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Development of the First Certified Reference Materials for Several Brominated Flame Retardants in Polymers

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The first reference materials certified for several polybrominated flame retardants in polymers were developed. Commercially available polyethylene and polypropylene were fortified with technical mixtures of Pentabrominated diphenylether (Penta-BDE), Octa-BDE, Deca-BDE, and Decabrominated biphenyl (BB) (where the capitalized forms refer to the technical mixtures). Homogeneity was tested on 20 units of each material, and between-unit variation was confirmed to be below 4% for all congeners. Stability was assessed after storage of samples for 1 year at 4, 18, and 60 °C. Uncertainty of degradation during transport was found negligible for all congeners, whereas uncertainty of degradation for storage of 24 months at 4 °C was estimated between 2% and 11%. A characterization intercomparison involving 16 laboratories was organized. After exclusion of technically doubtful results, between-laboratory standard deviations ranged from 3% to 12%, making this intercomparison the best for this field of analysis so far. Statistical analysis revealed that the use of isotopically labeled internal standards did not improve analytical precision in this study. The good comparability, together with the independent confirmation of the assigned mass fractions via the total bromine content as well as by using non-GC/MS-based methods, allowed for the first time the certification of polymer materials for several brominated flame retardants.

Brominated diphenylethers (BDEs) belong to a class of brominated compounds which are, apart from the presence of the oxygen atom between the phenyl rings, structurally similar to polychlorinated biphenyls (PCBs) and, therefore, share the same numbering of congeners as proposed by Ballschmiter et al.¹ Brominated biphenyls (BBs) are the bromine homologues of PCBs; hence, the same numbering system is used. They are commercially available as technical mixtures of various congeners of which the name is derived from the average degree of bromination. For example, technical Penta-BDE consists of various tetra-, penta-, and hexabrominated congeners. To avoid confusion we will in this manuscript follow the convention that names in

capital letters refer to the technical mixtures, whereas lowercase letters refer to the congeners themselves. Therefore, “Octa-BDE” refers to the technical mixture with an average degree of bromination of 8, whereas “octa-BDEs” refers to all octabrominated congeners. Technical Deca-BDE and Deca-BB are relatively pure substances, consisting of more than 97% pure BDE-209 and BB-209, respectively. Congener patterns of the technical mixtures depend on the reaction conditions and vary between producers and even batches.

The European Commission Directive on the “Restriction of the use of certain hazardous substances in electrical and electronic equipment” (RoHS)² bans the use of certain brominated flame retardants (BFRs) in electric and electronic devices since July 1, 2006 unless no technical substitutes exist, and limit values of 1 g/kg (0.1%) for the sum of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) have been set.³ Similar legislation has been adopted by, e.g., Australia, Canada, Korea, and Taiwan, the People’s Republic of China, Japan, and several states in the United States (e.g., Washington, California, Maine). Enforcement of this legislation requires, among other measures, testing of materials and products for their content of BFRs. Reliable quality of the determination of BFRs is therefore crucial.

Although chemical analysis of BFRs seems quite straightforward (extraction, cleanup, quantification by gas chromatography/mass spectrometry (GC/MS)), experience has shown that the opposite is true.^{4,5} Several aspects that are inherently coupled to this group of chemicals can hamper sound analysis. Most problems are situated in the final quantification step.

Several injection techniques for the introduction into the GC system, all with their specific drawbacks, are available. Split/splitless injectors are robust, and perform well if injected extracts are dirty, but temperature-induced degradation of analytes may occur if the injector temperature is too high. This technique is also known to discriminate analytes with high molecular weight. Lowering the injector temperature will discriminate even more

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(3) Decision 2005/618/EC of the European Commission of 18 August 2005 amending Directive 2002/95/EC of the European Parliament and of the Council for the purpose of establishing the maximum concentration values for certain hazardous substances in electrical and electronic equipment, OJ L 214, 19.8.2005, 65–65.

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against high molecular weight analytes. This can be overcome by application of a pressure pulse.⁶ The issue of discrimination of high molecular weight analytes is of special importance when analyzing BFRs with high bromine content, such as nona-BDEs and BDE-209. An alternative is offered by the programmed temperature vaporization (PTV) injector, whose injection parameters can be modified to optimize the transfer of BFRs from the liner to the column.

PBDEs with a low to medium degree of bromination (tri- to hepta-BDEs) usually are analyzed on capillary columns of 30–50 m length to achieve sufficient resolution for all congeners of interest. Column diameter is preferably <0.25 mm to minimize possible on-column degradation.

For the analysis of PBDEs with high degree of bromination, such as BDE-209, short columns (preferable 10–15 m) with thin film thickness (0.1–0.2 μm) are recommended in order to reduce the residence time (and hence possible degradation) in the column.^{6,7} Especially BDE-209 should receive special attention because of its sensitivity to heat and the higher susceptibility for degradation in the GC system, which seems to necessitate specific column stationary phases.⁶ Even columns with comparable stationary phases from different manufacturers can have varying results concerning BDE-209 elution.⁶ Due to the different needs for low- and high-brominated congeners, column selection is always a matter of compromises.

As mentioned earlier, BDE-209 is a BFR that deserves special attention concerning chemical analysis. Apart from the crucial column selection, also the oven programming and injector settings and condition can compromise the analysis of BDE-209 or even render it impossible. Degradation to some extent is unavoidable and can vary greatly depending on the system status, oven temperature, and the residence time in the injector and column. Fast temperature programming leads to less degradation but can hamper the analysis of complex samples because of lower resolution.⁸

In order to maintain an adequate analyte transfer to and through the column, all injector parts, the liner, and column (head) need to be completely free from activated sites. Therefore, the liner needs to be replaced often and the column is shortened on a regular basis. A dirty liner and/or column head can lead to debromination (degradation) of BDE-209. Upon injection of BDE-209, other BDE congeners are formed in the inlet system, such as BDE-206, BDE-207, and BDE-208. In an optimized GC system, this degradation is under control and negligible. A contaminated injection system leads to significant formation of debromination products,⁸ which can interfere with the quantification of BDEs -206, -207, -208, and -209. Degradation of BDE-209 itself can be compensated for with the proper use of a mass-labeled internal standard (IS).

