



Institute for Reference
Materials and Measurements



European Reference Materials

CERTIFICATION REPORT

**Certification of the mass fractions of various
polybrominated diphenyl ethers (PBDEs),
decabrominated biphenyl and total Br and total Sb in two
polymer reference materials**

**Certified Reference Materials
ERM[®]-EC590 & ERM[®]-EC591**

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The mission of the JRC-IRMM is to promote a common and reliable European measurement system in support of EU policies.

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Certification of the mass fractions of various polybrominated diphenyl ethers (PBDEs), decabrominated biphenyl and total Br and total Sb in two polymer reference materials

**Certified Reference Materials
ERM[®]-EC590 & ERM[®]-EC591**

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Disclaimer

Certain commercial equipment, instruments, and materials are identified in this report to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

ABSTRACT

This report describes the preparation and certification of the polymer certified reference materials (CRM) ERM-EC590 and ERM-EC591. The CRMs have been certified by the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

The CRMs were prepared from a low-density polyethylene granulate and polypropylene granulate spiked with technical mixtures of brominated diphenylethers (BDEs) and brominated biphenyls (BB). Technical Penta-BDE, Octa-BDE, Deca-BDE and Deca-BB were added.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The CRMs have been certified for their content of Br as well as for several BDE congeners and decabrominated biphenyl (BB-209). Indicative values have been established for Sb. Additional information about several BDE-congeners is given.

These CRMs are intended for use in quality assurance of measurements of BDEs, BB-209 and elements in polymers and related matrices.

Uncertainties are expanded uncertainties estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95 %. The following values were assigned.

Certified values

	ERM-EC590 [g/kg]	ERM-EC591 [g/kg]
Br	2.13 ± 0.09	2.08 ± 0.07
2,4,4'-TriBDE (BDE-28)		0.0025 ± 0.0006
2,2',4,4'-TetraBDE (BDE-47)	0.23 ± 0.04	0.245 ± 0.023
2,2',3,4,4'-PentaBDE (BDE-99)	0.30 ± 0.06	0.32 ± 0.04
2,2',4,4',6-PentaBDE (BDE-100)	0.063 ± 0.016	0.066 ± 0.007
2,2',4,4',5,5'-HexaBDE (BDE-153)	0.047 ± 0.012	0.044 ± 0.010
2,2',4,4',5,6'-HexaBDE (BDE-154)	0.026 ± 0.007	0.026 ± 0.006
2,2',3,4,4',5,6'-HeptaBDE (BDE-183)	0.132 ± 0.012	0.087 ± 0.008
2,2',3,3',4,4',6,6'-OctaBDE + 2,2',3,4,4',5,6,6'-OctaBDE (BDE-197+204)	0.076 ± 0.015	0.052 ± 0.009
DecaBDE (BDE-209)	0.65 ± 0.010	0.78 ± 0.09
DecaBB (BB-209)	0.63 ± 0.10	0.74 ± 0.08

Indicative values

	ERM-EC590 [g/kg]	ERM-EC591 [g/kg]
Sb	0.756 ± 0.025	0.713 ± 0.022

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GLOSSARY

ANOVA	Analysis of variance		electronic equipment", Directive 2002/95/EC
BFR	Brominated flame retardant		
CRM	Certified reference material	SF-MS	Sectorfield mass spectrometer
ECNI	Electron capture negative ionisation	SRM [®]	Standard reference material
ERM [®]	European Reference Materials	UV	Ultraviolet
GC	Gas chromatography	WDXRF	Wavelength-dispersive X-ray fluorescence spectrometry
HPLC	High performance liquid chromatography	<i>MSB</i>	Mean square among groups from an ANOVA
IA-MS	Ion attachment-mass spectrometry	<i>MSW</i>	Mean square within groups from an ANOVA
IC	Ion chromatography	<i>p</i>	Number of laboratories
ICP-MS	Inductively coupled plasma-mass spectrometry	<i>s</i>	Standard deviation of dataset means in the characterisation study
IEC	International Electrotechnical Commission	<i>S_{bb}</i>	Between-unit variability
(I)NAA	(Instrumental) neutron activation analysis	<i>S_{between}</i>	Standard deviation between-groups (ANOVA)
ISO	International Organization for Standardization	<i>S_R</i>	Reproducibility standard deviation
<i>k₀</i> NAA	Neutron activation analysis using the <i>k₀</i> -method for quantification	<i>S_{wb}</i>	Standard deviation within bottle
MS	Mass spectrometry	<i>S_{within}</i>	Standard deviation within groups (ANOVA)
(P)BB	(Poly) brominated biphenyl	<i>u_{bb}[*]</i>	<i>Between-bottle</i> heterogeneity that could be hidden by method repeatability
(P)BDE	(Poly)brominated diphenyl ether	<i>u_{bb}</i>	Uncertainty related to a possible between-bottle heterogeneity
PCB	Polychlorinated biphenyl	<i>U_{CRM}</i>	Combined uncertainty of the certified value
PE	Polyethylene	<i>u_{char}</i>	Uncertainty of the characterisation
PLE	Pressurized liquid extraction (= accelerated solvent extraction)	<i>U_{CRM}</i>	Expanded uncertainty of a certified value
PP	Polypropylene	<i>u_{lts}</i>	Uncertainty of long-term stability
PTV	Programmable temperature vaporizer	<i>u_{outl}</i>	Uncertainty estimated from outliers
Q-MS	Quadrupole mass spectrometer	<i>u_{sts}</i>	Uncertainty of short-term stability
QCM	Quality control material		
RoHS	EU Directive on "Restriction of the use of certain hazardous substances in electrical and		

1 INTRODUCTION

The European Commission's Directive on the "Restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS) [1] bans the use of certain polybrominated flame retardants (BFRs) in electric and electronic devices since the 1st of July 2006 unless no technical substitutes exist. Commission Decision 2005/618/EC sets limit values of 1 g/kg (0.1 %) for the sum of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in plastics [2]. Decabrominated diphenylether (Deca-BDE) was originally exempted [3], but this exemption was annulled by the European Court of Justice [4] for procedural errors. Similar legislation to the European RoHS Directive has been adopted by Australia, Canada, Korea, Taiwan, 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 BFRs. Reliable quality of the determination of BFRs is therefore crucial.

PBDEs belong to a class of brominated compounds that are structurally comparable to polychlorinated biphenyls (PCBs), and therefore share the same numbering of congeners as proposed by Ballschmiter *et al.* [5]. PBDEs are commercially available as technical mixtures, consisting of various congeners, the average degree of bromination of which is used to derive the name. For example, technical Penta-BDE has on average 5 bromine atoms per diphenylether, although it consists of various tetra-, penta- and hexabrominated congeners. The composition of two technical mixtures of Penta- and Octa-BDE is given in Table 1 [6]. Technical Deca-BDE and Deca-BB are relatively pure substances, consisting of at least 97 % BDE-209 and BB-209, respectively. Congener patterns depend on the reaction conditions and can vary from producer to producer and even from batch to batch.

Table 1: Composition of the technical mixtures of Penta- and Octa-BDE from Great Lakes Chemicals. Number in brackets give the main congeners.

	technical Penta-BDE	technical Octa-BDE
tetrabrominated BDEs	35% (BDE-47)	
pentabrominated BDEs	56 % (BDE-99, -100)	
hexabrominated BDEs	9 % (BDE-153, 154)	8 % (BDE-153)
heptabrominated BDEs		40 % (BDE-183)
octabrominated BDEs		36 % (BDE-196, BDE-197, BDE-203)
nonabrominated BDEs		15 % (BDE-207)

Mass fractions of intentionally added BFRs to polymers range from 10 to 30 % and are thus far above the limits stipulated by the RoHS Directive, but concentrations near the legal limit are possible for recycled plastics. Considerable loads of BFRs in videocassettes made from recycled plastics have been already reported [7].

Several organisations developed standardised methods in order to improve analytical performance in the determination of PBDEs in polymers, but none of these include PBBs. The German Federal Environment Agency (UBA) commissioned the Federal Institute for Materials Research and Testing (BAM) to develop and validate a method for the analysis of technical mixtures of Penta- and Octa-BDE in plastics. Relative repeatability and reproducibility standard deviations in four polymers fortified around 1 g/kg were 4 and 25 %, respectively [8]. In addition, Working Group 3 of the technical committee 111 of the International Electrotechnical Commission has developed a standard method for all RoHS relevant substances, which includes a method for BFRs in an informative annex. This draft standard follows largely the German method for BFRs, but also includes Deca-BDE. At present, the voting draft has been accepted.

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 (JRC), has decided to produce two reference materials for PBDEs and PBBs in polymers. The materials should be certified for individual PBDE and PBB congeners as well as for total Br, as screening for Br is frequently used to identify potentially non-compliant samples. Only indicative values for Sb were regarded necessary, as Sb itself is not restricted by the RoHS directive, but, as Sb_2O_3 is commonly used as synergist for BFRs, is also sometimes used for screening purposes.

2 PARTICIPANTS

Processing

DSM Resolve, Geleen (NL) (preparation of the granulates)

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE) (bottling)

Homogeneity and stability studies

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE) (Br, Sb)

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Tests under 17025 accreditation BELAC 015-TEST

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3 PROCESSING

3.1 MATERIAL SELECTION

After consultation with experts in the field, it was decided to produce two materials based on a polymer partly soluble in common solvents and a polymer insoluble in common solvents, 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. Finally, polyethylene (PE) was selected as soluble polymer and polypropylene (PP) as insoluble polymer.

Penta-BDE, Octa-BDE, Deca-BDE and Deca-BB were chosen as substances banned by the RoHS directive. 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.

3.2 PROCESSING

Two batches of 90 kg of material were prepared from commercial PE and PP (both from Sabic, NL). No additives were added to the PE material. The lubricant Ca-stearate and the antioxidants Irgafos 168 and Irganox 1010 were added to the PP material.

The granulates were fortified with technical mixtures of Penta-, Octa- and Deca-BDE as well as with a technical mixture of Deca-BB. Deca-BDE (Saytex 102™) and Deca-BB (Adine 102™) were provided by Albemarle Corp, Louvain-La-Neuve (BE). The supplier of the technical mixture of Penta-BDE and Octa-BDE wished to remain confidential. In addition, Sb₂O₃ was added to simulate real samples, where Sb₂O₃ is usually added as synergist to the BFRs. The approximate composition of the two materials is given in Table 2.

Table 2: Nominal composition of the two reference materials.

	ERM-EC590	ERM-EC591
Matrix	Polyethylene	Polypropylene
Additives	none	Ca-stearate, Irgafos 1638, Irganox 1010
technical Penta-BDE	0.7 g/kg	0.7 g/kg
technical Octa-BDE	0.25 g/kg	0.20 g/kg
technical Deca-BDE	0.7 g/kg	0.7 g/kg
technical Deca-BB	0.7 g/kg	0.7 g/kg
Sb ₂ O ₃	0.8 g/kg	0.8 g/kg

Samples were extruded several times and 20 g each were filled into amber glass bottle. Samples have been stored at 4 °C ever since.

4 ASSESSMENT OF HOMOGENEITY

Key requirement for any reference material is equivalence between the various units. In this respect, it is not relevant whether the variation between units is significant compared to the analytical variation, but whether this variation is significant to the certified uncertainty. Consequently, ISO Guide 35 demands RM producers to quantify the between bottle variation. This aspect is covered in between-unit homogeneity studies.

Within-unit heterogeneity does not influence the uncertainty of the certified value, but determines the minimum size of subsample that is representative for the whole unit. Quantification of within-unit heterogeneity is therefore necessary to determine the minimum sample intake.

4.1 BETWEEN-BOTTLE HOMOGENEITY

Quantification of between-bottle heterogeneity is most easily done by analysis of variance (ANOVA), which can separate the between-bottle variation (s_{bb}) from the within-bottle variation (s_{wb}). The latter is equivalent to the analytical variation if the individual subsamples are representative for the whole bottle. Evaluation by ANOVA requires bottle averages to follow at least a unimodal distribution and results for each bottle to follow unimodal distributions with approximately the same standard deviations. Distribution of the bottle averages can easily be checked, but too few data are available for each bottle to make a clear statement of the distribution of individual results. Therefore, it was checked whether all individual data follow a unimodal distribution. Minor deviations from unimodality of the individual values do not grossly affect the estimate of between-unit standard deviations.

One has to bear in mind that s_{bb} and s_{wb} are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups (MSB) can be smaller than the mean squares within groups (MSW), resulting in negative arguments under the square root used for the estimation of the between-bottle variation, whereas the true variation cannot be lower than zero. In this case, u_{bb}^* , the maximum heterogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [9]. u_{bb}^* is comparable to the limit of detection of an analytical method, yielding the maximum heterogeneity that might be undetected by the given study setup.

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. Four replicate determinations per bottle were performed under repeatability conditions by wavelength dispersive x-ray fluorescence spectrometry (WDXRF) (Br, Sb) and ultrasonic extraction with toluene and subsequent quantification by GC-MS (BFRs). Sample intakes were 4 g for WDXRF and 0.5 g for GC-MS.

A second subset of 20 bottles covering the whole batch had been taken for the stability testing during storage (see below). Also these samples were selected from the whole batch following a random stratified sampling scheme. Also these samples were analysed under repeatability conditions in one analytical run. As no influence of time and temperature was found for any of the conditions tested for the congeners concerned, the data from these studies were used to gain additional information on material homogeneity when outliers, bimodal distributions or trends in the filling sequence were found. To do this, storage information was ignored and only the bottle number was taken into consideration. These data were subjected to the same evaluations as the samples originally used for homogeneity.

Grubbs-tests at 99 % confidence levels 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 normal

distributions using normal probability plots and whether the individual data are unimodally distributed using histograms.

Results were corrected for their trend in the analytical sequence if the trend was significant on at least a 95 % confidence level as shown below.

$$\text{corrected result} = \text{measured result} - b \cdot i$$

b slope of the linear regression

i position of the result in the analytical sequence

As the analytical sequence and the bottle numbers were not correlated, this correction improved the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities.

4.1.1 Descriptive evaluation of ERM-EC590 and ERM-EC591

The results of these evaluations are shown in Table 3 and Table 4, the results of the measurements themselves are depicted in Annex A.

Table 3: Descriptive evaluation of the results for individual PBDE congeners in ERM-EC590. The level of significance for statistically significant slopes is given for the trendtests. Results for trends in the filling sequence, outliers and distribution refer to the dataset after correction of trends in the analytical sequence.

	Trends		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Bottle means	Individual results	Bottle means
total Br	no	95 %	none	none	normal	normal
Sb	no	no	none	none	normal	normal
BDE-47	no	no	none	none	normal	normal
BDE-42+66	no	no	none	none	normal	normal
BDE-85	no	no	none	none	normal	normal
BDE-99	no	no	one	none	normal	normal
BDE-100	no	no	none	none	normal	bimodal
BDE-100 (stab)	99 %	no	none	none	normal	normal
BDE-127	no	no	none	none	unimodal	normal
BDE-183	no	no	none	none	slightly bimodal	normal
BDE-196	99 %	no	none	none	normal	normal
BDE-197	no	no	none	none	bimodal	slightly bimodal
BDE-197 (stab)	99 %	no	none	none	normal	normal
BDE-203	no	no	none	none	normal	normal
BDE-206	no	no	none	none	unimodal	unimodal
BDE-207	no	95 %	none	none	normal	normal
BDE-207 (stab)	99 %	no	none	none	normal	normal
BDE-209	95 %	no	none	none	unimodal	normal
BB-209	no	no	none	none	normal	normal

(stab): Data from the long-term stability study were used.

Only total Br and BDE-207 showed a trend in the filling sequence. Trends were apparent in the analytical sequence for some congeners. However, as the analytical sequence was randomised and is not correlated with the filling sequence, trends in the analytical sequence were corrected as described above in order to improve the sensitivity of the study for potential between-unit heterogeneity.

Distributions of bottle means were normal or at least unimodal for all congeners except BDE-100 and to a much lesser extent, BDE-197. For the latter, two bottles 1190 and 3587 had means 10 % above the other bottle means, but were not flagged as outliers. Individual results generally followed normal distributions except in the case of BDE-197, where the results were clearly bimodally distributed. There are some indications of potential bimodality in the individual results for BDE-183, but this does not influence the distribution of bottle means.

No technical reason for the outlier of individual replicates for BDE-99 could be found. Tentative removal of the outlier did not change the result of the final heterogeneity determination. The outlier was therefore retained to provide a conservative measure of homogeneity.

Table 4: Descriptive evaluation of the results for individual PBDE congeners in ERM-EC591. The level of significance for statistically significant slopes is given for the trendtests. Results for trends in the filling sequence, outliers and distribution refer to the dataset after correction of trends in the analytical sequence.

	Trends		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Bottle means	Individual results	Bottle means
total Br	99 %	no	two	none	unimodal	normal
Sb	no	no	two	none	unimodal	normal
BDE-47	99 %	no	none	none	normal	normal
BDE-42+66	no	no	none	none	unimodal	normal
BDE-85	no	no	none	none	normal	normal
BDE-99	99 %	no	none	none	normal	unimodal
BDE-100	99 %	no	none	none	unimodal	unimodal
BDE-127	no	no	none	one	unimodal	unimodal
BDE-127 (stab)	95 %	no	none	none	normal	unimodal
BDE-183	99 %	no	none	none	unimodal	unimodal
BDE-196	no	no	none	none	unimodal	unimodal
BDE-197	no	no	none	none	normal	normal
BDE-203	no	no	none	none	normal	unimodal
BDE-206	99 %	no	none	none	normal	unimodal
BDE-207	95 %	no	none	none	normal	unimodal
BDE-209	no	no	none	none	slight bimodality	normal
BB-209	99 %	no	none	none	normal	unimodal

(stab): Data from the long-term stability study were used.

None of the analytes in ERM-EC591 showed a trend in the filling sequence. Trends were apparent in the analytical sequence for more than half of the analytes. However, as the analytical sequence was randomised and is not correlated with the filling sequence, trends in the analytical sequence were corrected as described above in order to improve the sensitivity of the study for potential between-unit heterogeneity.

Outlying individual results were found for Br and Sb, but these outliers did not result in outlying bottle means.

Distributions for the individual results were in all cases normal or at least unimodal. The same is true for the distributions of bottle averages, with the exception of BDE-209.

From this descriptive evaluation it was concluded that using all data available for ERM-EC590 and ERM-EC591 would result in reliable estimates for the between-bottle

heterogeneity for Br, Sb and all BFRs when the results from long-term stability are used as well.

4.1.2 Quantification of heterogeneity

Results were evaluated using single-factor ANOVA. Standard deviations within bottles (s_{wb}) and between bottles (s_{bb}) as well as u_{bb}^* were calculated. The results of these evaluations are shown in Table 5.

