex A "Elimination" of the Stockholm Convention on Persistent Organic Pollutants (POPs), with specific exemption available for the production of HBCD and use of HBCD for Expanded Polystyrene (EPS) and Extruded Polystyrene (XPS) in buildings.<sup>ii</sup> The Stockholm Convention is implemented in EU law by way of the POP Regulation.<sup>iii</sup> The inclusion of HBCD in Annex A of the Stockholm Convention has not yet been implemented under the EU POP Regulation. Once a substance is listed in Annex I to the POP Regulation, its production, placing on the market and use, whether on its own, in a preparation or as a constituent of articles, is prohibited, except for specific exemptions eventually listed.

In order to ensure an efficient end of life management of future PS foam waste containing HBCD, a suitable analytical test method is needed, able to distinguish between HBCD and HBCD-free foams. Waste has a different management status if the HBCD levels are below a certain "low POP content" threshold, as defined and agreed upon by the Stockholm and Basel Conventions. At higher HBCD levels, such waste must 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<sup>iv</sup>. The Stockholm and Basel Conventions have introduced preliminary low POP content levels (LPCL), with the objective to decide on a final value within the next two years whether such level will be placed at 1000 ppm or at 100 ppm. Industry is advocating for the 1000 ppm level, taking into consideration a number of key factors such as the fact that the 1000 ppm level is at least 7-fold lower than a regular use of HBCD in foam formulations and hence accounting for several (unlikely) recycling cycles whilst emphasizing among others the constraints related to the analytical capabilities. The aim is towards the development of a robust and reliable method, capable of providing the necessary confidence in legal compliance. The viable and acceptable chosen method is designed in such a way, that it can find broad acceptance, not only in the developed but also in the developing countries since the laboratory infrastructure required to implement it is widely available, affordable and yet reliable, and the locally trained personnel are well positioned to perform the test.



## 1. Rationale and Short Method Description

This technical document summarizes the work done at present to meet the demands for the development of a fast and cost-effective method allowing for the qualitative and quantitative analysis of HBCD in waste polystyrene foams. Although the low POP content and hence the detection limits remain to be defined, industry has now engaged in developing a method based on the analytical expertise and the capabilities available in industry's laboratories or in literature references.

A working group of industry experts was established for the joint development of the analytical method. Indeed to date no such specific, robust and reliable standard method exists to determine trace amounts of HBCD in polystyrene foams. Findings from the recently completed large-scale co-incineration trial highlighted the occurrence of potential variations as recorded for the tested foams<sup>iv</sup>. The experts concluded that a reliable analysis of HBCD in polymers necessitates firstly an efficient sample extraction process of the additive from the matrix. The experts also took note of the fact that for the analysis in other matrices such as soil, water or sediment no international standards are available<sup>v</sup>. Having hence reviewed the various analytical approaches and in view of the urgency to deliver a solution, the working group decided to select one of the proposed methods that was deemed most appropriate for the task.

In short the method can be described as follows:

*The qualitative and quantitative determination of hexabromocyclododecane (HBCD) in Polystyrene (PS) foams is performed using Gas-Chromatographic (GC) analysis using a GC equipped with a Split or Splitless Injector and a Flame Ionization Detector (FID). Samples are prepared by dissolving the polymer and additives in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and by precipitation of the polymer through the slow addition under stirring of i-propanol (i-PrOH), followed by GC analysis of the resulting solution. The presence of HBCD is validated by means of the retention time, comparing it with a known standard. The quantification of HBCD in a given sample is performed by using the Internal Standard (ISTD) technique.*

A number of key criteria, including among others, has determined the selection of the method:

- The method ought not to be complex. It must be practical and easy to use even in less sophisticated laboratories in developing countries, with commonly used and widely available analytical hardware and equipment.
- The detection limit is adapted to allow for a correct analysis at a content level of 1000 ppm HBCD.
- There is no necessity to report the individual amounts of each of the HBCD stereo-isomers. The total amount of HBCD is sufficient for identification and meets the purpose.
- The necessity to avoid co-elution of HBCD with interfering compounds, in due recognition for the selection of the FID detector.
- Should there be a need (e.g. to detect a lower level of HBCD) then a more sensitive method can be put in place.