Most data on analytical quality in BFR determination is available for environmental samples. The first international interlaboratory exercise organized in 1999 included five biological samples, two sediments, and two standard solutions.⁴ Only the

results for BDE-47 were acceptable with between-laboratory RSDs ranging from 17% to 40%. Also, most studies organized since 1999 were oriented toward environmental samples such as sediment, sewage sludge, fish tissues, marine mammal blubber, and human serum and milk. The Arctic Monitoring and Assessment Programme (AMAP) organizes a study on human serum three times a year. Average between-laboratory RSDs for 2007 and 2008 were between 20% and 40%, with sometimes outliers for, e.g., BDE-209 (90%), and do not indicate a clear improvement of results.⁹ Average mass fractions of PBDE congeners range from 0.15 to 1.0 $\mu\text{g}/\text{kg}$ in these studies. An intercomparison between eight laboratories for organic contaminants in marine mammal tissues in 2005 reported between-laboratory RSDs between 15% and 75% for five congeners not including BDE-209 (mass fractions between 8 and 120 $\mu\text{g}/\text{kg}$).¹⁰ In an interlaboratory comparison exercise organized by QUASIMEME (European Union project “Quality Assurance of Information for Marine Environmental Monitoring in Europe”) in 2007, a relative between-laboratory standard deviation of 74% for a mass fraction of 6 $\mu\text{g}/\text{kg}$ was found for BDE-209 in marine sediment,¹¹ in accordance with previous exercises, for which coefficients of variation around 50–60% were documented for BDE-209 in sediments.¹²

To our knowledge, the best results for an intercomparison exercise for environmental samples so far were obtained in a study organized by the network of reference laboratories and carefully selected related organizations for monitoring and biomonitoring of emerging environmental pollutants.¹³ There, only BDE-209 was analyzed in a standard solution and a dust sample (NIST SRM 2585). Proper selection of participants and the rigorous implementation of previous recommendations resulted in relative reproducibility and repeatability standard deviations below 10% for both samples, and all reported results for the dust samples were not significantly different from the certified value. A follow-up study was organized comprising now both routine and some expert laboratories (10 participants in total). For this exercise, a standard solution and a dust (NIST SRM 2585) and sediment sample had to be measured, and the between-laboratory variation coefficient varied between 15% and 30%, depending on the matrix.

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 1 g/kg are possible for recycled plastics. Considerable loads of BFRs in videocassettes made from recycled plastics have already been reported.¹⁴ The limit of 1 g/kg stipulated in the RoHS directive is several orders

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of magnitude above those values usually encountered in environmental samples,¹⁵ and better comparability of results than in environmental analysis would therefore be expected for polymer samples. However, a recent intercomparison on PBDEs in poly(ethylene terephthalate) gave relative reproducibility standard deviations between 24% and 47%.¹⁶ The German Federal Environment Agency (UBA)¹⁷ and the International Electrotechnical Commission (IEC) developed standardized methods in order to improve comparability of analytical results, but none of these include PBBs. Validation of the method by the German Federal Environment Agency in an intercomparison which comprised four polymers fortified with technical mixtures of Penta- and Octa-BDE gave repeatability and reproducibility standard deviations of 4% and 25%, respectively. Intercomparisons of the draft IEC standard, which follows largely the German standard method, were considered by the IEC members as showing insufficient agreement between results, and the method for the determination of BFRs was therefore only included as an informative annex. Significant improvement of the determination method is therefore needed to allow reliable quantification of BFRs in polymers. Moreover, as shown by the results obtained with the German standard method, within-laboratory repeatability is in this case a particularly poor estimator of measurement uncertainty, with reproducibility standard deviation exceeding repeatability standard deviation by a factor 6.

In order to provide the analytical laboratories with the necessary tools for adequate quality assurance and quality control for BFR analysis in polymers, the Institute for Reference Materials and Measurements (IRMM), one of the institutes of the European Commission's Joint Research Centre (JRC), therefore decided to produce two reference materials for PBDEs and PBBs in polymers. The materials should be certified for individual congeners of PBDEs and PBBs as well as for total Br, as screening for Br is frequently used to identify potentially noncompliant samples. The steps leading to the certification of total Br is described in detail in the certification report.¹⁸ This project was necessary, as so far only two certified reference materials (CRMs) for BFRs are available, both from the National Metrology Institute of Japan and only certified for BDE-209 (NMIJ-8108a and 8110-a).

Production of CRMs is a multistep process that includes processing, homogeneity testing, stability testing, characterization, assignment of property values, as well as after-sales service. Many of these steps require reliable measurements, most noteworthy characterization, i.e., the measurements used to obtain the certified values. This, however, creates a problem for the first

Table 1. Nominal Composition of the Two Reference Materials

	ERM-EC590	ERM-EC591
matrix	polyethylene	polypropylene
additives	none	lubricant (calcium stearate), antioxidants (Irgafos 1638, Irganox 1010)
Penta-BDE techn	0.7 g/kg	0.7 g/kg
Octa-BDE techn	0.25 g/kg	0.2 g/kg
Deca-BDE techn	0.7 g/kg	0.7 g/kg
Deca-BB techn	0.7 g/kg	0.7 g/kg
Sb ₂ O ₃	0.8 g/kg	0.8 g/kg

CRM of a kind, as demonstration of high measurement quality requires CRMs itself. Production of a first CRM of a certain type is therefore an especially difficult task, as no reliable quality control tools are available to ascertain the accuracy of the measurement results of the various studies. This paper describes the successful certification of the two materials for their mass fraction of BFRs.

