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Standard measurement method for the determination of polybrominated flame retardants (pentabromo diphenylether, octabromo diphenylether) in products

by

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16. Abstract

In accordance with the Directive 2003/11/EC amending the Council Directive 76/769/EEC for the 24th time, pentabromo and octabromo diphenylethers may not be used or put on the market in concentrations higher than 0.1 % by mass.
To verify this threshold value a standard measurement method for the determination of selected pentabromo diphenylethers (pentaBDE-isomers) and octabromo diphenylethers (octaBDE-isomers) in polymers based on gas chromatography mass spectrometry (GC/MS) was developed.
The following target compounds were selected for the investigations: BDE85 (2,2',3,4,4'-pentaBDE), BDE99 (2,2',4,4',5-pentaBDE), BDE100 (2,2',4,4',6-pentaBDE), BDE203 (2,2',3,4,4',5,5',6-octaBDE), BDE196 (2,2',3,3',4,4',5,6'-octaBDE), BDE197 (2,2',3,3',4,4',6,6'-OctaBDE). The following reference materials were prepared: polyurethane (PUR-H) and epoxy resin (EP) containing 0.1 % by mass of sum of pentaBDE isomers, polystyrene (PS) and acrylnitril-butadiene-styrene-copolymer (ABS) containing 0.1 % by weight of sum of octaBDE isomers. For quality assurance of the standard measurement method an interlaboratory comparison was conducted between 1 June and 30 November 2004 where 18 participants were involved.
Data assessment was performed in accordance with DIN ISO 5725-2:2002-12 "Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic methods for the determination of repeatability and reproducibility of a standard measurement method". The following general mean values and standard deviations were obtained: 1.09 ± 0.16 mg g^{-1} (15 %) (sum pentaBDE isomers/EP), 1.3 ± 0.19 mg g^{-1} (15 %) (sum pentaBDE isomers/PUR-H), 0.99 ± 0.27 mg g^{-1} (27 %) (sum octaBDE isomers/PS), 0.42 ± 0.11 mg g^{-1} (26 %) (sum octaBDE isomers/ABS).
The reproducibility standard deviation s_{Rj} and repeatability standard deviation s_{rj} were calculated as statistical parameters. The repeatability of the sum of pentaBDE isomers in EP was s_{rj}= 0.044 mg g^{-1} (4.0 %) and the reproducibility was s_{Rj} = 0.167 mg g^{-1} (15 %). s_{rj} and the s_{Rj} were 0.038 mg g^{-1} (2.9 %) and 0.195 mg g^{-1} (15 %), respectively, for the sum of pentaBDE isomers in PUR-H. For the sum of octaBDE isomers in ABS s_{rj} and s_{Rj} were determined to 0.029 mg g^{-1} (6.9 %) and 0.114 mg g^{-1} (27 %), respectively. For the sum of octaBDE isomers in PS the s_{rj} = 0.043 mg g^{-1} (4.3 %) and s_{Rj} = 0.255 mg g^{-1} (26 %) were obtained.

17. Keywords
pentabromo diphenylether (pentaBDE), octabromo diphenylether (octaBDE), polymer, reproducibility, repeatability, Directive 2003/11/EC, Directive 76/769/EEC, GC/MS, polybrominated flame retardants

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Abstract

Introduction

Flame retardants (FR) are being used in various products, e.g. electrical components, synthetics, textiles and furniture foams, in order to reduce their flammability. Polybrominated diphenylethers belong to the most important halogenated FRs: they are – due to the production process – bromohomologous mixes of different isomers and congeneres (Σ_{Br} = 1 to 10). Technical products based on penta (PENTA-BDE), octa (OCTA-BDE) and decabromo diphenylether (DECA-BDE) are available as commercial products.

Numerous studies prove the persistence and ubiquitous spread of PBDE in the different environmental spheres and indicate bioaccumulation.

Based on European risk assessments on penta and octabromo diphenylethers the Guideline 2003/11/EC was passed as the 24th amendment of Guideline 76/769/EEC for the restriction of marketing and use of certain dangerous substances and preparations (octabromo diphenylether, pentabromo diphenylether). In Germany this guideline was implemented within the scope of the ”Ordinance on prohibitions and limitations of the manufacture and use of hazardous substances, preparations and products according to the Law on Chemicals” (Chemikalien-Verbotsverordnung – ChemVerbotsV) and “Ordinance on Hazardous Substances” (Gefahrstoffverordnung-GefStoffV). As a consequence of this, since 30 June 2004, substances, preparations and products with a content of more than 0.1 % by mass of penta or octaBDE isomers may not be marketed, used or applied. Based on this prohibition the aim of the work was to develop a standard analysis technique for the determination of these regulation-relevant PBDE isomers in various polymers.

Analytical methods and materials

In order to develop the analysis method the individual steps (sample homogenization, extraction, GC/MS) had to be tested and optimised.

A centrifugal mill was used for sample homogenization. The sample was prepared by means of soxhlet extraction using toluene as an extraction agent.

Identification and quantitative determination of PBDE took place with the help of gas chromatography and mass spectrometry (GC/MS) in single ion monitoring (SIM) mode using three typical ion traces per isomer.

The selection of the penta and octabrominated diphenylether isomers to be tested took place using the main isomers of the PENTA-BDE and OCTA-BDE technical products: 2,2',4,4',6-pentaBDE (BDE100), 2,2',4,4',5-pentaBDE (BDE99), 2,2',3,4,4'-pentaBDE (BDE85), 2,2',3,4,4',5,5',6-octaBDE (BDE203), 2,2',3,3',4,4',5,6'-octaBDE (BDE196) and 2,2',3,3',4,4',6,6'-octaBDE (BDE197). Decachloro biphenyl (CB209) was used as an internal standard for the correction of syringe error, and dibromo octafluoro biphenyl (DBOFB) as an internal standard to check the analyte recovery rate.

The polymer types were compiled using published data on the application of the PENTA-BDE and OCTA-BDE technical products. Therefore acrylnitril-butadien-styrene-copolymer (ABS), polystyrene (PS), polyurethane hard foam (PUR H) and epoxy resin (EP) polymers were selected for the production of the interlaboratory test materials. These polymers were provided by manufacturers or, as in the case of epoxy resin, mixed and cast.

Various statistical parameters were determined for quality control and method validation of the analytical method. Linearity and variance homogeneity were proved for the calibration of the six selected isomers and the internal standard DBOFB, in addition, the relative method standard deviations (3 - 7 %) were determined. 2 to 9 % was determined for the reproducibility of the GC/MS system depending upon the isomer.

The analyte recovery functions and the repeatability standard deviations (5 – 7 %) of the isomers serve to characterise the method. The lower limit of the analytical method was determined by the limit of detection as 0.02 to 0.04 mg g^{-1} and limit of quantitation as 0.06 to 0.12 mg g^{-1}.

An international interlaboratory test was carried out where data were checked by graphic compatibility tests (Mandel's h-statistics and Mandel's k-statistics) and numerical outliers' tests (Grubbs' test and Cochran test) to determine the repeatability standard deviation and reproducibility standard deviation as statistical parameters of the standard measurement method,

Results

The interlaboratory test led to the results summarized in Table A1.

Table A1: Summarized results of the interlaboratory test.

Polymer	**Isomer sums**	p_j	m_j [mg g^{-1}]	s_{rj} [mg g^{-1}]	s_{Rj} [mg g^{-1}]
Epoxy resin	PentaBDE	15	1.09	0.044	0.167
Polyurethane	PentaBDE	15	1.3	0.038	0.195
Polystyrene	OctaBDE	18	0.99	0.043	0.255
ABS	OctaBDE	17	0.42	0.029	0.114

p_j: number of laboratories; m_j: general mean value; s_{rj}: repeatability standard deviation; s_{Rj}: reproducibility standard deviation

When specifying the repeatability and reproducibility standard deviations it must be considered that these statistical parameters were determined on the basis of specified model polymers. A higher matrix load in real samples clearly leads to a change of these parameters.

The 18 participants of the interlaboratory test were asked to record comments, improvements and lack of clarity of the standard measurement method.

The analysis of octaBDE isomers was accompanied with certain problems, such as insufficient resolution and tailing of the peaks in the chromatogram. In particular the lowest concentration of the calibration solutions which should be used (50 ng mL^{-1}) could not, or only poorly, be evaluated in certain cases, as the peaks were very small and sometimes close to or below the detection limit (related to the signal-noise ratio).

The documentation by the participants of the actual test conditions showed certain deviations from the standard measurement method (e.g. in the calibration range, extraction volume, weighed portion, quantification not using single standards but a technical product). These changes may have led to a degradation of the reproducibility standard deviation, in particular for the determination of octaBDE isomers.

The repeatability and reproducibility standard deviations of the tested polymers show a good agreement, thus the standard measurement method provides reproducible analytical results under repeatability and reproducibility conditions regardless of the polymer type tested. The standard deviation under reproducibility conditions however exhibits a value higher by a factor 4 to 6 compared to the standard deviation under repeatability conditions. This can have different causes, for instance the effect of variously configured GC/MS systems of the participants or the influence of different analysts on the analytical results.

In addition, the developed standard measurement method was tested on some real samples. Due to the higher matrix load it might be reasonable to perform a clean-up between extraction and measurement. A mini silicagel column proved useful in removing the turbidity and colouring which occurred in the sample extracts.

Summing up, it can be shown that, based on the results, the developed standard measurement method provides precise measurement results for the

determination of the sum penta and sum octaBDE isomers respectively, in particular within the range of the limiting value of 0.1 % by mass [1 mg g^{-1}] under the specified conditions.

1 Lists

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1.4 Abbreviations

A	ABS sample with PENTA-BDE for interlaboratory comparison
a, b, c	coefficients of regression analysis
ABS	acrylonitrile-butadiene-styrene-copolymer
ANOVA	analysis of variance (one-factorial)
B	ABS sample with OCTA-BDE for interlaboratory comparison
BDE100	2,2',4,4',6-pentaBDE
BDE196	2,2',3,3',4,4',5,6'-octaBDE
BDE197	2,2',3,3',4,4',6,6'-octaBDE
BDE203	2,2',3,4,4',5,5',6-octaBDE
BDE85	2,2',3,4,4'-pentaBDE
BDE99	2,2',4,4',5-pentaBDE
BSEF	Bromine Science and Environmental Forum
C_{TV}	test value in Cochran's test
C	PS sample with OCTA-BDE for interlaboratory comparisons
CB209	decachlorobiphenyl
C_{crit}	table value in Cochran's test /12/
CV	relative standard deviation
D	PUR sample with PENTA-BDE for interlaboratory comparisons
DBOFB	4,4'-dibromo octafluorobiphenyl
DE-71	PENTA-BDE of Great Lakes Co.
DE-79	OCTA-BDE of Great Lakes Co.
decaBDE	decabrominated diphenylether-isomers
DECA-BDE	technical product
df	film thickness
E	EP sample with PENTA-BDE for interlaboratory comparisons
EI	electron impact ionization

EP	epoxy resin
EUROLAB	Chemische Analytik; Mess- und Prüftechnik e.V. (Chemical Analysis, Measurement and Testing Non-profit Org.)
F	table value of F-test /12/
f	degree of freedom
FR	flame retardant
G	test value in Grubbs' test (two outlying observations)
GC	gas chromatography
G_{crit}	table value Grubbs' test /12/
heptaBDE	heptabrominated diphenylether isomers
hexaBDE	hexabrominated diphenylether isomers
ID	internal diameter
L	laboratory code in interlaboratory comparisons
MS	mass spectrometry
m_j	general mean in interlaboratory comparisons
N	number of repetitions
nonaBDE	nonabrominated diphenylether isomers
NS	normal section
octaBDE	octabrominated diphenylether isomers
OCTA-BDE	technical product
P	confidence level
PBDE	polybrominated diphenylether
pentaBDE	pentabrominated diphenylether isomers
PENTA-BDE	technical product
PS	polystyrene
PTV	programmable temperature vaporizer
PUR-H	polyurethane hard foam
TV	test value in F-test
IC	material for interlaboratory comparison

SIM	single ion monitoring
s_{rj}	standard deviation under repeatability conditions
s_{Rj}	reproducibility standard deviation
STDev	standard deviation to laboratory average
s_{xo}	method's standard deviation
s_y	residual standard deviation
T	test value in Grubbs' test (one outlying observation)
t	Student's t-factor (table value /12/)
T_{crit}	table value in Grubbs' test /12/
TetraBDE	tetrabrominated diphenylether isomers
TriBDE	tribrominated diphenylether isomers
CI	confidence interval
DS-water	fully desalinated water
V_{xo}	relative method's standard deviation
x_{dtr}	determination limit
x_{dtc}	detection limit

2 Introduction and objectives

Flame retardants (FRs) are added to many polymers in the form of additives or bound reactively in the macromolecules in order to lower their flammability in accordance with relevant fire protection regulations. They are used for instance in insulation and foam materials, electronic components, fire protection clothing and textiles, leisure equipment, in the furniture industry and in aeroplane and vehicle manufacture.

FRs can be divided into various groups with different chemical bases and functional behaviour.
Inorganic FRs (e.g. $Al(OH)_3$), organophosphorus FRs (e.g. tris(2-chloro-isopropyl)phosphat) and halogenated organic FRs (e.g. polybrominated diphenylether (PBDE)) are the most important groups.

Industrial production of PBDE is carried out by bromination of diphenylether. The production process yields technical products with bromine-homologues of various bromine numbers. Depending on the number and position of bromine atoms on the two phenyl rings, 209 different compounds can be formed (Figure 1).

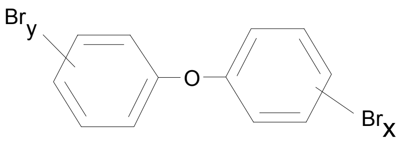

Figure 1: PBDE basic structure; Σ x,y: 1-10

Products based on penta- (PENTA-BDE), octa- (OCTA-BDE) and decabromo diphenylether (DECA-BDE) are of commercial interest (Table 1).
The *Bromine Science and Environmental Forum* (BSEF) calculated in 1999 a total quantity of 54.800 t DECA-BDE. It is used mainly in plastics, textiles and in

preparations for protective coatings. BSEF found that 3,825 t of OCTA-BDE was used in 1999. OCTA-BDE is used as an additive flame retardant mainly in ABS applications. The output of PENTA-BDE according to BSEF was about 9,500 t in 1999, the majority being used in the upholstery and furniture industry (polyurethane foam, textiles) /1/.

Table 1: Composition of commercial PBDE.

Composition according to /8/								
Product	TriBDE	TetraBDE	PentaBDE	HexaBDE	HeptaBDE	OctaBDE	NonaBDE	DecaBDE
DECA-BDE							0.3 - 3%	97 - 98%
OCTA-BDE				10 - 12%	43 - 44%	31 - 35%	9 - 11%	0 - 1%
PENTA-BDE	0 - 1%	24 - 38%	50 - 62%	4 - 8%				

The necessary reduction of fire risk in polymers by suitable additives threatens the environment with anthropogenic pollutants due to production, application, usage and disposal. PBDEs exhibit high boiling points and/or decomposition temperatures, a high adsorption capability and a high chemical stability which are desirable qualities for fire protection. However, these very characteristics have an unfavourable effect in the environment since PBDEs are not very susceptible to biological degradation and are therefore characterised by a high persistence. Due to their marked lipophilic behaviour these compounds are inclined to accumulate in different environmental compartments (air, water, soil). Numerous studies indicate that they are ubiquitous in the environment, in particular the commonly found pentabrominated diphenylether, even in regions remote from industry /1, 2, 3/. Our knowledge about the degradation behaviour in the environment and the eco and human toxicology is rather limited and potential long-term consequences for humans and the environment cannot currently be estimated. In accordance with the No. 793/93 European Union regulation (EEC) for evaluation and control of the environmental risks of chemical waste materials, a risk evaluation was carried out for the estimation of the threat to the environment by PENTA-BDE, OCTA-BDE and DECA-BDE /5, 6, 7/. Based on existing toxicological data, ecotoxicology and the results of environmental monitoring studies, an evaluation showed that action is needed to curb any further threat to the environment due to PENTA-BDE and OCTA-BDE. The formal announcement took place in the Official Journal of the European Union of 15.02.2003 with the Directive 2003/11/EC to the 24th Amendment of the Directive 76/769/ECC on the restriction of marketing and use of certain hazardous materials and preparations (octabromo diphenylether, pentabromo diphenylether) /15/. The implementation in national law was carried out within the framework of the German Chemicals Prohibition Order /16/ and the Dangerous Substances Order /17/., An analytical method for sampling and investigation corresponding to scientifically recognized test procedures is essential for identifying the limiting value of 0.1 % by mass of pentaBDE isomers and 0.1 % by mass of octaBDE isomers in materials, preparations and products as set in the Directive.