For those measurands for which outlying bottle means were detected, another measure of heterogeneity was estimated. Between-bottle heterogeneity was modelled as rectangular distribution limited by the highest outlying average. The uncertainty using these outliers (u_{outl}) was then estimated as

$$u_{outl} = \frac{|widest\ outlier - study\ average|}{\sqrt{3} \cdot study\ average}$$

A similar approach was used for total Br and BDE-207 for EC590, where a trend in the filling sequence was detected. Here, u_{outl} was estimated using the half-width of a rectangular distribution between the highest and lowest bottle average:

$$u_{outl} = \frac{|highest\ result - lowest\ result|}{2 \cdot \sqrt{3} \cdot study\ average}$$

Also these data are shown in Table 5.

Table 5: Results of the homogeneity test for ERM-EC590 and ERM-EC591. n.c.= cannot be calculated as $MSB < MSW$. u_{outl} : uncertainty estimated from trends in the filling sequence or outliers.

	EC590				EC591			
	s_{wb} [%]	s_{bb} [%]	u_{bb}^* [%]	u_{outl} [%]	s_{wb} [%]	s_{bb} [%]	u_{bb}^* [%]	u_{outl} [%]
total Br	0.31	0.22	0.07	0.32	0.68	n.c.	0.14	
Sb	0.38	0.30	0.08		0.60	0.19	0.13	
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	8.3	0.2	1.8		6.8	n.c.	1.5	
BDE-100 (stab)	7.1	n.c.	1.5					
BDE-127	4.1	0.8	0.9		5.0	n.c.	1.1	3.8
BDE-127 (stab)					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	7.4	0.7	1.6	2.35	6.8	1.0	1.5	
BDE-197 (stab)	12.2	2.3	2.6					
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	7.2	nc	1.5		7.5	n.c.	1.6	
BDE-207 (stab)	8.0	n.c.	1.7					
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	

(stab): data from the long-term stability study were used.

The good repeatability of the measurements for Br and Sb allows setting very tight limits for potential heterogeneity. The studies demonstrated that the potential between-unit variation in both materials for Br and Sb is below 0.4 %, which is small enough to make the materials suitable as reference materials.

For BFRs, the frequent occurrence of $MSB < MSW$ (n.c. in Table 5) demonstrates that material heterogeneity is smaller than can be detected for many congeners. For four congeners (BDE-100, -197 and -207 in EC590 and BDE-127 in EC591), assessments were made using data from the stability studies. The question now arises which results are more reliable. For this, it has to be borne in mind that BDE-127, BDE-197, BDE-203 and BDE-207 were not added as single compounds but as parts of mixtures of several congeners. The physicochemical characteristics of the various congeners cover a continuum from the lower brominated ones to the highly brominated ones. A de-mixing of selected congeners during processing was therefore deemed impossible. It was therefore concluded that the bimodal distributions for BDE-100 and -197 (EC590), the trend in the filling sequence for BDE-207 (EC590) and the outlying bottle average for BDE-127 (EC591) are results of analytical artefacts and do not reflect the real distribution of these analytes in the material. Therefore, the results from the stability data were used.

The assessment of homogeneity for individual congeners demonstrated that between-unit variation for the individual congeners is below 3 % for all congeners, which is negligible compared to the method variability usually observed.

The materials are therefore sufficiently homogeneous to serve as reference materials.

BDE-28, -153 and -154 were not determined in the study. As stated above, the two congeners were not added individually but as part of technical mixtures of various congeners. The distribution of these congeners in the material can only be heterogeneous, if selective de-mixing or enrichment or evaporation of these congeners occurred during processing. The chemical properties of BDE-28, -153 and -154 are very similar to those of the other congener. The same is true for the physical properties: While it is true that BDE-28 is more volatile than the other congeners, its vapour pressure at processing temperatures is still low enough to make selective evaporation unlikely. Therefore, homogeneity of these congeners was assessed from the homogeneity of the other congeners. The highest uncertainty contribution of all congeners for a particular material was therefore used as conservative estimate of the uncertainty of homogeneity for BDE-28, -153 and -154.

The between-unit heterogeneity (u_{bb}) was therefore estimated as the larger value of s_{bb} or u_{bb}^* . The results from the stability studies were used for BDEs-100, 197 and -207 (EC590) and BDE-127 (EC591) whereas u_{outl} was used for total Br for EC590. For BDE-28, -153 and BDE-154 which were not determined in the study, the highest result of the other congeners for the material in question was used. The values are listed in Table 6.

Table 6: Summary of the estimates of between-unit heterogeneity for ERM-EC590 and ERM-EC591.

	EC590 u_{bb} [%]	EC591 u_{bb} [%]
Total Br	0.32	0.14
Sb	0.30	0.19
BDE-28	2.6	2.3
BDE-47	1.5	2.2
BDE-42+66	2.1	0.9
BDE-85	2.1	2.3
BDE-99	1.7	2.0
BDE-100	1.5	1.5
BDE-127	0.9	1.6
BDE-153	2.6	2.3
BDE-154	2.6	2.3
BDE-183	2.4	1.6
BDE-196	2.0	1.3
BDE-197	2.6	1.5
BDE-203	1.6	1.5
BDE-206	1.4	1.0
BDE-207	1.7	1.6
BDE-209	2.3	1.8
BB-209	1.9	1.0

4.2 WITHIN-BOTTLE HETEROGENEITY AND MINIMUM SAMPLE INTAKE

Within-bottle heterogeneity is closely correlated to the minimum sample intake. Due to the intrinsic heterogeneity, individual subsamples of a material will not contain the same amount of analyte. The minimum subsample that is representative for the complete bottle is the minimum sample intake. The larger the intrinsic heterogeneity, the larger the minimum sample intake.

Minimum sample intake was determined from the results of the characterisation study, using the method information supplied by the participants. The smallest sample intake that still yielded results with a repeatability and accuracy acceptable to be included in the respective studies was taken as minimum sample intake. Using the data from Annex C and D, the following minimum sample intakes are derived:

Total Br: 30 mg

Sb: 200 mg

BFRs: 30 mg of ground material

5 ASSESSMENT OF STABILITY

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

The most relevant degradation pathway was assumed to be "blooming", i.e. a diffusion of the flame retardants to the surface of the polymer. Blooming is well documented and results in increased loads of some BFRs in household dust [10]. Blooming usually follows Fick's law [11], with higher temperatures leading to faster diffusion.

Stability testing is necessary to establish conditions for dispatch to the customers as well as conditions for storage. The stability studies were conducted as isochronous stability studies [12]. 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.

Samples were stored for 0, 4, 8 and 12 months at 4 °C, 18 °C 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 8 results per time/temperature combination (2 bottles x 4 replicates). Measurements were performed by WDXRF (Br, Sb) and ultrasonic extraction with toluene and subsequent quantification by GC-MS (BFRs), respectively.

The studies were evaluated individually for each temperature. Results were screened for outliers using a Grubbs test, but only outliers that were dubious on technical grounds were excluded. Linear regressions were performed and the slopes were tested for significance on 95 % confidence levels. In addition to the evaluation per temperature, data for all temperatures for a given congener were combined into a single dataset. This was possible as all measurements for each study had been randomised over the whole analytical sequence. The data therefore can be regarded as forming one large dataset. This combination therefore increases the power of the statistical regression analysis for the combined studies. The results of these evaluations are summarised in Table 7 and Table 8, whereas graphical representations of the studies are given in Annex B.

Table 7: Results of the evaluation of the one-year stability studies for ERM-EC590.

Analyte	4 °C		18 °C		60 °C		All temp. combined	
	Outl.	Slope	Outl.	Slope	Outl.	Slope	Outl.	Slope
Br	none	not sig.	none	sig.	none	99 %	not combined	
Sb	1 (ret.)	not sig.	none	not sig.	1 (ret.)	not sig.	not combined	
BDE-47	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-42+66	2 (ret)	95 %	none	95 %	none	not sig.	1(ret)	not sig
BDE-85	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-99	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-100	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE127	none	not sig.	none	not sig.	none	99 %	none	not sig.
BDE-183	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-196	1 (ret)	not sig.	1 (ret)	not sig.	none	not sig.	none	not sig.
BDE-197	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-203	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-206	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-207	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-209	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BB-209	1 (ret)	not sig.	none	not sig.	1 (ret)	not sig.	none	not sig.

Outl.: number of outlying individual values; (ret): outlier was retained; sig./not sig.: significance on a 95 % confidence level.

Table 8: Results of the evaluation of the stability studies for ERM-EC591.

Analyte	4 °C		18 °C		60 °C		All temp. combined	
	Outl.	Slope	Outl.	Slope	Outl.	Slope	Outl.	Slope
Br	1 (ret)	not sig.	none	not sig.	2(ret)	99 %	not combined	
Sb	none	not sig.	none	not sig.	none	not sig.	not combined	
BDE-47	1 (ret)	not sig.	none	not sig.	none	not sig.	1 (ret)	not sig.
BDE-42+66	none	not sig.	none	not sig.	1 (ret)	not sig.	2 (ret)	not sig.
BDE-85	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-99	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-100	none	not sig.	none	not sig.	1 (ret)	not sig.	2 (ret)	not sig.
BDE-127	none	not sig.	1 (ret)	not sig.	none	not sig.	1 (ret)	not sig.
BDE-183	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-196	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-197	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-203	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-206	1 (ret)	not sig.	none	not sig.	2 (ret)	not sig.	2 (ret)	not sig.
BDE-207	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BDE-209	none	not sig.	none	not sig.	none	not sig.	none	not sig.
BB-209	none	not sig.	none	not sig.	none	not sig.	none	not sig.

Outl.: number of outlying individual values; (ret): outlier was retained; sig./not sig.: significance on a 95 % confidence level.

Some outlying individual results were found for both materials. However, removal of these results did not affect the result on the significance of the slopes. As no technical reason for exclusion was found and as retention leads to a conservative estimate for the uncertainty of degradation, the results were retained.

The slopes for Br were significant for storage at 18 and 60 °C in ERM-EC590 and for storage at 60 °C in ERM-EC591. These slopes indicate loss of Br, which can be explained by evaporation of some BFRs. In contrast, BDE-127 shows a statistically significant increasing trend at 60 °C, which would only be possible by selective degradation of other congeners. This was considered very unlikely. None of the other slopes was found significant on a 95 % confidence level. The same holds true for the combined datasets for the BFRs. This indicates slight changes of the total Br content upon storage at 60 °C, whereas no indication of degradation of any of the other analytes, regardless of the temperatures was found. However, due to the intrinsic variability of results, degradation cannot be completely ruled out even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be obscured by the method repeatability, i.e. to estimate the uncertainty of stability.

As explained above, degradation is expected to proceed faster at 18 and 60 °C than at 4 °C. The combination of the 4, 18 and 60 °C studies therefore gives a conservative estimate for the stability at 4 °C, while minimising the influence of method repeatability on the uncertainty estimate due to the higher number of results per time.

Uncertainties of stability during dispatch and storage were estimated as described in [13] for each analyte. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution is then estimated as a chosen shelf life multiplied with the uncertainty of the regression lines. The following uncertainties were estimated:

- u_{sts} , the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies for a time of 0.25 months (1 week). The uncertainty therefore describes the possible change during a dispatch at 60 °C lasting for one week.
- u_{lts} , the stability during storage. This uncertainty contribution was estimated from the 4 °C studies (total Br, Sb) or from the combined studies for a shelf life of 24 months (BFRs). The uncertainty contribution therefore describes the possible degradation for 24 months at 4 °C.

The results of these evaluations are summarised in Table 9.

Table 9: Results of the evaluation of the uncertainties of stability for ERM-EC590 and ERM-EC591. u_{sts} was estimated for a period of 1 week storage at 60 °C. u_{lts} was estimated for a storage of 24 months at 4 °C from the 1 year/4 °C study for Br and Sb and from the combination of all temperatures for BFRs.

Analyte	ERM-EC590		ERM-EC591	
	u_{sts} 60 °C, 1 week [%]	u_{lts} 4°C, 2 years [%]	u_{sts} 60 °C, 1 week [%]	u_{lts} 4°C, 2 years [%]
Br	0.009	0.402	0.004	0.306
Sb	0.008	0.632	0.005	0.432
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

As can be seen in Table 9, u_{sts} is negligible in all cases. The material can therefore be dispatched under ambient conditions.

Uncertainties of stability during storage are about 0.5 % for total Br and Sb. Due to the significantly worse repeatability of the determination of BFRs, their uncertainties range from 2 to 12 %, depending on the congener. These uncertainties are taken up in the final uncertainties of the certified values and might be reduced in the future, based on the results of the stability monitoring after certification.

BDE-28, -153 and -154 were not determined in the study. Based on the chemical similarity and the known persistence of the congeners, more rapid degradation than for the other congeners can be unlikely for BDE-28, -153 and -154. While BDE-28 is more volatile than the others, its vapour pressure at processing temperatures is still low enough as to prevent significant evaporation losses. Therefore, the highest of value of the study for each material can be taken as conservative estimate for the uncertainty of stability for BDE-28, -153 and -154.

6 CHARACTERISATION

6.1 SELECTION OF PARTICIPANTS

Participants in the characterisation studies were selected based on criteria that comprised both technical aspects as well as aspects regarding quality management.

Participants for the characterisation of total Br had demonstrated their competence in the determination of Br and Sb in polymers in previous certification exercises. Participants for the characterisation of PBDEs were selected based on participation in intercomparisons for BFRs [8, 14] or method validation reports.

Fulfilment of the quality management requirements ensured that the technical standard was maintained from the time of demonstration to the actual measurement. Most participating laboratories are accredited to ISO 17025, even if the measurements are in many cases not covered by the scope of accreditation. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (section 2),.

6.2 SETUP

Guiding principle of the characterisation study was randomisation of laboratory bias. To achieve this, the following measures were taken

- Several laboratories were selected to perform independent measurements.
- Different methodologies were employed whenever possible to confirm the absence of method bias. Laboratories were therefore free to select a method of their choice. Results for Br were obtained by k_0 -neutron activation analysis (k_0 NAA), instrumental neutron activation analysis (INAA), combustion-ion chromatography (IC), combustion-sectorfield inductively coupled plasma-mass spectrometry (SF-ICP-MS) and combustion – titration. Sb was only determined by k_0 NAA and INAA, as these methods can simultaneously determine Sb and Br and as only indicative values were aimed for. The methods are described in tabular form in Annex C. Results for BFRs were obtained using different sample preparation techniques (Soxhlet extraction, complete dissolution, ultrasonic extraction, pressurised liquid extraction). Individual BFRs were quantified using gas chromatography-mass spectrometry (GC-MS) with different ionisation (electron impact, negative ionisation) and mass separation techniques (quadrupol, sectorfield). In addition, direct ion-attachment mass-spectrometry (IA-MS) and high performance liquid chromatography (HPLC) with UV detection were applied for confirmatory purposes. The methods are described in tabular form in Annex D.
- Six independent measurements per laboratory were performed. These measurements were spread over at least two days, to ensure within-laboratory reproducibility conditions.
- Independent calibration lines were prepared for all measurements.
- Laboratories performed and reported results for method blanks.

Samples for the characterisation study covered the whole batch and were selected using a random stratified sampling scheme.

Laboratories received quality control samples to demonstrate traceability of their results. For total Br and Sb, the certified reference material ERM-EC681k, "Trace metals in LDPE" with a Br-mass fraction of 770 mg/kg was used. For BFRs, blinded candidate SRM[®]s 2257 and 2258 (PBDEs in isooctane) from the US National Institute for Standards and Technology (NIST) were used. Laboratories were requested to report the results on these materials together with the results on candidate CRMs ERM-EC590 and EC591.

Laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the six results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

6.3 TECHNICAL EVALUATION

6.3.1 Br and Sb

All laboratories received a bottle of ERM-EC681k as quality control sample. The results on this sample could therefore directly be used to check for absence of significant bias. This material has a certified Br content of 770 ± 40 mg/kg, which is about 1/3 of the Br content of the new materials and an Sb content of 99 ± 6 mg/kg.

The three sets of results obtained by k_0 NAA and INAA as well as the results obtained by combustion-IC and combustion-SF-ICP-MS agreed with the certified value for Br within the respective uncertainties. Results by combustion-titration were 10 % below the certified values, with combined uncertainty being only 8.3 %. This agreement was regarded as sufficient to prove traceability of the results of the method. Results from neutron activation tended to be higher than those from destructive methods. However, the results agree within the respective uncertainties. All results were therefore accepted on technical grounds.

As only an indicative value for Sb had been aimed at, only three datasets by k_0 NAA were obtained for Sb. The results for the certified quality control sample agreed in all cases with the certified values. Therefore, all three datasets were accepted for value assignment. No statistical evaluation was performed, as the number of datasets was too low.

The results of these studies are depicted in Annex E.

6.3.2 PBDEs and BB-209

Two quantitative indicators of technical problems were used, namely the results on the quality control solution and the calculated total Br content. Results on the quality control solution were compared to the candidate certified values, with strong deviations indicating technical problems. Total Br content was calculated from the results submitted by the participants and compared to the total Br content as determined by element specific methods. While the calculated Br content can be below the one determined by element specific methods as often not all congeners were reported, it cannot be above. Results were discussed with the participants. The discussion aimed at identification of potential technical problems in the submitted data:

Laboratory 7 reported results in agreement with the quality control solution. However, results for the polymers were consistently higher than those of the other laboratories. While this is not a problem *per se*, the Br-content as calculated from these results is 35-40 % above the Br mass fraction as determined by element analysis methods, indicating calibration problems. The results of laboratory 7 were therefore excluded from the evaluation.

Laboratory 8 reported that partial dissolution of the polymers led to a formation of a film in the liner of the GC. This resulted in degradation of BDE-209, as shown by the relatively high ratio of BDE-206/BDE-209 for EC590. EC591 does not dissolve in toluene and is therefore not affected by these issues. Nevertheless, the reported results for BDE-209 and BB-209 were two to three times above the spiking levels, resulting in calculated Br mass fractions far above the ones measured by elemental analysis techniques. The results for the congeners BDE-209 and BB-209 for both materials were therefore excluded from the evaluation.

Laboratory 10 reported that it had corrected its results for the recovery of an internal QC sample, which was 80-85 %. The corrected results were therefore 15-20 % above the results of the other participants. The laboratory re-submitted the uncorrected values after the discussion. As at that time the results of the other laboratories had already been disclosed,

these results are not included in the set of results used for value assignment, but are shown for comparison in Annex E.

Laboratory 11 reported low results for all congeners for EC590 except BDE-209 and BB-209. As the laboratory used a high sample intake (1000 mg), a small volume of solvent (10 mL) and a solvent that dissolves EC590 (toluene), matrix effects may have influenced the results for EC590. The results from Laboratory 11 for EC590 were therefore excluded from the evaluation.

Results for BDE-209 and BB-209 for EC591 were twice to three times the spiking levels. Due to these results, the Br content calculated from the BFRs for EC591 was 50 % above the mass fraction as determined from elemental methods. The results for BDE-209 and BB-209 for EC591 were therefore also excluded from the evaluation.

Laboratory 12 reported calibration problems for BDE-47. When crosschecked against another standard, the standard used showed only a recovery of 80 %. The results for BDE-47 were therefore excluded from the further evaluation.