EXPERIMENTAL SECTION

Material Selection and Processing. The materials selected should address all main problems encountered in the determination of BFRs in polymers:

One material should at least be partially soluble in common solvents to mimic the problem of separation of dissolved polymer in the extract.

One material should be hardly soluble in common solvents, as extraction of such a polymer is more difficult.

Samples should be in a coarse form, possibly requiring some grinding to cover also this part of the measurement process.

Target mass fractions should be close to the limits of 1 g/kg.

The materials were processed by DSM (Geleen, The Netherlands). Polyethylene was chosen as partly soluble polymer and polypropylene as insoluble polymer. Commercial polyethylene and polypropylene were fortified with technical mixtures of Penta-BDE, Octa-BDE, Deca-BDE, and Deca-BB. Sb₂O₃ was added to both materials, as it is commonly used as synergist for BFRs. The nominal composition of materials is given in Table 1. This nominal composition was unknown to the participants at the time of the characterization study. The materials are in granular form (particle diameter about 2 mm) and are packed in units of 20 g each. Approximately 3300 units of each material were prepared.

Homogeneity Study. For each material, homogeneity was tested on 20 units selected by a random stratified scheme covering the whole batch. Four BFRs analyses were performed on each unit by ultrasonic extraction with toluene and subsequent quantification by GC/MS (BFRs). Sample intake was 0.5 g. Measurement sequences were randomized to be able to discriminate between possible trends in the filling sequence and trends in the analytical sequence. Significant trends in the analytical sequences for BDEs -100, -196, -197, -207, and -209 (polyethylene) and BDEs -47, -99, -100, -127, -183, -206, -207, and BB-209 (polypropylene) were corrected prior to the subsequent evaluation steps.

The studies were evaluated by one-way analysis of variance (ANOVA) as described by ISO Guide 35.¹⁹ The between-unit standard deviation (s_{bb}) and within-unit standard deviation (s_{wb}),

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repeatability of the measurements) were calculated. In addition, the maximum heterogeneity that could be hidden by the method variability, u_{bb}^* ,²⁰ was calculated as

$$u_{bb}^* = \sqrt{\frac{MSW}{n}} \sqrt[4]{\frac{2}{\nu_{MSW}}}$$

with MSW being the mean squares within groups from the ANOVA, n the number of replicates per bottle, and ν_{MSW} the degrees of freedom of MSW. In some cases, results from the stability studies were used to give an additional assessment of homogeneity.

Stability Study. The most relevant degradation pathway was assumed to be “blooming”, i.e., a diffusion of the flame retardants to the surface of the polymer and consecutive evaporation. This blooming is well documented and leads to increased loads of BFRs in household dust.²¹ Blooming usually follows Fick’s law,²² and higher temperatures lead to faster diffusion.

Stability was tested using an isochronous design.²³ In this type of study, 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.

Samples were stored for 0, 4, 8, and 12 months at 4, 18, and 60 °C, respectively. Storage at –20 °C was defined as reference condition 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 eight results per time/temperature combination (two bottles × four replicates). Measurements were performed by ultrasonic extraction with toluene and subsequent quantification by GC/MS.

Linear regressions were performed for each analyte and temperature, and the slopes were tested for significance. Even in absence of indication of degradation, the results cannot completely rule out degradation. The extent to which degradation is possible within the repeatability of the measurements is captured by the uncertainty of stability. This uncertainty was estimated as

$$u_s = u_b t$$

with u_s being the uncertainty of stability, u_b the uncertainty of the slope of the regression line with a slope of 0, and t the chosen duration.²⁴ Two uncertainties were estimated, namely, the uncertainty of short-term stability (u_{sts} , the uncertainty of degradation during transport) and the uncertainty of long-term stability (u_{lts} , the uncertainty of degradation during storage). The former was estimated for a period of 1 week at 60 °C, the

Table 2. Overview of Methods Used for the Determination of BFRs in the Two Polymer Materials

grinding	samples taken as is and various grinding techniques (scissors, laboratory mill, cryogrinding)
sample intake	particle sizes from 0.25 to 2 mm
extraction	20 to 1000 mg Soxhlet extraction with toluene or dichloromethane ultrasonic-assisted extraction with toluene or isooctane pressurized liquid extraction with toluene or isooctane static extraction with toluene complete dissolution in xylene/dimethyl glutarate
internal standards	one or multiple PCBs fluorinated diphenylethers unlabeled diphenylethers ¹³ C-labeled analogues for some or all measurands
GC injectors	cool-on-column split/splitless PTV
GC columns	one column only: DB-HT, DB-5MS, ZB-5HT, Rtx-5-Sil-MS, Rtx CLP, Rtx-5MS, ZB-5HT Inferno two columns (DB-5MS/CP-Sil8; DB-5/Rtx-5MS)
ionization technique	electron impact electron capture negative ionization
MS systems	quadrupole MS sectorfield MS with resolutions >5000 amu

latter for a period of 2 years for storage at 4 °C. For the uncertainty contribution for 2 years of storage, all studies were combined to have more data points per time point. As degradation proceeds faster at higher temperatures, combining results from 4 °C with those from 18 and 60 °C still results in a conservative estimate of stability. In this way, the 1 year study could be extrapolated to estimate potential degradation over 2 years without falsely inflating the uncertainties.