The aim of the work was to develop a standard measurement method for testing the limiting value mentioned in different relevant materials. The statistical validation took place using a suitable interlaboratory comparison in order to demonstrate the practicability and comparability of the reference procedure. For the development of the standard measurement method, quantitative analysis of pentabromo diphenylether isomers (pentaBDE) and octabromo diphenylether isomers (octaBDE) was performed based on the relevant instruction in Directive 2003/11/EC with the help of gas chromatography and mass spectrometry (GC/MS).

3 Analytical determination of PBDE in polymer samples

For the determination of the substance concentrations in polymer samples, suitable sample preparation and analytical methods are necessary. For the development of the analytical method, individual steps (sample preparation, storage, processing, measuring method) must be tested and the design parameters suitably adapted. For quality assurance and validation of the analysis method a test of variance homogeneity of the calibration range must take place and the regression model (linear one, 2nd-order) determined. The sensitivity is limited at its lower boundary by the limit of detection and quantitation. The accuracy will be tested by the analyte recovery function. Thus the influence of each step of sample preparation on the measured value can be checked.

Polymer samples are prepared using soxhlet extraction with suitable organic solvents. The selection of the solvent for maximum solubility of the components, prevention of transverse contamination etc. is part of the method development. Identification and quantitative determination take place using gas chromatography and mass spectrometry (GC/MS). In this combined procedure the substances are separated as a function of time based on their chemical and physical properties in the gas chromatography system using a suitable separation capillary column. Actual detection and quantification take place using a mass spectrometer.

3.1. General preparation

All solvents were checked before application for trace contaminants and blank values. Glass devices and materials were cleaned after use by heating at 450°C, cleaned in a laboratory dishwasher (demineralised water), dried at 150°C and rinsed with toluene and/or acetone before renewed use. In order to protect the UV-susceptible PBDE from light-induced decomposition, brown glass was used and/or protected with aluminium foil against light.

3.2. Selected guide substances for the development of the standard measurement method

The standard measurement method was developed for penta and octabrominated diphenylethers regulated by the Directive 2003/11/EC.
The selection of the pentabrominated and octabrominated diphenylether isomers took place based on the known isomers in technical products and commercially available standards.
The actual composition of the technical, commercially available PENTA-BDE varies depending upon manufacturer. It seems however that the available information about the composition of a product is representative for and/or comparable with other products. In addition to DE-71 commercial products are Bromkal 70 and Saytex 115, though the two latter products are no longer produced and marketed in the European Union. A fraction of 50 – 62 % of pentaBDE isomers can be assumed in the technical PENTA-BDE /7/.
In the PENTA-BDE technical product DE-71 there are three pentaBDE isomers (s. Annex 2.1):

- 2,2’,4,4’,6-pentaBDE (BDE100)
- 2,2’,4,4’,5-pentaBDE (BDE99)
- 2,2’,3,4,4’-pentaBDE (BDE85)

The actual composition of the technical OCTA-BDE also varies depending upon manufacturer; therefore normally only a certain percentage range of the individual congener groups contained in the technical products can be specified in each case. The fraction of octaBDE isomers in technical OCTA-BDE products varies between 26 –36 % /6/.

There are three octaBDE isomers in the OCTA-BDE DE-79 technical product (see Annex 2.2):

- 2,2’,3,4,4’,5,5’6-octaBDE (BDE203)
- 2,2’,3,3’,4,4’,5,6’-octaBDE (BDE196)
- 2,2’,3,3’,4,4’,6,6’-octaBDE (BDE197)

Altogether the six isomers mentioned are commercially available as single standards.

For simplicity's sake in the following text the technical mixes will be denoted by capital letters (PENTA-BDE and OCTA-BDE) and the penta and octabrominated diphenylether isomers termed as pentaBDE isomers and octaBDE isomers.

4,4'-dibromo octafluoro biphenyl (DBOFB) is used as an internal standard to check the analyte recovery rates, and decachloro biphenyl (CB209) applied for the correction of the injection volume.

3.3. Specification of the used technical PBDEs

3.3.1. PENTA-BDE preparation (Annex 2)

Commercial name	Great Lakes DE-71™		
CAS number	32534-81-9		
Composition	Bromine content 70.8 %		
	Major components:	TetraBDE	30 %
		PentaBDE	52 %
		HexaBDE	12 %
Main applications	Polyurethane (PUR); Epoxy resin (EP), rubber, polyvinyl chloride, textiles		

3.3.2. OCTA-BDE preparation (Annex 2)

Commercial name	Great Lakes DE-79™		
CAS number	32536-52-0		
Composition	Bromine content 79.8 %		
	Major components:	HexaBDE	13 %
		HeptaBDE	44 %
		OctaBDE	42 %
Main applications	Acrylonitrile-butadiene-styrene-copolymer (ABS); Polystyrene (PS), polyamide		

3.4. GC/MS

GC/MS system used:
Agilent GC Series 6890/ Bear Instruments Kodiak 1200 (mass range 10 - 1500 amu)

Carrier gas	Helium
Injection system	PTV injector
Injection	Splitless
Purge time	1 min
Purge flow	50 mL min^{-1}
Temperature programme (PTV)	90°C (0 min) - 300°C/min - 350°C (15 min)
GC column	DB-5-ms; 15 m; 0.25 mm ID; 0.1 µm df
Column pre-pressure	constant flow: 1.2 mL min^{-1}
Temperature programme	70 °C (2 min)-20 °C/min-300 °C (15 min)
Transfer line	310 °C
Ionisation method	EI; 70 eV
Ion source T	200 °C

The analysis of the polybrominated flame retardants took place in the SIM (Single Ion Monitoring) mode using the following mass traces (quantification: underlined mass trace; mass spectra see Annex 6).

PentaBDE Isomers	(M^+-2Br)+2, (M^+-2Br)+4, M^++4	403.7, 405.7, 563.6
OctaBDE Isomers	(M^+-2Br)+6, (M^+-2Br)+8, M^++8	641.6, 643.6, 801.5

Internal Standard for the correction of the injection volume:

CB209	M^++4, M^++6, (M^+-2Cl)+4	497.5, 499.6, 427.6

Internal Standard for the control of the analyte recovery rate:

DBOFB	M^++3, M^++2, (M^+-FBr)+2	455.8, 454.4, 357.5

3.5. Selection and preparation of the sample material

3.5.1. Specification of the polymers used

The following materials were selected for method development and for the preparation of the interlaboratory test materials (Table 2) based on available information on the ranges of application /6, 7/ of the PENTA-BDE and OCTA-BDE technical products in the literature.

- Acrylonitrile-butadiene-styrene-copolymer (ABS)
- Polystyrene (PS)
- Polyurethane hard foam (PUR-H)
- Epoxy resin (EP)

The polymer materials were obtained with specified FR content from manufacturers and/or, in the case of the EP, self mixed and cast (see Section 8.2). The production of the compound took place depending upon polymer by adding the FR during the extrusion (ABS and PS) or during the foaming (PUR-H).

In addition to the flame-retarded polymers, pure polymer materials (without additives) were provided. The exact specifications and the manufacturers of the polymers are listed in Annex 4.

Table 2: Flame-retarded polymers.

Polymer master batch	**Added FR preparation**	**FR preparation content (manufacturer's data)**
ABS	PENTA-BDE	approx. 1 %
ABS	OCTA-BDE	2.95 %
PS	OCTA-BDE	2.96 %
PUR-H	PENTA-BDE	approx. 2 %
EP	PENTA-BDE	2 %

3.5.2. Production of the polymers with an octaBDE or a pentaBDE isomer content of approx. 0.1 % by mass

Polymers, whose sum content of pentaBDE or octaBDE isomers is near the legally specified limiting value of 0.1 % by mass were produced for the interlaboratory test. The polymer master batch (see Section 3.5.1, Annex 4) was mixed with an additive-free polymer. The three polymers available as granulates (ABS/PENTA-BDE, ABS/OCTA-BDE, PS) could be mixed directly with additive-free granulates. The epoxy resins and the polyurethane hard foams with and without FR additives were first roughly comminuted (by a pair of scissors and pliers and/or a knife) and then mixed.

The PENTA-BDE DE-71 technical formulation used consists of approx. 50 % of pentabromo diphenylether isomers; the OCTA-BDE DE-79 technical formulation of approx. 30 % (see Annex 2) comprises isomers of octabromo diphenylether. This must be considered when polymers are diluted to specified isomer contents (see Table 3).

The produced polymers were comminuted (see Section 8.3) and ground to a particle size of 500 µm and statistically homogenised using the cross-riffling scheme (Section 8.4) /11/.

80 sub-samples were prepared for each polymer (Table 4) and marked with the letters A to E and a sequential number.

Table 3: Interlaboratory comparison materials (IC materials).

	Master batch content		**Mix ratio Polymer with FR + Polymer without FR**	**Isomer content in IC material**
	FR addition	**Sum isomers**		
ABS/ PENTA-BDE	Approx. 1 %	Approx. 0.5 % pentaBDE	200 g + 800 g	Approx. 0.1 % pentaBDE
ABS/ OCTA-BDE	Approx. 3 %	Approx. 1 % octaBDE	100 g + 900 g	Approx. 0.1 % octaBDE
PS	Approx. 3 %	Approx. 1 % octaBDE	100 g + 900 g	Approx. 0.1 % octaBDE
PUR-H	Approx. 2 %	Approx. 1 % pentaBDE	100 g + 900 g	Approx. 0.1 % pentaBDE
EP	Approx. 2 %	Approx. 1 % pentaBDE	100 g + 900 g	Approx. 0.1 % pentaBDE

Table 4: Number and denotation of sub-samples of polymers to be tested for homogeneity.

Polymer	**Sub-sample**	**Fill-in mass per sub-sample [g]**
ABS with DE-71	A 1 to A 80	2.03 ± 0.07
ABS with DE-79	B 1 to B 80	2.01 ± 0.06
PS with DE-79	C 1 to C 80	1.98 ± 0.29
PUR-H with DE-71	D 1 to D 80	0.54 ± 0.02
EP with DE-71	E 1 to E 80	1.93 ± 0.09

4 Method validation

4.1. Determination of the calibration function and method parameters

The concentration range of 50 to 500 ng mL^{-1} of the selected guide substances (Chapter 3.2) and 10 to 100 ng mL^{-1} of the Internal Standard DBOFB, resp. (10 equidistant calibration solutions; the internal standard decachloro biphenyl was used for the correction of the injection volume) were tested using Mandel's adjustment test /9/ (see Annex 3) to check the linearity of the calibration function used:

$$DS^2 = (N-2)\, s^2_{y1} - (N-3) s^2_{y2}$$
$$TV = DS^2 / s^2_{y2}$$

with N = number of the selected concentration steps (= 10)
s_{y1} = residual standard deviation of a function of 1st degree
s_{y2} = residual standard deviation of a function of 2nd degree
DS^2 = difference of variances
TV = test value

The difference of the variances DS^2 can be calculated from the residual standard deviations s_{y1} (of the linear calibration function) and the residual standard deviations s_{y2} (of the 2nd degree calibration function). The test value TV is calculated and compared with the table value F (f_1 = 1, f_2 = N-3, P = 99 %) for Mandel's adjustment test. If TV is smaller or equal to F, the 2nd degree calibration function does not guarantee any significantly better adjustment; the calibration is linear.

Linearity was tested for the selected guide substances (Section 3.2).

The test values determined for the concentration range used were under the F-value (1; 7; 99 %) of 12.25 (see Annex 3 for all guideline substances examined). Therefore all calibrations were regarded as linear.
The relative method's standard deviations V_{xo} of the linear calibration functions were between 3-7 %.

4.2. Reproducibility of the GC/MS system for PBDE

To determine reproducibility, multiple determinations (n=10) were carried out using GC/MS for the selected guide substances (concentration: 250 ng mL^{-1}). The areas of the guide substances (A) were corrected by the areas of the internal standard CB209 (A_{CB209}). Table 5 shows the relative standard deviation (%) of the values A/A_{CB209}.

Table 5: Relative standard deviation of the repeated measurements

	Rel. standard deviation [%]
2,2',4,4',6-pentaBDE (BDE100)	2.4
2,2',4,4',5-pentaBDE (BDE99)	2.2
2,2',3,4,4'-pentaBDE (BDE85)	2.6
2,2',3,3',4,4',6,6'-octaBDE (BDE197)	9.4
2,2',3,4,4',5,5',6-octaBDE (BDE203)	5.3
2,2',3,3',4,4',5,6'-octaBDE (BDE196)	4.7
DBOFB	2.0

4.3. Variance homogeneity

10 standard samples each of the lowest (x_1) and the highest (x_N) concentrations of the selected guide substances (Section 3.2) were separately analysed within the provisional range (PBDE: 50 - 500 ng mL^{-1}; DBOFB 10 - 100 ng mL^{-1}) to

check for variance homogeneity. The areas of the guideline substances (A) were corrected by the area of the internal standard CB209 (A_{CB209}).

The variance of the respective two measured value series s_1^2 and s_N^2 (see Annex 3.2) were investigated by the F-test for homogeneity /9/.

$TV = s^2_N / s^2_1$

$F\ (f_1 = 9;\ f_2 = 9,\ P = 99\ \%) = 5.35$

The determined test value TV is compared with the table value F ($f_1 = f_2 = N - 1$, P = 99 %). If TV is smaller or equal to F, homogeneity can be assumed within the series.

The test values determined for the guideline substances were under the F-value within the specified work area (see Annex 3.2). Variance homogeneity is thus ensured.

4.4. Testing the standard measurement method and investigation for matrix influences

A significant quality criterion of an analytical method is its applicability to natural samples. Process steps and matrix effects may result in the increase of imprecision and/or as systematic deviations (constant systematic or proportional systematic) of the analytical results from the "real" values.

The calculation of the analyte recovery function, which enables systematic deviations to be uncovered /9/, is suitable for checking both individual process steps and a potential matrix influence.

Each calibration standard is checked against the analytical method.

The analytical results x_f can be calculated with the help of the analysis function (calibration function of the basic method solved with respect to x):

$$x_f = \frac{y_f - a_c}{b_c}$$

If the "determined" concentration (x_f) is plotted on the ordinate against the calibration concentration (x_c) on the abscissa, one obtains the analyte recovery straight line which can mathematically described by the analyte recovery function

$$x_f = a_f + b_f \cdot x_c \,.$$

In an ideal case the analyte recovery function is a straight line with $a_f = 0$ and $b_f = 1$.

4.4.1. Control of analytical precision

A prerequisite for the plausibility of the analyte recovery function is the similarity between the method's standard deviation s_{xoc} of the basic method and the residual standard deviation s_{yf} of the analyte recovery function.

The method's standard deviation of the calibration function of the basic method s_{xoc} and the residual standard deviation of the analyte recovery function s_{yf} are tested for significant difference by the F-test.

$$TV = \left(\frac{s_{yf}}{s_{xoc}} \right)^2$$

If TV is greater than F ($f_1 = f_2 = N_c - 2$, P = 99%), there is a significant difference between the two standard deviations. In this case no final statement can be made concerning the non-existence of systematic deviations.