Laboratory 13 reported results for the quality control solution that deviated up to an order of magnitude from the candidate certified values, indicating calibration problems. The complete dataset was therefore excluded from evaluation.

Laboratory 18 reported that BB-209 is normally not determined by the laboratory. Evaluation was performed with without internal calibration, which, as confirmed by another laboratory, is inappropriate for this compound. The results for BB-209 were therefore excluded from further evaluation.

Laboratory 19 reported a coelution between BDE-196 and BDE-203 on an RTx-5 column. Measurements on a second column (LC-50) were performed, where a separation is possible. The laboratory also reported separate results for BDE-198 (see also discussion next page).

Laboratory 20 reported results in agreement with the candidate certified value for the quality control solution but consistently high values for all congeners in the polymers. The total Br content as calculated from these results is twice the Br content as determined by element analysis methods. As this is impossible, the complete dataset was excluded from further evaluation.

Laboratory 21 reported problems with a commercial standard: A "certified" commercial standard mixture it had used as internal quality control contained only 50 % of the stated concentration of BDE-209. As this standard mixture had not been used for quantification, results were retained.

Only Laboratory 21 had sieved its milled powder to obtain different particle size fractions, which were analysed independently. It reported a strong influence of the particle size on results for higher BDEs: recoveries decrease for larger particle sizes. Finally, the results on the smallest particle size fraction was chosen for reporting of results. This effect seems to be due to a combination of solvent and particle size: Laboratory 21 deliberately chose a solvent (isooctane) with little interaction with the matrix to minimise interferences by with the polymer. Other laboratories using e.g. toluene reported good results, even for samples taken "as is".

The results from the laboratories that use PCB-209 as internal standard do not form a cluster, not even for the determination of BDE-209. PCB-209 therefore seems in principle to be a suitable internal standard.

Literature on possible coelutions on different GC columns indicates that for the columns used in this study, a separation of BDE-197/BDE-204 is often not possible [15]. The results therefore give the sums of these two congeners.

Literature data suggest that BDE-198 usually coelutes with BDE-203 [15], whereas no information on BDE-196 is given in this paper. The results for BDE-203 may therefore also be the sum of BDE-198 and -203. However, while laboratories 8, 16, 18 and 21 reported results for BDE-196 and -203, laboratory 19 reported coelution of BDE-196 and 203 on an apparently equivalent column, whereas BDE-198 could be separated. All of these 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 are assigned.

Another potentially critical issue is the method blank for BDE-209, as this congener is used frequently in electric equipment of furniture upholstery and contamination is therefore possible. The method blanks submitted by the participants were investigated. The majority of laboratories that delivered accepted results could not detect any method blanks. The remaining laboratories usually found blanks corresponding to less than 10 mg/kg in a sample. This amount is negligible compared to the mass fraction of BDE-209 in the material (700 mg/kg).

The results of these studies are depicted in Annex E.

Note: The graphs in Annex E show expanded uncertainties, not standard deviations. Results with a low standard deviation may well have a large uncertainty.

6.4 STATISTICAL EVALUATION

The datasets accepted on technical grounds were tested for outlying means using the Grubbs test and using the Cochran test for outlying standard deviations, (both at a 99 % confidence level) as well as for normality of dataset means using kurtosis/skewness tests and normal probability plots. Standard deviation within (S_{within}) and between ($S_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 10 and Table 11.

Table 10: Statistical evaluation of the technically accepted datasets for ERM-EC590.

Measurand	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Average [mg/kg]	s [mg/kg]	$S_{between}$ [mg/kg]	S_{within} [mg/kg]
Br	6	none	none	yes	2131	105	102	54
Sb	3	n.a.	n.a.	n.a.	755.7	19.2	17.3	20.1
BDE-28	5	none	n.a.	yes	2.440	0.276	0.265	0.193
BDE-47	11	none	Labs 9, 18	yes	233.9	30.8	28.9	26.2
BDE-99	11	Lab 19	Labs 9, 18	about	302.1	32.4	30.74	24.8
BDE-100	11	none	Labs 9, 19	yes	63.02	3.66	3.45	3.01
BDE-153	11	none	Labs 9, 18	yes	47.412	3.376	3.123	3.139
BDE-154	7	none	Lab 18	yes	25.73	1.80	1.43	2.66
BDE-183	11	none	Labs 9, 14, 18	yes	132.37	9.26	7.82	12.17
BDE-197+204	10	none	Lab 18	yes	76.00	6.42	5.69	7.27
BDE-209	10	none	Lab 9	yes	654.8	36.4	17.7	77.9
BB-209	8	none	Lab 9	yes	634.0	76.83	74.3	47.5

p: number of accepted sets of results; s: standard deviation of dataset means; averages and standard deviations in mg/kg.n.a. Not applicable (too few data).

Table 11: Statistical evaluation of the technically accepted datasets for ERM-EC591.

Measurand	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Average [mg/kg]	s [mg/kg]	S _{between} [mg/kg]	S _{within} [mg/kg]
Br	6	none	none	yes	2083	75	68	75
Sb	3	n.a.	n.a.	n.a.	712.8	17.8	16.9	13.6
BDE-28	6	none	none	yes	2.549	0.344	0.330	0.158
BDE-47	12	none	Lab 9	about	245.1	28.4	26.4	23.9
BDE-99	12	Lab 19	Lab 9	about	316.6	34.1	33.5	14.6
BDE-100	12	none	Labs 9, 18	yes	65.99	4.15	3.91	3.41
BDE-153	12	none	Labs 9, 18	yes	44.04	3.62	3.53	2.03
BDE-154	8	none	none	yes	26.27	2.01	1.89	1.70
BDE-183	12	none	Labs 14, 18	yes	86.54	7.63	7.02	7.34
BDE-197+204	11	none	Labs 14, 18	yes	51.87	6.43	5.91	6.25
BDE-209	10	none	Lab 9	yes	783.6	45.3	n.a.	221.0
BB-209	8	none	none	yes	742.6	60.7	58.5	39.7

p: number of accepted sets of results; *s*: standard deviation of dataset means; averages and standard deviations in mg/kg. n.a. Not applicable (too few data).

As can be seen in Table 10 and Table 11, laboratories 9 and 18 are frequently flagged as outliers of variance. This is mainly due to the fact that a large part of the uncertainties on their results is captured by the standard deviations, whereas standard uncertainties of other laboratories usually are much larger than the standard deviations. The results were therefore retained. This retention has little influence on the average, but has some influence on the results of the ANOVA: Data for within- and between-laboratory standard deviations are not very reliable if outliers of variance are present.

Table 10 and Table 11 also show that the technical discussion removed nearly all potentially outlying mean values. Only in the case of BDE-99 the Grubbs-tests shows outlying mean values. This was retained, as no technical reason for exclusion was found and as the value agrees with several other values for this congener.

Standard deviations between laboratories are in many cases larger than standard deviations within laboratories, indicating that repeatability is not the main contribution to measurement uncertainty. As highlighted in the technical discussion, issues like standards, matrix effects and use of inappropriate quality control samples are much more important impediment to comparability of results. Using the data for the standard deviation within and between-laboratories standard deviations, relative reproducibility standard deviations (s_R), defined as $s_R = \sqrt{s_{between}^2 + s_{within}^2}$, ranging from 7 to 17 % were calculated. The only exception is BDE-209, where s_R for EC591 is 30 %, respectively. These results represent a significant improvement over a previous intercomparison [14], where reproducibility standard deviations ranged from 24 to 47 %.

All datasets follow or are close to normal distributions. Average and standard deviations are therefore meaningful estimators for the expected value and its variation.

7 VALUE ASSIGNMENT

For these materials, certified, indicative and informative values have been assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM require generally pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets in accordance with the Guide to the expression of uncertainty in measurement [16] must be established.

Indicative values are values where either the uncertainty is deemed too large or where too few independent datasets were available to allow certification. Uncertainties are evaluated according to the same rules as for certified values.

Additional material information refers to values that have been obtained in the course of the study. For example, results reported from only one or two laboratories in cases where individual measurement uncertainty is high, would fall under this category.

7.1 CERTIFIED VALUES

The unweighted means of the means of the accepted datasets as shown in Table 10 and Table 11 were used as assigned values for all measurands.

The certified uncertainty consists of uncertainties related to characterisation (u_{char}), between-bottle heterogeneity (u_{bb}), degradation during long-term storage (u_{lts}) and transport to the customer (u_{sts}) [17].

- u_{char} was estimated as the standard error of the mean of laboratory means, i.e. s/\sqrt{p} with s and p taken from Table 10 and Table 11.
- u_{bb} was estimated as the larger value of the standard deviation between-units (s_{bb}) or the maximum heterogeneity potentially hidden by method repeatability (u_{bb}^*), or as u_{outl} in the case of Br (EC590). The values are taken from Table 6. The highest of these values was taken as estimate for BDE -153 and -154.
- u_{sts} was estimated from stability tests and was taken from Table 9. For BDE-28, -153 and BDE-154, which were not determined in the study, the highest result of the study was taken.
- u_{lts} was estimated from stability tests and was taken from Table 9. For BDE-28, -153 and BDE-154, which were not determined in the study, the highest result of the study was taken.

These uncertainties were regarded as uncorrelated and combined quadratically to estimate the uncertainty of the certified value (u_{CRM}) as shown below.

$$u_{CRM} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{sts}^2}$$

The various uncertainty contributions and the combined uncertainty are shown in Table 12 and Table 13.

Table 12: Uncertainty budget and certified values for ERM-EC590.

	u_{char}	u_{bb}	u_{lts}	u_{sts}	u_{CRM}	Certified value	U_{CRM}
	[%]	[%]	[%]	[%]	[%]	[g/kg]	(k=2) [g/kg]
Br	2.01	0.32	0.402	0.009	2.1	2.13	0.09
2,2',4,4'-Tetra BDE (BDE-47)	4.0	1.5	6.1	0.1	7.4	0.23	0.04
2,2',3,4,4'-PentaBDE (BDE-99)	3.2	1.7	9.2	0.1	9.9	0.30	0.06
2,2',4,4',6-PentaBDE (BDE-100)	1.8	1.5	12.1	0.2	12.3	0.063	0.016
2,2',4,4',5,5'-HexaBDE (BDE-153)	2.1	2.6	12.1	0.2	12.6	0.047	0.012
2,2',4,4',6,6'-HexaBDE (BDE-154)	2.6	2.6	12.1	0.2	12.7	0.026	0.007
2,2',3,4,4',5,6'-HeptaBDE (BDE-183)	2.1	2.4	3.1	< 0.1	4.5	0.132	0.012
2,2',3,3',4,4',6,6'-OctaBDE + 2,2',3, 4,4',5,6,6'-OctaBDE (BDE-197+204)	2.7	2.6	8.9	0.1	9.6	0.076	0.015
DecaBDE (BDE-209)	1.8	2.3	6.3	0.1	6.9	0.65	0.10
DecaBB (BB-209)	4.3	1.9	5.4	0.1	7.2	0.63	0.10

Table 13: Uncertainty budget and certified values for ERM-EC591.

	u_{char}	u_{bb}	u_{lts}	u_{sts}	u_{CRM}	Certified value	U_{CRM}
	[%]	[%]	[%]	[%]	[%]	[g/kg]	(k=2) [g/kg]
Br	1.469	0.14	0.306	0.004	1.507	2.08	0.07
2,4,4'-TriBDE (BDE-28)	5.5	2.3	10.8	0.2	12.3	0.0025	0.0006
2,2',4,4'-TetraBDE (BDE-47)	3.3	2.2	2.2	< 0.1	4.6	0.245	0.023
2,2',3,4,4'-PentaBDE (BDE-99)	3.1	2.0	4.3	0.1	5.7	0.32	0.04
2,2',4,4',6-PentaBDE (BDE-100)	1.8	1.5	4.2	0.1	4.8	0.066	0.007
2,2',4,4',5,5'-HexaBDE (BDE-153)	2.4	2.3	10.8	0.2	11.3	0.044	0.010
2,2',4,4',5,6'-HexaBDE (BDE-154)	2.7	2.3	10.8	0.2	11.4	0.026	0.006
2,2',3,4,4',5,6'-HeptaBDE (BDE-183)	2.5	1.6	3.4	0.1	4.5	0.087	0.008
2,2',3,3',4,4',6,6'-OctaBDE + 2,2',3, 4,4',5,6,6'-OctaBDE (BDE-197+204)	3.7	1.5	6.8	0.1	7.9	0.052	0.009
DecaBDE (BDE-209)	1.8	1.8	4.8	0.1	5.4	0.78	0.09
DecaBB (BB-209)	2.9	1.0	4.4	0.1	5.4	0.74	0.08

A graphical depiction of all assigned values, together with averages and standard deviations and submitted uncertainties of the individual laboratories is shown in Annex E.

7.2 INDICATIVE VALUES

Indicative values were assigned for Sb. Only three laboratories submitted results and all results were obtained by NAA-techniques. However, as two of the three laboratories had recently successfully participated in the characterisation of Sb in polyethylene and as INAA is now considered a primary method of measurement, the results were regarded as sufficiently trustworthy to assign indicative values. The uncertainty budgets were set up as for the certified values and are listed together with the assigned values in Table 14.

Table 14: Uncertainty budget and certified values for Sb in ERM-EC590 and ERM-EC591.

	u_{char} [%]	u_{bb} [%]	u_{lts} [%]	u_{sts} [%]	u_{CRM} [%]	Indicative value [g/kg]	U_{CRM} (k=2) [g/kg]
Sb-EC590	1.46	0.30	0.63	0.01	1.62	0.756	0.025
Sb-EC591	1.44	0.19	0.43	0.01	1.52	0.713	0.022

7.3 ADDITIONAL MATERIAL INFORMATION

Some laboratories reported additional BDE-congeners. These values are listed in Table 15. Results from laboratories that were excluded from the value assignment were not taken into consideration. Due to the doubts on the coelution of BDE-196, -198 and -203, no information value is given for these congeners.

Table 15: Additional material information for ERM-EC590 and ERM-EC591.

Congener	ERM-EC590	ERM-EC591
	Mass fraction [mg/kg]	Mass fraction [mg/kg]
2,2',4-TriBDE (BDE-17)	0.9	0.9
2,4,4'-TriBDE (BDE-28)	2.4	
2,2',4,5'-TetraBDE (BDE-49)	5.5	5.5
2,3',4,4'-TetraBDE (BDE-66)	4.6	4.6
2,4,4',5-TetraBDE (BDE-74)	2.5	2.4
2,4,4',6-TetraBDE (BDE-75)	0.3	0.4
2,2',3,4,4'-PentaBDE (BDE-85)	17.7	19.1
2,2',3',4,5-Penta BDE + 2,3',4,4',5-PentaBDE (BDE-97+118)	1.4	1.3
2,2',4,5,5'-PeBDE (BDE-101)	2.1	2.1
2,3',4,4',6-PentaBDE (BDE-119)	0.4	
2,2',3,4,4',5'-HexaBDE (BDE-138)	5.6	5.5
2,2',3,4,4',6-HexaBDE (BDE-139)	4.9	5.1
2,2',4,4',6,6'-HexaBDE (BDE-155)	1.2	1.4
2,2',3,3',4,5,6'-HeptaBDE + 2,3,3',4,4',5,6-HeptaBDE (BDE-173+190)	5.9	4.3
2,2',3,4,4',5,5'-HeptaBDE (BDE-180)		5.4
2,2',3,4,4',5,6-HeptaBDE (BDE-181)	2.0	0.8
2,2',3,4,4',5,6'-HeptaBDE (BDE-182)	3.2	2.3
2,2',3,3',4,4',5,6,6'-NonaBDE (BDE-207)	90.3	43.8
2,2',3,3',4,5,5',6,6'-NonaBDE (BDE-208)	15.0	6.6

7.4 CONFIRMATION OF ASSIGNED VALUES

Correctness of the calibration lines was verified by the quality control solution, a candidate CRM. On average, results submitted by the laboratories for this solution agree with the candidate certified value, as can be seen in Figure 1 **Error! Reference source not found.** The only deviation is for BDE-203, which coelutes with BDE-198 on various columns, which is also present in the solution.

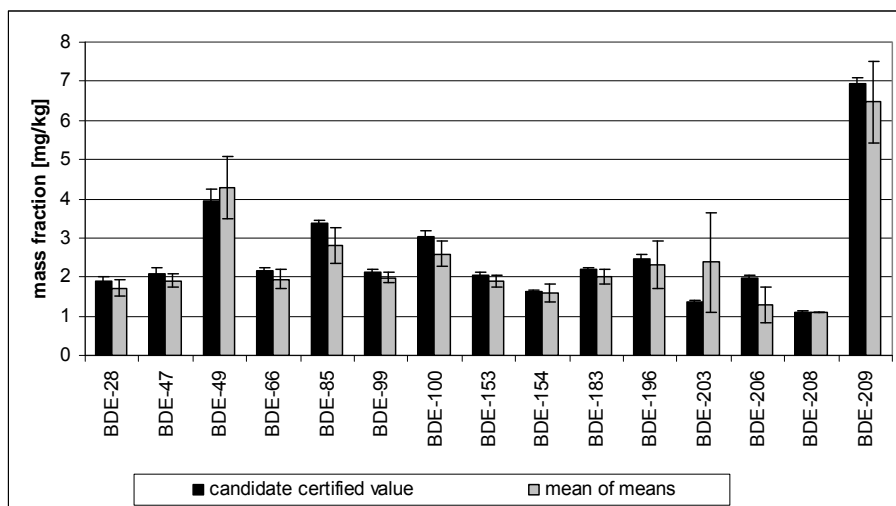


Figure 1: Comparison of results for the certified quality control solution. Error bars are expanded uncertainties for the certified values or confidence interval of the mean of means.

Two datasets from non-GC methods were received. One set was obtained by IA-MS, the other by HPLC. In IA-MS, the sample (almost 1mg) without pretreatment is introduced and heated directly, then the evaporated. BFRs are determined by mass spectrometry. This method gives the sum of each homologue group. Also measurements by HPLC give the sum of penta-, hexa-, hepta-, octa- and nonabrominated BFRs together with BDE-209 and BB-209. The two methods are both plagued by specific problems:

- IA-MS requires a matrix material for calibration. In the absence of other materials, quality control material IRMM-310 was used for calibration. As the assigned values of IRMM-310 are of an informative character only, the results by IA-MS cannot be included in the set of values for certification.
After disclosure of results, a second set of results for BDE-209 using CRM NMIJ CRM-8108-a (Deca-BDE in polystyrene) for calibration was received.
- The HPLC method was optimised for commonly occurring PBDE patterns. The pattern in EC590 and EC591, containing four technical mixtures of BFRs rather than only one, was highly unusual, thus leading to potentially biased results. Nevertheless, the results confirm that the order of magnitude of the values assigned by GC is accurate. Results from these two methods are compared to the results obtained by GC in Figure 2. Certified, indicative and informative values were combined for this comparison.