Characterization. Setup of the Study. Characterization aimed at randomization of significant laboratory bias. Therefore, an intercomparison of laboratories that participated successfully in previous intercomparisons on the determination of BFRs in polymers was organized. Fulfilment of quality management requirements ensured that the technical standard had been maintained from the time of demonstration of competence to the actual measurement. Most participating laboratories were accredited to ISO 17025, even if the measurements are in many cases not covered by the scope of accreditation. Most laboratories were specialized in analysis of industrial and polymer samples, although also two environmental analysis laboratories participated in the study. The environmental laboratories had demonstrated their competence in the analysis of polymer samples by submitting results on a quality control material consisting of BFRs in poly(ethylene terephthalate). Laboratories were free to choose their own methods, i.e., methods they were familiar with. The predominance of industrial analytical laboratories led to deviations of the usual practice in environmental analysis laboratories with regards to the choice of columns and injectors.

Sixteen laboratories were selected to cover different extraction and quantification methods. A short summary of the methods is given in Table 2; a detailed description is given in the Supporting

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Information. Before the start of the measurements, a telephone conference was organized in which the detailed measurement protocol was discussed and during which potential misunderstandings were solved.

As can be seen in Table 2, a wide variety of extraction techniques, internal standards, and GC/MS systems were employed.

Extraction: Most laboratories used toluene as extraction solvent, with Soxhlet extraction being the dominant technique. Extraction times ranged from 1 to 24 h. Other techniques included ultrasonic-assisted extraction, pressurized liquid extraction, and static extraction. One laboratory dissolved the samples completely.

Internal standards: A variety of internal standards was used. Several laboratories used either one or several PCBs as internal standard for all analytes, whereas others employed a suite of PCBs, fluorinated diphenylethers, isotopically labeled as well as nonlabeled PBDEs.

GC systems: GC systems varied widely with respect to injection systems and columns used. Most laboratories determined all samples on one column, but two laboratories employed two columns. In one case, only nona- and decabrominated BDEs as well as BB-209 were analyzed on the second column, whereas the second laboratory also analyzed octabrominated congeners on the second column. Determination of all congeners on a single column is usually not recommended as a long GC run leads to degradation of BDE-209. However, the samples contained few of the lower brominated congeners due to their industrial origin, thus making long GC runs superfluous. Temperature programs for laboratories using only one column ranged from 15 to 28 min, which is short enough to avoid degradation. Yet another laboratory used two columns to avoid some coelutions, delivering two complete data sets.

Quantification: All laboratories used mass spectrometry as quantification technique, but also here the MS systems (quadrupole, two sectorfield) and ionization techniques varied. In addition, two laboratories performed measurements by high-performance liquid chromatography with UV detection (HPLC-UV) and ion-attachment mass spectrometry (IA-MS), respectively, to confirm the results from GC/MS measurements. Each laboratory received two bottles of each of the two materials and two ampules of a quality control solution. These two quality control solutions were candidate CRMs provided by the U.S. National Institute for Standards and Technology (NIST), which had not been released yet, but whose certificates were in the final review stage. The materials consisted of BDE-209 in isooctane (candidate SRM 2258) and a PBDE mix in isooctane (candidate SRM 2257). The use of these solutions was preferred over the possibility to use one of the Japanese CRMs, as those are only certified for BDE-209. Each laboratory was requested to perform six independent measurement series. Each measurement series consisted of a complete calibration line, determination of a method blank, measurement of a quality control sample, and measurement of one extract of the two materials. Two quantitative assessments for the technical quality were available. Laboratories' results for the quality control solution were compared to the candidate certified values. Results deviating significantly from the candidate certified

values were excluded from the evaluation. In addition, the Br content calculated on the results for the various congeners was compared to the Br content, which had been determined independently by several laboratories using neutron activation analysis as well as destructive methods. Data sets were excluded if the calculated Br content was significantly above the candidate certified Br content. A technical discussion was held with the laboratories after receipt of the results. This discussion aimed at identification of analytical problems that would result in exclusion of data sets on technical grounds.

Statistical Evaluation. Results accepted on technical grounds were subjected to a further statistical evaluation.

It was checked whether the data followed normal distributions and whether variances for each congener were homogeneous. ANOVAs were performed to evaluate average within- and between-laboratory standard deviations. These evaluations were performed with a modified version of the software SoftCRM.²⁵ No outliers were eliminated solely on statistical grounds.

In addition, within-laboratory standard deviations were investigated more deeply using the set of results accepted on technical grounds: regression analyses of absolute/relative within-laboratory standard deviation versus mass fraction were performed. With the use of ANOVA, it was investigated whether the within-laboratory standard deviation differed between congeners. A regression analysis of recovery of the assigned value versus the particle size used was performed to investigate a potential influence of the particle size on the results. Finally, repeatability of results obtained using isotopically labeled standards was compared to the one obtained using nonisotopically labeled standards. Results obtained using a different isotopically labeled congener than the one quantified were classified as obtained by "nonlabeled" standards. For these investigations, results from both materials were pooled into one data set. Statistical evaluation was performed using Statistica 7.0.

RESULTS AND DISCUSSION

Homogeneity. The results of the homogeneity evaluations are shown in Table 3.

As can be seen in Table 3, between-bottle variation was confirmed to be below 4% for all congeners, proving the suitability of the materials as CRMs.

Stability. Of the 84 regression lines (14 congeners \times 3 temperatures \times 2 materials), only the slope of BDE-127 in the polyethylene material was found significant after 1 year of storage at 60 °C. This finding is actually below the expected value of 4 statistically significant slopes at a confidence level of 95%. In addition, the mass fraction of BDE-127 apparently increases, which could only be explained by degradation of another congener, forming BDE-127, which is extremely unlikely and is most likely an analytical artifact. In any case, BDE-127 is not certified, so the slope, even if real, is irrelevant. The uncertainties of stability during dispatch and storage are listed in Table 4.