The final choice of the method took into account the challenges related to the complexity of a polymer matrix, including a possible lack of homogeneity of the HBCD distribution in the polymer matrix.



The working group of analytical experts has drawn its attention to those factors that were likely to influence or distort the results,

- such as the nature and the quantity of solvents for the dissolution and the precipitation,
- the precipitation rate,
- the shaking duration,
- the selection of the column,
- the choice of the internal standard,
- the injection mode,
- the rate of recovery of the HBCD in the precipitation including the dissolution steps, etc.

The impact of these factors and the influence they could have on the outcome of the results has been examined in one or the other of the participating laboratories.

Finally, in order to verify the robustness and the reproducibility of the method, a Round Robin Test was conducted. If the limited number of participating laboratories (4) did not enable a fully representative statistical analysis and data processing, it did however provide very valuable results.

**The resulting method is described in this technical document. The findings of the Round Robin Test as well as some specific work on the recovery are also reported.**

The results obtained clearly demonstrate that the analytical approach based on GC-FID for the determination of HBCD in polystyrene foams can meet the requirements set out at the beginning of the test series and is able to fulfil the expectations.

**An additional validation of the method can and should be considered to further assess the reproducibility, the detection limit, the accuracy profile at different concentrations and to prepare the way for standardization.**



## 2. Method parameters

### 2.1. Equipment

Gas Chromatograph (GC) equipped with a Split or a Splitless Injector and a Flame Ionisation Detector (FID).

### 2.2. Column (indicative)

Stationary phase : Polydimethylsiloxane, e.g. HP-1 (J. W. Scientific) or equivalent  
 Length : 25 m or 30 m  
 Diameter : 0.32 mm  
 Film thickness : 0.52 µm

*Note: Alternative column dimensions are acceptable as long as the chromatographic peaks of HBCD and of the internal standard do not interfere with each other.*

### 2.3. Operational Parameters

Detector gas mix:

Hydrogen	35 ml/min
Air	350 ml/min
Makeup (He)	30 ml/min

Detector temperature: 320 °C

Injector temperature: 180°C

Carrier flow (He): Constant flow rate: 6 ml/min

Oven program: Start at 80 °C, rise (10°C/min) to 320 °C

Injection technique: Splitless (Split injection is also possible)

Injection volume: 1.0 µl

### 2.4. Reagents

CH <sub>2</sub> Cl <sub>2</sub> or CHCl <sub>3</sub>	Reagent grade
i-PrOH	Reagent grade

### 2.5. Internal Standard (ISTD) Solution Preparation

- Use a clean 25 ml flask
- Select a suitable internal standard. It should not become interfered by other signals on the chromatogram and have a time of retention suitably close to the HBCD signal. For example, n-hexadecane or 2-ethyl-1-hexanol or a similar compound.
- Prepare a solution of 500 ppm of internal standard in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, recording the exact concentration.

*Note: In line with the traditional analytical know-how, the internal standard solution should be prepared in such a way that the actual signal of the internal standard peak displays a comparable area as the HBCD signal. However, since samples can have a content of HBCD ranging from 500-1000 ppm up to some % points a compromise has to be sought.*



## 2.6. Sample Preparation

- Use a clean 25 ml flask

*Note:* The sample may have a very low density and therefore extra volume will be required before dissolution. Use a flask able to accommodate the sample amount, the exact flask volume is not relevant.

- Completely dissolve 0.5 g of sample, accurately weighted, in 4 ml of internal standard solution, recording weight.