A second confirmation of the accuracy of the results comes from a comparison of the total Br values as calculated from the BFRs and from elemental methods. For this calculation, certified, indicative and informative values were used. The results are shown in Figure 2.

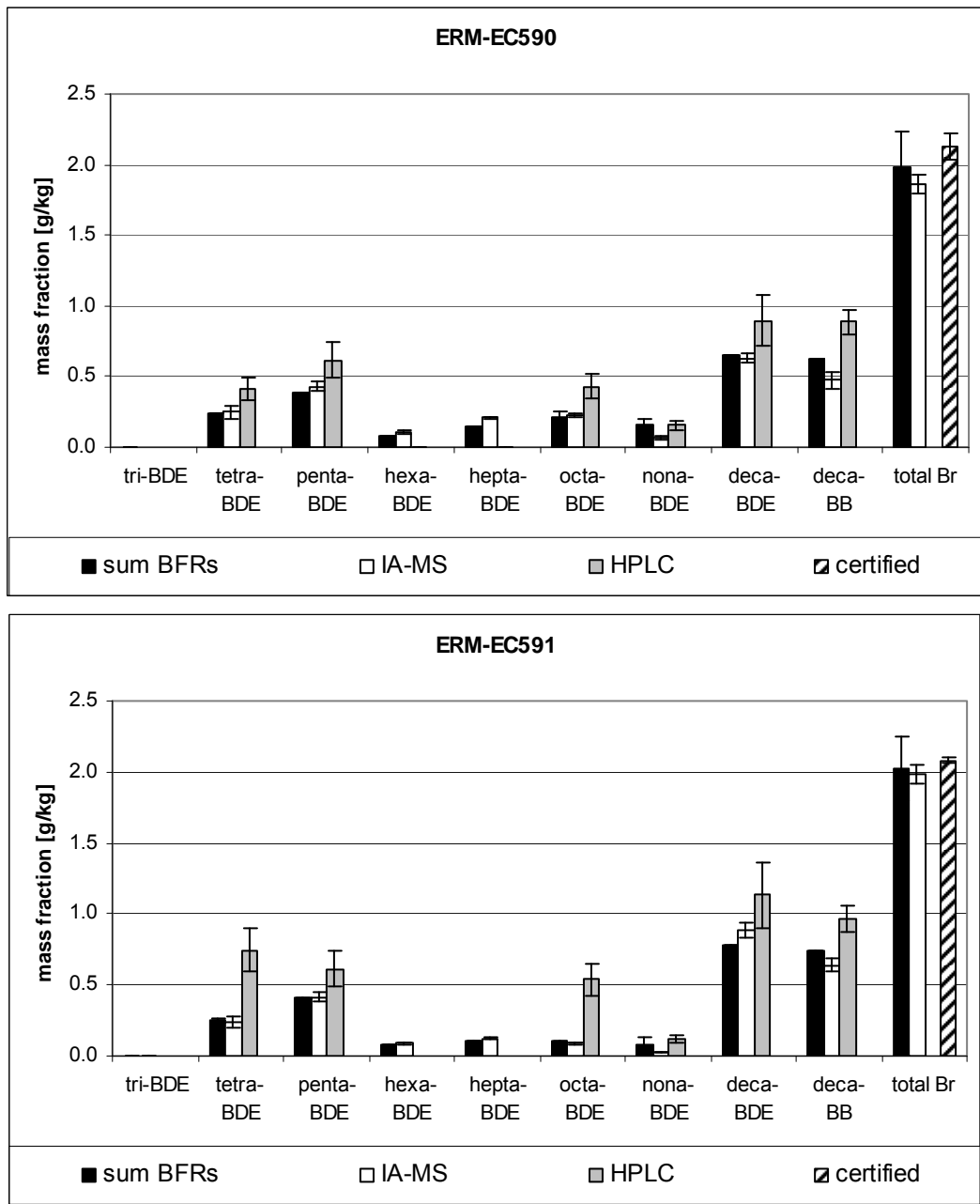


Figure 2: Comparison of results from GC, HPLC, IA-MS and elemental analysis methods. All Error bars are expanded uncertainties ($k=2$). Uncertainties for the sums of results from GC were calculated as square root of the squared uncertainties of the individual contributions.

As can be seen in Figure 2, results for tetra to octa-BDEs from IA-MS agree within the respective uncertainties with the sum of results obtained by GC. Results for nona-BDEs, and Deca-BB from IA-MS are slightly lower than those obtained by GC.. The opposite is true for results by HPLC, the results of which are above those obtained by GC. Total bromine content as calculated from the GC-results agrees with the total Br content as determined by element-specific methods, confirming completeness of extraction. The values found also agree with the theoretical contents from the composition, which is 1.9 to 2.0 g/kg for ERM-EC590 and ERM-EC591. This agreement confirms the correctness of the assigned values.

8 METROLOGICAL TRACEABILITY

Bromine

Laboratories used instrumental as well as destructive methods, eliminating potential influences of method preparation. Quantification was based on completely independent measurement principles. Agreement between the results therefore confirms absence of any significant method bias and demonstrates the identity of the analyte being Br.

Only validated methods were used. Agreement with the certified value of the quality control materials proved absence of significant bias for the individual methods. This agreement also demonstrated the correctness of the individual calibrations. The certified values are therefore traceable to the international system of units (SI).

Antimony

Only NAA-methods were used. Although, based on the knowledge of the performance of NAA methods for polymer samples, a method bias is unlikely, absence of method bias cannot be unequivocally demonstrated. Identity of the analyte is therefore defined as "Sb as determined by NAA".

The methods were validated. Agreement with the certified values of the control sample confirmed the absence of bias and the correctness of calibration (where applicable) for the individual results. The assigned quantity values are therefore traceable to the SI.

Brominated flame retardants

PBDEs and PBBs are chemically clearly defined molecules. The participants used different GC columns and different ionisation techniques. In addition, agreement with the certified mass fractions of the candidate CRM that was distributed together with the polymer materials confirms the identity of the molecules.

Different extraction methods (Soxhlet, ultrasound assisted, PLE) and solvents (toluene, CH₂Cl₂, isooctane) were used. In addition, one laboratory dissolved the complete sample, hence avoiding extraction altogether. Agreement between the results therefore demonstrates absence of any systematic influence of the extraction technique on the assigned values.

Results were obtained applying GC methods with different ionisation techniques (electron impact, chemical ionisation). While the agreement of the sum of assigned values with the results from IA-MS and the agreement of the total Br mass fraction calculated from the results with the certified Br mass fraction strongly indicates absence of method bias, this absence could not be demonstrated. Identity of the BFR congeners are therefore defined as "as determined by GC-MS".

Only validated methods were used. Correctness of calibration was confirmed by agreement of results with the certified values for the candidate CRM used as quality control. The assigned quantity values are therefore traceable to the SI.

9 COMMUTABILITY

CRMs must exhibit the same analytical behaviour for given methods as a normal laboratory sample. The laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding digestion/extraction, calibration and detection. The good agreement between the results obtained shows the commutability of the materials.

10 INSTRUCTIONS FOR USE

10.1 STORAGE CONDITIONS

The material shall be stored at +4 °C in the dark.

10.2 SAFETY AND PROTECTION OF THE ENVIRONMENT

The usual laboratory safety measures apply.

10.3 HANDLING OF THE MATERIAL

Grinding of the materials to particle diameters < 0.5 mm if extraction methods are used is highly recommended, although the influence of particle size on extraction efficiency strongly depends on the extraction technique and extraction solvent. Milling conditions should be chosen so that the ground material remains colourless to avoid potential changes of the analyte content.

Especially for ERM-EC591, cryogrinding is recommended, as the polymer tends to become plastic when ground without cooling.

10.4 USE OF THE CERTIFIED VALUES

The material is intended to be used for method validation and for demonstration of laboratory proficiency.

Comparing an analytical result with the certified value

A result is unbiased if the combined uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1 [18]).

Use in quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same result as heterogeneity was included in the uncertainties of the certified values.

Use as a calibrant

It is not recommended to use these matrix materials as calibrants, unless the method in question requires calibration with matrix materials. If used nevertheless, the uncertainty of the certified value shall be taken into account in the final estimation of measurement uncertainty.

11 REFERENCES

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12 ACKNOWLEDGEMENTS

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13 ANNEX(ES)

Annex A: Results of the homogeneity tests for ERM-EC590 and ERM-EC591

Annex B: Graphical representation of stability tests for ERM-EC590 and ERM-EC591

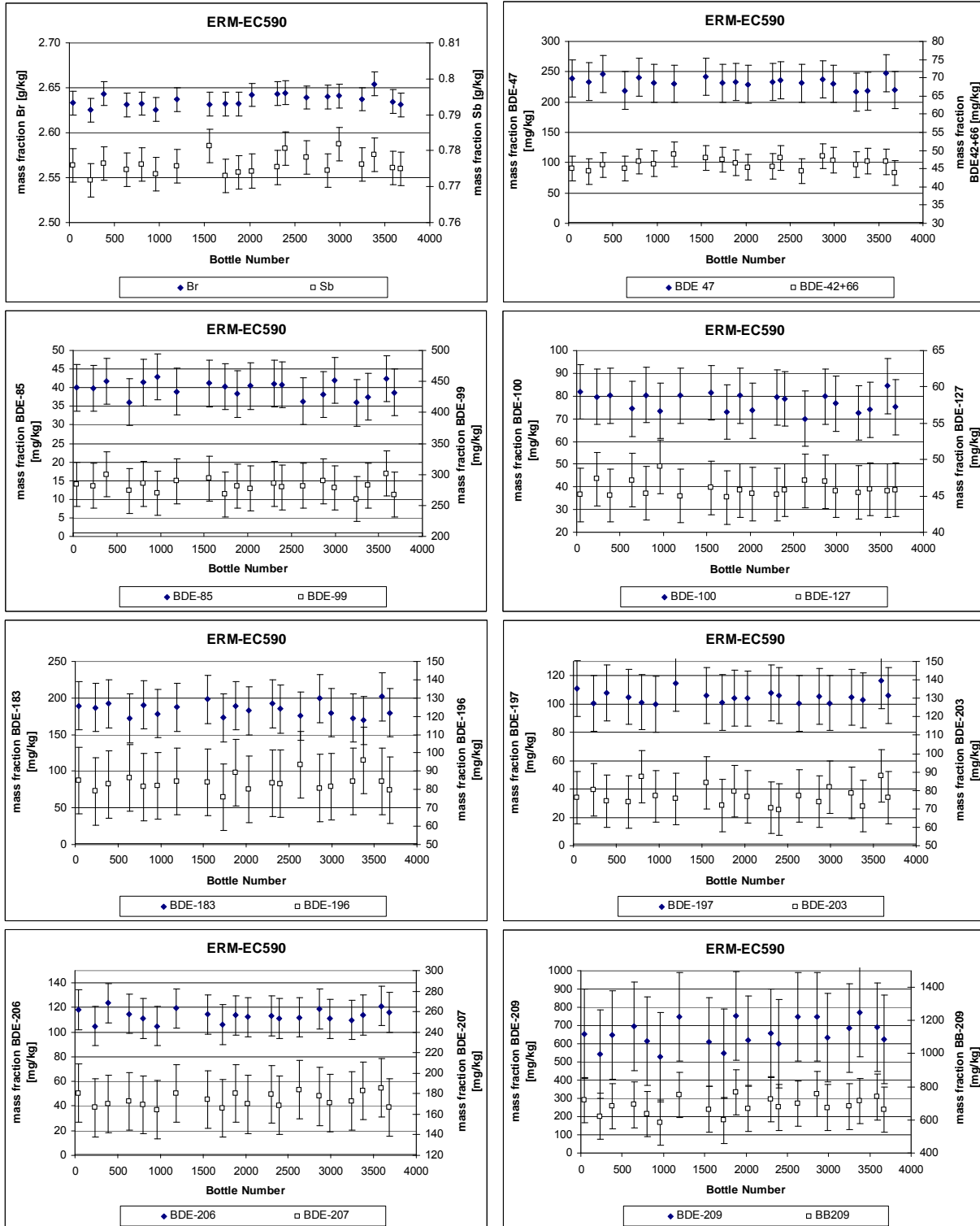
Annex C: Methods used for characterisation of total Br and Sb

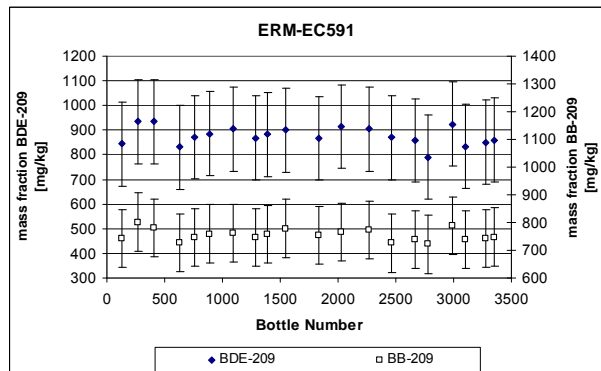
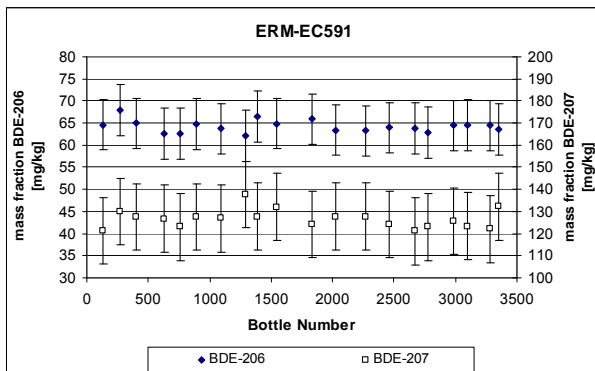
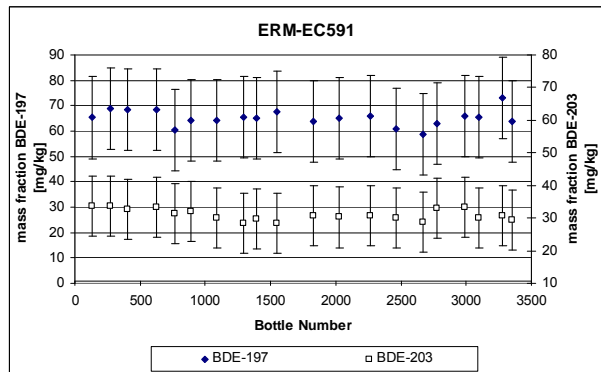
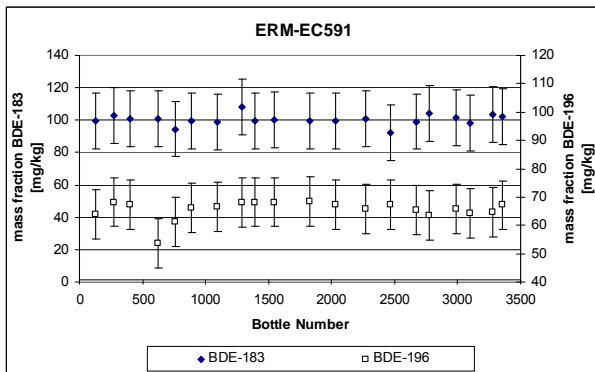
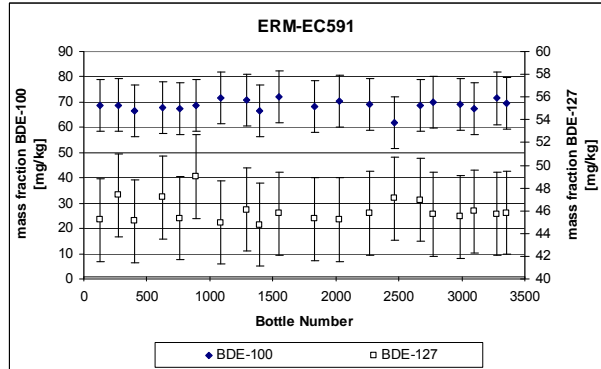
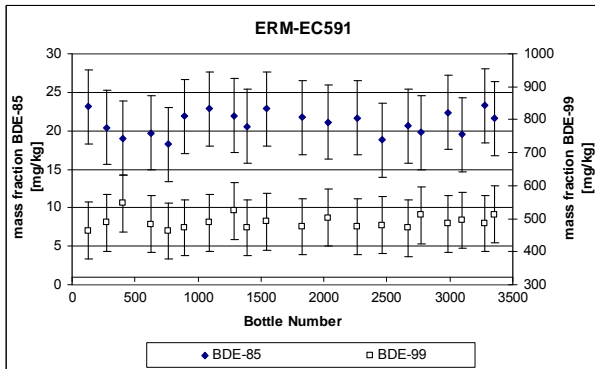
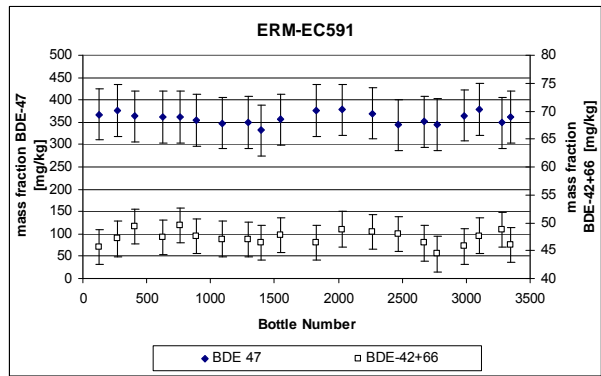
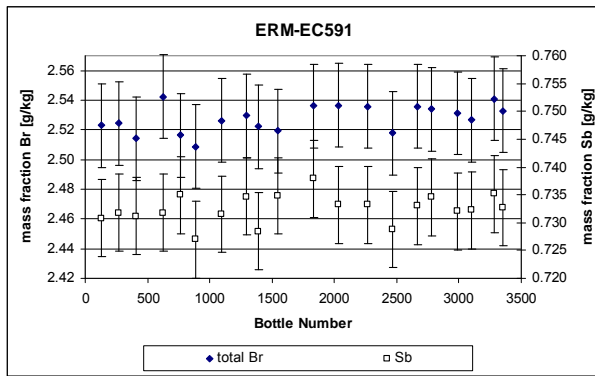
Annex D: Methods used for characterisation of PBDEs and BB-209

Annex E: Graphical and tabular presentation of the results of the characterisation studies