As can be seen in Table 4, potential degradation during transport is <0.3% and therefore negligible in all cases. Uncertainties of degradation during storage range from 3% to 12%. These uncertainties do not so much reflect any real degradation but are

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Table 3. Results of the Homogeneity Study for ERM-EC590 and ERM-EC591^a

	EC590			EC591		
	s_{wb} [%]	s_{bb} [%]	u_{bb}^* [%]	s_{wb} [%]	s_{bb} [%]	u_{bb}^* [%]
BDE-47	6.8	0.6	1.5	10.1	n.c.	2.2
BDE-42 + -66	4.6	2.1	1.0	4.2	1.8	0.9
BDE-85	9.6	1.5	2.1	10.7	n.c.	2.3
BDE-99	8.1	n.c.	1.7	9.1	n.c.	2.0
BDE-100	7.1	n.c.	1.5	6.8	n.c.	1.5
BDE-127	4.1	0.8	0.9	7.4	n.c.	1.6
BDE-183	11.2	n.c.	2.4	7.4	n.c.	1.6
BDE-196	9.2	n.c.	2.0	6.2	n.c.	1.3
BDE-197	12.2	2.3	2.6	6.8	1.0	1.5
BDE-203	7.6	3.4	1.6	6.9	n.c.	1.5
BDE-206	6.5	n.c.	1.4	4.7	n.c.	1.0
BDE-207	8.0	n.c.	1.7	7.5	n.c.	1.6
BDE-209	10.9	n.c.	2.3	8.4	n.c.	1.8
BB-209	9.1	1.7	1.9	4.7	n.c.	1.0

^a n.c. = cannot be calculated as the mean squared error between bottles is larger than the mean squared error within bottles.

Table 4. Results of the Evaluation of the Uncertainties of Stability for ERM-EC590 and ERM-EC591^a

analyte	ERM-EC590		ERM-EC591	
	$u_{sts60^\circ C, 1week}$ [%]	$u_{lts4^\circ C, 2years}$ [%]	$u_{sts60^\circ C, 1week}$ [%]	$u_{lts4^\circ C, 2years}$ [%]
BDE-47	0.1	6.1	<0.1	2.2
BDE-42 + -66	0.1	6.7	<0.1	2.9
BDE-85	0.2	11.5	0.1	7.4
BDE-99	0.1	9.2	0.1	4.3
BDE-100	0.2	12.1	0.1	4.2
BDE-127	0.1	3.4	<0.1	3.2
BDE-183	<0.1	3.1	0.1	3.4
BDE-196	0.1	4.4	0.1	5.9
BDE-197	0.1	8.9	0.1	6.8
BDE-203	0.1	6.0	0.2	10.8
BDE-206	0.1	5.8	0.1	6.2
BDE-207	0.1	6.8	0.1	5.2
BDE-209	0.1	6.3	0.1	4.8
BB-209	0.1	5.4	0.1	4.4

^a u_{sts} was estimated for a period of 1 week of storage at 60 °C.

the combined effect of the method variability and the extrapolation of the results of the 12 months study to a shelf life of 24 months. This is especially true for the estimates for BDE-85 and -203, where the higher repeatability standard deviation of the study makes setting tighter limits for potential degradation impossible. Further stability studies lasting 24, 36, 72, and 108 months are ongoing. On the basis of the findings of these studies, the uncertainty of stability might be decreased in the future.

Characterization. Technical Evaluation. The technical discussion highlighted some analytical pitfalls, such as grinding of samples, quality of available commercial standards, partial dissolution of the polymers, and coelutions.

Grinding of the samples, especially the polypropylene material, posed a specific problem to many laboratories. Results at IRMM indicate that extraction efficiency strongly depends on the particle size, with samples of smaller particle sizes giving higher results (data not shown). The effect was especially pronounced for the polypropylene sample. This result was obtained with isooctane as extraction solvent to avoid dissolution of polymers. Other laboratories, however, used the granulate without grinding and

still achieved results in good agreement with the other laboratories' data. The effect of particle size seems therefore to be a combination of extraction method (solvent, technique) and particle size.

Two laboratories reported problems with the commercial standard solutions they used. A single congener standard for BDE-47 gave only 80% of the response of a single congener standard from another supplier. Our own results indicated that a certified BDE mix, also from the same producer, contained only 55% of the stated mass fraction of BDE-209 when calibrated against a standard from yet another supplier. Using the results on the certified standard solutions SRM 2257 and 2258 allowed confirmation that the standard used was incorrect in former case but confirmed the correctness of the calibration standard in the other case. Therefore, the results were excluded in the former case but retained in the latter. Quality of the standards therefore is still an issue in the determination of BFRs, and the recent release of the NIST certified solutions SRM 2257 and SRM 2258 should lead to an improvement in this field.

Several laboratories reported problems caused by the partial dissolution of the polymer matrix, which caused film formation in the liner of the GC, resulting in degradation of BDE-209. Also, sensitivity was affected by residual polymer. In one case, results for the polyethylene material were therefore withdrawn. Approaches used to counter this problem included reducing the sample intake dramatically, choice of another solvent, or a cleanup of the extract.

Two laboratories reported that accurate determination of BB-209 using the recovery of BDE-209 was not possible.

One laboratory reported results for the quality control solution that were a factor of 5–10 above the candidate certified values, without any visible pattern that would hint at a dilution error. This data set was excluded. Two laboratories reported results that were consistently high, resulting in calculated Br mass fractions of 50% and 150% above the ones determined by element-specific methods. Also these results were excluded from the further evaluation. The fact that the results for one of the two data sets for quality control solution agreed with the candidate certified values clearly shows that traceability of results cannot be guaranteed by correct calibration alone—a thorough control of all measurement steps is crucial for comparability of results. A third laboratory reported results 15–25% above those of the other laboratories. This laboratory had corrected its result for the recovery obtained on a noncertified quality control material. The laboratory submitted the uncorrected data set after the technical discussion. As at this stage the tentative averages had been revealed, the data set was not included in the calculation of the certified values.

