TOWARDS THE FIRST CERTIFIED REFERENCE MATERIAL FOR POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND POLYBROMINATED BIPHENYLS (PBBs) IN TWO TYPES OF POLYMERS

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Introduction

The European Commission Directive on the "Restriction 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 since the 1st of July 2006 unless no technical substitutes exist [1]. Commission Decision 2005/618/EC has set limit values of 1 g/kg (0.1 %) for the sum of polybromobiphenyls (PBBs) and polybromodiphenyl ethers (PBDEs) in plastics [2]. The European RoHS Directive has also been adopted by Australia, Canada, Korea and Taiwan, while similar legislation is planned or has already been passed in the People's Republic of China, Japan and several states in the USA (e.g. Washington, Maine). Actual enforcement of this directive requires – amongst other measures - also testing of materials and products for their content of brominated flame retardants (BFRs). Reliable quality of the determination of BFRs is therefore crucial.

Originally, deca-BDE was exempted from this legislation and was still allowed, but since April 1, 2008 a ruling by the European Court of Justice has annulled this exemption starting from June 30, 2008 [3]. From then on, the use of PBDEs is no longer allowed in the EU.

Mass fractions of intentionally added BFRs to polymers range from 10-30 % and are thus far above the limits stipulated by the RoHS Directive, but concentrations near this limit are possible for recycled plastics. Considerable loads of BFRs in videocassettes made from recycled plastics have been already reported [4], showing that this scenario is not only a theoretical possibility.

In order to provide the analytical laboratories with the necessary tools for adequate quality assurance and quality control during PBDE analysis in polymers, the Institute for Reference Materials and Measurements (IRMM), one of the institutes of the European Commission's Joint Research Centre, has decided to produce two certified reference materials for PBDEs and PBBs in polyethylene (PE) and polypropylene (PP). Both materials will be certified for the total Br and Sb content and for the mass fraction of selected PBDEs, PBBs and Sb_2O_3. The materials will therefore be valuable quality control instruments for both XRF-based techniques that are used in screening of plastics for Br and Sb as well as for techniques that determine exact mass fractions of the individual flame retardants (e.g. GC/MS). Both materials are in the final stage of the certification process and their release is planned for end 2008/beginning 2009.

Materials and Methods
Material selection
Two materials based on a (partly) soluble polymer (PE) and an insoluble polymer (PP) were selected in order to cover as many analytical challenges as possible. The first case would test the removal of dissolved matrix, which can strongly interfere with the determination of BFRs, whereas the second material would be more challenging to extract.

Penta-BDE, Octa-BDE and Deca-BB technical mixtures were chosen as substances banned by the RoHS directive at the time the production of the reference materials started. It was aimed at achieving mass fractions not too far away from the legal limit for each technical mixture, while being not too far above the legal limit for the sum of all substances. In addition, Deca-BDE was added to give laboratories a means to confirm their ability to distinguish Deca-BDE from other BDEs, as it was still allowed at that time. As exemptions from the EU RoHS Directive need to be regularly reviewed and as other states regulate also Deca-BDE, there is a clear need for inclusion of this material as well. This approach has proven successful seeing the recent annulment of the exemption by the European Court of Justice [3].

Processing

Two batches of 90 kg of material were prepared from commercial PE and PP. No additives were added to the PP material. Ca-stearate, Irgafos 168 and Irganox 1010 were added to the PE material.

The granulates were fortified with technical mixtures of Penta-, Octa- and Deca-BDE as well as with a technical mixture of Deca-BB. In addition, Sb_2O_3 was added to simulate real samples, where Sb_2O_3 is usually added as synergist to the BFRs. Samples were extruded several times and the pellets (around 5 mm diameter) were filled into amber glass bottles of 20 g each. The approximate composition of the two materials is given in Table 1.