Annex A Results of the homogeneity studies

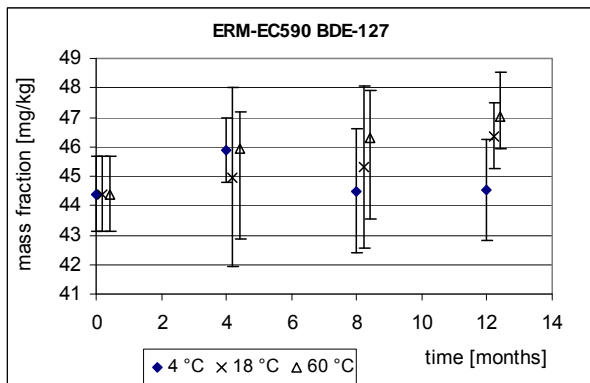
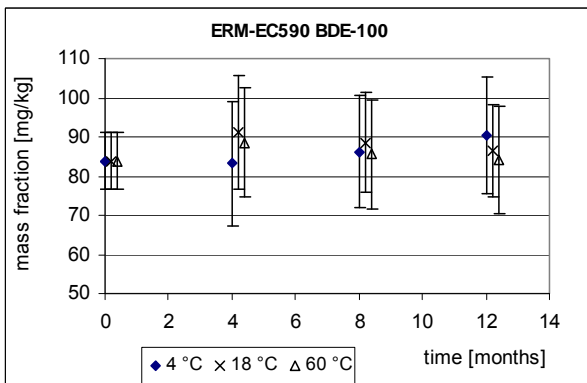
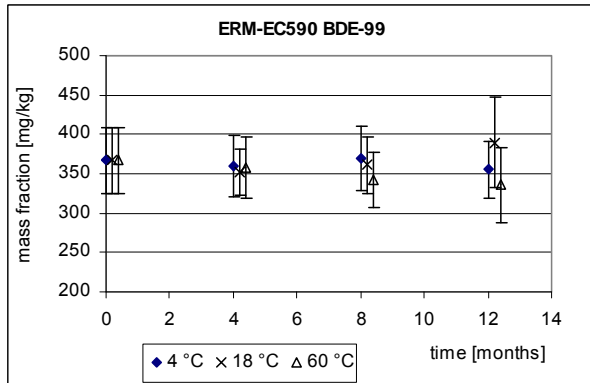
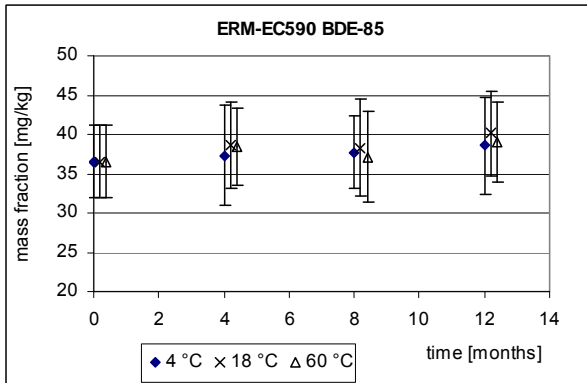
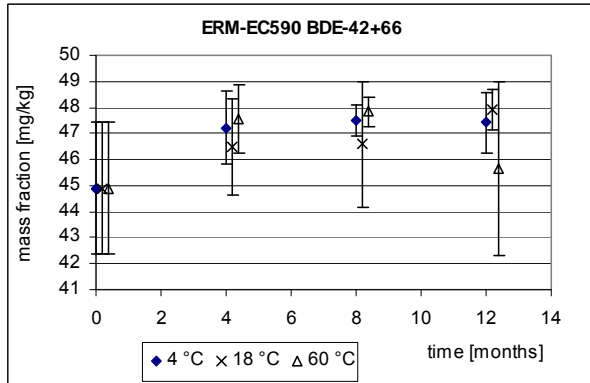
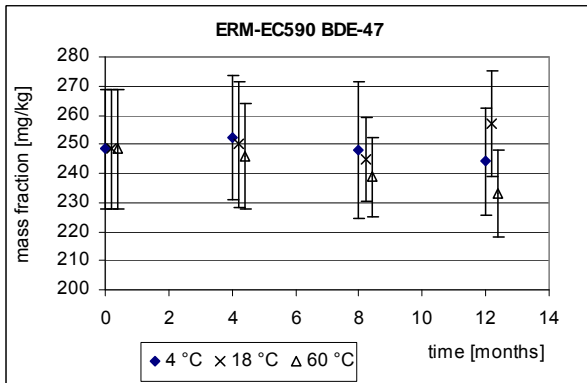
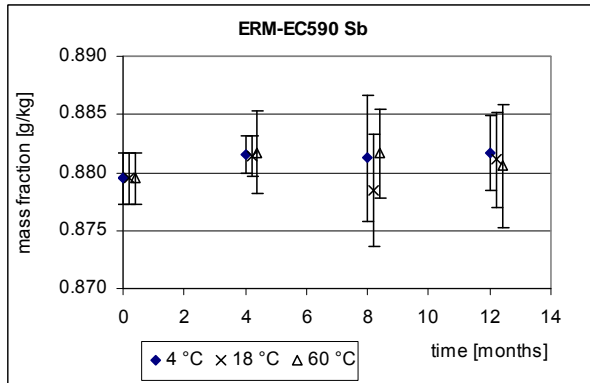
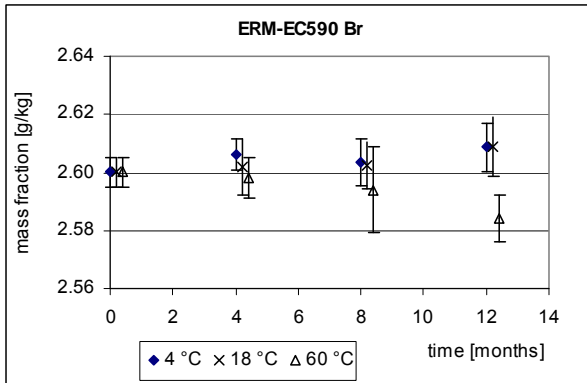
The graphs show bottle averages and their 95 % confidence intervals. Confidence intervals were based on the "within-bottle" standard deviation for each congener rather than on the standard deviation of the 4 replicates per bottle. Absolute values do not agree with the certified values, most likely due to different calibrations.

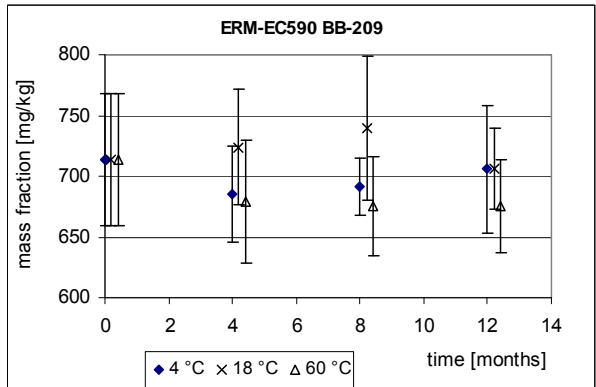
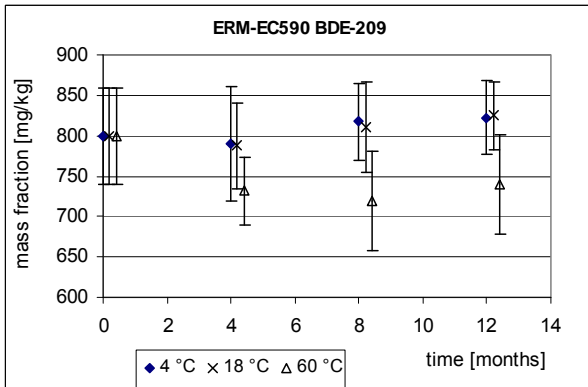
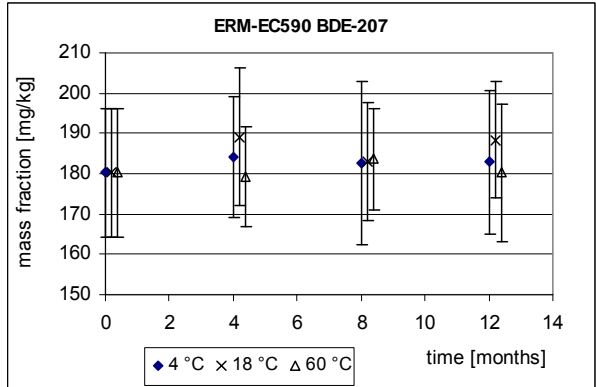
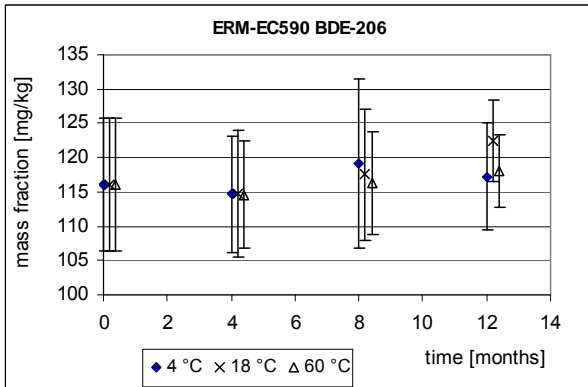
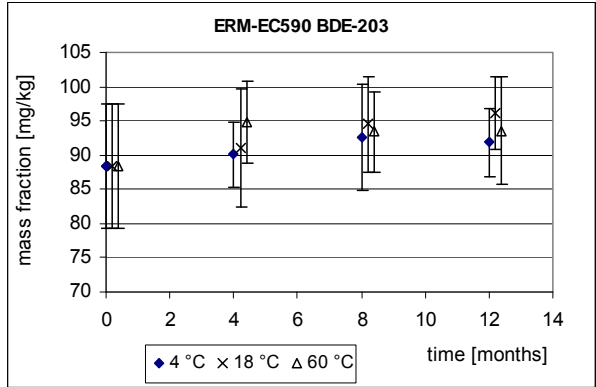
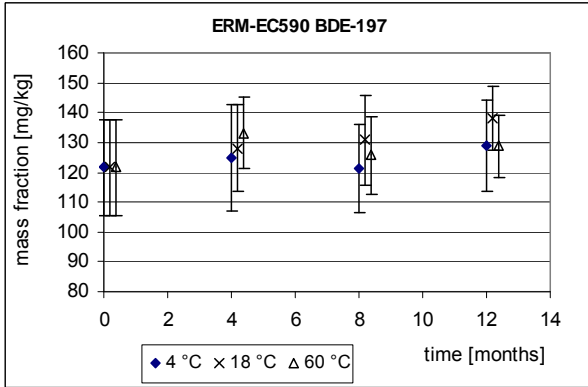
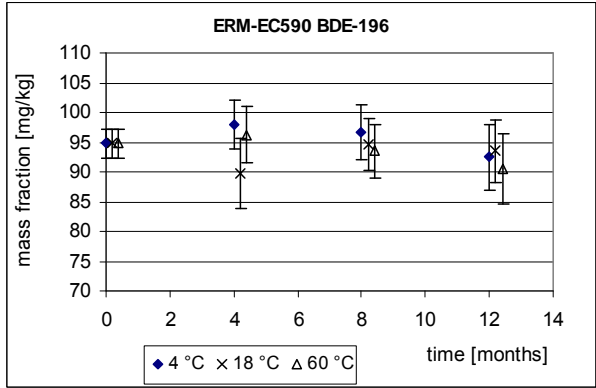
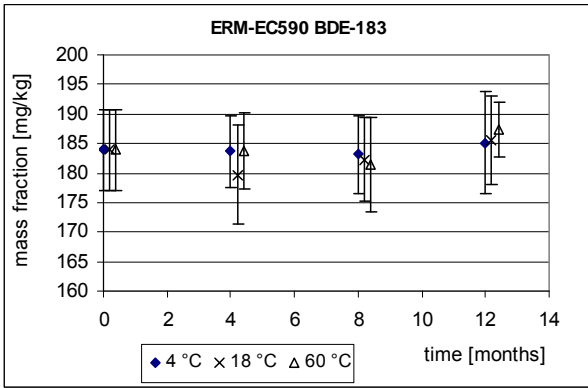


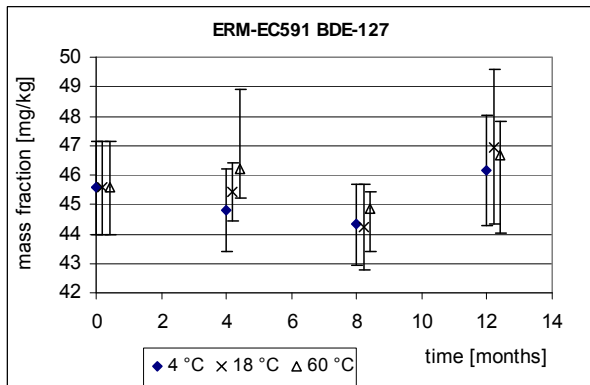
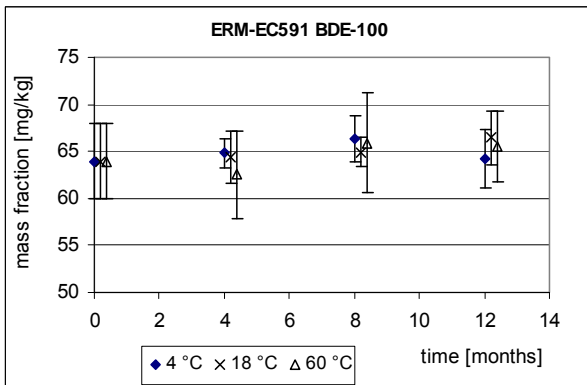
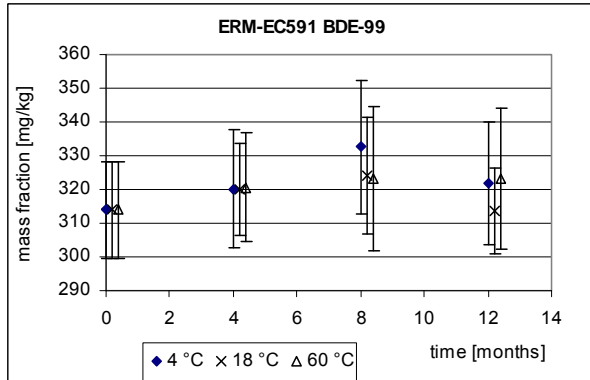
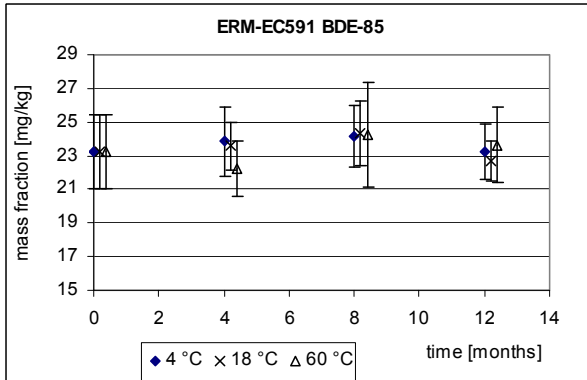
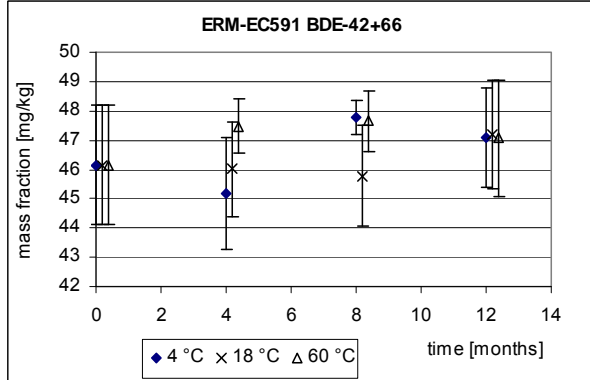
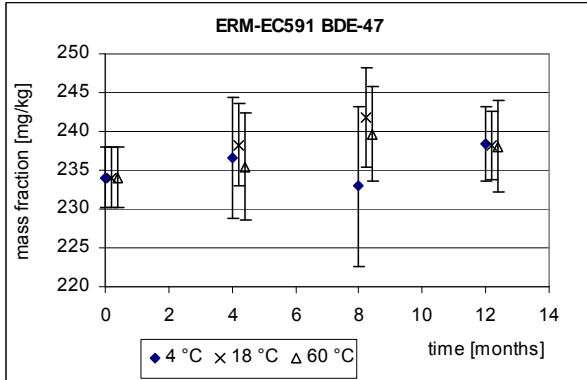
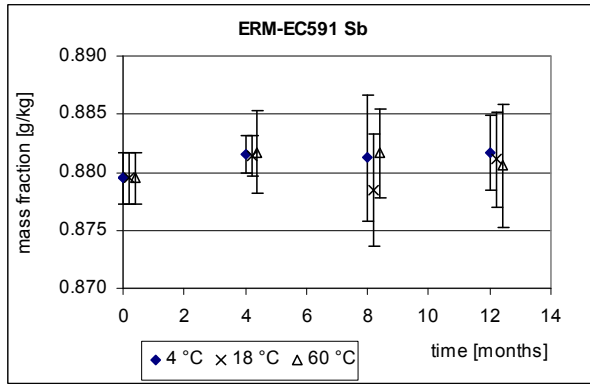
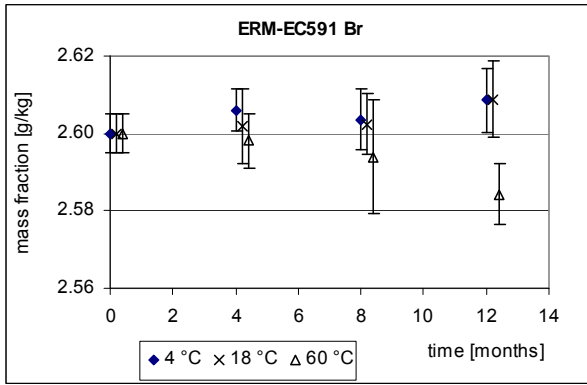