Additive-free polymers (EP and/or ABS) with different concentrations of the technical products PENTA and/or OCTA-BDE (specified by the composition of the technical products: BDE99: 100 to 500 ng mL^{-1}, BDE100: 20 to 100 ng mL^{-1}, BDE197: 100 to 420 ng mL^{-1}, BDE203: 50 – 220 ng mL^{-1}, in five concentration; equidistant levels) were spiked to determine the analyte recovery rates and investigated by standard measurement methods as described in Annex 1. The test values shown in Table 6 were determined for the pentaBDE isomers BDE99, BDE100 and octaBDE isomers BDE197 and BDE203.

Table 6: Determined test values to control analytical precision.

	Epoxy resin		**ABS**	
	BDE99	**BDE100**	**BDE197**	**BDE203**
s_{xoc}	39.99	10.87	11.20	5.6
s_{yf}	35.55	28.31	25.51	4.38
TV	0.79	6.79	5.19	0.61
F (f1 = f2 =Nc-2, 99%)	29.46			

The results in Table 6 show that analytical precision has been achieved.

4.4.2. Constant-systematic deviations

In the case of constant-systematic deviations the error (deviation) is independent of the concentration of the analysed component which leads to a parallel displacement of the matrix calibration plot straight lines in relation to the straight line calibration obtained with pure standard solutions. One cause of this deviation can be that a matrix component is also included, i.e. the analytical method is not specific enough. The confidence interval of the axis intercept a_f is calculated to determine the constant-systematic deviation.

Determination of the confidence interval CI (a_f)

$$CI\ (a_f) = a_f \pm t_{(p,f)} \bullet s_{yf} \sqrt{\left(\frac{1}{N_f} + \frac{\bar{x}_c^2}{Q_{xx}}\right)}$$

with $Q_{xx} = \sum x_i^2 - \frac{1}{N} \times \left(\sum x_i\right)^2$

a_f = *axis intercept*

N_f = *number of concentration levels = 5*

$t_{p,f}$ = *table value (Student's t-test at probability P and degree of freedom $f = N_f - 2$); $t_{95\%,3} = 3.18$*

s_{yf} = *residual standard deviation of the analyte recovery function*

Q_{xx} = *sum of quadrates*

$\bar{x}_c$ = *arithmetical average of concentration interval*

x_i = *concentration level*

A constant-systematic deviation is there at a confidence level of 95 % if the confidence interval does not include the value $a_f = 0$. Table 7 shows the calculated confidence intervals of the axis intercepts.

Table 7: Calculation of the calculated confidence intervals of the axis intercepts of the analyte recovery functions.

	BDE99	**BDE100**	**BDE197**	**BDE203**
CI (a_f) for P = 95 %	-29.74 ± 118.57	19.56 ± 94.41	-36.48 ± 90.93	-11.94 ± 15.15
Is the value a_f = 0 included?	**Yes**	**Yes**	**Yes**	**Yes**
Is there a constant-systematic deviation?	No	No	No	No

There are no constant-systematic deviations at a confidence level of 95 % for all tested isomers (BDE99, BDE100, BDE197, BDE203).

4.4.3. Proportional-systematic deviations

In the case of proportional-systematic deviations the extent of the error depends on the concentration of the analysed component. This leads to a change of the slope of the matrix calibration plot straight lines. These deviations from the true value can be due to individual process steps or matrix effects. To determine the proportional-systematic deviation, the confidence interval $CI(b_f)$ of the slope b_f is calculated.

$$CI(b_f) = b_f \pm \frac{t_{(p,f)} \times s_{yf}}{\sqrt{Q_{xx}}}$$

with b_f = *slope*

$t_{p,f}$ = *table value (Student's t-factor at probability P and degree of freedom* $f = N_f - 2$*);* $t_{95\%,\,3} = 3.18$; $t_{99\%,\,3} = 5.841$; $t_{99{,}9\%,\,3} = 12.92$

s_{yf} = *residual standard deviation of the analyte recovery function*

Q_{xx} = *sum of quadrates (see Chapter 4.4.2)*

If the confidence interval (P = 95 %) includes the value $b_f = 1$, then there is no proportional-systematic deviation at a confidence level of 95 %. If the confidence interval (P = 99 %) does not include the value $b_f = 1$, then there is a proportional-systematic deviation.

Table 8 shows the confidence intervals of the slopes.

The following conclusions can be drawn:

For BDE100 there is no proportional-systematic deviation with a statistical probability of 95 %.

For BDE99 and BDE197 the value $b_f = 1$ is enclosed with a statistical probability of 99 % only. Thus a slight proportional-systematic deviation is there.

For BDE203 the value $b_f = 1$ is enclosed with a statistical probability of 99.9 % in the confidence interval of the slope. Thus a proportional-systematic deviation is there.

Table 8: Calculation of the confidence intervals of the slopes of the analyte recovery functions.

	BDE99	**BDE100**	**BDE197**	**BDE203**
CI (b_f) for P = 95 %	1.41 ± 0.36	1.16 ± 0.28	1.41 ± 0.32	1.31 ± 0.10
Is the value $b_f = 1$ included?	No	Yes	No	No
CI (b_f) for P = 99 %	1.41 ± 0.66		1.41 ± 0.59	1.31 ± 0.19
Is the value $b_f = 1$ included?	Yes		Yes	No
CI (b_f) for P = 99.9 %				1.31 ± 0.43
Is the value $b_f = 1$ included?				Yes
Is there a proportional-systematic deviation?	Yes (light)	No	Yes (light)	Yes

4.4.4. Determination of the repeatability standard deviation of the standard measurement method

To determine the random error of the standard measurement method (Annex 1), the standard deviation was determined under repeatable conditions. This quantity is determined from a number of repetitive, independent measurements on a homogeneous sample material.

A tenfold analysis of the sum of pentaBDE isomers in ABS/PENTA-BDE (see Table 3 IC material) using the standard measurement method (Annex 1) yielded 0.0622 mg g^{-1} with a relative standard deviation of 5.1 %.

A tenfold analysis of the sum of octaBDE isomers in PS/OCTA-BDE (see Table 3 IC material) using the standard measurement method (Annex 1) yielded 0.0778 mg g^{-1} with a relative standard deviation of 6.9 %.

4.4.5. Determination of the detection and quantitation limit according to DIN 32 645 (modification of the direct method)

To determine the detection limit according to DIN 32 645 the blank value procedure can be used as a direct method. A modification of the blank value procedure was used: instead of a direct determination of the blank value dispersion, the resultant dispersion of an analysis sample, whose content is near the detection limit, is determined /10/.

The equation for the calculation of the limit of detection x_{LOD} reads:

$$x_{LOD} = s_x \times t_{\alpha;f} \times \sqrt{\frac{1}{m} + \frac{1}{n}}$$

with

s_x = standard deviation of the contents in the sample

t = table value (Student's t-factor); $t_{0.01;\,9}$ = 2.821

α = significance level (probability for the error of 1st kind), per standard = 0.01

f = number of degrees of freedom = n-1

m = number of measurements of the analysis sample, per standard = 1

n = number of calibration data, per standard = 10

One obtains for the limit of detection:

$$x_{LOD} = s_x \times 2.821 \times \sqrt{1 + \frac{1}{10}} = s_x \times 2.96$$

The limit of quantitation x_{LOQ} (minimum content in a sample from which a quantitative determination is permissible) can only be estimated and not calculated exactly without knowing the dispersion data of the calibration straight lines. Since for standard conditions according to DIN 32 645 the limit of quantitation should be the content at which the half prognosis interval of the value equals 33 %, the limit of quantitation can be estimated as

$$x_{LOQ} \approx 3 \times x_{LOD}\,.$$

The threshold value for the sum of penta- and octaBDE isomers respectively is about 0.1 % by mass. This corresponds to a content of 1 mg g^{-1}. To determine the detection and quantiation limits, polymers were tested whose content was 0.1 mg g^{-1}. To obtain a pentaBDE isomer content that is near the detection limit, the flame retardant-treated epoxy resin (Table 3 IC material) is mixed in the soxhlet thimble during weighing with epoxy resin without FR additive at a ratio of 1:9 and analysed ten times in accordance with the standard measurement method (Annex 1). A higher detection limit is expected for octaBDE isomers, therefore in this case the polymer ABS with OCTA-BDE (Table 3 IC material) is tested ten times without further dilution steps.
As an example for the calculation of the analytical limits of the pentaBDE isomers the main isomer BDE99 in the technical product was selected.
The average value of the tested sample became 0.116 ± 0.0061 mg g^{-1}.

Thus the following analytical limits were obtained:

$$x_{LOD} = s_x \times 2.96 = (0.061 \times 2.96)\, mg\ g^{-1} = 0.02\, mg\, g^{-1}$$

$$x_{LOQ} \approx 3 \times x_{LOD} = (3 \times 0.02)\, mg\ g^{-1} = 0.06\, mg\, g^{-1}$$

As an example for the calculation of the analytical limits of the octaBDE isomers the main isomer BDE197 in the technical product was selected.

The mean value of the tested sample became 0.257 ± 0.0138 mg g^{-1}. Thus the following analytical limits were obtained:

$$x_{LOD} = s_x \times 2.96 = (0.0138 \times 2.96)\, mg\, g^{-1} = 0.04\, mg\, g^{-1}$$

$$x_{LOQ} \approx 3 \times x_{LOD} = (3 \times 0.04)\, mg\, g^{-1} = 0.12\, mg\, g^{-1}$$

4.5. Homogeneity test of the polymers

A reference material is considered homogeneous with respect to a certain parameter when the parameter value determined by tests on random samples within a specified extent is within the specified uncertainty limits.

A homogeneity study on eight systematically selected sub-samples from the existing 80 sub-sample sets is planned within the quality control (see Chapter 3.5.2). The dispersion of the contents inside the sub-sample ("inside the bottle") and between the different sub-samples ("between the bottles") is determined using the analysis of variance (F-test) by four simultaneous and independent determinations of the analyte contents in each of these selected sub-samples. Due to time limitations, in some cases only three simultaneous determinations of the sub-samples were performed.
The obtained test value TV is compared with the table value F(P, f_1, f_2). If TV is smaller than F, the material can be regarded as homogeneous at the specified significance P, random sample size and test procedure.

The formulae for calculation are listed in Annex 5 due to their complexity. The computer-aided evaluation of the measured values can take place with the help of a one-factorial analysis of variance (analysis of variances - ANOVA table).

4.5.1. ABS with PENTA-BDE (material A)

Table 9 and Figure 2 display the contents measured over three or four simultaneous tests on selected sub-samples for the ABS/PENTA-BDE polymer (Table 3 IC material). Table 10 shows the results of the one-factorial analysis of variance.

Table 9: Analytical data of homogeneity tests of the ABS/PENTA-BDE polymer.

Sub-sample	**A-01**	**A-15**	**A-28**	**A-34**	**A-47**	**A-54**	**A-63**	**A-74**
Sum of pentaBDE isomers, measured content [mg g^{-1}]	0.990	1.285	1.202	1.309	1.085	1.148	1.103	1.129
	1.139	1.336	1.188	1.354	1.245	1.288	1.178	1.166
	1.173	1.235	1.266	1.197	1.154	1.154	1.151	1.178
		1.180	1.164	1.243	1.207	1.148	1.174	1.126
MV_i [mg g^{-1}]	1.101	1.259	1.205	1.276	1.173	1.185	1.152	1.150
s_i [mg g^{-1}]	0.0973	0.0669	0.0436	0.0695	0.0694	0.0691	0.0345	0.0262
V_i [%]	8.8	5.3	3.6	5.5	5.9	5.8	3.0	2.3
MV_{total} [mg g^{-1}]	1.187							
s_{total} [mg g^{-1}]	0.058							
V_{total} [%]	4.9							

MV_i: mean value of sub-sample i, s_i: standard deviation of sub-sample i, V_i: relative standard deviation of sub-sample i, MV_{total}: general mean value, s_{total}: standard deviation of mean values of sub-samples, V_{total}: relative standard deviation of mean values of sub-samples

Table 10: ANOVA table ABS/PENTA-BDE.

	Sum of squares	**Degrees of freedom**	**Variance**	**TV $= s_v^2 / s_r^2$**	**F (0.95; 7; 23)**	**F (0.99; 7; 23)**
Dispersion between the sub-samples	SQ_1 = 0.087	$f_1 = 7$	$s_v^2 = 0.012$	3.289	2.442	3.539
Dispersion within the sub-samples	SQ_2 = 0.087	$f_2 = 23$	$s_r^2 = 0.004$			

TV: test value, F(P, f_1, f_2): F-value (table value) at significance P and degrees of freedom f_1 and f_2

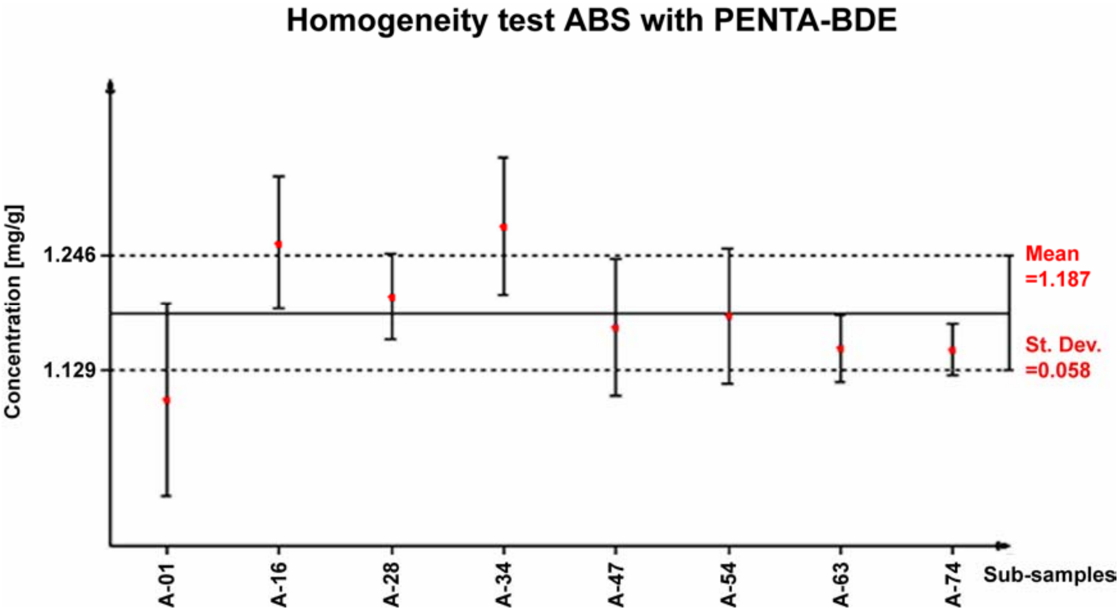

Figure 2: Mean and standard deviation (St. Dev.) of the tested sub-samples ABS/PENTA-BDE as a sum of penta-BDE isomers in mg g^{-1}.

The ABS/PENTA-BDE polymer can be considered as homogeneous at the actual test conditions (8 sub-samples, altogether 31 tests, significance 99%).

4.5.2. ABS with OCTA-BDE (material B)

Table 11 (also see Figure 3) illustrates the contents measured over three or four simultaneous measurements of selected sub-samples for the ABS/OCTA-BDE polymer (Table 3 IC Material). Table 12 shows the results of the one-factorial analysis of variance.

Table 11: Analytical data of homogeneity tests of the ABS/OCTA-BDE polymer.

Sub-sample	**B-05**	**B-14**	**B-27**	**B-32**	**B-46**	**B-58**	**B-66**	**B-79**
Sum of octaBDE isomers, measured content [mg g^{-1}]	0.524	0.504	0.502	0.570	0.527	0.532	0.458	0.542
	0.524	0.547	0.591	0.568	0.481	0.536	0.505	0.593
	0.495	0.541	0.525	0.542	0.532	0.443	0.455	0.600
	0.487	0.604						
MV_i [mg g^{-1}]	0.508	0.549	0.539	0.560	0.513	0.504	0.473	0.578
s_i [mg g^{-1}]	0.0193	0.0413	0.0462	0.0156	0.0281	0.0526	0.0280	0.0317
V_i [%]	3.8	7.5	8.6	2.8	5.5	10.4	5.9	5.5
MV_{total} [mg g^{-1}]	0.528							
s_{total} [mg g^{-1}]	0.035							
V_{total} [%]	6.6							

MV_i: mean value of sub-sample i, s_i: standard deviation of sub-sample i, V_i: relative standard deviation of sub-sample i, MV_{total}: general mean value, s_{total}: standard deviation of mean values of sub-samples, V_{total}: relative standard deviation of mean values of sub-samples

Table 12: ANOVA table ABS/OCTA-BDE.

