Introduction

From the 1st of July 2006, the Directive 2002/95/EC on the “Reduction of the use of certain hazardous substances in electrical and electronic equipment” (RoHS) bans the use of certain polybrominated flame retardants in electric and electronic devices unless no technical substitutes exist. Commission Decision 2005/680/EC has set limit values of 1 g/kg (0.1 %) for polybromobiphenyls (PBBs) and polybromodiphenyl ethers (PBDEs) in plastics. Compared to the levels generally encountered in environmental samples, these limit values in plastics are relatively high. Therefore, analysis of plastics and thus enforcement of the RoHS-Directive might seem straightforward and easy to implement. In practice however, things are a little more complicated: (1) The majority of BFR-analysing laboratories handled environmental samples and do not have experience with polymers, (2) the polymer matrix poses new, previously not encountered analytical problems and (3) the focus of the analysis is put more on higher brominated congeners that are more prone to degradation during analysis.

The first international inter-laboratory exercise was organised in 1999 and included five biological samples, two sediments and two standard solutions (de Boer and Cofino, 2002). These materials were sent to 26 participants in nine different countries. Only the results for BDE 47 were acceptable with RSDs ranging from 17 to 40 %. Results of all the other reported PBDEs (99, 100, 153, and 154) showed that a further improvement of the analyses was needed. The BDE 209 analysis was not under control by the participating laboratories. The conclusion of that study stated that “the performance of the laboratories can substantially be improved by ensuring a better calibration, good blanks, a better GC resolution, better internal standards, and protecting BDE 209 from high temperatures, incoming daylight and UV light” (de Boer and Cofino, 2002). Since 1999, several intercomparison studies have been organised to improve the quality in the analysis of BFRs (Voorspoels, 2006). All of these studies were directed towards environmental samples, such as sediment, sewage sludge, fish tissues, marine mammal blubber and human serum and milk. In parallel with the increasing number of participating laboratories in time, a general tendency for qualitative improvements of results and thus of analytical methods was observed. This was possible due to the continuous advice given by the organisers after each exercise and to the increased availability of (labelled) standards. Nevertheless, these interlaboratory studies have shown that most laboratories have improved their analytical methodology for PBDEs, except for BDE 209, for which several difficulties still persist.

In order to provide the analytical laboratories with the necessary tools for adequate quality assurance and quality control during PBDE analysis in polymers, a suitable certified reference material (CRM) is necessary. Such a CRM is commonly produced by characterisation through multiple expert laboratories. As mentioned above however, the expertise in the analysis of environmental samples does not necessarily imply the same expertise in polymer analysis. Therefore, an intercomparison study to assess the performance of expert-laboratories in the analysis of BFRs in polymers was organised and the results are presented.

Sample Preparation and Characterisation

Twenty kg of commercial poly(ethyleneterephthalate) (PET) granulate was prepared from commercially PET that was spiked with technical mixtures of Penta-BDE, Octa-BDE and Deca-BDE as well as the technical mixture of Deca-BB. The spiking levels were 0.7 g/kg (Penta-BDE, Deca-BDE and Deca-BB) and 0.4 g/kg (Octa-BDE). In addition, 0.8 g/kg Sb2O3 was added. Samples were extruded several times and bottled. Two hundred amber glass bottles were filled with approximately 10 g granulate each after re-homogenisation.
The total PBDE and PBB content of the sample was theoretically above the limits stipulated by the European RoHS directive. Taking into consideration that Deca-BDE is presently exempted from the RoHS directive, the total amount of RoHS relevant substances is 1.8 g/kg, with 1.2 g/kg deriving from the various tri- to nona-BDEs.

**Homogeneity**
Ten bottles were analysed in duplicate for their total Br-content by wavelength-dispersive XRF (WDXRF). The between-bottle variation of the Br-content was estimated as 0.32 % from one-way analysis of variance.