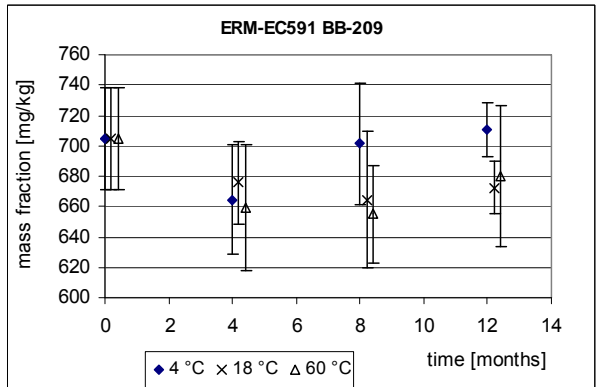
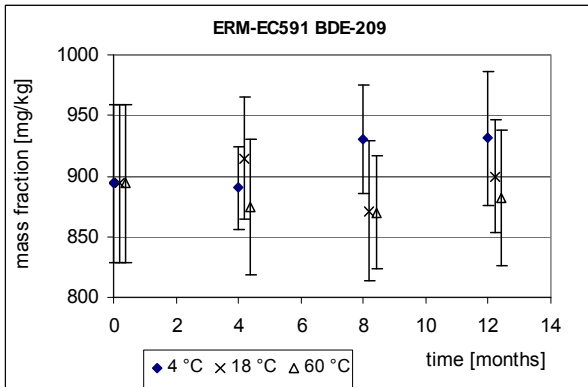
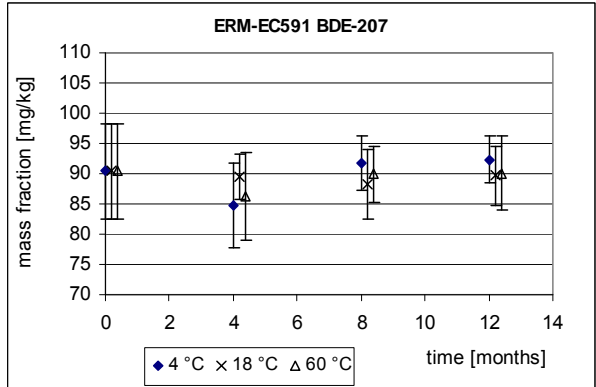
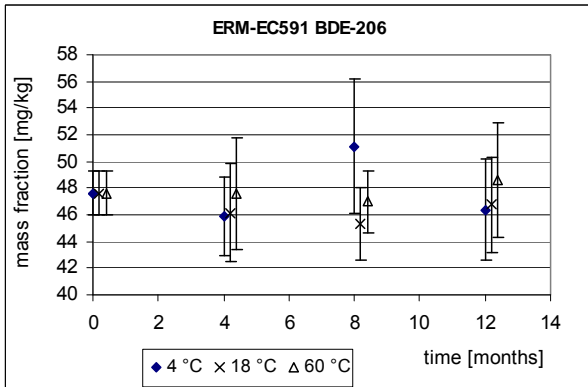
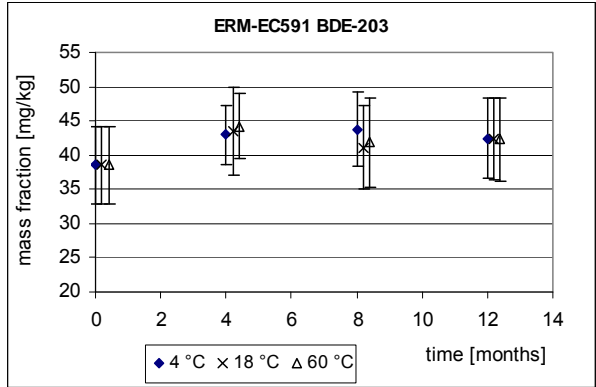
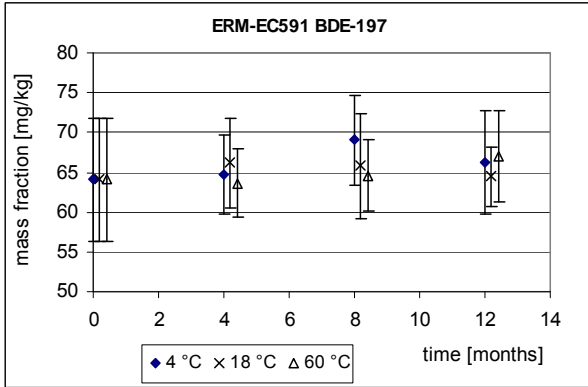
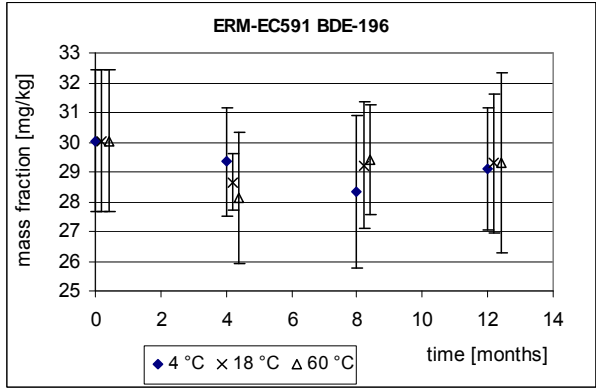
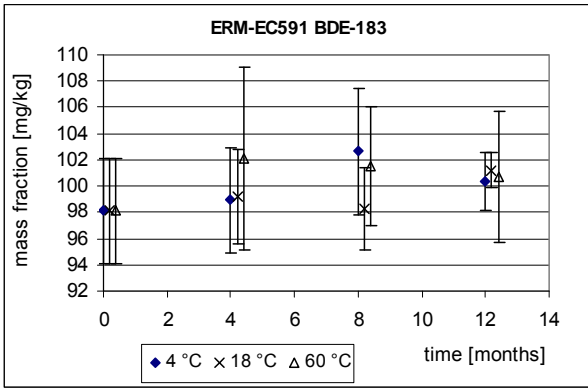
Annex B: Results of the stability studies

The graphs show averages per time point and their 95 % confidence intervals. Confidence intervals are based on the standard deviations of the 8 replicates per time/temperature combination. Data for different temperatures were measured at the same time but are graphically separated to make the graphs easier readable. Only one set of results per measurand was measured for t=0, which was entered three times in the graphs. Absolute values do not agree with the certified values, most likely due to different calibrations.









Annex C: Methods used for characterisation of total Br and Sb

Data-set	Sample intake [mg]	Sample preparation	Calibration	Quantification
1	170 - 240	none	IRMM-530 flux monitors (99.9 % Al, 0.1 % Au) Blank: empty vial	k_0 NAA: Irradiation: 7 h (Br); 4 h (Sb) with a flux of $3 \cdot 10^{11}$ neutrons/(cm ² s) Decay time 2-5 d (Br), 15-25 d (Sb), Measuring time 2 h Lines (keV): 554.3, 619.1, 776.5; 1044, 1317.5 (Br); 564.2, 602.7 (Sb)
2	150-220	none	Al-Au (0.1%), Zn (99.99%), Zr (99.8%) Validated using several BCR-CRMs Blank: SPRONK 0908, supra pure polyethylene	k_0 NAA: Irradiation: 6 h with a flux of $1 \cdot 10^{12}$ neutrons/(cm ² s) Decay time 3 and 4 days (Sb), Measuring time 35 min Lines (keV): 776.5 (Br); 564.2 (Sb)
3	400	none	NIST SRM 3184 (Br anion- solutions) and NIST SRM (multielement standard solution)	INAA: Irradiation: 1 h with a flux of $2.8 \cdot 10^{11}$ neutrons/(cm ² s) Decay time 5 to 7 days, Measuring time 7200 s Lines (keV): 221, 554, 606, 619, 698, 776, 828, 1008, 1044, 1317, 1475 (Br); 564, 603, 646, 693, 723 (Sb)
4	20-30	Combustion in an oxygen bomb (Schöninger flask); Combustion gases trapped in an aqueous solution of sodium disulfite	Titer of the titrant is established from the analysis of characterized organic compounds with known content of bromine.	Potentiometric titration with 0.001 N silver nitrate in a suitable acetone/water solution
5	320 - 400	Combustion in an oxygen bomb (10 bar O ₂); Combustion gases trapped in ultra pure water	Monoelement standard (Merck) traceable via NIST NaBr in water; calibration checked against an independent Quality control from SPEX Certiprep	sectorfield ICP-MS masses 79, 80 (79 reported) Internal standard Se
6	300 – 500	Combustion in an oxygen bomb (10 bar O ₂); Combustion gases trapped in ultra pure water	Monoelement standard (Merck) traceable via NIST, NaBr in water; calibration checked against an independent Quality control from SPEX Certiprep	Ion chromatography with UV detection Resin: strong basic low capacity anion exchanger

Annex D: Methods used for characterisation of PBDEs

Data-set	Sample intake [mg]	Sample preparation	Calibration	Quantification
7	250	Grinding to < 0.5 mm Ultrasonic extraction (toluene, 70 °C, 3 h) Precipitation of dissolved polymer UV protection: not specified	Internal standard: PCB-209 Calibration with pure congeners from AccuStandard	GC-quadrupole-MS Column: DB 5HT (15 m x 0.25 mm x 0.1 µm) Injection: Pulsed splitless; 310 °C
8	100	Cutting to particles of 2 x 2 mm (scissors) Extraction (toluene, 100 °C, 4 h) No additional clean-up UV protection: use of amber glass vials	Internal standard PCB-209 Calibration with a custom mix from AccuStandard	GC-quadrupole-MS; resolution 0.3 amu Column: DB 5MS (15 m x 0.25 mm x 0.1 µm) Injection: 310 °C
9	110	Samples taken as is Dissolution in xylene/ dimethyl glutarate Precipitation of the polymer and subsequent filtration UV protection: not specified	Internal standards: ¹³ C labelled BFR-mix, Wellington Laboratories Calibration: BB-209, PBDE-mix, Wellington Laboratories	GC-quadrupole-MS Column: ZB 5HT (15 m x 0.25 mm x 0.1 µm) Injection: Cold injection with subsequent desorption (90-320 °C)
10	1700-3800	Grinding to about 0.5 mm (IKA A11 analytical mill) Soxhlet extraction (toluene, 110 °C, 24 h) Dilution, addition of internal standard UV protection: Protection from light (6 samples were re-extracted to check for completeness of extraction)	¹³ C labelled BFRs from Cambridge Isotope Laboratories/Wellington Laboratories for all congeners Calibration: Native congeners from CIL/Wellington Laboratories	GC-SF-MS; resolution 8000-9000 amu Column: RTX5 Sil-MS (30 m x 0.25 mm x 0.1 µm) Injection: Splitless, 280 °C
11	1000	Information on grinding not given Extraction with 10 mL solvent (toluene, 100 °C, 1 h)	Internal standard: PCB-209 Calibration: Standards from Accustandard	GC-quadrupole-MS; Column: DB 5HT 30 m x 0.25 mm x 0.25 µm) Injection: not given
12	500	Samples taken as is Soxhlet extraction (CH ₂ Cl ₂ , 24 h) Dilution UV protection: yes	Internal standards: ¹³ C labelled BDE 209 (nona-BDEs, BDE-209, BB-209), unlabelled BDE-58 (all others) Calibration: Native congeners from Accustandard, Chiron and Wellington Laboratories	GC-quadrupole-ECNI-MS Column: DB-5 (15 m x 0.25 mm x 0.25 µm) (nona and deca BDEs, Deca-BB); CP-SIL8 (50 m x 0.25 mm x 0.25 µm) (others); Injection: Splitless, 275 °C

Data -set	Sample intake [mg]	Sample preparation	Calibration	Quantification
13	200	<u>Modified US EPA method 3541</u> Cryo-grinding to 5 mm (ZM200, Retsch) Soxhlet extraction (toluene, 2 h) Acidic silica column cleanup UV protection: Glassware wrapped in aluminium foil	Internal standards: D ₁₀ fluranthene Calibration: Native congoeners from Wellington Laboratories	GC-quadrupole-MS; resolution 0.1 amu Column: DB-5MS (30 m x 0.25 mm x 0.25 µm) Injection: PTV, splitless mode, 90-350 °C
14	500	Grinding to < 0.5 mm (EC590) and < 1 mm (EC591), respectively (centrifugal mill ZM100, Retsch) Soxhlet extraction (toluene, 2 h) UV protection: equipment wrapped in aluminium foil	Internal standards: ¹³ C labelled BDE-47, -99, -153, 183, -209, BB-209 from Wellington Laboratories Calibration: Native congeners from Accustandard and Wellington Laboratories	GC-SF-MS; resolution 5000 amu Column: DB5-HT (15 m x 0.25 mm x 0.1 µm) Injection: cool on column
15	100	<u>Method according to IEC FDIS 62321</u> Grinding to 0.5 mm (Pulverisette 14) Soxhlet extraction (toluene , 2 h) Filtration (0.45 µm membrane) UV protection: yes	Internal standard: PCB-209 Calibration: Native congeners from Wellington Laboratories	GC-quadrupole-MS; resolution 0.5 amu Column: J&W (15 m x 0.21 mm x 0.1 µm) Injection: 280 °C
16	110-170	Grinding to < 0.75 mm (Centrifugal Mill ZM100, Retsch) PLE (toluene, 125 °C, 140 bar) no further clean-up UV protection: yes	Internal standards: F-BDE-47, F-BDE-100, BDE-190, F-BDE-201, ¹³ C BDE 209 Calibration: Native congeners from Accustandard, Wellington Laboratories and Cambridge Isotope Laboratories	GC-quadrupole-MS; Column: Rtx CLP (30 m x 0.25 mm x 0.25 µm) Injection: PTV 125-325 °C
17	200	<u>Method according to IEC FDIS 62321</u> Grinding to < 1 mm (Centrifugal Mill ZM200, Retsch) Soxhlet extraction (toluene, 2 h) Florisil column clean-up UV protection: yes	Internal standard: PCB-209 Calibration: Native congeners from AccuStandard	GC-quadrupole-MS Column: DB-5HT (15 m x 0.25 mm x 0.1 µm) Injection: Pulsed splitless, 280 °C

Data-set	Sample intake [mg]	Sample preparation	Calibration	Quantification
18	500	Sample taken as is Soxhlet extraction (toluene, 12 h) Clean-up with sulphuric acid, mixed-layer column and alumina column	Internal standards: ¹³ C labelled BDE-28, BDE-47, BDE-77, BDE-99, BDE-100, BDE-126, BDE-153, BDE-154, BDE-183, BDE-197 and BDE-209	GC-SF-MS; resolution 7000-9000 amu Column: RTX5MS (15 m x 0.25 mm x 0.25 μm) (Octa- to Decabrominated congener), J&W DB5(60 m x 0.25 mm x 0.25 μm) (other congeners) Injection: 40 -350 °C
19	500	Grinding to < 0.1 mm (SPEX Certiprep 6850 Freezer/mill) Soxhlet extraction (toluene, 21 h) Solvent evaporated under nitrogen, residue re-dissolved in n-hexane Removal of plastic by centrifugation UV protection: glassware wrapped in aluminium foil	Internal standards: Chlorinated diphenylethers (CDE, from Ultra Scientific) CDE-66, CDE-118, CDE-209 and ¹³ C-BDE-209 (Cambridge Isotope Laboratories) Native congeners prepared from NIST SRM 2258 and NIST SRM 2257	GC-quadrupole-MS; Column: RTxi-5MS (15 m x 0.25 mm x 0.25 μm) Injection: cool on column Confirmation and BDE-196, 203 on a LC-50 (15 m x 0.25 mm x 0.15 μm) Injection: cool on column
20	500	Samples used as is Ultrasound extraction (CH ₂ Cl ₂ , 25 °C, 1 h) No cleanup UV protection by using amber vials	Internal standards: ¹³ C BDE-47, BDE-99, BDE-153, BDE-183; PCB-209 Native standards from Accustandard, Cambridge Isotope Laboratories, Wellington Laboratories, Promochem	GC-quadrupole-MS; resolution 0.1 amu Column: J&W DB-5 (10 m x 0.25 mm x 0.32 μm) Injection: PTV, 100 °C
21	20	Grinding and sieving, size fraction between 0.125 and 0.25 mm taken (jet milling under liquid nitrogen cooling) Ultrasound extraction (iso-octane, 20 °C, 1.25 h) No cleanup UV protection by using amber vials	Internal standards: BDE-77, BDE-128, ¹³ C BDE-209 Native standards from Wellington Laboratories	GC-quadrupole- ECNI-MS; resolution 0.6 amu Column: J&W DB-5MS (15 m x 0.25 mm x 0.1 μm) Injection: PTV, 90-300 °C
22	1000	Grinding to < 0.5 mm (cryogenic mill) EC590: Ultrasonic extraction (toluene, 80 °C); EC591: PLE (toluene, 3 cycles 100 °C, 140 bar) UV protection: yes	Internal standards ¹³ C BDE-47, -99, -100, -153, -183, -97, -200 and BB-209 from Wellington Laboratories Native congeners from Wellington Laboratories	GC-quadrupole-MS; resolution Column: ZB-5HT Inferno (10 m x 0.25 mm x 0.10 μm) Injection: PTV (Gerstel CIS), 90-360 °C

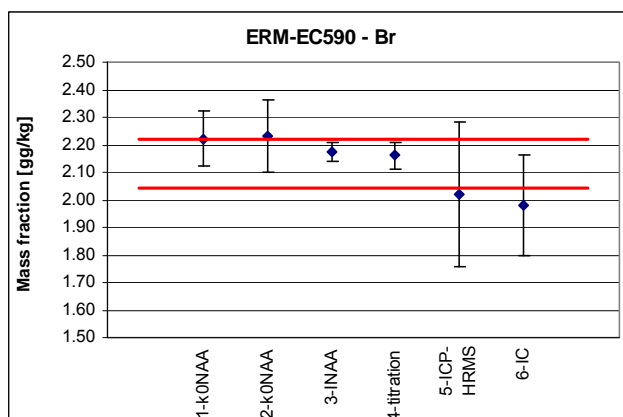
Data-set	Sample intake [mg]	Sample preparation	Calibration	Quantification
23	100	Grinding to < 1 mm (centrifugal Mill ZM100 with iron distance sieve, Retsch) Soxhlet extraction (n-propanol, 3 h) Filtration (paper filter) UV protection: yes	Internal standards: BDE-209, Tetrabromobisphenol A Native congeners: Technical mixtures LGC Standards and Fluka	HPLC-UV Column: Macherey Nagel Nucleosil® 100-7 C ₁₈ Nautilus (25 cm x 4 mm)
24	0.8 – 1.2	Cryo-grinding to 0.1 mm No further treatment	IRMM-310 (QCM BFRs in PET) for Tetra-nona-BDEs and BB-209; NMIJ CRM 8108-a for BDE-209	IA-Quadrupole-MS

Annex E: Graphical depiction of the results of the characterisation study.