	Sum of quadrates	**Degrees of freedom**	**Variance**	**TV = s_v^2 / s_r^2**	**F (0.95; 7; 18)**	**F (0.99; 7; 18)**
Dispersion between the sub-samples	SQ_1 = 0.026	f_1 = 7	s_v^2 = 0.004	3.096	2.577	3.841
Dispersion within the sub-samples	SQ_2 = 0.022	f_2 = 18	s_r^2 = 0.001			

TV: test value, F(P, f_1, f_2): F-value (table value) at significance P and degrees of freedom f_1 and f_2

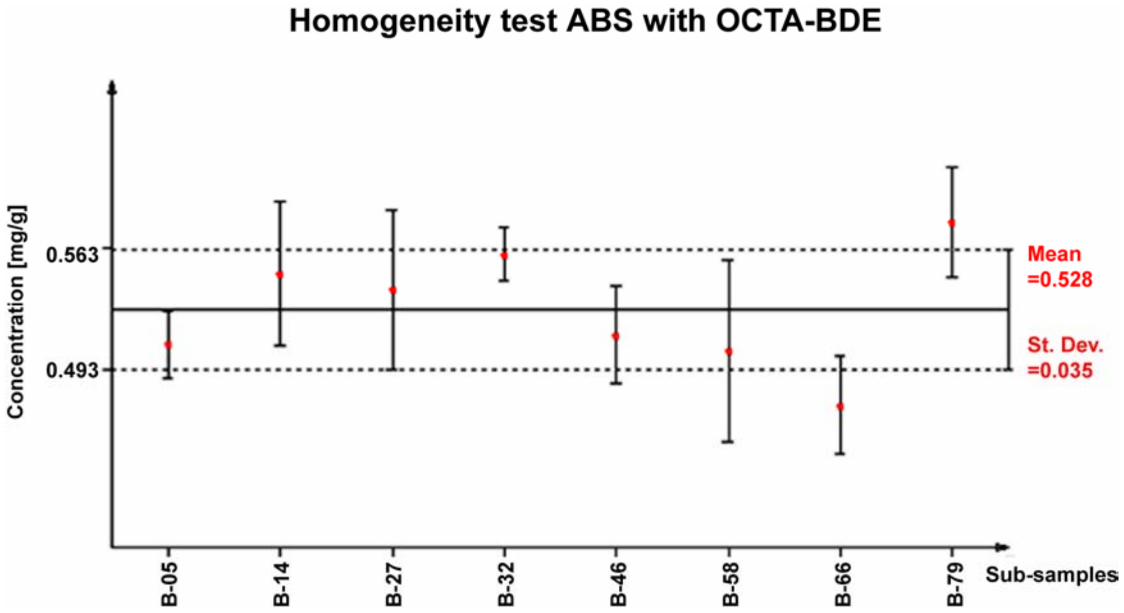

Figure 3: Mean and standard deviation (St. Dev.) of the tested sub-samples ABS/OCTA-BDE as a sum of octaBDE isomers in mg g^{-1}.

The ABS/OCTA-BDE polymer can be considered as homogeneous at the actual test conditions (8 sub-samples, altogether 26 tests, significance 99%).

4.5.3. PS mit OCTA-BDE (material C)

Table 13 (also see Figure 4) displays the contents measured over three or four simultaneous measurements of selected sub-samples for the PS/OCTA-BDE polymer (Table 3 IC material). Table 14 shows the results of the one-factorial analysis of variance.

Table 13: Analytical data of homogeneity tests of the PS/OCTA-BDE polymer.

Sub-sample	**C-01**	**C-15**	**C-28**	**C-36**	**C-44**	**C-57**	**C-65**	**C-78**
Sum of octaBDE isomers, measured content [mg g^{-1}]	1.131	1.050	1.222	1.206	0.915	1.121	1.069	1.061
	1.122	1.114	0.950	0.965	1.078	1.009	1.092	0.968
	1.175	1.178	1.085	1.005	0.896	1.025	0.914	0.969
	1.132	1.182						
MV_i [mg g^{-1}]	1.140	1.131	1.086	1.059	0.963	1.052	1.025	0.999
s_i [mg g^{-1}]	0.0238	0.0623	0.1360	0.1292	0.1000	0.0606	0.0968	0.0534
V_i [%]	2.1	5.5	12.5	12.2	10.4	5.8	9.4	5.3
MV_{total} [mg g^{-1}]	1.057							
s_{total} [mg g^{-1}]	0.061							
V_{total} [%]	5.8							

MV_i: mean value of sub-sample i, s_i: standard deviation of sub-sample i, V_i: relative standard deviation of sub-sample i, MV_{total}: general mean value, s_{total}: standard deviation of mean values of sub-samples, V_{total}: relative standard deviation of mean values of sub-samples

Table 14: ANOVA table PS/OCTA-BDE.

	Sum of quadrates	**Degrees of freedom**	**Variance**	**TV = s_v^2 / s_r^2**	**F (0.95; 7; 18)**	**F (0.99; 7; 18)**
Dispersion between the sub-samples	SQ_1 = 0.091	$f_1 = 7$	$s_v^2 = 0.013$	1.721	2.577	3.841
Dispersion within the sub-samples	SQ_2 = 0.136	$f_2 = 18$	$s_r^2 = 0.008$			

TV: test value, F(P, f_1, f_2): F-value (table value) at significance P and degrees of freedom f_1 and f_2

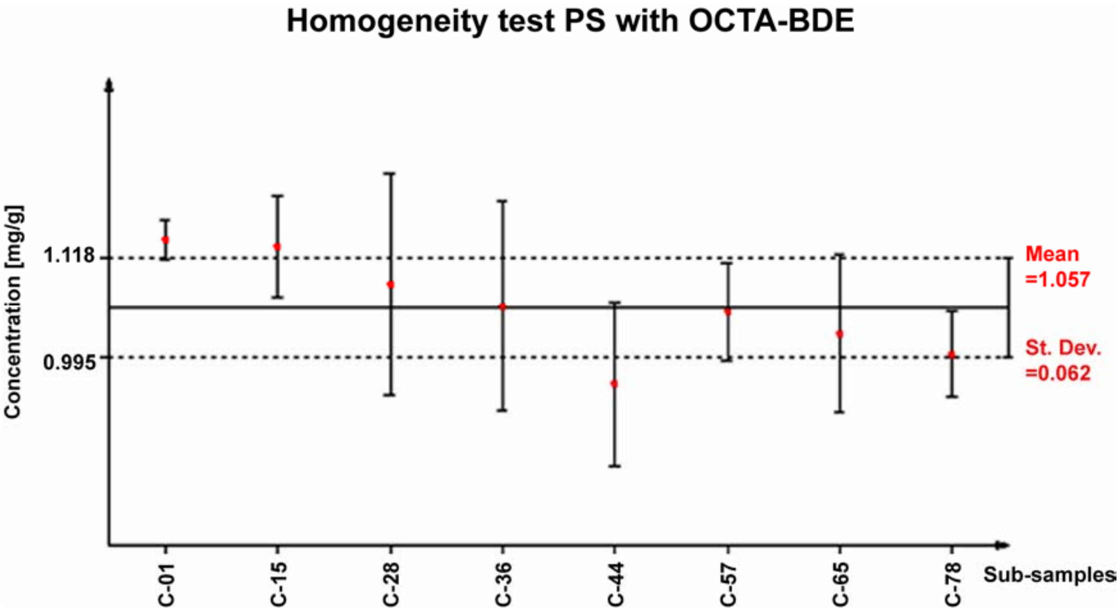

Figure 4: Mean and standard deviation (St. Dev.) of the tested PS/OCTA-BDE sub-samples as a sum of octaBDE isomers in mg g^{-1}.

The PS/OCTA-BDE polymer can be considered as homogeneous at the actual test conditions (8 sub-samples, altogether 26 tests, significance 99%). Even if a significance of 95 % is supposed, homogeneity can be assumed.

4.5.4. PUR with PENTA-BDE (material D)

Table 15 (also see Figure 5) displays the contents measured over three or four simultaneous measurements of selected sub-samples for the PUR/PENTA-BDE polymer (Table 3 IC material). Table 16 shows the results of the one-factorial analysis of variance.

Table 15: Analytical data of homogeneity tests of the PUR/PENTA-BDE polymer.

Sub-sample	**D-03**	**D-15**	**D-28**	**D-34**	**D-47**	**D-59**	**D-66**	**D-78**
Sum of pentaBDE isomers, measured content [mg g^{-1}]	1.429	1.255	1.570	1.395	1.283	1.464	1.453	1.377
	1.314	1.552	1.434	1.519	1.421	1.360	1.324	1.368
	1.155	1.379	1.490	1.499	1.512	1.464	1.430	1.380
	1.413	1.424						
MV_i [mg g^{-1}]	1.328	1.403	1.498	1.471	1.405	1.429	1.402	1.375
s_i [mg g^{-1}]	0.1259	0.1226	0.0684	0.0666	0.1153	0.0600	0.0688	0.0062
V_i [%]	9.5	8.7	4.6	4.5	8.2	4.2	4.9	0.5
MV_{total} [mg g^{-1}]	1.414							
s_{total} [mg g^{-1}]	0.053							
V_{total} [%]	3.8							

MV_i: mean value of sub-sample i, s_i: standard deviation of sub-sample i, V_i: relative standard deviation of sub-sample i, MV_{total}: general mean value, s_{total}: standard deviation of mean values of sub-samples, V_{total}: relative standard deviation of mean values of sub-samples

Table 16: ANOVA table PUR/PENTA-BDE.

	Sum of quadrates	**Degrees of freedom**	**Variance**	**TV = s_v^2 / s_r^2**	**F (0.95; 7; 18)**	**F (0.99; 7; 18)**
Dispersion between the sub-samples	SQ_1 = 0.067	f_1 = 7	s_v^2 = 0.017	1.112	2.577	3.841
Dispersion within the sub-samples	SQ_2 = 0.154	f_2 = 18	s_r^2 = 0.093			

TV: test value, F(P, f_1, f_2): F-value (table value) at significance P and degrees of freedom f_1 and f_2

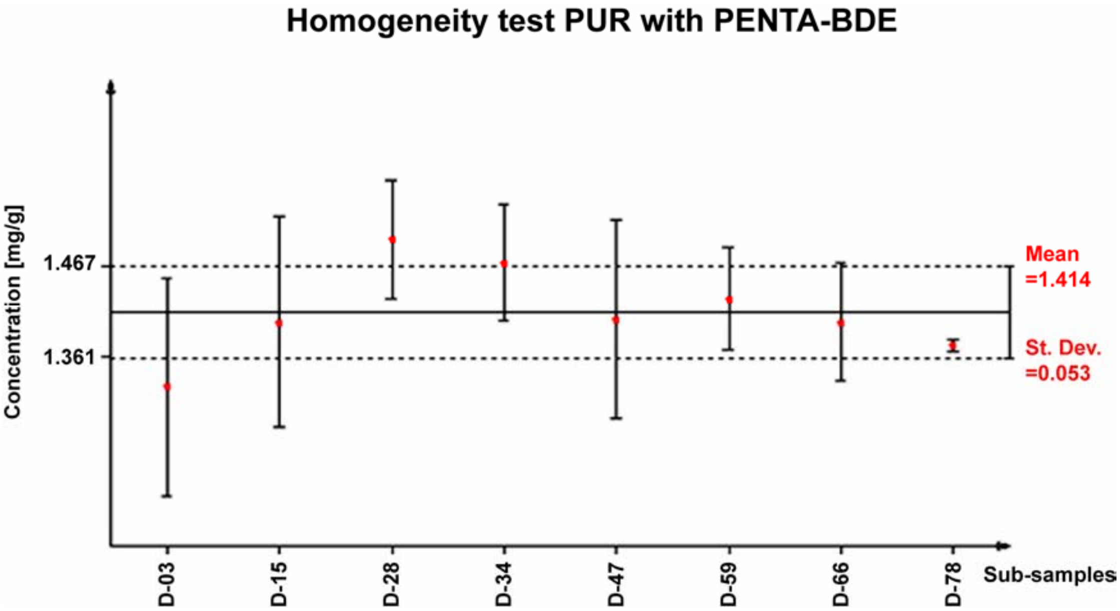

Figure 5: Mean and standard deviation (St. Dev.) of the tested PUR/PENTA-BDE sub-samples as a sum of pentaBDE isomers in mg g^{-1}.

The PUR/PENTA-BDE polymer can be considered as homogeneous at the actual test conditions (8 sub-samples, altogether 26 tests, significance 99%). Even if a significance of 95 % is supposed, homogeneity can be assumed.

4.5.5. EP with PENTA-BDE (material E)

Table 17 (also see Figure 6) shows the contents measured over three or four simultaneous measurements of selected sub-samples for the EP/PENTA-BDE polymer (Table 3 IC material). Table 18 shows the results of the one-factorial analysis of variance.

Table 17: Analytical data of homogeneity tests of the EP/PENTA-BDE polymer.

Sub-sample Teilprobe	**E-04**	**E-16**	**E-24**	**E-36**	**E-44**	**E-56**	**E-64**	**E-77**
Sum of pentaBDE isomers, measured content [mg g^{-1}]	1.090	1.130	1.705	1.347	1.455	1.565	1.397	1.471
	1.159	1.154	1.681	1.561	1.555	1.512	1.359	1.402
	1.169	1.267	1.416	1.606	1.359		1.334	1.337
	1.111	1.686						
MW_i [mg g^{-1}]	1.132	1.309	1.601	1.505	1.456	1.539	1.363	1.403
s_i [mg g^{-1}]	0.0379	0.2582	0.1604	0.1384	0.0980	0.0375	0.0317	0.0670
V_i [%]	3.3	19.7	10.0	9.2	6.7	2.4	2.3	4.8
MW_{total} [mg g^{-1}]	1.414							
s_{total} [mg g^{-1}]	0.148							
V_{total} [%]	10.5							

MV_i: mean value of sub-sample i, s_i: standard deviation of sub-sample i, V_i: relative standard deviation of sub-sample i, MV_{total}: general mean value, s_{total}: standard deviation of mean values of sub-samples, V_{total}: relative standard deviation of mean values of sub-samples

Table 18: ANOVA table EP/PENTA-BDE polymer.

	Sum of quadrates	**Degrees of freedom**	**Variance**	**TV = s_v^2 / s_r^2**	**F (0.95; 7; 17)**	**F (0.99; 7; 17)**
Dispersion between the sub-samples	SQ_1 = 0.524	$f_1 = 7$	$s_v^2 = 0.075$	3.909	2.614	3.927
Dispersion within the sub-samples	SQ_2 = 0.326	$f_2 = 17$	$s_r^2 = 0.019$			

TV: test value, F(P, f_1, f_2): F-value (table value) at significance P and degrees of freedom f_1 and f_2

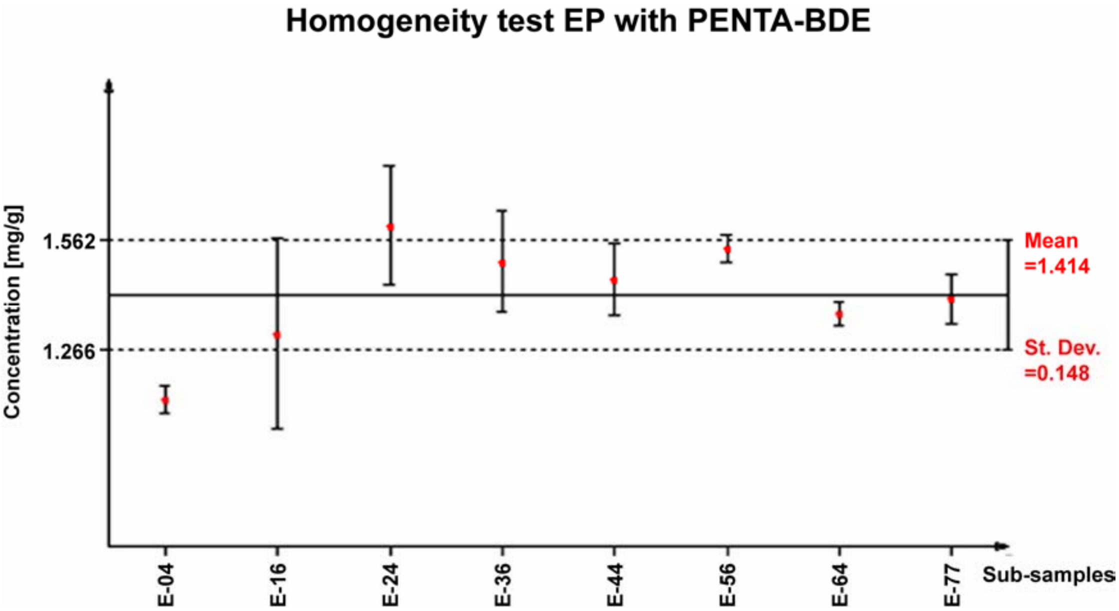

Figure 6: Mean and standard deviation (St. Dev.) of the tested EP/PENTA-BDE sub-samples as a sum of pentaBDE isomers in mg g^{-1}.