*Note:* Consider preparing a second sample for a double analysis as a means to balance out any possible differences, given that HBCD may not always be evenly distributed throughout a particular foam sample.

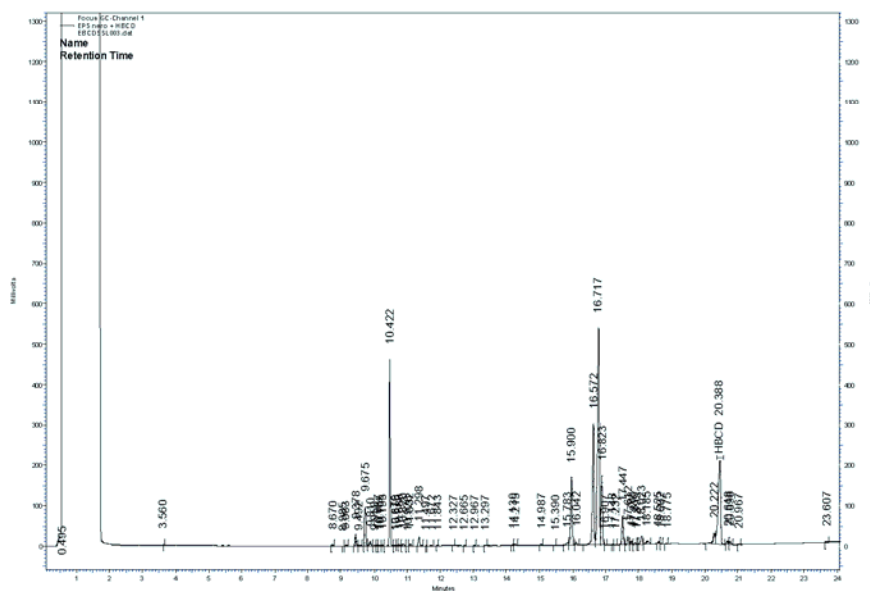
- Carefully precipitate the polymer by slowly adding 8 ml of a precipitating solvent *i*-PrOH under controlled stirring or swirling, recording weight.
- Filter the solution through a 0.45 µm PTFE filter.
- Inject 1 µl of the resulting solution into the GC, recording areas for both ISTD and HBCD signals.

## 2.7. Identification of HBCD

The presence of HBCD is confirmed through the time of retention (comparing it with a known standard of HBCD in the same solvents).

Detection limit: 35 ppm of HBCD in the sample.

## 2.8. Chromatogram



**Figure 1** - Chromatogram of expanded polystyrene (EPS) solution containing HBCD with splitless injection

HBCD Analysis in PS Foams



### 3. Quantification of HBCD

#### 3.1. Principle of Quantification

Quantification is performed through internal standard technique.

#### 3.2 Calculation of the Concentration of HBCD in a given sample

The concentration of HBCD in a given sample is obtained by applying the following formula:

$$[\text{HBCD}] = W_{\text{ISTD}} * (A_{\text{HBCD}} / A_{\text{ISTD}}) * R_{\text{HBCD}} / W_{\text{sample}}$$

Where:

[HBCD] = Concentration of HBCD in the sample (in ppm)

$W_{\text{ISTD}}$  = Weight of ISTD added to the sample preparation (in  $\mu\text{g}$ )

$A_{\text{ISTD}}$  = Area of the ISTD peak in the chromatogram

$A_{\text{HBCD}}$  = Area of the HBCD peak in the chromatogram

$R_{\text{HBCD}}$  = Response factor for HBCD (for details see chapter 3.3)

$W_{\text{sample}}$  = Weight of sample (in grams)

#### 3.3. Response Factor calculation

Prepare a response factor solution consisting of 50 ppm of HBCD and 50 ppm of ISTD in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ , calculating the exact concentration for each component.

Inject 1  $\mu\text{l}$  of the response factor solution into the GC, recording the areas for both the ISTD and the HBCD signals.