The technical discussion resulted in exclusion of four complete data sets plus the additional exclusion of one data set for the polyethylene material. After this technical evaluation, 5–12 data sets were retained for BDEs -28, -99, -100, -153, -154, -196, -197, -209, and BB-209.

Literature on possible coelutions on different GC columns indicates that for the columns used in this study, a separation of BDE-198/BDE-203 is generally impossible.²⁶ This coelution is confirmed by the results of the quality control solution, which

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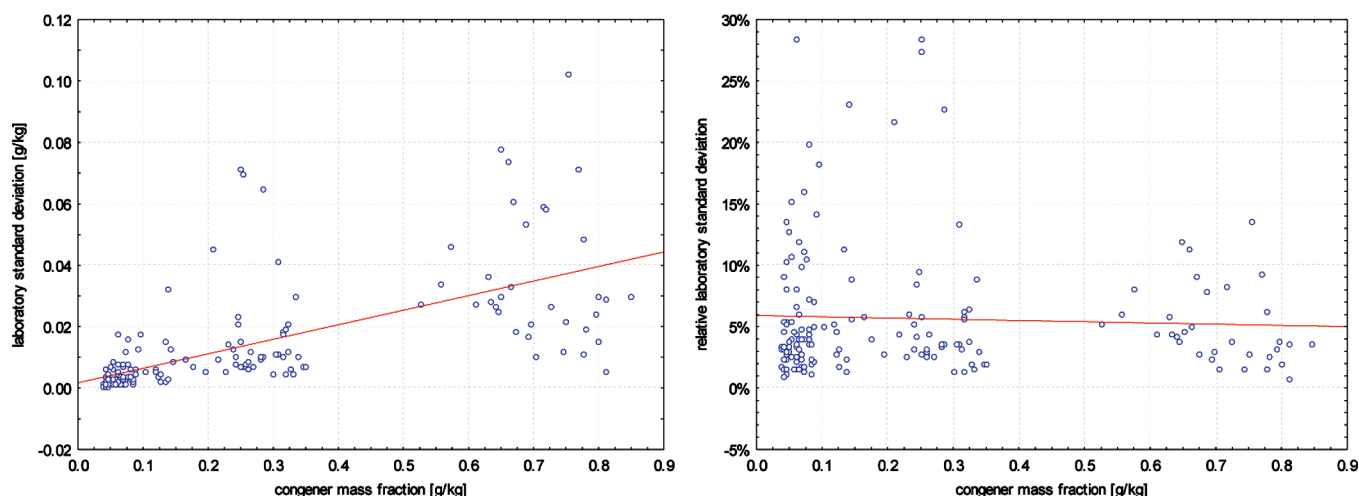


Figure 1. Regression analysis of within-laboratory standard deviations.

contained both BDE-198 and BDE-203: Many laboratories did not report results for BDE-198 but reported results for the quality control solution for BDE-203 that agrees well with the sum of BDE-198 and -203. The results for the polymer material, however, revealed another potential coelution, namely, for BDE-196 and BDE-198/BDE-203: four laboratories reported separate results for BDE-196 and -203 (and did not report BDE-198), whereas one laboratory reported coelution of BDE-196 and -203 an apparently equivalent column and separate results for BDE-198. Separation between BDE-196 and BDE-198/BDE-203 was therefore apparently possible for the first set of laboratories, whereas the other laboratory managed to separate BDE-198 from BDE-196/BDE-203. All laboratories confirmed the identity of the congeners by the retention time of individual standards. Slight differences between theoretically identical columns therefore seem to cause different coelutions. Due to this unclear situation, no values for BDE-196, -198, and -203 were assigned. Also between BDEs -197 and -204 coelution is highly likely. The certificate of SRM 2257 only gives one certified value for BDE-197/BDE-204, which highlights the obvious coelution between these two congeners. The participating laboratories reported either BDE-197 or BDE-204, but as the values were consistent, one value was assigned to the sum of BDE-197 and -204.

Statistical Evaluation. Several outliers of variance were detected using the Cochran procedure. These results were retained, as the measurement uncertainties reported by these laboratories was not significantly higher than those of the other laboratories. It was concluded that for these laboratories a higher fraction of the combined measurement uncertainty is covered by the within-laboratory repeatability. For three congeners (BDE-99 and -196 in the polyethylene material and BDE-99 in the polypropylene material) one outlying laboratory mean was detected. Also this value was retained as the result agreed with the others within the respective uncertainties. The assumption of normal distribution was accepted for all data sets based on normal probability plots and kurtosis/skewness tests.

ANOVA showed no difference in within-laboratory repeatability between the various congeners on a significance level of 95%, confirming that results for different congeners can indeed be pooled. Results in the various groups frequently did not follow normal distributions, thus putting into doubt the validity of the

statistical *F*-tests. Visualizations, however, show that the 95% confidence intervals of the averages for the various congeners overlap widely, confirming the nonsignificance of the ANOVA.

The regression analysis (Figure 1) showed a significant increase of absolute within-laboratory standard deviation with increasing congener mass fraction, while relative within-laboratory standard deviations remained constant. The various relative standard deviations therefore can be combined into a single data set.

The correlation between final particle size and the recovery of the assigned values was not significant, confirming the assumptions made in the technical discussion that this influence is only visible for certain combinations of solvents and extraction techniques.