The EP/PENTA-BDE polymer can be considered as homogeneous at the actual test conditions (8 sub-samples, altogether 25 tests, significance 99%).

5 Checking the standard measurement method: results of the interlaboratory comparison

The standard measurement method developed within the project (Annex 1) was tested to determine precision under repeatability and reproducibility conditions with the help of an international interlaboratory comparison with 18 participating laboratories.
The following time schedule has been applied:

30.04.2003	First call for interlaboratory comparison to selected laboratories
31.08.2003	Second call for interlaboratory comparison to selected laboratories by EUROLAB
31.12.2003	Registration deadline for interested laboratories
11.03.2004	Distribution of method description, software and test material PENTA-BDE/ABS for a voluntary pre-interlaboratory comparison
30.04.2004	Deadline for sending in the results of the pre-interlaboratory comparison
10.06.2004	Distribution of interlaboratory comparison material
03.09.2004	Expected deadline for sending in the results
15.10.2004	Receipt of the last results
03.11.2004	Information on outliers to affected laboratories
26.11.2004	Distribution of the results to the participants in the form of a final report

The flame-protected polymers manufactured in accordance with Chapter 3.5.2 were used as test materials (material A to E).
Evaluation was performed in accordance with DIN ISO 5725 /12/.
A computer-aided evaluation was performed on the measurement results using the SoftCRM (Version 1.2.2) software /13/.

The results of a trial interlaboratory comparison on PENTA-BDE in ABS (material A) are described in Chapter 5.2. This test was carried out to detect any grave error of the standard analysis guideline and to test the software for its applicability. The determined data were tested using Cochran's test and Grubbs' test for any outlier (Annexes 8 and 9).

The following polymer samples were tested in the main interlaboratory comparison:

- Material E: sum of pentaBDE isomers in epoxy resin (Chapter 5.3)
- Material D: sum pentaBDE isomers in polyurethane (Chapter 5.4)
- Material C: sum of octaBDE isomers in polystyrene (Chapter 5.5)
- Material B: sum of octaBDE isomers in ABS (Chapter 5.6)

To determine the precision of the standard measurement method under conditions of repeatability and reproducibility, data from the main interlaboratory comparison were tested using graphical compatibility tests and numerical outlier tests.

Two test quantities were used in the graphical consistency technique: Mandel's h-statistic and Mandel's k statistic (Annex 7) /12/.

Cochran's and Grubbs' tests were used as numerical outlier tests (Annexes 8 and 9) /12/.

5.1. Participants in the interlaboratory comparison

In addition to BAM IV.2 (co-ordinator), 17 other testing bodies from Germany, Austria, Switzerland, China, Italy, Korea and the USA participated in the interlaboratory comparison. Previous experience of these laboratories in PBDE handling and polymer analysis is listed in Table 19.

Table 19: Previous experience of the participants in the interlaboratory comparison.

Laboratory code	**Experience in PBDE analysis**	**Matrix**
L001	Yes	Sediment, water, biological samples
L003	Yes	Polymers, textiles, wood wool
L004	Yes	Household dust, textiles
L012	Yes	Polymers, cuddly toys
L013	Yes	Polymers, textiles
L014	Yes	Polymers, textiles
L019	Yes	Polymers, sediment, water, biological samples
L021	No	-
L026	Yes	Biological samples
L027	No	-
L030	Yes	Polymers, textiles
L037	No	-
L040	Yes	Sediment, water
L041	Yes	Sediment, water
L044	Yes	Polymers
L045	Yes	Polymers
L046	Yes	Polymers

5.2. PentaBDE isomers in ABS (IC material A)

Table 20 displays the results in mg g^{-1} obtained using the standard measurement method (Annex 1) (sum of pentaBDE isomers, see Chapter 3.2) for ABS with PENTA-BDE flame retardant (see Chapter 3.5.2).

Table 20: Test results of repeat analyses as a sum of pentaBDE isomers in mg g^{-1} in ABS, with PENTA-BDE flame retardant.

No.	Laboratory code	Sample number				Mean [mg g^{-1}]	STDev [mg g^{-1}]	CV [%]
		A-XX-1	A-XX-2	A-XX-3	A-XX-4			
1	Co-ordinator	0.994	1.06	1.0695	1.0345	*1.040*	*0.034*	*3.2*
2	L001	0.934	0.952	0.956	0.944	*0.947*	*0.010*	*1.0*
3	L003	1.06	1.15			*1.105*	*0.064*	*5.8*
4	L004	0.822	0.765	0.742	0.778	*0.777*	*0.034*	*4.3*
5	L013	0.88	0.84	0.9	0.85	*0.868*	*0.028*	*3.2*
6	L014	0.89	0.98	1.07	1.04	*0.995*	*0.079*	*8.0*
7	L019	1.008	1.021	1.089	1.008	*1.032*	*0.039*	*3.8*
8	L021	0.88	0.87	0.79		*0.847*	*0.049*	*5.8*
9	L026	0.85	0.86	0.89	0.86	*0.865*	*0.017*	*2.0*
10	L030	0.686	0.677	0.691	0.677	*0.683*	*0.007*	*1.0*
11	L040	0.733	0.793	0.736	0.752	*0.754*	*0.028*	*3.7*

STDev: standard deviation to laboratory mean; CV: coefficient of variation

0.901 ± 0.134 mg g^{-1} was obtained as the mean value for the sum of the pentaBDE isomers from the data determined in the interlaboratory comparison. The relative standard deviation is 15 %. No outlier could be detected by either Cochran's test of laboratory variances (Annex 8) or Grubbs' test of laboratory mean values (Annex 9).

Figure 7 shows a graphical representation of the laboratory mean values for the sum of pentaBDE isomers in mg g^{-1} in ABS with PENTA-BDE flame retardant.

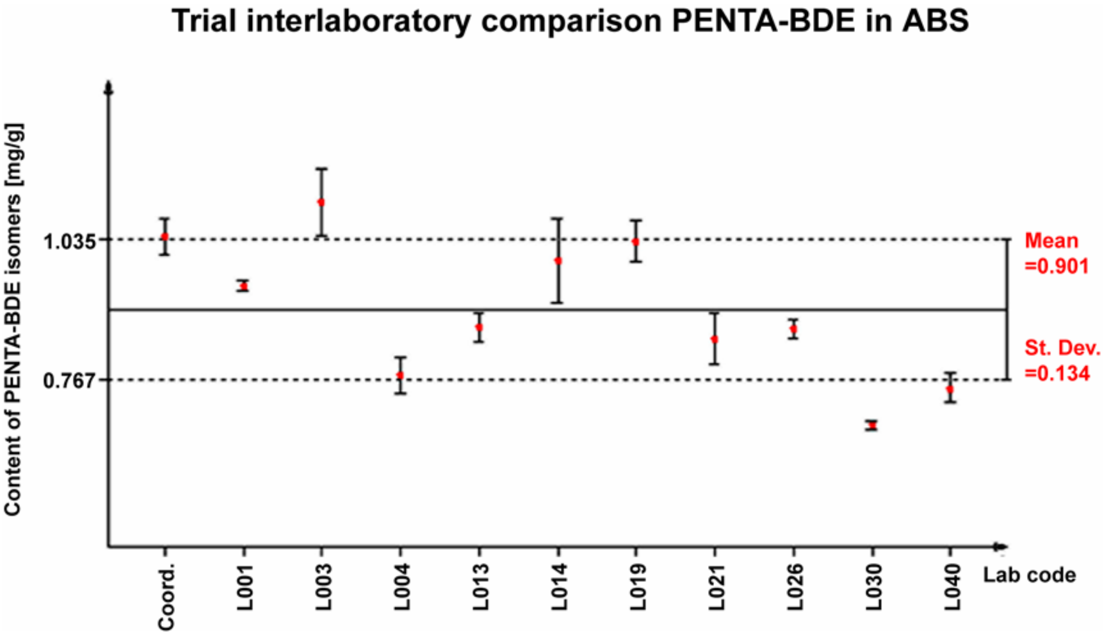

Figure 7: Graphical representation of the sum of pentaBDE isomers [mg g^{-1}] in ABS with PENTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 11 laboratories.

5.3. PentaBDE isomers in epoxy resin (IC material E)

Table 21 and Figure 8 show test results as a sum of pentaBDE isomers in mg g^{-1} in epoxy resin with PENTA-BDE flame retardant (see Section 3.5.2).

Table 21: Test results of repeat analyses as a sum of pentaBDE isomers in mg g^{-1} in epoxy resin with PENTA-BDE flame retardant.

No.	**Labor Code**	**Sample number**				**Mean [mg g^{-1}]**	**STDev [mg g^{-1}]**	**CV [%]**
		E-XX-1	**E-XX-2**	**E-XX-3**	**E-XX-4**			
1	001	0.89	0.97	0.88	0.92	*0.914*	*0.040*	*4.4*
2	003	1.78	1.68	2.26	1.75	*1.868*	*0.265*	*14.2*
3	004	1.07	1.14			*1.107*	*0.046*	*4.1*
4	012	1.28	1.26	1.31	1.27	*1.279*	*0.023*	*1.8*
5	013	0.79	0.75	0.84	0.76	*0.786*	*0.040*	*5.0*
6	014	1.19	1.14	1.15	1.1	*1.145*	*0.037*	*3.2*
7	019	1.19	1.29	1.23	1.28	*1.250*	*0.045*	*3.6*
8	021	0.95	0.88	0.85		*0.893*	*0.051*	*5.7*
9	026	1.11	1.05	1.13	1.16	*1.113*	*0.046*	*4.2*
10	027	1.20	1.19	1.15		*1.181*	*0.024*	*2.0*
11	030	1.30	1.20	1.27	1.23	*1.250*	*0.044*	*3.5*
12	037	0.85	0.73		0.91	*0.832*	*0.092*	*11.1*
13	040	1.25	1.33	1.31		*1.297*	*0.041*	*3.2*
14	041	1.09	1.09	1.04	1.06	*1.070*	*0.024*	*2.3*
15	044	1.08	1.16	1.18	1.08	*1.125*	*0.053*	*4.7*
16	045	1.75	1.91	1.73		*1.795*	*0.099*	*5.5*
17	046	0.96	1.16	1.34		*1.152*	*0.190*	*16.5*
18	Coord.	1.09	1.16	1.17	1.11	*1.132*	*0.038*	*3.3*

STDev: standard deviation to laboratory mean; CV: coefficient of variation

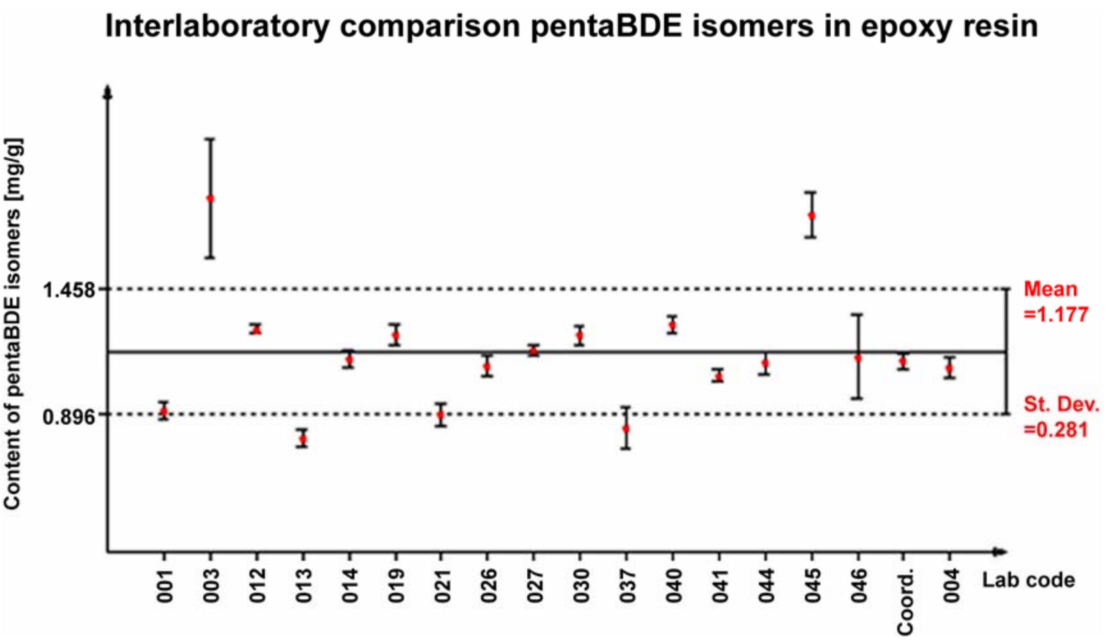

Figure 8: Graphical representation of the laboratory means as a sum of pentaBDE isomers [mg g^{-1}] in epoxy resin with PENTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 18 laboratories.

5.3.1. Statistical evaluation – pentaBDE isomers in epoxy resin

5.3.1.1. Results of Mandel's h statistic (pentaBDE isomers in epoxy resin)

Figure 9 illustrates graphically the values calculated as per Annex 7 for h in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's consistency parameters h and k /12/) are at 2.36 (level of significance 1 %) and 1.88 (level of significance 5 %).

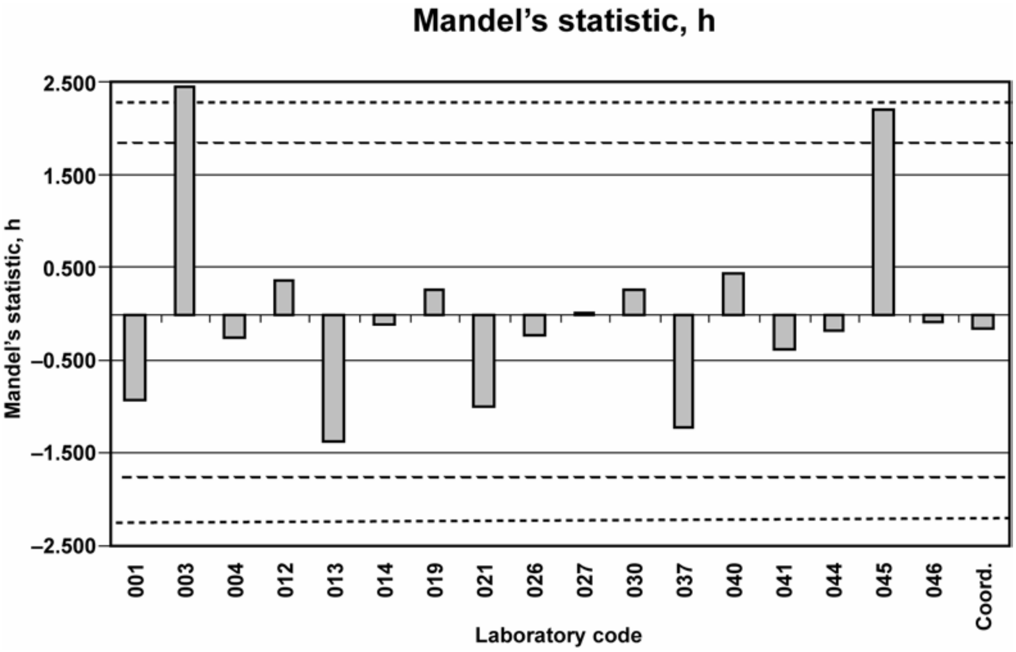

Figure 9: Calculated values for h (pentaBDE isomers in epoxy resin); indicator lines: 1.88 (level of significance 5%); 2.36 (level of significance 1%).