**Stability**
Stability was tested on samples stored for 1, 2 and 3 weeks at 60 °C and 8 weeks at 20 °C. In addition, samples were UV irradiated for 17 and 40 hours in their bottles to check for the influence of sunlight on the closed bottles. All samples were analysed by WDXRF. No significant decrease of the Br content of these samples occurred in these treatments, showing that no evaporation of PBBs or PBDEs had taken place over this period. UV irradiated samples did also not exhibit any discoloring or smell on opening. Stability of the PBDEs and PBBs in regard to interconversion of congeners was not directly assessed, but inferred from the stability of the total Br content. The agreement of the laboratory means with the target values confirms the assumption of stability.

**Target values**
A certificate of analysis was available for Deca-BB. No certificates of analysis of the batches of the technical BDE-mixtures were available, but samples from other batches from the same manufacturer are sold as reference materials. These certificates were used to calculate a nominal congener composition. This nominal composition is shown in Table 1. Using these certificates, a Br-content of 2.07 g/kg was calculated. Total Br content was determined by $k_0$-neutron activation analysis and a Br-mass fraction of 2.30 ± 0.10 g/kg was determined (expanded uncertainty in line with the ISO Guide to the expression of uncertainty in measurement (GUM); ISO, 1993). This result agrees with the theoretical calculated result of 2.1 g/kg, taken into consideration that certificates of analysis of the actual batches used were only available for decaBB. This good agreement allows confirmation of trueness of analytical methodologies through independently derived measurements.

### 3 STUDY SETUP

#### 3.1 Participants
In total 63 laboratories, of which 30 were from Europe (mostly Germany), 27 from Asia (mostly China) and 6 from the Americas (mostly USA) expressed their interest in the study, of which 37 sets of results were received. Participants submitted 2 to 12 individual results per congener in the PET material and 1-2 results per congener in the solution.

#### 3.2 Analytical methodology and target analytes
No method was prescribed, i.e. participants were free to use their own analytical methods. This freedom extended to sample preparation, cleanup and quantification. Participants received a method questionnaire to give more information on their analytical method used. One laboratory used HPLC, whereas all other laboratories used GC. Only one laboratory used isotopically labelled internal standards, whereas the other laboratories used PCB 209 (most), PAHs, or F-PBDEs as internal standard. Several laboratories based their results on external calibration.

### 4 RESULTS AND DISCUSSION
A detailed statistical analysis was only performed for results of BDE 47, BDE 99, BDE 100, BDE 153, BDE 183, BDE 196, BDE 197, BDE 203, BDE 206, BDE 209 and BB 209 as the number or datasets for the other congeners was too small to obtain meaningful results.
Repeatability and reproducibility

Data were screened for outliers of variance using the Cochran procedure (ISO, 1994) at a confidence level of 99% and outliers of mean values using Hampel (Davies, 1988) procedure with k = 4.5 (p = approx. 95%). An arbitrary maximum number of outliers of 5 for each procedure was defined. This limit was only exceeded once for Cochran outliers and never for Hampel outliers. In this case, visual inspection of the datasets resulted in final exclusion of 3 datasets on the basis of outlying variances.

Within (s_r) and between-laboratory (s_L) standard deviations, respectively, were calculated from one-way analysis of variance (ANOVA) as described in ISO 5725 (ISO, 1994). Reproducibility standard deviation was calculated as the square root of the squares of s_r and s_L. The results of this evaluation are shown in Table 1. Dependence of both s_r and s_L on the concentration was tested visually and via regression analysis.

Table 1: Grand means and their 95% confidence interval (CI), repeatability standard deviation (s_r), between-laboratory standard deviation (s_L) and reproducibility standard deviation (s_R); n: number of datasets