An ANOVA of within-laboratory standard deviation versus the type of internal standard showed that results obtained in this study with ^{13}C -labeled internal standards for the congener in question had on average higher within-laboratory standard deviations than those obtained without ^{13}C -labeled standards. Although this difference was significant on a 95% confidence level, it is highly influenced by the results of two laboratories with high standard deviations using ^{13}C -labeled internal standards. The distribution of results is therefore not normal. After removal of the results from these two laboratories, results obtained by ^{13}C -labeled internal standards still showed higher variations but differences were no longer significant. Nevertheless, this study does not indicate any superiority of results obtained using isotopically labeled internal standards. This result is unlikely to be due to selective removal of laboratories using nonlabeled standards in the technical evaluation: Three of the four laboratories excluded indeed used nonlabeled standards, the fourth used ^{13}C -labeled standards for four congeners. The fact that also one data set using isotopically labeled internal standards had to be excluded for technical grounds shows that also in this type of analysis isotopically labeled internal standards are no “silver bullet” and are also prone to technical errors.

Mean of accepted means, standard deviations of data set means, as well as within- and between-laboratory standard deviations are shown in Table 5. As can be seen in Table 5, standard deviations between laboratory means ranged from 5% to 12%, with the exception of BDE-196, where it was 27%. This high variation is most likely due to coelutions possible for this congener. Between-laboratory standard deviations were in several cases (nota

Table 5. Statistical Evaluation of the Technically Accepted Data Sets for ERM-EC590 and ERM-EC591^a

measurand	polyethylene (ERM-EC590)					polypropylene (ERM-EC591)				
	<i>p</i>	average [mg/kg]	<i>s</i> [mg/kg]	relative <i>s</i> _{between} [%]	relative <i>s</i> _{within} [%]	<i>p</i>	average [mg/kg]	<i>s</i> [mg/kg]	relative <i>s</i> _{between} [%]	relative <i>s</i> _{within} [%]
BDE-28	5	2.440	0.276	11	8	6	2.549	0.344	13	6
BDE-47	11	233.9	30.8	12	11	12	245.1	28.4	11	10
BDE-99	11	302.1	32.4	10	8	12	316.6	34.1	11	5
BDE-100	11	63.02	3.66	5	5	12	65.99	4.15	6	5
BDE-153	11	47.412	3.376	7	7	12	44.04	3.62	8	5
BDE-154	7	25.73	1.80	6	10	7	26.27	2.01	7	7
BDE-183	11	132.37	9.26	6	9	12	86.54	7.63	8	8
BDE-197+204	10	76.00	6.42	7	10	11	51.87	6.43	11	12
BDE-209	10	654.8	36.4	3	12	10	783.6	45.3	n.a.	28
BB-209	8	634.0	76.83	12	7	8	742.6	60.7	8	5

^a *p*: number of accepted sets of results. *s*: standard deviation of data set means; averages and standard deviations in mg/kg. n.a.: not applicable (cannot be calculated as mean squared error between laboratories is larger than the mean squared error within laboratories).

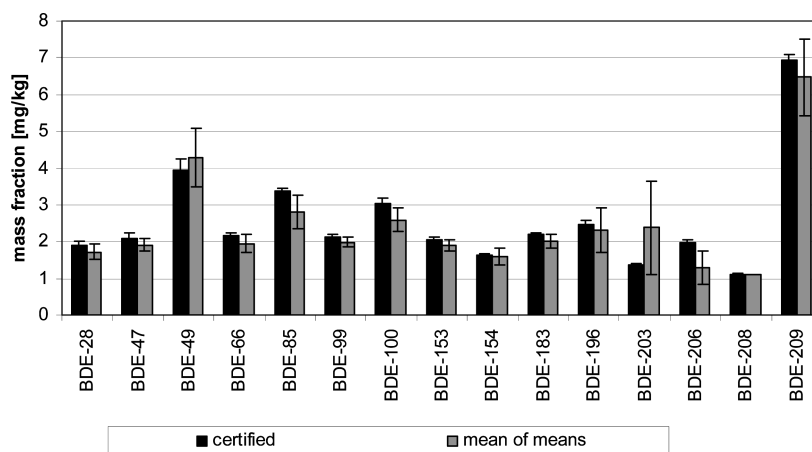


Figure 2. Comparison of results on the certified quality control solution. Error bars are expanded uncertainties for the certified values and confidence interval of the mean of means.

bene for BDE-209 in the polyethylene material) below 3% and were below 10% for several other congeners. It should be highlighted that no outliers were removed to obtain this level of agreement between laboratories, only technically dubious results were excluded. This is the best comparability of analytical results of BFRs reported so far.

Confirmation of Results. In addition to the good agreement among each other, evidence was obtained that the mean of laboratory means is unbiased within its uncertainty.

The average results obtained on the quality control solution are compared to the candidate certified values in Figure 2. The results agree with the candidate certified values, demonstrating correct calibration by the laboratories of which data sets were accepted. Figure 2 also clearly shows the issue of coelution for BDE-203: the candidate SRM also contained BDE-198, hence the high result for this congener.

One laboratory dissolved both samples in xylene/dimethyl glutarate, thus entirely removing the problem of incomplete extraction. Another evidence of completeness of extraction comes from the calculated Br mass fractions: these agree with the ones obtained by element-specific methods within the respective uncertainties (2130 ± 90 mg/kg vs 1980 ± 250 mg/kg for the polyethylene material and 2080 ± 21 mg/kg vs 2020 ± 225 mg/kg for the polypropylene material).