Figure 9 indicates that the h value for Laboratory 003 is outside the indicator lines, thus should be considered as an outlier. The h value of Laboratory 045 is between the two indicator lines and should be considered as a straggler.

5.3.1.2. Results of Mandel's k statistic (pentaBDE isomers in epoxy resin)

Figure 10 illustrates graphically the values calculated as per Annex 7 for k in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's consistency parameters h and k /12/) are at 1.88 (level of significance 1%) and 1.59 (level of significance 5%).

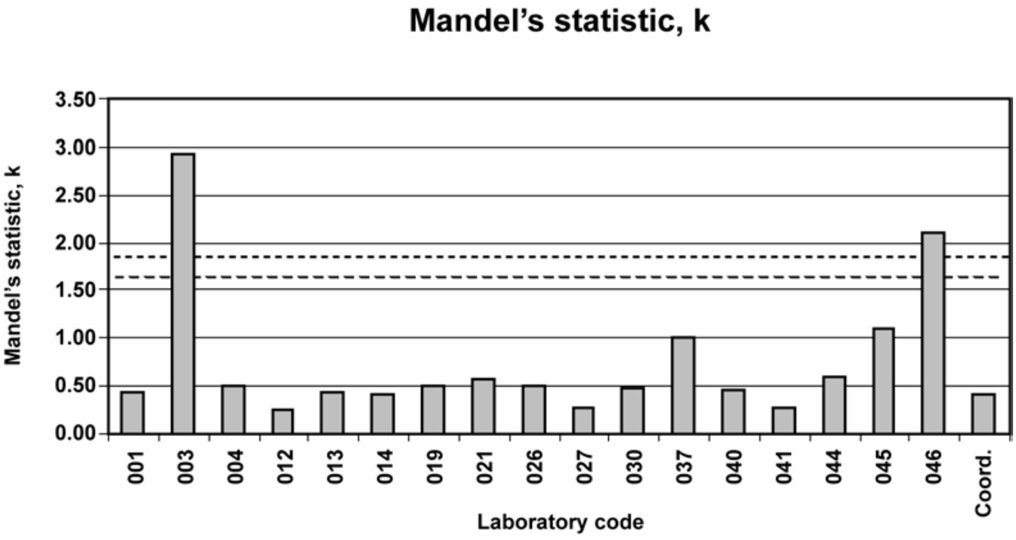

Figure 10: Calculated values for k (pentaBDE isomers in epoxy resin); indicator lines: 1.59 (level of significance 5%); 1.88 (level of significance 1%).

As Figure 10 indicates, the k values for Laboratory 003 and Laboratory 046 are outside the indicator lines and should be considered as outliers.

5.3.1.3. Checking variances – Cochran's test (pentaBDE isomers in epoxy resin)

In accordance with Annex 8 the test quantity C_{TV} has been calculated for the Laboratory with the highest variance (Laboratory 003) which yielded the test quantity C_{TV} = 0.476 for Laboratory 003.

For a maximum of four repeat analyses with a number of 18 laboratories based on the Table for critical values of Cochran's test /12/ the following table values have been obtained:

C-crit = 0.288 (level of significance 0.01)

C-crit = 0.240 (level of significance 0.05)

Since the determined test quantity C_{TV} is above the critical value for the level of significance 0.01, Laboratory 003 has to be considered as an outlier and will be expunged.

For Laboratory 046 the test quantity C_{TV} = 0.465 has been calculated.

For a maximum of four repeat analyses with a number of 17 laboratories (18 minus one outlier) based on the Table for critical values of Cochran's test, the following test values have been obtained:

C-crit = 0.301 (level of significance 0.01)
C-crit = 0.250 (level of significance 0.05)

Laboratory 046 must then be considered as an outlier and will be expunged.

A follow-up control of laboratory variances has found no further outliers.

5.3.1.4. Controlling laboratory means – Grubbs' test (pentaBDE isomers in epoxy resin)

In accordance with Annex 9 the smallest (L013) and the greatest (L003) laboratory means will be controlled using Grubbs' test.

The test has delivered the following test values for the respective outliers:

for Laboratory 013: T1 = 1.391
for Laboratory 003: Tn = 2.457

For 18 laboratories the following table values can be obtained from the Table for critical values of Grubbs' test for one outlier /12/:

T-crit = 2.821 (level of significance 0.01)
T-crit = 2.504 (level of significance 0.05)

In the current case the determined test values T1 and Tn are below T-crit (0.05), thus there is no outlier.

In accordance with Annex 9 Grubbs' test has been applied to the two smallest (L013 and L037) and the two greatest (L045 and L003) laboratory means.

The following test values have been obtained using Grubbs' test for two outliers:

for Laboratories 013 and 037: G1,2 = 0.772

for Laboratories 003 and 045: Gn-1,n = 0.281

For 18 Laboratories the following table values have been obtained based on the Table for critical values of Grubbs' tests for two outliers /12/:

G-crit = 0.353 (level of significance 0.01)

G-crit = 0.446 (level of significance 0.05)

In the current case Gn-1,n is smaller than G-crit (0.01), thus Laboratories L003 und L045 have to be considered as outliers.

5.3.2. Results of pentaBDE isomers in epoxy resin

Table 22 summarises the results of the statistical tests.

Table 22: Summary of results of the statistical tests for the determination of pentaBDE isomers in epoxy resin.

Statistical test	**See Chapter**	**Result**
Mandel's h statistic	5.3.1.1	L003 outlier L045 straggler
Mandel's k statistic	5.3.1.2	L003 outlier L046 outlier
Cochran's test	5.3.1.3	L003 outlier L046 outlier
Grubbs' test	5.3.1.4	L003 outlier L045 outlier

Based on these results Laboratories L003, L045, L046 will be expunged.

Figure 11 gives a graphical representation of the laboratory means, the general mean and the standard deviation.

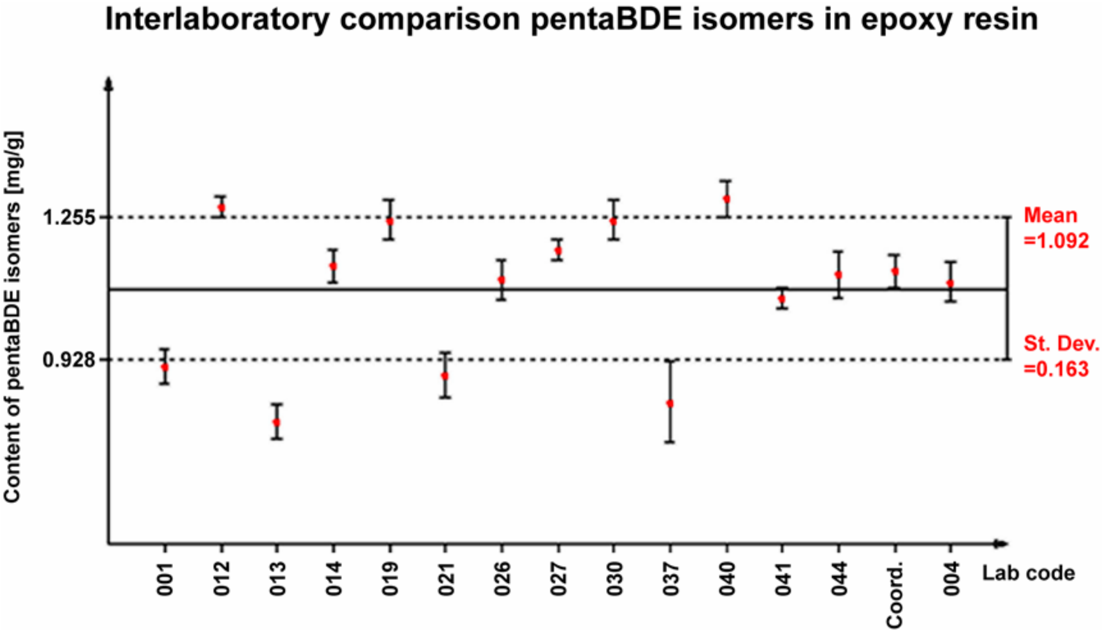

Figure 11: Graphical representation of the sum of pentaBDE isomers [mg g^{-1}] in epoxy resin with PENTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 15 laboratories (outliers expunged).

1.092 ± 0.163 mg g^{-1} has been obtained for the general mean of the tested sample as a sum of pentaBDE isomers in epoxy resin. The relative standard deviation is 14.9 %.

5.4. PentaBDE isomers in polyurethane (IC material D)

Table 23 illustrates the test results as a sum of pentaBDE isomers in mg g^{-1} in polyurethane with PENTA-BDE flame retardant (Section 3.5.2).

Table 23: Test results of repeat analyses as a sum of pentaBDE isomers in mg g^{-1} in polyurethane with PENTA-BDE flame retardant.

No.	**Lab code**	**Sample number**				**Mean [mg g^{-1}]**	**STDev [mg g^{-1}]**	**CV [%]**
		D-XX-1	**D-XX-2**	**D-XX-3**	**D-XX-4**			
1	001	1.08	1.07	1.057	1.069	*1.069*	*0.009*	*0.9*
2	004	1.1611	1.2431			*1.202*	*0.058*	*4.8*
3	003	0.97	2.86	1.79	1.77	*1.848*	*0.776*	*42*
4	012	1.503	1.464	1.421	1.411	*1.450*	*0.042*	*2.9*
5	013		0.841	0.896	0.873	*0.870*	*0.028*	*3.2*
6	014	1.4	1.39	1.4	1.41	*1.400*	*0.008*	*0.6*
7	019	1.418	1.415	1.425	1.505	*1.441*	*0.043*	*3.0*
8	021	1.12	1.16	1.15		*1.143*	*0.021*	*1.8*
9	026	1.31	1.3	1.29	1.35	*1.313*	*0.026*	*2.0*
10	027	1.35393	1.40678	1.34249		*1.368*	*0.034*	*2.5*
11	030	1.64	1.65	1.65	1.67	*1.653*	*0.013*	*0.8*
12	037	1.19		1.12	1.23	*1.180*	*0.056*	*4.7*
13	040	1.26	1.371	1.334		*1.322*	*0.057*	*4.3*
14	041	1.2	1.18	1.22	1.28	*1.220*	*0.043*	*3.5*
15	044	1.35	1.349	1.411	1.365	*1.369*	*0.029*	*2.1*
16	045	2.0893	1.9269	2.2308		*2.082*	*0.152*	*7.3*
17	046	0.9748	1.2378	1.2326		*1.148*	*0.150*	*13.1*
18	Coord.	1.57	1.434	1.49		*1.498*	*0.068*	*4.6*

STDev: standard deviation to laboratory mean; CV: coefficient of variation

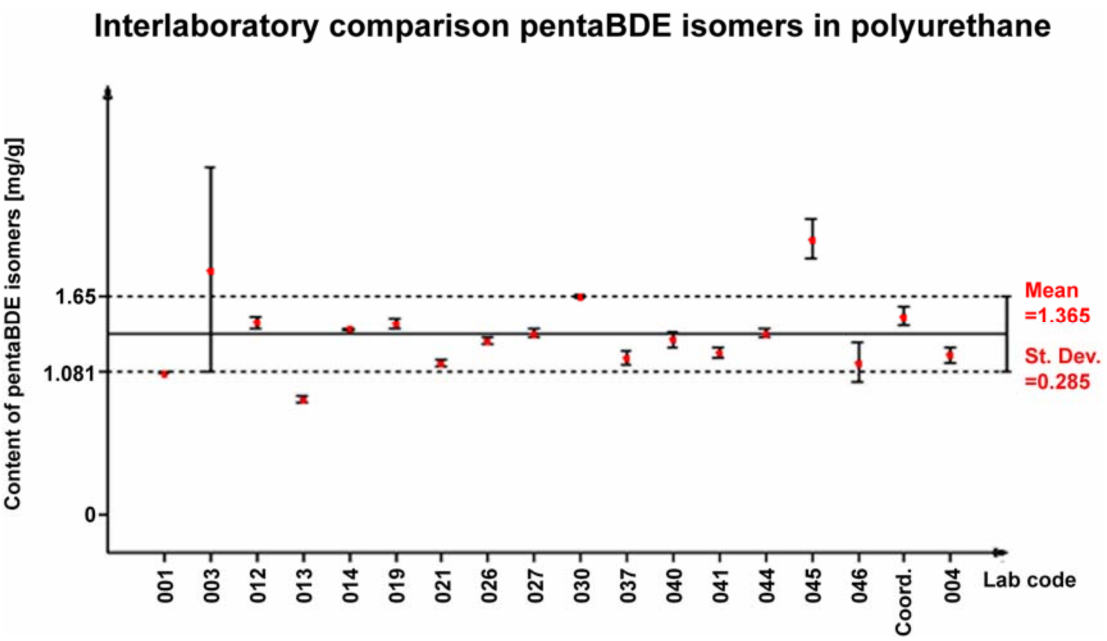

Figure 12: Graphical representation of the laboratory means as a sum of pentaBDE isomers [mg g^{-1}] in polyurethane with PENTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 18 laboratories.

5.4.1. Statistical evaluation – pentaBDE isomers in polyurethane

5.4.1.1. Results of Mandel's h statistic (pentaBDE isomers in polyurethane)

Figure 13 illustrates graphically the values calculated as per Annex 7 for h in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's compatibility test quantities h and k /12/) are at 2.36 (level of significance 1 %) and 1.88 (level of significance 5 %).

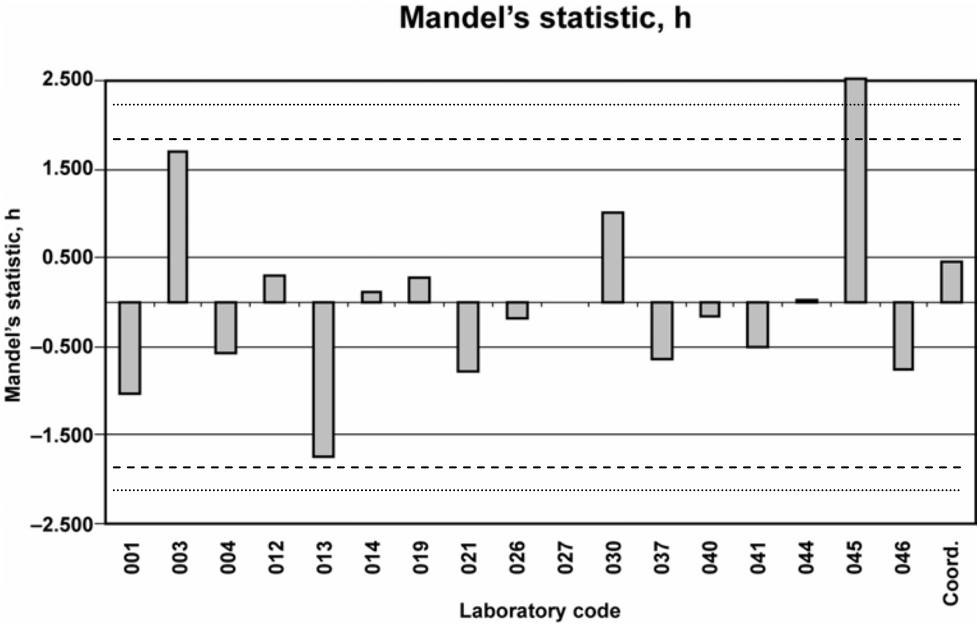

Figure 13: Calculated values for h (pentaBDE isomers in polyurethane); indicator lines: 1.88 (level of significance 5%); 2.36 (level of significance 1%).