Table 1. Nominal composition of the two reference materials

| Matrix	Polyethylene	Polypropylene
Additives	none	Ca-stearate, Irgafos 1638, Irganox 1010
Penta-BDE tech.	0.7 g/kg	0.7 g/kg
Octa-BDE tech.	0.25 g/kg	0.2 g/kg
Deca-BDE tech.	0.7 g/kg	0.7 g/kg
Deca-BB tech.	0.7 g/kg	0.7 g/kg
Sb_2O_3	0.8 g/kg	0.76 g/kg

Results and Discussion

Between-bottle homogeneity

Homogeneity was assessed through determination of the total Br-content using wavelength dispersive x-ray fluorescence (WD-XRF). This technique uses an x-ray source to remove electrons from inner shells. Subsequent decay of these excited states leads to element specific photon emission. Between-bottle-homogeneity was tested on 20 samples. Samples were taken using a random-stratified sampling scheme, thus ensuring that the complete batch was covered.

Statistical tests were performed to detect potentially outlying individual results as well as outlying bottle averages. Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. It was furthermore checked whether the individual data and bottle averages follow a normal distribution using normal probability plots and whether the individual data are unimodally distributed using histograms. All distributions are normal or unimodal, allowing evaluation by one-way analysis of variance (ANOVA). Examples are shown in Figure 1.

Although homogeneous distribution of the total bromine is a good indication that the technical mixtures are homogeneously distributed or not, homogeneity of individual BFRs will be determined by GC/MS.

Figure 1. Results of a homogeneity study; the graph shows bottle averages of the Br-content and their 95 % confidence intervals.
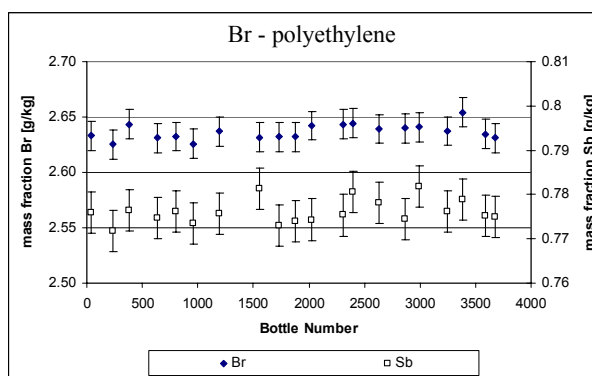
Assessment of stability

Stability testing is necessary to establish conditions for dispatch (short-term stability) to the customers as well as conditions for storage (long-term stability). All stability studies were conducted as isochronous stability studies [5]. In this type of studies, samples are stored for a certain interval at the test conditions. After that time, samples

are moved to conditions where further degradation is negligible ("reference condition"), effectively "freezing" the degradation status of the materials. This setup allows analysis of materials of various exposure times under repeatability conditions, thus greatly improving the sensitivity of the study to detect degradation.

Time, temperature and radiation were regarded as the most relevant influences on stability of the materials. The influence of radiation was minimised by the choice of a brown glass container, which eliminates most of the incoming radiation. In addition, materials are stored and dispatched in the dark, thus practically eliminating the possibility of degradation by radiation. Therefore, only the influences of time and temperature needed to be investigated.

PBDEs themselves are chemically stable compounds. Their high boiling points (up to above 400 °C) indicate that they are not subject to thermal degradation at temperatures encountered during everyday life. As stated above, possible degradation through radiation was minimised by the bottle material and storage and shipping in the dark. A known effect of "additive" BFRs like PBDEs and PBBs, i.e. BFRs that are not incorporated into the polymer matrix is diffusion of the flame retardants to the outer surface. The degree of this migration (also often called "blooming") depends on the type of polymer and BFR, geometry of the polymer matrix and temperature. Generally, increased temperature will increase blooming potential [6]. Therefore, temperature and time were regarded as the main factors influencing the stability of the two materials.

Stability during transport

Samples were stored for up to 4 weeks at different temperatures. Reference conditions were defined as storage at – 20 °C in the dark. Samples stored at these conditions form the time zero of this study. Two bottles were stored for each time/temperature combination. After the end of the study measurements were performed by WDXRF (Br, Sb). Because the total Br-content does not give any information whether the individual BFR compounds are stable or not, the WD-XRF results still need confirmation. Analysis of individual BFRs by GC/MS will be used for this purpose.