The response factor is obtained by applying the following formula:

$$R_{\text{HBCD}} = ([\text{HBCD}]_{\text{rf}} / [\text{ISTD}]_{\text{rf}}) * (A_{\text{ISTD}} / A_{\text{HBCD}})$$

Where:

$R_{\text{HBCD}}$  = Response factor for HBCD

$[\text{HBCD}]_{\text{rf}}$  = Concentration of HBCD in the response factor solution (in ppm)

$[\text{ISTD}]_{\text{rf}}$  = Concentration of ISTD in the response factor solution (in ppm)

### 4. Recovery

The determination of the recovery of HBCD can represent a significant hurdle when no known standards with certified amounts of HBCD are available as references. As a matter of fact, the industrial as well as the laboratory production of PS foams have shown that the manufacture of a PS foam sample with a precisely known amount of HBCD is not feasible and that the additive distribution of HBCD in the polymer matrix may show certain variations. This consideration would also apply to the dry blending of an HBCD-free PS foam with an HBCD-containing PS foam in the preparation of a low concentration material.





It follows that, in due consideration for the limitations mentioned, two different test series have been carried out to demonstrate that the method is capable to provide a robust and satisfactory recovery.

#### **4.1. Co-precipitation of the internal standard and/or HBCD verified**

The co-precipitation of HBCD has been verified using a blank foam sample (i.e.: one without HBCD) and adding known amounts of HBCD. The test aims to determine if the precipitation step will lead to any significant co-precipitation of the internal standard and/or of the HBCD with the polymer.

[HBCD] Theoretical conc.	[HBCD] Recovered	Recovery
ppm	ppm	%
0	0	-
0	0	-
0	0	-
514	484	94.2
514	491	95.5
514	487	94.7
953	954	100.0
953	946	99.2
953	954	100.1
2550	2394	93.9
2550	2406	94.3
2550	2396	94.0
	<b>Average</b>	96.2
	<b>SD</b>	2.7
	<b>RSD</b>	2.8%

**Table 1** – Recovery of HBCD from PS foam samples 'spiked' with HBCD

The recoveries are > 90% across all the concentration ranges, indicating that no significant co-precipitation of the internal standard or HBCD occurs under the applied method specifications.

#### **4.2. Recovery of HBCD verified through repetitive analyses of a same sample**

In order to better understand if one single recovery step will be sufficient or not, two foam samples were subjected to a 1<sup>st</sup> analysis, followed by a 2<sup>nd</sup> precipitation and a 2<sup>nd</sup> analysis and then a 3<sup>rd</sup> precipitation with a 3<sup>rd</sup> analysis. In the absence of a sample with a certified and homogeneously distributed known amount of HBCD, this test shall provide evidence of how much HBCD can be recovered with this method and/or how much is likely to remain in the sample.

To perform this investigation, in a first step each foam sample is analyzed as described in chapters 2 and 3 of this method development: the resulting solvent has been discarded, leaving only the precipitated polymer. The latter is then dried under a flux of N<sub>2</sub>, re-dissolved and precipitated (as if it was a virgin sample), followed by the analysis of the solution via GC-FID.



Next, the solvent has been discarded again, and the remaining polymer is dried once more under a flux of N<sub>2</sub>. A third re-dissolution and re-precipitation has provided another solution analyzed in turn via GC-FID.

This particular test protocol has been performed on two foam samples, whereby each foam sample has been analyzed several times (i.e. each time a different sectional amount for every sample), by two different labs. One participating lab has performed the testing by using two different internal standards (2-ethyl hexanol and n-hexadecane) so as to verify if, by changing the internal standard, differences in the method performance can result.

### 4.3 Investigating sample S1

#### 4.3.1. Internal Standard 2-ethyl hexanol (Lab 1)

Laboratory 1 has investigated 6 foam sections taken from the same sample S1, using as an Internal Standard 2-ethyl hexanol. The results from the 3 subsequent extraction steps and their totals are given in table 2.