Figure 13 indicates that the h value for Laboratory 045 is outside the indicator lines, thus has to be considered as a potential outlier.

5.4.1.2. Results of Mandel's k statistic (pentaBDE isomers in polyurethane)

Figure 14 illustrates graphically the values calculated as per Annex 7 for k in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's compatibility test quantities h and k /12/) are at 1.88 (level of significance 1 %) and 1.59 (level of significance 5 %).

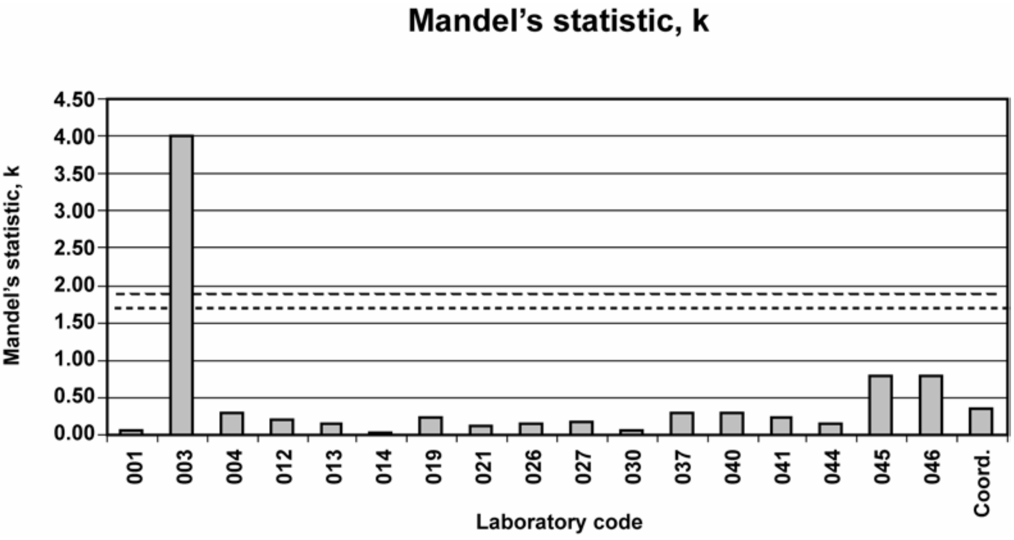

Figure 14: Calculated values for k (pentaBDE isomers in polyurethane); indicator lines: 1.59 (level of significance 5%); 1.88 (level of significance 1%).

Figure 14 indicates clearly that the k value for Laboratory 003 is outside the indicator lines and has to be considered as an outlier.

5.4.1.3. Checking variances – Cochran's test (pentaBDE isomers in polyurethane)

In accordance with Annex 8 the test quantity C_{TV} has been calculated for the Laboratory with the highest variance (L003) which yielded the test quantity $C_{TV} = 0.896$ for Laboratory 003. For a maximum of four repeat analyses with a number of 18 laboratories based on the Table for critical values of Cochran's test /12/ the following table values have been obtained:

C-crit = 0.288 (level of significance 0.01)
C-crit = 0.240 (level of significance 0.05)

Since the determined test quantity C_{TV} is above the critical value for the level of significance 0.01, Laboratory 003 has to be considered as an outlier and will be expunged.

For Laboratory 045 the test quantity C_{TV} = 0.331 has been calculated.
For a maximum of four repeat analyses with a number of 17 laboratories (18 minus one outlier) based on the Table for critical values of Cochran's test the following table values have been obtained /12/:

C-crit = 0.301 (level of significance 0.01)
C-crit = 0.250 (level of significance 0.05)

Laboratory 045 must then be considered as an outlier and will be expunged.

For Laboratory 046 the test quantity C_{TV} = 0.484 has been calculated.
For a maximum of four repeat analyses with a number of 16 laboratories (18 minus two outliers) based on the Table for critical values of Cochran's test the following table test have been obtained /12/:

C-crit = 0.316 (level of significance 0.01)
C-crit = 0.262 (level of significance 0.05)

Laboratory 046 must then be considered as an outlier and will be expunged.

Another test of laboratory variances yielded no further outliers.

5.4.1.4. Checking the laboratory means – Grubbs' test (pentaBDE isomers in polyurethane)

In accordance with Annex 9 the smallest (L013) and the greatest (L045) laboratory means have been tested using Grubbs' test.
The test for one outlier provided the following test values:

for Laboratory 013: T1 = 1.740
for Laboratory 045: Tn = 2.520

For 18 laboratories the following table values can be obtained from the Table for critical values of Grubbs' test for one outlier /12/:

T-crit = 2.821 (level of significance 0.01)
T-crit = 2.504 (level of significance 0.05)

In the current case the determined test value Tn is between the critical values of the level of significance 0.05 and 0.01. Therefore Laboratory 045 has to be considered as a straggler.

5.4.2. Results of pentaBDE isomers in polyurethane

Table 24 recapitulates the results of the statistical tests.

Table 24: Summary of the results of the statistical tests for the determination of the pentaBDE isomers in polyurethane.

Statistical test	**See Chapter**	**Result**
Mandel's h statistic	5.4.1.1	L045 outlier
Mandel's k statistic	5.4.1.2	L003 outlier
Cochran's test	5.4.1.3	L003 outlier L045 outlier L046 outlier
Grubbs' test	5.4.1.4	L045 straggler

Based on these results the Laboratories 003, 045, 046 will be expunged.

Figure 15 gives a graphic illustration of laboratory means, general mean and standard deviation.

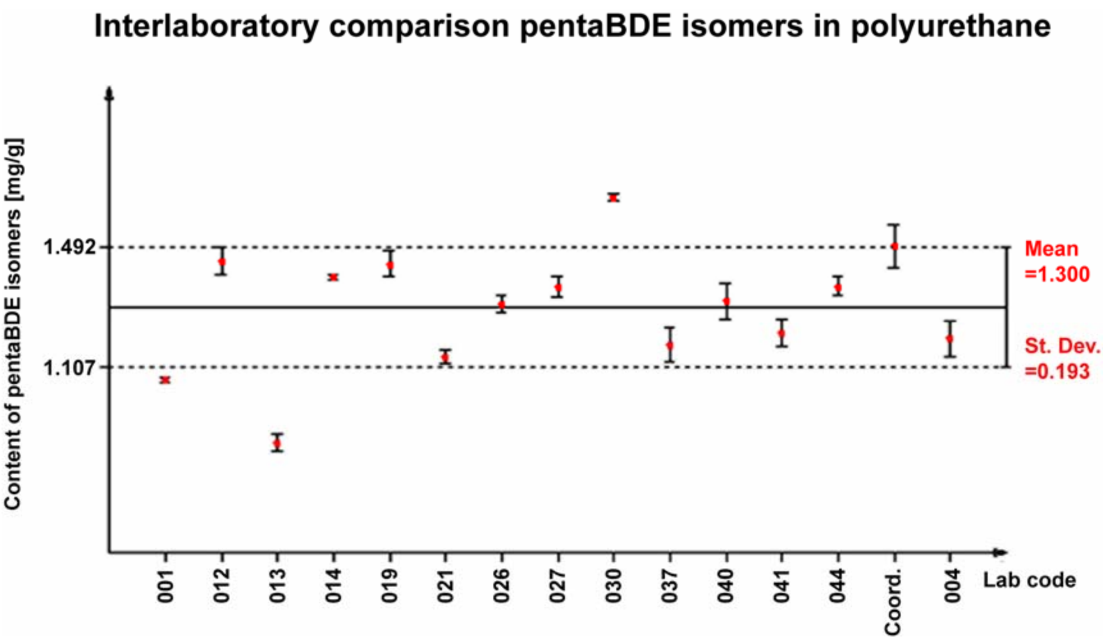

Figure 15: Graphical representation of the sum of pentaBDE isomers [mg g^{-1}] in polyurethane with PENTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 15 laboratories (outliers expunged)

The general mean of the sample tested is 1.3 ± 0.19 mg g^{-1} as a sum of the pentaBDE isomers in polyurethane. The relative standard deviation is 14.8 %.

5.5. OctaBDE isomers in polystyrene (IC Material C)

Table 25 and Figure 16 show the test results as a sum of octaBDE isomers in mg g^{-1} in polystyrene with OCTA-BDE flame retardant (see Section 3.5.2).

Table 25: Test results of repeat analyses as a sum of octaBDE isomers in mg g^{-1} in polystyrene with OCTA-BDE flame retardant.

No.	**Laboratory code**	**Sample number**				**Mean [mg g^{-1}]**	**STDev [mg g^{-1}]**	**CV [%]**
		C-XX-1	**C-XX-2**	**C-XX-3**	**C-XX-4**			
1	001	0.934	0.979	1.006	0.902	*0.955*	*0.046*	*4.8*
2	003	1.62	1.56	1.54		*1.573*	*0.042*	*2.6*
3	004	1.4453	1.527			*1.486*	*0.058*	*3.9*
4	012	1.345	1.244	1.366	1.398	*1.338*	*0.067*	*5.0*
5	013	0.849	0.839	0.857	0.808	*0.838*	*0.021*	*2.6*
6	014	0.919	0.924	0.902	0.912	*0.914*	*0.010*	*1.0*
7	019	1.047	1.031	1.024	1.123	*1.056*	*0.046*	*4.3*
8	021	0.61	0.61	0.61		*0.610*	*0.000*	*0*
9	026	0.87	0.8	0.85	0.82	*0.835*	*0.031*	*3.7*
10	027	0.92229	1.03997	1.03656		*1.000*	*0.067*	*6.7*
11	030	0.74	0.7	0.71	0.69	*0.710*	*0.022*	*3.0*
12	037		0.953	1.05	1.01	*1.004*	*0.049*	*4.9*
13	040	0.8928	0.9154	0.9116		*0.907*	*0.012*	*1.3*
14	041	0.852	0.854	0.86	0.871	*0.859*	*0.009*	*1.0*
15	044	1.007	0.917	1.022	1.044	*0.998*	*0.056*	*5.6*
16	045	0.5948	0.5723	0.4785		*0.549*	*0.062*	*11.2*
17	046	1.1389	1.0819	1.0959		*1.106*	*0.030*	*2.7*
18	Coord	1.05	1.114	1.18	1.182	*1.132*	*0.063*	*5.6*

STDev: standard deviation to laboratory mean; CV: coefficient of variation

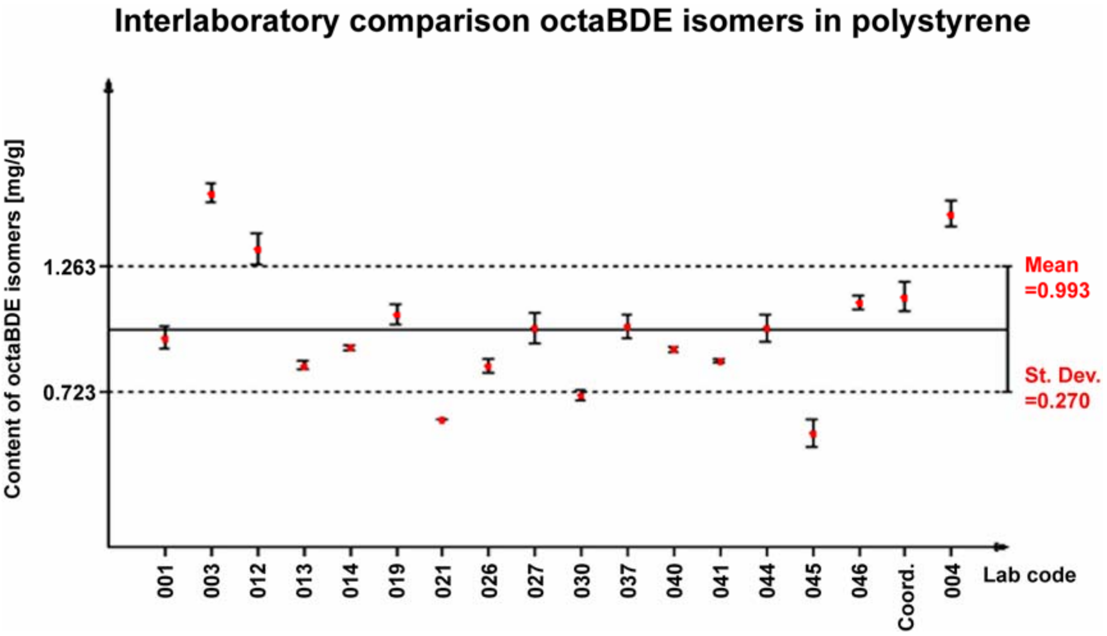

Figure 16: Graphical representation of the laboratory means as a sum of octaBDE isomers [mg g^{-1}] in polystyrene with OCTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 18 laboratories.

5.5.1. Statistical evaluation – octaBDE isomers in polystyrene

5.5.1.1. Results of Mandel's h statistic (octaBDE isomers in polystyrene)

Figure 17 illustrates graphically the values calculated as per Annex 7 for h in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's compatibility test quantities h and k /12/) are at 2.36 (level of significance 1 %) and 1.88 (level of significance 5 %).

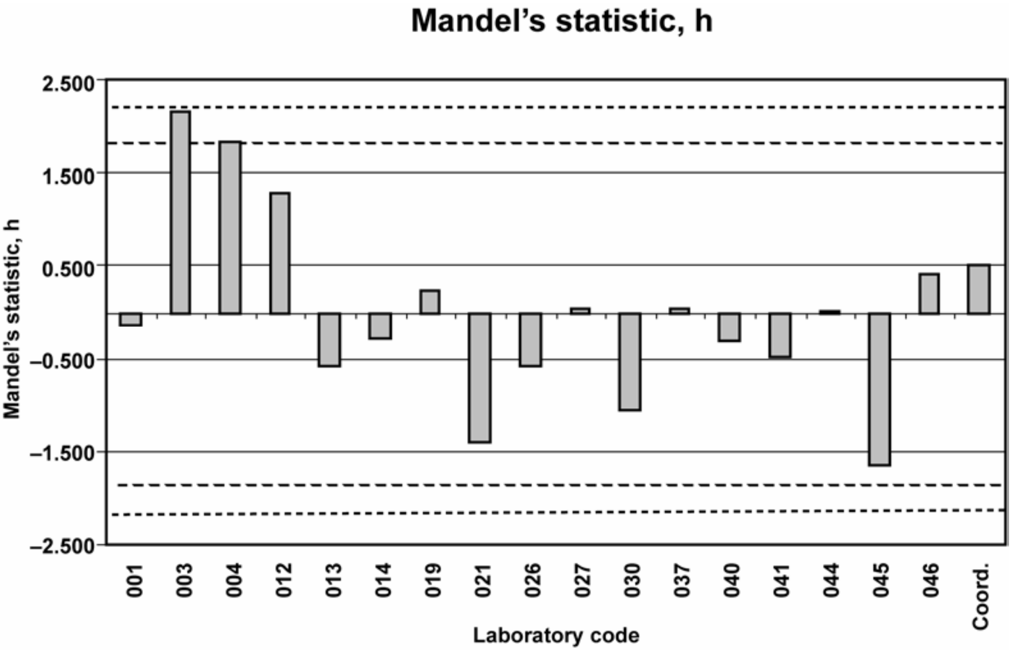

Figure 17: Calculated values for h (octaBDE isomers in polystyrene); indicator lines: 1.88 (level of significance 5%); 2.36 (level of significance 1%).

Figure 17 indicates that the h value for Laboratory L003 is between the two indicator lines and has therefore to be considered a straggler.

5.5.1.2. Results of Mandel's k statistic (octaBDE isomers in polystyrene)

Figure 18 illustrates graphically the values calculated per Annex 7 for k in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's compatibility test quantities h and k /12/) are at 1.88 (level of significance 1 %) and 1.59 (level of significance 5 %).