Laboratories marked with an asterisk (*) are used for confirmation only (Laboratory 15; alternative column laboratory 19); Q-MS: Quadrupol-MS; SF-MS: Sectorfield-MS

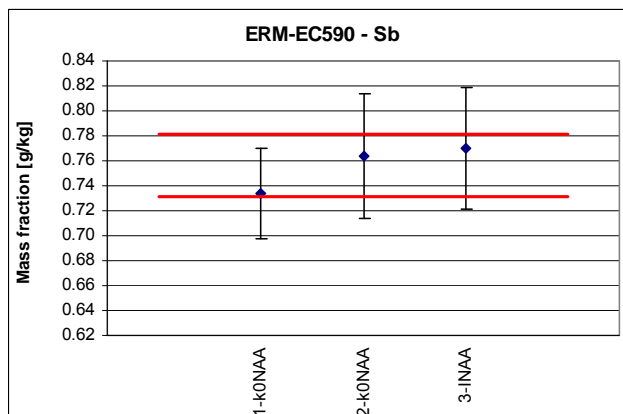
ERM-EC590 – Br

Lab	Method	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
1	kONAA	2.2207	0.0104	0.0999
2	kONAA	2.2293	0.0303	0.1315
3	INAA	2.1752	0.0426	0.0326
4	titration	2.1613	0.0737	0.0497
5	ICP- HRMS	2.0210	0.0693	0.2627
6	IC	1.9810	0.0643	0.1842



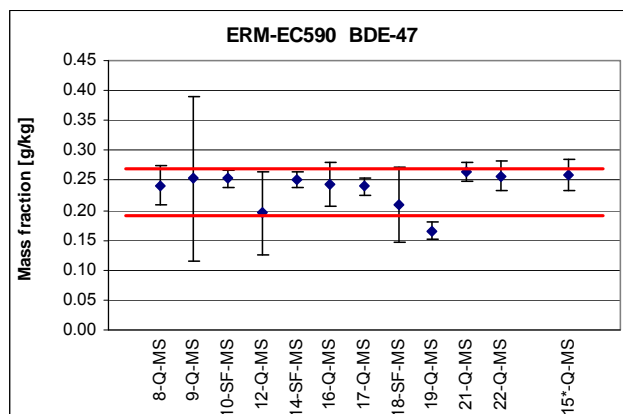
ERM-EC590 - Sb

Lab	Method	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
1	kONAA	0.7340	0.0067	0.0360
2	kONAA	0.7632	0.0074	0.0500
3	INAA	0.7700	0.0333	0.0490



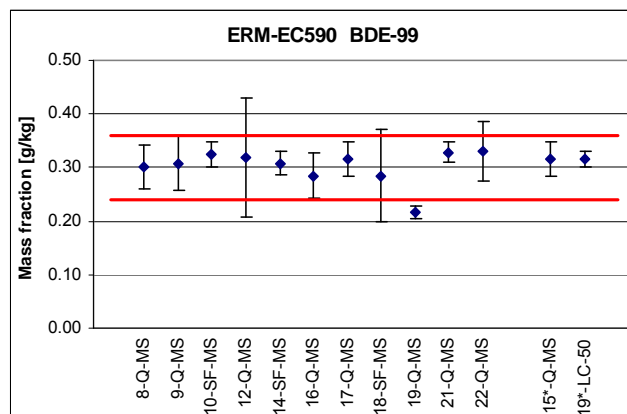
ERM-EC590 BDE-47

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.2417	0.0075	0.0335
9	Q-MS	0.2525	0.0692	0.0138
10	SF-MS	0.2531	0.0070	0.0140
12	Q-MS	0.1950	0.0055	0.0683
14	SF-MS	0.2515	0.0070	0.0140
16	Q-MS	0.2434	0.0100	0.0365
17	Q-MS	0.2400	0.0126	0.0149
18	SF-MS	0.2083	0.0454	0.0625
19	Q-MS	0.1657	0.0097	0.0150
21	Q-MS	0.2637	0.0116	0.0158
22	Q-MS	0.2576	0.0073	0.0245
15*	Q-MS	0.2600		0.0260



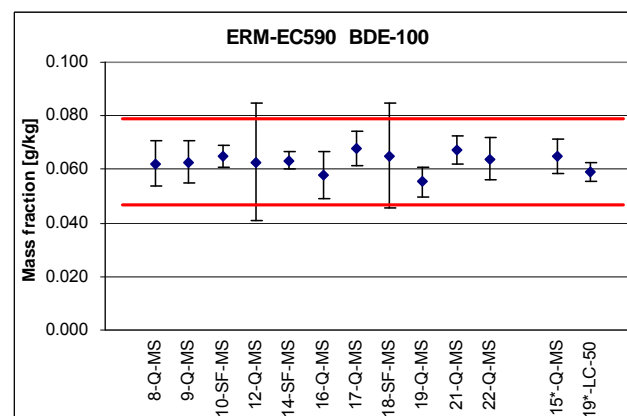
ERM-EC590 BDE-99

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.3017	0.0041	0.0418
9	Q-MS	0.3082	0.0411	0.00509
10	SF-MS	0.3246	0.0120	0.0240
12	Q-MS	0.3183	0.0041	0.1114
14	SF-MS	0.3079	0.0110	0.0220
16	Q-MS	0.2844	0.0100	0.0427
17	Q-MS	0.3167	0.0175	0.0323
18	SF-MS	0.2850	0.0647	0.0855
19	Q-MS	0.2167	0.0095	0.0120
21	Q-MS	0.3285	0.0062	0.0197
22	Q-MS	0.3306	0.0047	0.0565
15*	Q-MS	0.3160		0.0316
19*	LC-50	0.3150		0.0140



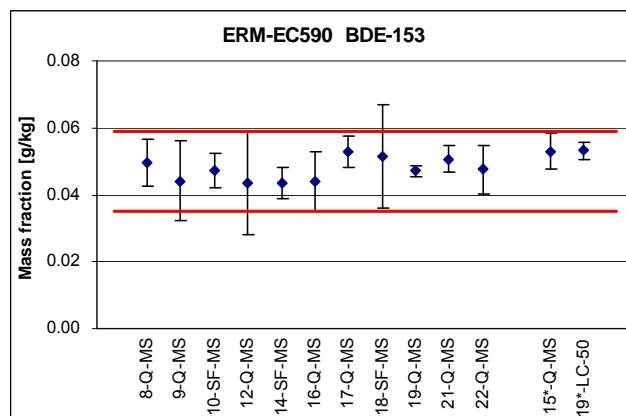
ERM-EC590 BDE-100

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0622	0.0010	0.0086
9	Q-MS	0.0628	0.0041	0.0008
10	SF-MS	0.0650	0.0020	0.0040
12	Q-MS	0.0627	0.0023	0.0219
14	SF-MS	0.0634	0.0016	0.0032
16	Q-MS	0.0579	0.0027	0.0087
17	Q-MS	0.0678	0.0026	0.0062
18	SF-MS	0.0652	0.0039	0.0196
19	Q-MS	0.0554	0.0059	0.0055
21	Q-MS	0.0671	0.0016	0.0054
22	Q-MS	0.0638	0.0020	0.0079
15*	Q-MS	0.0650		0.0065
19*	LC-50	0.0592		0.0035



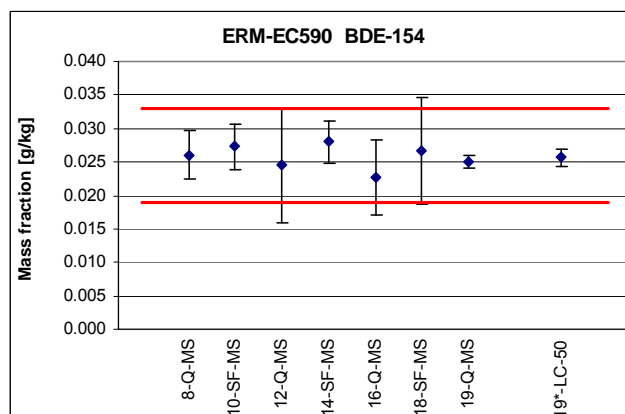
ERM-EC590 BDE-153

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0495	0.0016	0.0069
9	Q-MS	0.0441	0.0059	0.0012
10	SF-MS	0.0473	0.0026	0.0052
12	Q-MS	0.0435	0.0010	0.0152
14	SF-MS	0.0435	0.0023	0.0046
16	Q-MS	0.0441	0.0020	0.0088
17	Q-MS	0.0528	0.0021	0.0045
18	SF-MS	0.0515	0.0066	0.0155
19	Q-MS	0.0470	0.0006	0.0016
21	Q-MS	0.0506	0.0019	0.0040
22	Q-MS	0.0476	0.0011	0.0073
15*	Q-MS	0.0530		0.0053
19*	LC-50	0.0533		0.0026



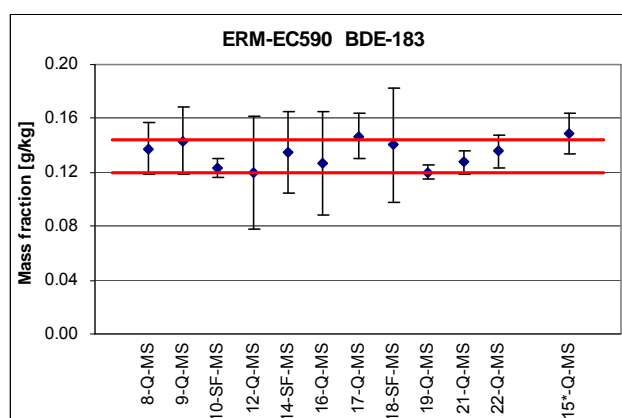
ERM-EC590 BDE-154

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0260	0.0006	0.0036
10	SF-MS	0.0273	0.0017	0.0034
12	Q-MS	0.0245	0.0005	0.0086
14	SF-MS	0.0280	0.0016	0.0032
16	Q-MS	0.0227	0.0009	0.0057
18	SF-MS	0.0267	0.0065	0.0080
19	Q-MS	0.0250	0.0003	0.0009
19*	LC-50	0.0257		0.0013



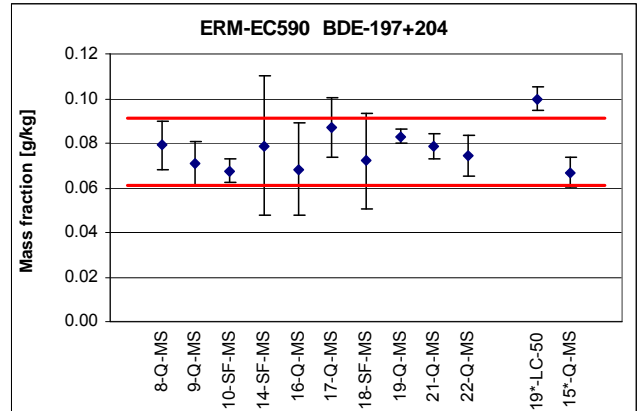
ERM-EC590 BDE-183

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.1373	0.0032	0.0191
9	Q-MS	0.1433	0.0126	0.0025
10	SF-MS	0.1234	0.0034	0.0069
12	Q-MS	0.1200	0.0063	0.0420
14	SF-MS	0.1344	0.0151	0.0302
16	Q-MS	0.1271	0.0040	0.0381
17	Q-MS	0.1467	0.0082	0.0170
18	SF-MS	0.1402	0.0325	0.0421
19	Q-MS	0.1203	0.0056	0.0050
21	Q-MS	0.1274	0.0022	0.0089
22	Q-MS	0.1359	0.0018	0.0122
15*	Q-MS	0.1490		0.0149



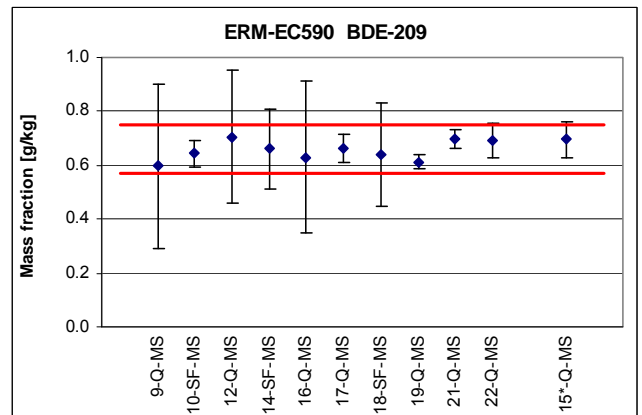
ERM-EC590 BDE-197+204

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0790	0.0037	0.0110
9	Q-MS	0.0708	0.0078	0.010
10	SF-MS	0.0677	0.0026	0.0053
14	SF-MS	0.0789	0.0157	0.0315
16	Q-MS	0.0684	0.0032	0.0205
17	Q-MS	0.0872	0.0061	0.0132
18	SF-MS	0.0720	0.0115	0.0216
19	Q-MS	0.0830	0.0030	0.0032
21	Q-MS	0.0787	0.0034	0.0055
22	Q-MS	0.0745	0.0013	0.0091
19*	LC-50	0.1000		0.0050
15*	Q-MS	0.0670		0.0067



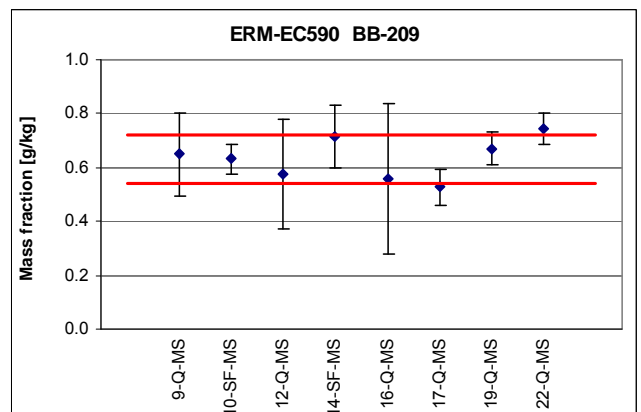
ERM-EC590 BDE-209

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
9	Q-MS	0.5980	0.2235	0.306
10	SF-MS	0.6449	0.0246	0.0491
12	Q-MS	0.7050	0.0105	0.2468
14	SF-MS	0.6606	0.0739	0.1480
16	Q-MS	0.6301	0.0364	0.2835
17	Q-MS	0.6650	0.0327	0.0519
18	SF-MS	0.6417	0.0264	0.1925
19	Q-MS	0.6120	0.0273	0.0270
21	Q-MS	0.6975	0.0203	0.0349
22	Q-MS	0.6934	0.0164	0.0638
15*	Q-MS	0.6950		0.0695



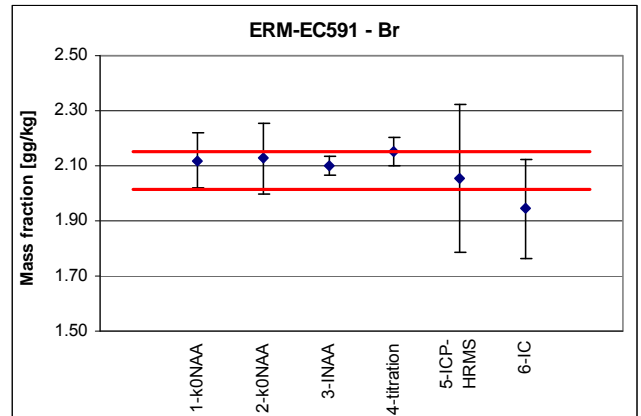
ERM-EC590 BB-209

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
9	Q-MS	0.6497	0.0774	0.155
10	SF-MS	0.6335	0.0277	0.0553
12	Q-MS	0.5750	0.0459	0.2013
14	SF-MS	0.7157	0.0590	0.1181
16	Q-MS	0.5571	0.0337	0.2785
17	Q-MS	0.5267	0.0273	0.0685
19	Q-MS	0.6703	0.0604	0.0600
22	Q-MS	0.7442	0.0114	0.0607



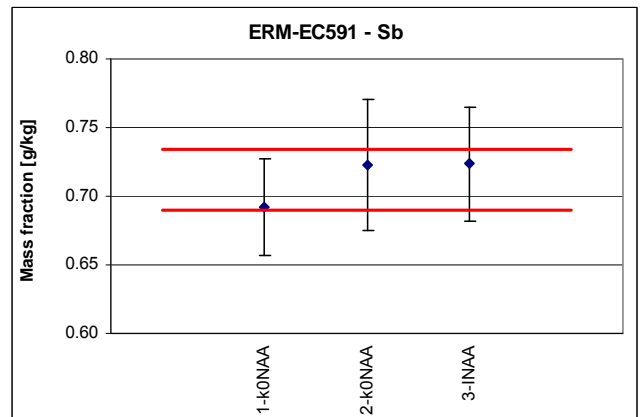
ERM-EC591 – Br

Lab	Method	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
1	kONAA	2.1183	0.0130	0.0996
2	kONAA	2.1258	0.0198	0.1275
3	INAA	2.1000	0.0510	0.0336
4	titration	2.1522	0.0717	0.0495
5	ICP-HRMS	2.0555	0.1311	0.2672
6	IC	1.9445	0.0908	0.1808



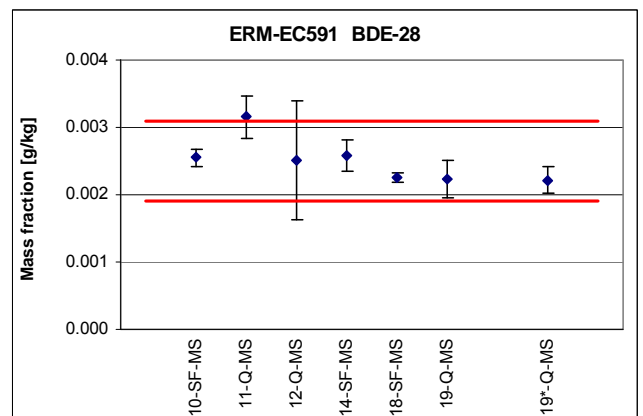
ERM-EC591 - Sb

Lab	Method	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
1	kONAA	0.6923	0.0117	0.0353
2	kONAA	0.7228	0.0059	0.0477
3	INAA	0.7233	0.0195	0.0412



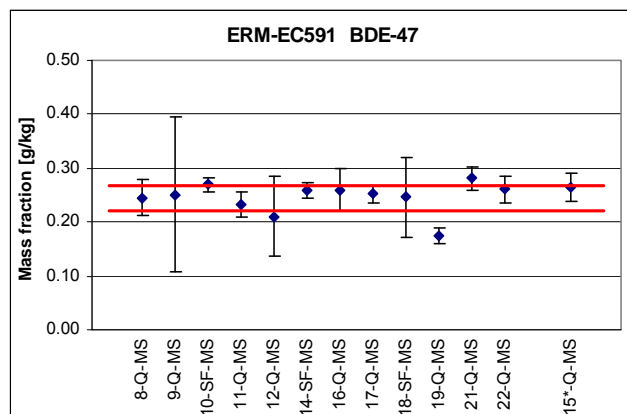
ERM-EC591 BDE-28

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
10	SF-MS	0.00255	0.0001	0.0001
11	Q-MS	0.00316	0.0001	0.00031
12	Q-MS	0.00252	0.0001	0.00088
14	SF-MS	0.00258	0.0001	0.00024
18	SF-MS	0.00225	0.0001	0.00007
19	Q-MS	0.00223	0.0003	0.00028
19*	Q-MS	0.00222	0.0000	0.00020



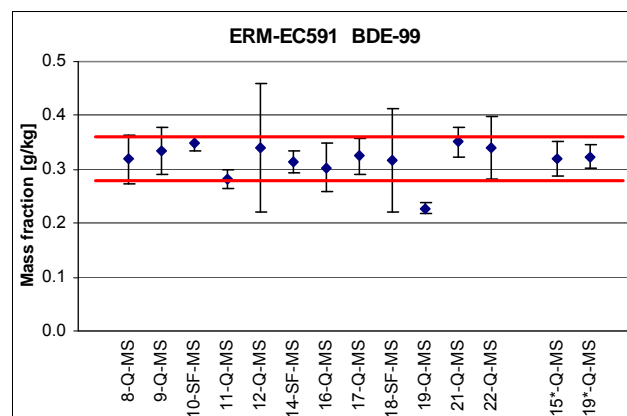
ERM-EC591 BDE-47

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.2450	0.0207	0.0341
9	Q-MS	0.2510	0.0713	0.1426
10	SF-MS	0.2693	0.0066	0.0132
11	Q-MS	0.2325	0.0140	0.0231
12	Q-MS	0.2100	0.0000	0.0735
14	SF-MS	0.2586	0.0072	0.0144
16	Q-MS	0.2601	0.0064	0.0390
17	Q-MS	0.2517	0.0147	0.0156
18	SF-MS	0.2467	0.0234	0.0740
19	Q-MS	0.1752	0.0071	0.0151
21	Q-MS	0.2805	0.0095	0.0224
22	Q-MS	0.2604	0.0083	0.0247
15*	Q-MS	0.2650		0.0265