Sample	Extraction 1	Extraction 2	Extraction 3	Total	% Extraction 1	% Extraction 2	% Extraction 3
	ppm	ppm	ppm	ppm			
S1	541	95	< LD	636	85	15	-
S1	656	129	< LD	785	84	16	-
S1	447	74	< LD	521	86	14	-
S1	407	58	< LD	465	87	13	-
S1	511	105	< LD	616	83	17	-
S1	435	118	< LD	553	79	21	-
				<b>Average</b>	84	16	

**Table 2** – Recovery of HBCD from PS foam sample S1 using 2-ethyl hexanol as ISTD

#### 4.3.2. Internal Standard n-hexadecane (Lab 1)

Laboratory 1 has also investigated 6 foam sections taken from the same sample S1, using as an Internal Standard n-hexadecane. The results from the 3 subsequent extraction steps and their totals are given in table 3.

Sample	Extraction 1	Extraction 2	Extraction 3	Total	% Extraction 1	% Extraction 2	% Extraction 3
	ppm	ppm	ppm	ppm			
S1	523	85	< LD	608	86	14	-
S1	632	115	< LD	748	85	15	-
S1	438	67	< LD	505	87	13	-
S1	388	52	< LD	440	88	12	-
S1	475	90	< LD	565	84	16	-
S1	413	104	< LD	517	80	20	-
				<b>Average</b>	85	15	

**Table 3** – Recovery of HBCD from PS foam sample S1 using n-hexadecane as ISTD



#### 4.3.3. Internal Standard n-hexadecane (Lab 2)

Laboratory 2 has investigated 2 foam sections taken from the same sample S1, using as an Internal Standard n-hexadecane. The results from the 3 subsequent extraction steps and their totals are given in table 4.

Sample	Extraction 1	Extraction 2	Extraction 3	Total	% Extraction 1	% Extraction 2	% Extraction 3
	ppm	ppm	ppm	ppm			
S1	696	101	<LD	797	87	13	-
S1	529	84	<LD	613	86	14	-
				<b>Average</b>	87	13	

**Table 4** – Recovery of HBCD from PS foam sample S1 using n-hexadecane as ISTD

#### 4.4 Investigating sample S4

##### 4.4.1. Internal Standard 2-ethyl hexanol (Lab 1)

Laboratory 1 has investigated 6 foam sections taken from the same sample S4, using as an Internal Standard 2-ethyl hexanol. The results from the 3 subsequent extraction steps and their totals are given in table 5.

Sample	Extraction 1	Extraction 2	Extraction 3	Total	% Extraction 1	% Extraction 2	% Extraction 3
	Weight-%	Weight-%	Weight-%	Weight-%			
S4	0,33	0,07	0,04	0,44	75	17	8
S4	0,35	0,07	0,02	0,44	79	17	4
S4	0,34	0,05	0,01	0,40	85	14	2
S4	0,33	0,08	0,01	0,42	78	19	3
S4	0,34	0,06	0,02	0,41	81	14	5
S4	0,32	0,05	0,04	0,42	78	13	9
				<b>Average</b>	79	16	5

**Table 5** – Recovery of HBCD from PS foam sample S4 using 2-ethyl hexanol as ISTD

##### 4.4.2. Internal Standard n-hexadecane (Lab 1)

Laboratory 1 has also investigated 6 foam sections taken from the same sample S4, using as an Internal Standard n-hexadecane. The results from the 3 subsequent extraction steps and their totals are given in table 6.