The WDXRF-studies were evaluated individually for each temperature. Results were screened for outliers using a Grubbs test, but only outliers also dubious on technical grounds were excluded. Linear regression lines were calculated for each study and the uncertainty of degradation for 1 week at 60 °C was calculated as described in [7] for each analyte. A significantly decreasing trend for the total Br-content was observed at 60 °C. This is probably associated with the volatility of the PBDE congeners. However, the associated uncertainty is very low and does not pose any problem for dispatching the samples (see Table 2). The results are summarised in Table 2, whereas graphical representations of the studies are given in Figure 2.

Table 2. Results of the evaluation of the short-term stability studies for the two polymer materials.

	Analyte	18 °C		60 °C	
		Outliers	Slope	Outliers	Slope
Polyethylene	Br	one (ret.)	not sig.	none	sig.
	Sb	one (ret.)	not sig.	one (ret.)	not sig.
Polypropylene	Br	none	not sig.	one (ret.)	not sig.
	Sb	none	not sig.	none	not sig.

sig./not sig.: significance on a 95 % confidence level; (ret): Outlier was retained

Stability during storage

Samples were stored up to 12 months at different temperatures. Storage at -20 °C was again defined as reference conditions for all studies. Two bottles were stored for each time/temperature combination. After the end of the study, four measurements were performed on each bottle, giving in total 8 results per time/temperature combination. Measurements were so far only performed by WDXRF (Br, Sb) and are being confirmed through analysis by GC/MS.

The studies were evaluated individually for each temperature. Results were screened for outliers using a Grubbs test, but only outliers also dubious on technical grounds were excluded. Linear regression lines were calculated for each study and tested for significance on a 95 % confidence level. Due to intrinsic variation of measurement

results no study can rule out degradation completely. Variation of measurement results therefore gives rise to an uncertainty component of degradation, which reflects the degree of uncertainty for the conclusion of negligible degradation. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is $0 \pm x$ % per time". In line with [7], this uncertainty component was estimated as uncertainty of the slope of the regression line multiplied with chosen shelf life. The results show that degradation occurs at 60 °C, but at 4 or 18 °C, the material appears stable. The selected reference temperatures applied throughout the production of the materials were valid and no storage difficulties are expected for the materials. An example of a study is given in Figure 3.

Figure 2. Results of a short-term stability study; the graph shows the average Br-content per time point and their 95 % confidence intervals.
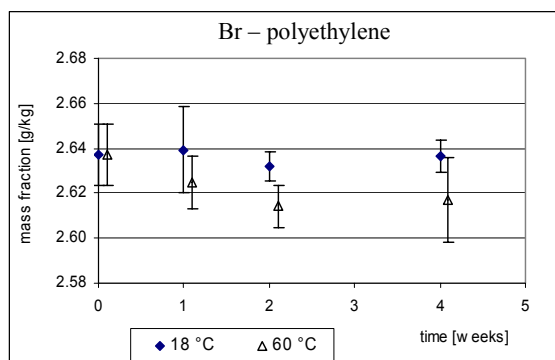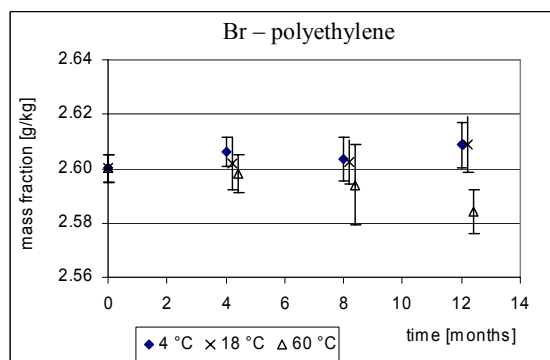
Figure 3. Results of a long-term stability study; the graph shows average Br-content per time point and their 95 % confidence intervals.

Characterisation and project finalisation

Characterisation of the content of the individual congeners is ongoing. Values of individual congeners will be assigned based on an interlaboratory comparison amongst laboratories of demonstrated competence. Laboratories were selected based results in a previous interlaboratory comparison [8]. Care was taken to maximise method variation in order to minimise the possibility of method bias. After a technical discussion of the results of the study (autumn 2008), values will be assigned. Uncertainty budgets comprising contributions of between-bottle heterogeneity, stability and characterization will be drawn up. Finally, the project will be subject to IRMM internal review as well as to peer-review by independent experts before release of the materials.

References

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