The results obtained by GC are also confirmed by results from non-GC-based methods: two laboratories were asked to perform

measurements by IA-MS and HPLC, respectively. In IA-MS, the sample (almost 1 mg) is heated and BFRs are directly evaporated without pretreatment. BFRs are determined by mass spectrometry. This method gives the sum of each homologue group. For HPLC, BFRs are extracted conventionally and the extract is quantified by HPLC-UV as the sum for each degree of bromination. Results from IA-MS and HPLC are shown in Figure 3: Results from IA-MS agree within the respective uncertainties for tetra, penta, hexa, octa-, and decabrominated homologues, whereas lower values were found for nona-BDEs and deca-BB. Due to the unusual congener pattern, resulting from the mixture of technical Penta-, Octa-, and Deca-BDE, results from HPLC differ usually from the GC results. Especially the high values for BDE-209 obtained by HPLC might hint at significant losses in the GC methods. However, this concern was dismissed as unlikely, as it would require equal degree of degradation in all GC methods, which would also have to be matched by an equal degree of degradation in the IA-MS. In addition, the values from GC/MS and IA-MS agree with the nominal values, whereas the results from HPLC are above the nominal values. It was therefore concluded that the higher value for BDE-209 obtained by HPLC is due to a positive bias of these measurements rather than due to a negative one of the GC and IA-MS methods.

Value Assignment. The unweighted means of laboratory means were assigned as certified values for BDE-47, -99, -100, -153, -154, -183, -209 and BB-209 for both materials. Due to the

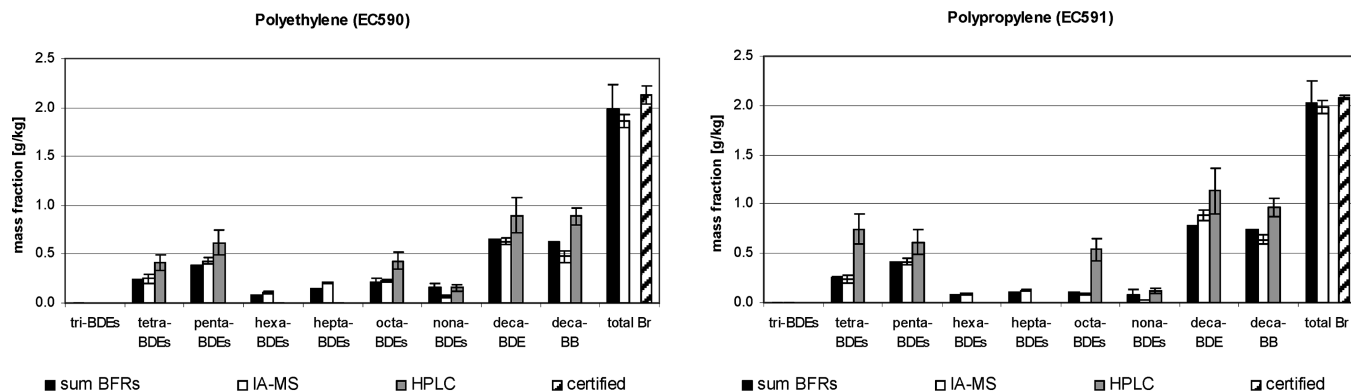


Figure 3. Comparison of results from GC, HPLC, IA-MS, and elemental analysis methods. Error bars are expanded uncertainties ($k = 2$). Uncertainties for the sums of results from GC were calculated as the square root of the squared uncertainties of the individual contributions.

Table 6. Certified Values and Their Uncertainty Budgets for the Two Polymer Materials

	polyethylene (ERM-EC590)		polypropylene (ERM-EC591)	
	certified value [g/kg]	$U_{\text{CRM}} (k = 2)$ [g/kg]	certified value [g/kg]	$U_{\text{CRM}} (k = 2)$ [g/kg]
BDE-28			0.0025	0.0006
BDE-47	0.23	0.04	0.245	0.023
BDE-99	0.30	0.06	0.32	0.04
BDE-100	0.063	0.016	0.066	0.007
BDE-153	0.047	0.013	0.044	0.010
BDE-154	0.026	0.007	0.026	0.006
BDE-183	0.132	0.012	0.087	0.008
BDE-197+204	0.076	0.015	0.052	0.009
BDE-209	0.65	0.10	0.78	0.09
BB-209	0.63	0.10	0.74	0.08

slightly higher number of data sets in the polypropylene material (ERM-EC591), values were also assigned for BDE-28. Assigned uncertainties include contributions from potential between-unit heterogeneity, potential degradation, as well as from characterization.²⁷ The final certified values and their expanded uncertainties (U_{CRM}) are shown in Table 6.

In addition, certified values for total Br, indicative values for Sb, and informative values for 18 other congeners have been assigned. Indicative and information values were based on 1–5 data sets received by the participants.¹⁸

CONCLUSIONS

Two polymer materials were prepared that are sufficiently homogeneous and stable to serve as reference materials.

In the characterization intercomparison of the two materials, a relative between-laboratory standard deviation of around 10% and below was obtained. According to our best knowledge, this outcome places the current exercise among the best ever reported. This allowed for the first time the certification of two polymer materials for their mass fractions of various PBDE congeners and BB-209. Confirmation of trueness for the assigned values was obtained with non-GC-based methods, giving increased confidence in the certified values. Although some analytical pitfalls, like incomplete separation of the matrix and poor quality of commercially available standards, could be identified, small, ill-

described laboratory specificities still seem to cause in some cases extreme deviations. However, the study also showed that a combination of only two simple quality indicators, i.e., the findings on a certified quality control solution and comparison of the certified Br content with the Br content calculated from the BFR determination, was sufficient to point out all technically doubtful results. The equivalence of results from industrial laboratories and environmental analysis laboratories, despite methodological differences (one vs two columns), demonstrated that not all recommendations for environmental analysis are valid for this kind of sample. As there is no evidence that results obtained using isotopically labeled internal standards are superior to results from other internal standards, these two CRMs will contribute significantly to higher confidence in measurements of BFRs in polymers.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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