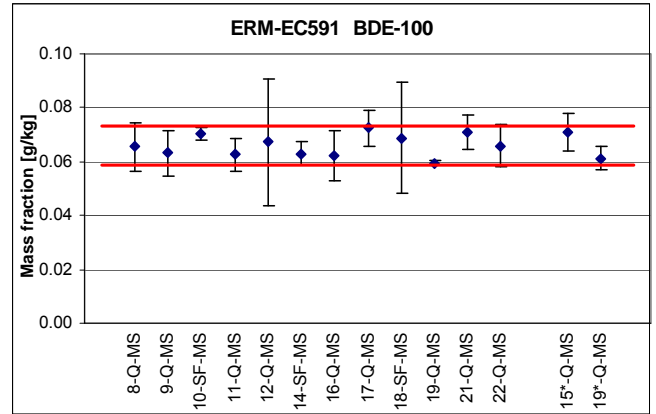
ERM-EC591 BDE-99

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.3183	0.0194	0.0442
9	Q-MS	0.3342	0.0293	0.0431
10	SF-MS	0.3476	0.0066	0.0132
11	Q-MS	0.2824	0.0099	0.0169
12	Q-MS	0.3400	0.0000	0.1190
14	SF-MS	0.3137	0.0100	0.0200
16	Q-MS	0.3035	0.0106	0.0455
17	Q-MS	0.3250	0.0207	0.0332
18	SF-MS	0.3167	0.0186	0.0950
19	Q-MS	0.2282	0.0056	0.0110
21	Q-MS	0.3507	0.0071	0.0281
22	Q-MS	0.3396	0.0099	0.0581
15*	Q-MS	0.3200		0.0320
19*	Q-MS	0.3240		0.0220



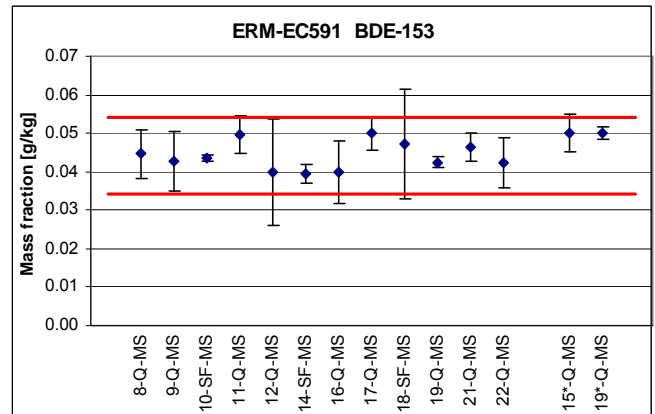
ERM-EC591 BDE-100

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0655	0.0010	0.0091
9	Q-MS	0.0632	0.0075	0.0085
10	SF-MS	0.0704	0.0012	0.0024
11	Q-MS	0.0626	0.0016	0.0062
12	Q-MS	0.0673	0.0019	0.0236
14	SF-MS	0.0630	0.0021	0.0043
16	Q-MS	0.0619	0.0013	0.0093
17	Q-MS	0.0727	0.0029	0.0067
18	SF-MS	0.0688	0.0068	0.0206
19	Q-MS	0.0594	0.0026	0.0008
21	Q-MS	0.0711	0.0010	0.0064
22	Q-MS	0.0660	0.0026	0.0081
15*	Q-MS	0.0710		0.0071
19*	Q-MS	0.0613		0.0044



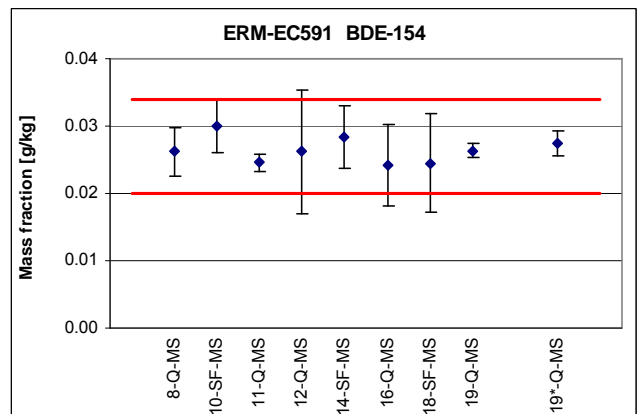
ERM-EC591 BDE-153

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0447	0.0012	0.0062
9	Q-MS	0.0429	0.0039	0.0078
10	SF-MS	0.0436	0.0004	0.0009
11	Q-MS	0.0496	0.0016	0.0049
12	Q-MS	0.0398	0.0013	0.0139
14	SF-MS	0.0395	0.0013	0.0025
16	Q-MS	0.0399	0.0006	0.0080
17	Q-MS	0.0500	0.0019	0.0043
18	SF-MS	0.0473	0.0038	0.0142
19	Q-MS	0.0424	0.0007	0.0015
21	Q-MS	0.0463	0.0024	0.0037
22	Q-MS	0.0424	0.0013	0.0065
15*	Q-MS	0.0500		0.0050
19*	Q-MS	0.0501		0.0017



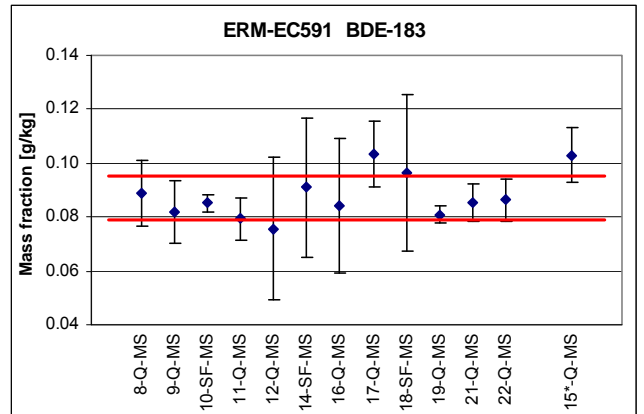
ERM-EC591 BDE-154

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0262	0.0004	0.0036
10	SF-MS	0.0299	0.0020	0.0039
11	Q-MS	0.0245	0.0007	0.0013
12	Q-MS	0.0262	0.0008	0.0092
14	SF-MS	0.0284	0.0023	0.0046
16	Q-MS	0.0241	0.0005	0.0060
18	SF-MS	0.0245	0.0035	0.0074
19	Q-MS	0.0264	0.0004	0.0010
19*	Q-MS	0.0274		0.0018



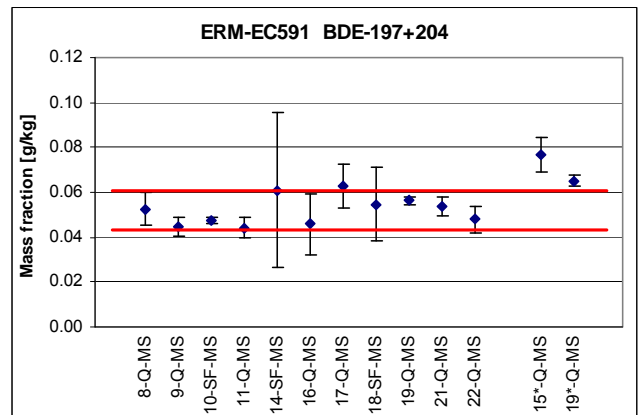
ERM-EC591 BDE-183

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0888	0.0044	0.0123
9	Q-MS	0.0818	0.0059	0.0117
10	SF-MS	0.0852	0.0016	0.0032
11	Q-MS	0.0795	0.0029	0.0079
12	Q-MS	0.0755	0.0079	0.0264
14	SF-MS	0.0910	0.0129	0.0259
16	Q-MS	0.0842	0.0019	0.0253
17	Q-MS	0.1033	0.0052	0.0120
18	SF-MS	0.0965	0.0175	0.0290
19	Q-MS	0.0810	0.0032	0.0032
21	Q-MS	0.0853	0.0009	0.0068
22	Q-MS	0.0863	0.0019	0.0078
15*	Q-MS	0.1030		0.0103



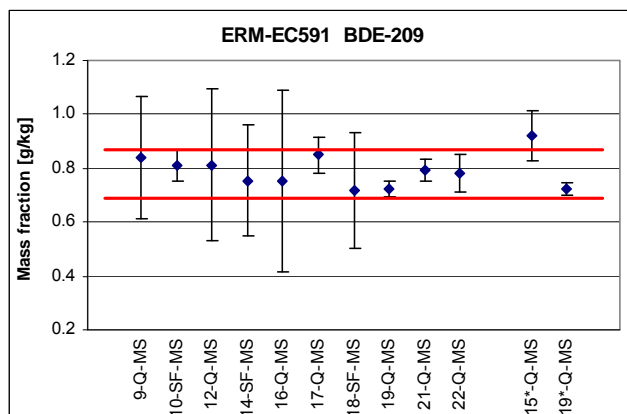
ERM-EC591 BDE-197+204

Lab	MS type	Average	s	Expanded uncertainty (k=2)
		[g/kg]	[g/kg]	[g/kg]
8	Q-MS	0.0527	0.0029	0.0073
9	Q-MS	0.0447	0.0046	0.0043
10	SF-MS	0.0475	0.0007	0.0014
11	Q-MS	0.0440	0.0015	0.0046
14	SF-MS	0.0608	0.0172	0.0345
16	Q-MS	0.0457	0.0013	0.0137
17	Q-MS	0.0628	0.0050	0.0096
18	SF-MS	0.0545	0.0083	0.0164
19	Q-MS	0.0562	0.0009	0.0016
21	Q-MS	0.0535	0.0014	0.0043
22	Q-MS	0.0480	0.0014	0.0059
15*	Q-MS	0.0770		0.0077
19*	Q-MS	0.0652		0.0023



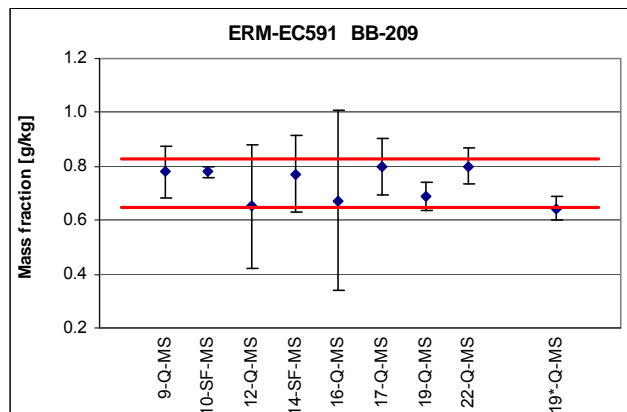
ERM-EC591 BDE-209

Lab	MS type	Average [g/kg]	s [g/kg]	Expanded uncertainty (k=2) [g/kg]
9	Q-MS	0.8383	0.6860	0.2280
10	SF-MS	0.8107	0.0288	0.0576
12	Q-MS	0.8133	0.0052	0.2847
14	SF-MS	0.7543	0.1024	0.2048
16	Q-MS	0.7512	0.0212	0.3380
17	Q-MS	0.8483	0.0299	0.0662
18	SF-MS	0.7183	0.0585	0.2155
19	Q-MS	0.7255	0.0267	0.0290
21	Q-MS	0.7947	0.0242	0.0397
22	Q-MS	0.7814	0.0191	0.0724
15*	Q-MS	0.9220		0.0922
19*	Q-MS	0.7240		0.0250



ERM-EC591 BB-209

Lab	MS type	Average [g/kg]	s [g/kg]	Expanded uncertainty (k=2) [g/kg]
9	Q-MS	0.7785	0.0480	0.0960
10	SF-MS	0.7786	0.0113	0.0226
12	Q-MS	0.6517	0.0293	0.2281
14	SF-MS	0.7711	0.0713	0.1426
16	Q-MS	0.6736	0.0180	0.3368
17	Q-MS	0.7983	0.0293	0.1038
19	Q-MS	0.6883	0.0533	0.0551
22	Q-MS	0.8005	0.0148	0.0657
19*	Q-MS	0.6430		0.0440



Annex E (continued): further results of the characterisation studies

ERM-EC590 av: average; p: number of results; U: expanded uncertainty (k=2) as reported by the laboratories: standard deviation; all results in mg/kg

BDE #	av	p	s	Lab 8		Lab 10		Lab 12		Lab 14		Lab 16		Lab 18		Lab 19 RTxi-5MS		Lab 19 LC-50		Lab 21	
				av	U	av	U	av	U	av	U	av	U	av	U	av	U	av	U	av	U
17	0.9	1														0.9	0.1				
28	2.4	6	0.3			2.6	0.2	2.4	0.8	2.8	0.5			2.3	0.7	2.1	0.3	2.2	0.2		
49	5.5	3	1.2											5.1	1.5	4.5	0.7	6.9	0.6		
66	4.6	6	0.6					4.3	1.5	4.1	1.1	4.2	2.5	5.2	1.6	4.2	0.4	5.6	0.5		
74	2.5	1														2.5	0.2				
75	0.3	2	0.0													0.3	0.1	0.3	0.1		
85	17.7	4	2.4					18.7	6.5	14.2	2.6			19.8	6.0	18.0	1.7				
97+118	1.4	1														1.4	0.1				
101	2.1	1														2.1	0.2				
119	0.4	1						0.4	0.2												
138	5.6	2	0.5					5.2	1.8							5.9	0.1				
139	4.9	3	0.6											4.2	1.3	5.3	0.1	5.1	0.3		
155	1.2	1														1.2	0.1				
173+190	5.9	2	0.1													5.9	0.3	5.8	0.5		
181	2.0	2												3.1	0.9			0.9	0.1		
182	3.2	1														3.2	0.2				
196	73.0	5	16.3	67.8	9.4							59.3	17.8	72.0	23.2			101	9	64.7	6.5
198	24.0	2	1.6													25.1	1.1	22.8	2.3		
203	40.9	4	3.1	45.5	6.3							38.4	19.2	39.8	12.0			39.8	3.9		
206	52.2	2	9.3					58.8	20.6			45.7	22.8								
207	90.3	4	21.1	118.8	16.5			82.7	28.9			68.8	34.4	90.8	27.3						
208	15.0	1						15.0	5.3												

ERM-EC591 av: average; p: number of results; s: standard deviation; all results in mg/kg

BDE #	av	p	s	Lab 8		Lab 11		Lab 12		Lab 14		Lab 16		Lab 18		19 RTxi-5MS		19 LC-50		Lab 21	
				av	U	av	U	av	U	av	U	av	U	av	U	av	U	av	U	av	U
17	0.9	1														0.9	0.1				
49	5.5	3	0.6					6.0	0.0					5.7	1.7	4.8	0.7				
66	4.6	5	0.7					4.6	1.6	3.9	1.4	4.2	2.5	5.9	1.8	4.5	0.4				
74	2.4	1														2.4	0.2				
75	0.4	2	0.0													0.4	0.1	0.4	0.0		
85	19.1	5	1.7			19.5	1.9	20.2	7.1	16.4	2.2			20.7	6.2	19.0	0.8				
97+118	1.3	1														1.3	0.1				
101	2.2	1																2.2	0.1		
138	5.5	2	0.3					5.3	1.9							5.7	0.1				
139	5.1	3	0.5											4.7	1.4	5.6	0.2	5.0	0.2		
155	1.4	1														1.4	0.1				
173+190	4.3	2	0.2													4.1	0.2	4.5	0.5		
180	5.4	1				5.4	0.5														
181	0.8	1																0.8	0.1		
182	2.3	1														2.3	0.1				
196	25.7	6	6.5	23.0	3.2	23.0	2.3					19.6	5.9	36.3	10.9			28.3	2.5	23.8	1.9
198	6.1	2	3.7													8.7	0.4	3.5	0.4		
203	15.3	5	3.4	16.2	2.2	14.4	1.4					12.7	6.4	20.8	6.3			12.6	1.2		
206	30.4	4	11.1	40.3	5.9	39.3	3.9	23.5	8.2			18.4	9.2								
207	43.8	5	22.6	68.3	9.5	15.5	1.5	38.5	13.5			31.4	15.7	65.2	19.6						
208	6.6	1						6.6	2.3												

EUR 23677 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: Certification of the mass fractions of various polybrominated diphenyl ethers (PBDEs), decabrominated biphenyl and total Br and Total Sb in two polymer reference materials, ERM[®]-EC590 and ERM[®]-EC591

Author(s): T. Linsinger, A. Birgersson-Liebich, F. Pellizzato, T. Venelinov, S. Voorspoels, A. Lamberty

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Abstract

This report describes the preparation and certification of the polymer certified reference materials (CRM) ERM-EC590 and ERM-EC591. The CRMs have been certified by the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

The CRMs were prepared from a low-density polyethylene granulate and polypropylene granulate spiked with technical mixtures of brominated diphenylethers (BDEs) and brominated biphenyls (BB). Technical Penta-BDE, Octa-BDE, Deca-BDE and Deca-BB were added.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The CRMs have been certified for their content of Br as well as for several BDE congeners and decabrominated biphenyl (BB-209). Indicative values have been established for Sb. Additional information about several BDE-congeners is given.

These CRMs are intended for use in quality assurance of measurements of BDEs, BB-209 and elements in polymers and related matrices.

Uncertainties are expanded uncertainties estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95 %. The following values were assigned.

Certified values

	ERM-EC590 [g/kg]	ERM-EC591 [g/kg]
Br	2.13 ± 0.09	2.08 ± 0.07
2,4,4'-TriBDE (BDE-28)		0.0025 ± 0.0006
2,2',4,4'-TetraBDE (BDE-47)	0.23 ± 0.04	0.245 ± 0.023
2,2',3,4,4'-PentaBDE (BDE-99)	0.30 ± 0.06	0.32 ± 0.04
2,2',4,4',6-PentaBDE (BDE-100)	0.063 ± 0.016	0.066 ± 0.007
2,2',4,4',5,5'-HexaBDE (BDE-153)	0.047 ± 0.012	0.044 ± 0.010
2,2',4,4',5,6'-HexaBDE (BDE-154)	0.026 ± 0.007	0.027 ± 0.006
2,2',3,4,4',5,6'-HeptaBDE (BDE-183)	0.132 ± 0.012	0.087 ± 0.008
2,2',3,3',4,4',6,6'-OctaBDE + 2,2',3,4,4',5,6,6'-OctaBDE (BDE-197+204)	0.076 ± 0.015	0.052 ± 0.009
DecaBDE (BDE-209)	0.66 ± 0.10	0.78 ± 0.09
DecaBB (BB-209)	0.63 ± 0.10	0.74 ± 0.08

Indicative values

	ERM-EC590 [g/kg]	ERM-EC591 [g/kg]
Sb	0.756 ± 0.025	0.713 ± 0.022

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