Sample	Extraction 1	Extraction 2	Extraction 3	Total	% Extraction 1	% Extraction 2	% Extraction 3
	Weight-%	Weight-%	Weight-%	Weight-%			
S4	0,30	0,07	0,03	0,40	76	16	8
S4	0,31	0,07	0,01	0,40	80	17	3

S4	0,31	0,05	0,01	0,37	85	13	2
S4	0,30	0,07	0,01	0,39	78	19	3
S4	0,29	0,05	0,02	0,36	82	13	5
S4	0,29	0,05	0,03	0,37	78	13	9
				<b>Average</b>	80	15	5

**Table 6** – Recovery of HBCD from PS foam sample S4 using n-hexadecane as ISTD

#### 4.4.3. Internal Standard n-hexadecane (Lab 2)

Laboratory 2 has investigated 2 foam sections taken from the same sample S4, using as an Internal Standard n-hexadecane. The results from the 3 subsequent extraction steps and their totals are given in table 7.

Sample	Extraction 1	Extraction 2	Extraction 3	Total	% Extraction 1	% Extraction 2	% Extraction 3
	<b>Weight-%</b>	<b>Weight-%</b>	<b>Weight-%</b>	<b>Weight-%</b>			
S4	0,38	0,08	0,01	0,47	81	17	2
S4	0,44	0,06	0,02	0,52	85	12	4
				<b>Average</b>	83	14	3

**Table 7** – Recovery of HBCD from PS foam sample S4 using n-hexadecane as ISTD

#### 4.5. Conclusions from the recovery investigations

The results confirm that the first extraction allows extracting between 80-87% of HBCD from the polymer matrix, which can be considered as a satisfactory recovery for the intended purpose of the method. The data also show that the choice of the internal standard has no particular influence on the recovery.

Variations found in sample S1 may have different origins, such as a potential uneven distribution of HBCD which need consideration when carrying out investigations with foam samples of such type.

### 5. Round Robin testing

In order to verify the robustness and the reproducibility of the method, four different laboratories from four different companies have participated in a Round Robin test.

#### 5.1 Sample description

Ten PS foam samples have been selected for the Round Robin test. The foam samples have been chosen so as to reflect the most currently available industry formulations representing actual market offerings and applications. The selected samples are described as follows:

S1 – EPS foam white with some 500-1000 ppm of HBCD. This sample has been specially manufactured through dry blending of a HBCD-free EPS with an HBCD-containing EPS for the purpose of this testing, since industry does not produce PS foams within this range of HBCD.

S2 - EPS foam white without FR

S3 - EPS foam white with polymeric FR

S4 - EPS foam white with HBCD

S5 - EPS foam grey with HBCD

HBCD Analysis in PS Foams

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S6 - XPS foam green with HBCD  
 S7 - XPS foam light blue with polymeric FR  
 S8 - XPS foam light blue with HBCD  
 S9 - XPS foam light blue without FR  
 S10 - XPS foam light blue with polymeric FR and a few hundred ppm of HBCD

All samples have been properly recorded, anonymized and shared with the four participating laboratories responsible for the respective analyses.

## 5.2. Results

The results from the Round Robin test are as follows:

		Lab.1	Lab.2	Lab.3	Lab.4
Foam Sample		Weight-%	Weight-%	Weight-%	Weight-%
S1		0,05	0,07	0,07	0,12
S2		<0,01	<0,01	<0,01	<0,01
S3		<0,01	<0,01	0,01	<0,01
S4		0,38	0,49	0,43	0,52
S5		1,09	1,17	0,87	1,00
S6		0,82	1,10	0,75	0,83
S7		<0,01	<0,01	<0,01	<0,01
S8		1,07	1,53	1,28	0,96
S9		<0,01	<0,01	0,01	<0,01
S10		0,03	0,04	0,05	0,02

**Table 8** - Results of the Round Robin test (LOQ < 0,01)

## 5.3. Conclusions from the Round Robin test

The results of the Round Robin provide solid evidence that the method is suitably robust and capable of demonstrating whether HBCD is present in the polystyrene foam or not, as per the rationale described in chapter 1.

In addition the method provides also the capability to quantify the amounts of HBCD in polystyrene foams with satisfactory and good accuracy, in line with the mentioned rationale.