<table>
<thead>
<tr>
<th>Congener</th>
<th># Br</th>
<th>target value [mg/kg]</th>
<th>n</th>
<th>grand mean ± CI [mg/kg]</th>
<th>s_r [mg/kg]</th>
<th>s_L [mg/kg]</th>
<th>s_R [mg/kg]</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDE 47</td>
<td>4</td>
<td>227</td>
<td>26</td>
<td>220 ± 25</td>
<td>37.3</td>
<td>17</td>
<td>71.8</td>
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<tr>
<td>BDE 99</td>
<td>5</td>
<td>307</td>
<td>25</td>
<td>299 ± 31</td>
<td>23.6</td>
<td>8</td>
<td>61</td>
</tr>
<tr>
<td>BDE 100</td>
<td>5</td>
<td>63</td>
<td>24</td>
<td>59.6 ± 7.7</td>
<td>8.0</td>
<td>13</td>
<td>30.6</td>
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<tr>
<td>BDE 153</td>
<td>6</td>
<td>52</td>
<td>20</td>
<td>48.8 ± 4.4</td>
<td>5.2</td>
<td>11</td>
<td>10.5</td>
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<tr>
<td>BDE 183</td>
<td>7</td>
<td>149</td>
<td>22</td>
<td>97 ± 17</td>
<td>9.7</td>
<td>10</td>
<td>37.6</td>
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<tr>
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<td>37</td>
<td>19</td>
<td>29.8 ± 6.3</td>
<td>3.6</td>
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<td>86</td>
<td>20</td>
<td>57 ± 14</td>
<td>4.1</td>
<td>7</td>
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<tr>
<td>BDE 203</td>
<td>8</td>
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<td>21</td>
<td>22.3 ± 6.0</td>
<td>2.9</td>
<td>13</td>
<td>13.3</td>
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<td>BDE 206</td>
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<td>25</td>
<td>48.4 ± 10.7</td>
<td>5.2</td>
<td>11</td>
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<td>BDE 209</td>
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<td>697</td>
<td>27</td>
<td>705 ± 128</td>
<td>71.4</td>
<td>10</td>
<td>321.6</td>
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<tr>
<td>BB 209</td>
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<td>608 ± 110</td>
<td>56.2</td>
<td>9</td>
<td>263.1</td>
</tr>
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</table>

As seen in Table 1, between-laboratory standard deviation exceed the within-laboratory standard deviations on average by a factor of 1.6 to 7.8 (average: 4). While relative between-laboratory standard deviation (relative s_L) is independent of the concentrations, there is a significant correlation between the relative s_L and the degree of bromination.

Repeatability standard deviations are comparable to those found in environmental analysis, reproducibility standard deviations are consistently worse than what is obtained in other intercomparisons. This verdict is made even more severe by the fact that the PBDE and PBB concentrations in the PET sample were several orders of magnitude above those found in environmental samples. Differences between labs are especially high for higher brominated compounds. Unfortunately, these congeners are the most relevant ones in regard to the RoHS directive. While Deca-BDE is exempted, discussions are ongoing whether this exemption also covers minor constituents of the technical mixture or not (such as nona- and octabrominated congeners). If octa- and nonabrominated-BDEs are present (from the technical Deca-mix or through degradation of BDE 209), the accuracy in the determination of these congeners can become crucial to have the material in question pass the test or not.
Trueness

Trueness of the methods was assessed by comparison of the outlier corrected mean of means for each congener with the theoretical value as shown in Table 1. The uncertainty of the theoretical value was considered negligible compared to the confidence interval of the mean of laboratory means. The 95% confidence interval of the mean of laboratory means was used as uncertainty estimate of the mean value. The confidence interval of the mean of laboratory means agrees for most of the analytes (exceptions are BDE 183, BDE 197 and BDE 206) with the theoretically calculated target value (Table 1).

More important from a practical point of view is the question whether the material would be correctly have been classified as non-RoHS compliant. Seven laboratories classified the material falsely as containing less than 1 g/kg BDEs when only PBDEs were summed up (sum: 1.2 g/kg). Still 9 laboratories falsely classified the material as RoHS compliant when also PBBs were taken into consideration and the sum of polybrominated substances was 1.8 g/kg.

5 CONCLUSION

Analytical reproducibility for higher brominated congeners is a quality limiting factor at this time. This insufficient reproducibility is most likely due to laboratory- and method related issues. The fact that only one lab used an isotopically labelled standard for the determination of BDE 209 can explain the high degree of interlaboratory variation for the higher brominated congeners. It seems that only few laboratories succeed in attaining an acceptable quality level. The results of this study indicate that the learning process that occurred in environmental analysis needs to be repeated in polymer analysis to attain acceptable accuracy to allow for reliable testing of RoHS compliance.

6 REFERENCES


Voorspoels S. 2006. PhD dissertation, University of Antwerp, Belgium