## 6. General Conclusions

An analytical methodology has been designed and tested to selectively identify the presence of HBCD in PS foams and to quantify HBCD, by applying a simple and cost-effective configuration consisting of GC-FID coupled with a Split or a Splitless Injector. The method provides for a robust and reliable recovery of HBCD, consolidated and confirmed by the coherent results delivered by the laboratories participating in a Round Robin test.

At this stage of development the method can be applied as such, but a further and desirable work extension by means of a full validation can be envisaged, thus providing additional confidence in its robustness and effectiveness, and preparing the way for standardisation.





### List of abbreviations (in alphabetical order)

EPS: Expanded Polystyrene  
 EU: European Union  
 FID: Flame Ionization Detector  
 FR: Flame Retardant (usually intended as flame retardant additive)  
 GC: Gas Chromatograph  
 HBBD: Hexabromocyclododecane  
 ISTD: Internal Standard  
 POP: Persistent Organic Pollutant  
*i*-PrOH: iso-Propanol  
 PS: Polystyrene  
 PTFE: Polytetrafluoroethylene  
 REACH: Registration, Evaluation, Authorization and Restriction of Chemicals  
 RRT: Round Robin Test  
 RSD: Relative Standard Deviation  
 SD: Standard Deviation  
 SVHC: Substance of Very High Concern  
 XPS: Extruded Polystyrene

### References

- <sup>i</sup> Regulation (EC) No 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, *OJ L 396, 30.12.2006, p.1.*
- <sup>ii</sup> Decision SC-6/13 of the Conference of the Parties ("CoP").
- <sup>iii</sup> Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC, *OJ L 158, 30.4.2004, p.7.*
- <sup>iv</sup> Mark FE, Vehlow J, Dresch H, Dima B, Grüttner W, Horn J. (2015). Destruction of the flame retardant hexabromocyclododecane in a full-scale municipal solid waste incinerator. *Waste Management & Research* 33, 165–174.
- <sup>v</sup> Rüdel H, Müller J, Quack M, Klein R. (2012). Monitoring of hexabromocyclododecane diastereomers in fish from European freshwaters and estuaries. *Environ Sci Pollut Res Int.* 19, 772-783.





## Annex

### **Role of analytical methods in ensuring that a low POP content value is implementable**

The need to identify HBCD in polystyrene foams below 1,000 mg/kg represents a significant challenge for the value chains actors such as the construction and demolition waste handlers, the recyclers and the enforcement authorities with respect to ensuring legal compliance.

The pragmatic identification and analysis of HBCD in polystyrene foams is an essential requirement for the environmentally sound management of POP containing waste foams. HBCD-containing foams in buildings can be *identified* through the information included with the Declaration of Performance (DoP) under the Construction Products Regulation (CPR) or by a Safety Data Sheet (SDS), or similar technical information when complying with REACH Article 33.1 notifying the presence of HBCD as SVHC. However, for all other foams where HBCD is suspected to be present there is a need for a robust analytical method to ensure compliance with the low POP limit.

There are today **two main challenges related to the analysis of HBCD**:

- Firstly, there is currently no standardised method to allow the analysis of HBCD in polystyrene foams.
- Secondly, there is a statistical uncertainty inherent in the analysis of HBCD in polystyrene foams which needs to be accounted for so as to give industry the needed confidence in their compliance efforts with any established threshold. To this end the necessary precision on the method has to be developed

Industry experience has shown that in order to ensure legal compliance with a given limit value, it is essential to be able to analyse the foam for the presence of HBCD in levels of at least 50% of that value. This means that even a limit of 1,000 mg/kg will present a considerable undertaking for the mentioned value chain actors, as polystyrene foams would have to be tested for levels of HBCD around 500 mg/kg in order to ascertain that they will be compliant or fall below a specified limit of 1,000 mg/kg. It is to be noted that the lower the low POP limit value is chosen, the higher the level of statistical uncertainty becomes.

It follows that the analysis of HBCD in polystyrene foams represents a challenge and at the same time a burden for said value chains actors. Analyses of HBCD carried out so far in environmental compartments (such as soil or water) cannot be transposed as such to the analysis in polystyrene foams. Polystyrene foams are a particularly difficult matrix when it comes to extracting HBCD for subsequent analysis.

Hence industry has been engaged in developing a robust and reliable analytical method for the identification of HBCD in polystyrene foams by means of gas chromatography with flame ionization detector (GC/FID). The method is designed to work on the basis of a 1,000 mg/kg threshold and aims to ensure a cost-effective and simple analysis that can be used by standard laboratories.



Other methods<sup>1</sup>, such as those relying on XRF (X-Ray Fluorescence) large or hand-held devices are useful in providing qualitative and quantitative indications as to the bromine content in polystyrene, but with limited ability to distinguish between different brominated compounds. The distinction between low molecular and polymeric-type brominated compounds has also been put in evidence by the XRF method. Until it becomes possible to cost-effectively identify HBCD with an appropriate level of confidence, recyclers will apply methods that only identify bromine. This will have much broader implications on plastics recycling as a whole (see note below).

Therefore, the availability of a reliable and accurate analytical method plays a significant role when determining a low POP limit under Annex IV and correspondingly an unintentional trace contamination limit under Annex I of the EU POP Regulation. Any threshold for HBCD in waste foams or new foams produced from recycling lower than 1,000 mg/kg becomes a significant hurdle for the operations of the value chains, likely to disrupt existing end-of-life material flows.

A low POP level of 1,000 mg/kg is considered both practical and pragmatic: it discontinues the use of construction and demolition waste foams that contain HBCD (since such foams contain HBCD above 5000 mg/kg). At the same time it supports the economic viability of recycling polystyrene foams that do not intentionally contain HBCD.

### Conclusion

Based on these considerations industry wishes to emphasize the following:

- Any limit lower than 1,000 mg/kg poses significant challenges for the polystyrene value chains actors including the plastics recycling and recovery industry, and hence these impacts should be carefully considered.
- Sufficient time allocation for the validation of the analytical methodology for a 1,000 mg/kg limit in polystyrene foams containing HBCD is essential in order to guarantee its reproducibility. Any lower limit will require the evaluation of an alternative method demanding a higher degree of precision. It is likely that such an endeavour will carry a significantly higher economic burden for the value chain actors, for the authorities and for the enforcement bodies.
- The international standardisation of the selected analytical method should be promoted.
- Industry asks that these essential considerations be accounted for by the authorities in charge of determining the low POP content limit under Annex IV to be consistent with the determination of the unintentional trace contamination limit under Annex I of the EU POP Regulation. Considerations to be seen in the context of industry's plea to avoid that the regulatory framework becomes a major barrier preventing a circular economy. The progressive complexity of the regulatory framework and its implementation for secondary raw materials such as the substance based REACH regulation imposing the need for multiple applications by recyclers can best be mitigated when sensible limits for classified products are being applied.

Nota: To be noted that both the XRF and the GC-FID methods should be considered complementary to each other, to the extent that they represent different degrees of differentiation regarding the identification of the chemical entities used in the PS foams. Whilst the XRF method provides primarily qualitative data as to the possible nature of said chemical entities, the presently developed method using GC-FID provides quantification of HBCD at the limit values specified in



the report. And whilst the XRF method is fast and cost-effective to be applied in the field, the GC-FID method requires stationary laboratory equipment that can delay data processing. Hence a certain hierarchy of method applications can be envisaged whereby the XRF method can be privileged but will never be a substitute for positive and quantitative identification of HBCD.

#### Reference

- <sup>1</sup> <http://www.ivv.fraunhofer.de/en/presse/presseinformationen/20150506-rapid-screening-test-for-hbcdd.html>