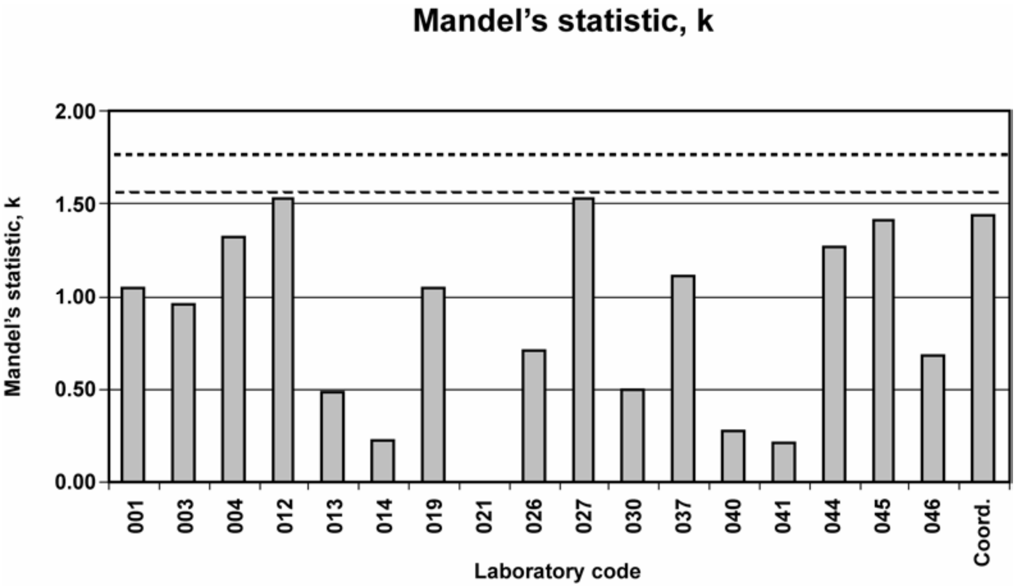

Figure 18: Calculated values for k (octaBDE isomers in polystyrene); indicator lines: 1.59 (level of significance 5%); 1.88 (level of significance 1%).

Figure 18 indicates that the k values for the laboratories involved are below the indicator lines, thus there are no outliers.

5.5.1.3. Checking variances – Cochran's test (octaBDE isomers in polystyrene)

An application of Cochran's test for the laboratory variances yielded no outliers.

5.5.1.4. Checking the laboratory means – Grubbs' test (octaBDE isomers in polystyrene)

In accordance with Annex 9 the smallest (L045) and the greatest (L003) laboratory means have been tested using Grubbs' test.

The test for one outlier provided the following test values:

for Laboratory 045: T1 = 1.644

for Laboratory 003: Tn = 2.148

For 18 laboratories the following table values have been obtained from the Table for critical values of Grubbs' test for one outlier /12/:

T-crit = 2.821 (level of significance 0.01)

T-crit = 2.504 (level of significance 0.05)

In the current case the test values determined are under T-crit (0.05) thus there is no outlier.

In accordance with Annex 9 the two smallest (L045 and L021) and the two greatest (L004 and L003) laboratory means have been tested using Grubbs' test.

Grubbs' test for two outliers provided the following test values:

for Laboratory 045 and 021: G1,2 = 0.689

for Laboratory 004 and 003: Gn-1,n = 0.474

For 18 laboratories the following table values have been obtained from the Table for critical values of Grubbs' test for two outliers /12/:

G-crit = 0.353 (level of significance 0.01)

G-crit = 0.446 (level of significance 0.05)

In both current cases G is greater than G-crit (0.05) thus there is no outlier.

5.5.2. Results of octaBDE isomers in polystyrene

Table 26 summarises the results of the statistical tests.

Table 26: Summary of the results of the statistical tests for the determination of octaBDE isomers in polystyrene.

Statistical test	**See Chapter**	**Result**
Mandel's h statistic	5.5.1.1	L003 straggler
Mandel's k statistic	5.5.1.2	No outlier
Cochran's test	5.5.1.3	No outlier
Grubbs' test	5.5.1.4	No outlier

Thus the results of the determination of octaBDE isomers in polystyrene have not indicated any outliers.

0.99 ± 0.27 mg g^{-1} has been obtained for the general mean of the tested sample as a sum of octaBDE isomers in polystyrene. The relative standard deviation is 27 %.

5.6. OctaBDE isomers in ABS (IC Material B)

Table 27 and Figure 19 show the test results as a sum of octaBDE isomers in mg g^{-1} in ABS with OCTA-BDE flame retardant.

Table 27: Test results of repeat analyses as a sum of octaBDE isomers in mg g^{-1} in ABS with OCTA-BDE flame retardant.

No.	Lab code	Sample number				Mean [mg g^{-1}]	STDev [mg g^{-1}]	CV [%]
		B-XX-1	B-XX-2	B-XX-3	B-XX-4			
1	001	0.413	0.446	0.412	0.423	*0.424*	*0.016*	*3.7*
2	003	0.5	0.31	0.33	0.74	*0.470*	*0.199*	*42.4*
3	004	0.4386	0.4413	-	-	*0.440*	*0.002*	*0.4*
4	012	0.588	0.59	0.633	0.641	*0.613*	*0.028*	*4.6*
5	013	0.331	-	0.306	0.273	*0.303*	*0.029*	*9.6*
6	014	0.468	0.495	0.524	0.506	*0.498*	*0.023*	*4.7*
7	019	0.47	0.428	0.379	0.395	*0.418*	*0.040*	*9.6*
8	021	0.32	0.31	0.23	-	*0.287*	*0.049*	*17.2*
9	026	0.55	0.56	0.6	0.62	*0.583*	*0.033*	*5.7*
10	027	0.25846	0.25903	0.3046	-	*0.274*	*0.026*	*9.7*
11	030	0.29	0.31	0.31	0.28	*0.298*	*0.015*	*5.0*
12	037	0.437	0.451	0.405	-	*0.431*	*0.024*	*5.5*
13	040	0.4764	0.5122	0.499	-	*0.496*	*0.018*	*3.7*
14	041	0.401	0.414	0.414	0.396	*0.406*	*0.009*	*2.3*
15	044	0.362	0.366	0.425	0.468	*0.405*	*0.051*	*12.5*
16	045	0.2606	0.2312	0.1893	-	*0.227*	*0.036*	*15.8*
17	046	0.455	0.4549	0.435	-	*0.448*	*0.012*	*2.6*
18	Coord	0.524	0.524	0.495	0.487	*0.508*	*0.019*	*3.8*

STDev: standard deviation to laboratory mean; CV: coefficient of variation

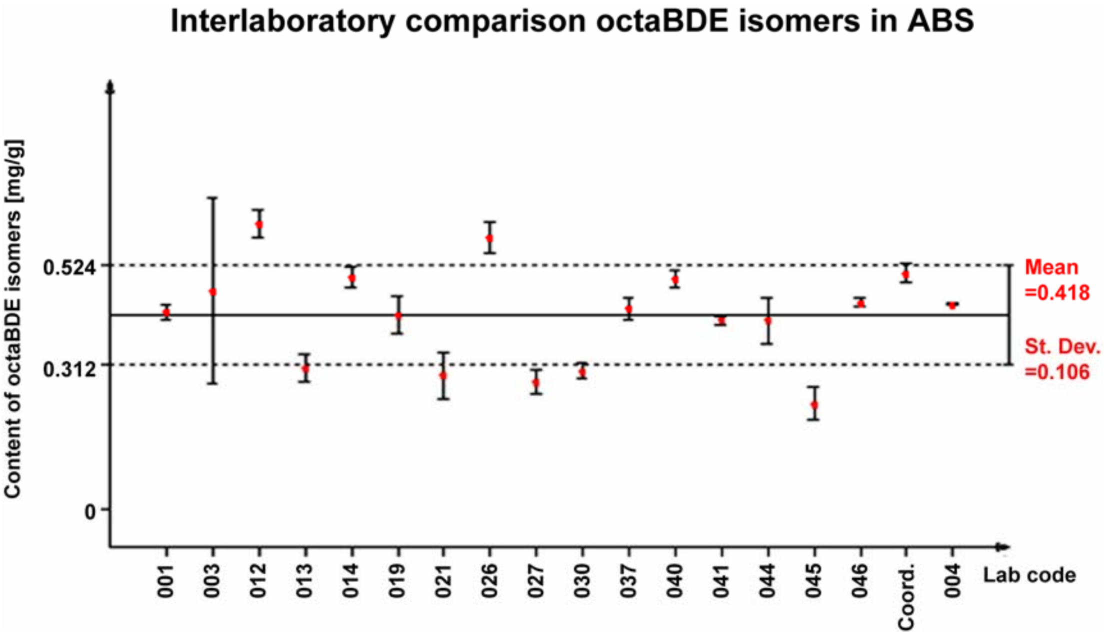

Figure 19: Graphical representation of the laboratory means as a sum of octaBDE isomers [mg g^{-1}] in ABS with OCTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 18 laboratories.

5.6.1. Statistical evaluation – octaBDE isomers in ABS

5.6.1.1. Results of Mandel's h statistic (octaBDE isomers in ABS)

Figure 20 gives a graphical illustration of the values calculated as per Annex 7 for h in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's compatibility test quantities h and k /12/) are at 2.36 (level of significance 1 %) and 1.88 (level of significance 5 %).

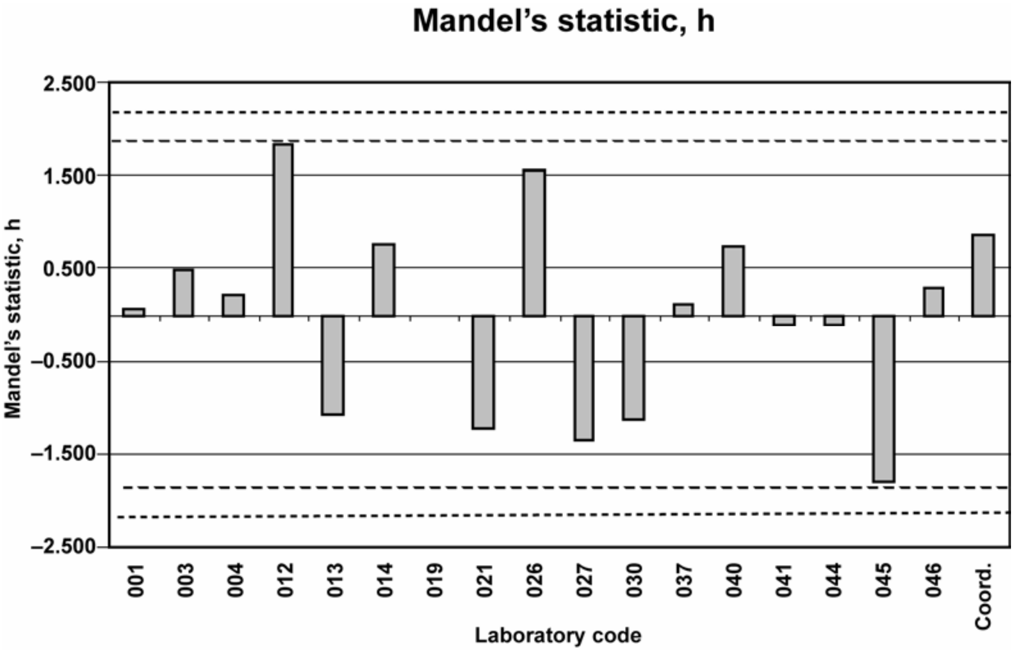

Figure 20: Calculated values for h (octaBDE isomers in ABS); indicator lines: 1.88 (level of significance 5%); 2.36 (level of significance 1%).

Figure 20 indicates that the h values for the laboratories shown are within the limits of the indicator lines. Thus there are no outliers.

5.6.1.2. Results of Mandel's k statistic (octaBDE isomers in ABS)

Figure 21 shows a graphical illustration of the values for k calculated as per Annex 7 in the order of the laboratories. The indicator lines shown (Table of indicators for Mandel's compatibility test quantities h and k /12/) are at 1.88 (level of significance 1 %) and 1.59 (level of significance 5 %).

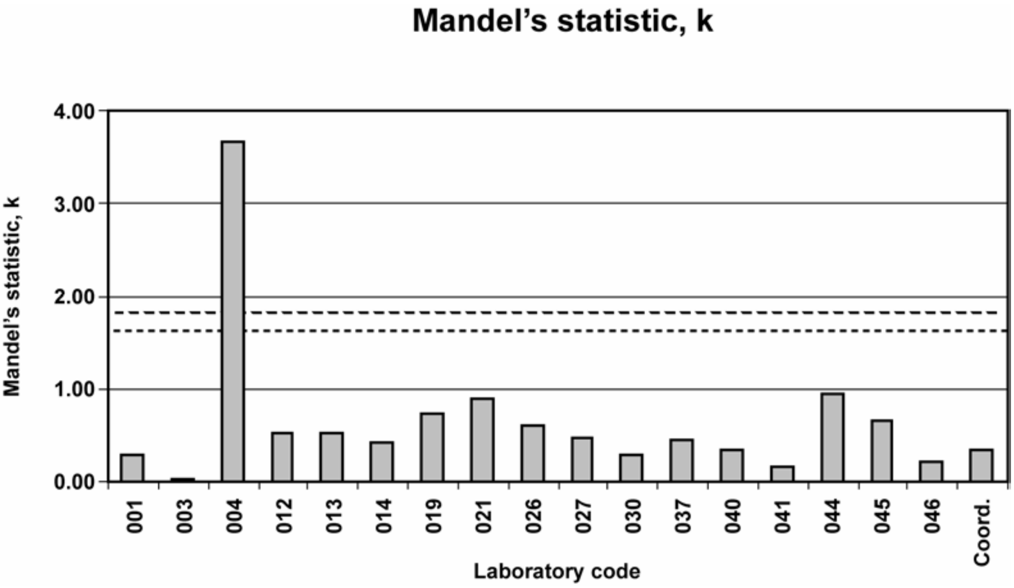

Figure 21: Calculated values for k (octaBDE isomers in ABS); indicator lines: 1.59 (level of significance 5%); 1.88 (level of significance 1%).

Figure 21 shows that the k value for Laboratory 003 is above the indicator lines. Laboratory 003 has therefore to be considered as an outlier.

5.6.1.3. Controlling variances – Cochran's test (octaBDE isomers in ABS)

In accordance with Annex 8 the test quantity C_{TV} has been calculated for the Laboratory with the highest variance (L003) which yielded the test quantity C_{TV} = 0.741 for Laboratory 003. For a maximum of four repeat analyses with a number of 18 laboratories based on the Table for critical values of Cochran's test /12/ the following table values have been obtained:

C-crit = 0.288 (level of significance 0.01)
C-crit = 0.240 (level of significance 0.05)

Since the test quantity C_{TV} obtained is above the critical value for the level of significance 0.01, Laboratory 003 must be considered as an outlier and will be expunged.

Another test of laboratory variances has provided no further outliers.

5.6.1.4. Controlling the laboratory means – Grubbs' test (octaBDE isomers in ABS)

In accordance with Annex 9 the smallest (L045) and the greatest (L003) laboratory means have been tested using Grubbs' test.

The test for one single outlier has provided the following test values:

for Laboratory 045: T1 = 1.798

for Laboratory 003: Tn = 2.831

For 18 laboratories the following table values have been obtained from the Table for critical values of Grubbs' test for one outlier /12/:

T-crit = 2.821 (level of significance 0.01)

T-crit = 2.504 (level of significance 0.05)

In the current case the test values T1 and Tn obtained are under T-crit (0.05) thus there is no outlier.

In accordance with Annex 9 the two smallest (L045 and L027) and the two greatest (L026 and L012) laboratory means have been tested using Grubbs' test.

Grubbs' test for two outliers has provided the following test values:

for Laboratory L045 and L027: G1,2 = 0.665

for Laboratory L026 and L012: Gn-1,n = 0.620

For 18 laboratories the following table values have been obtained from the Table for critical values of Grubbs' test for two outliers /12/:

G-crit = 0.353 (level of significance 0.01)

G-crit = 0.446 (level of significance 0.05)

In the current case the G values obtained are greater than G-crit (0.01) thus there is no outlier.

5.6.2. Results of octaBDE isomers in ABS

Table 28 recapitulates the results of the statistical tests.

Table 28: Summary of the results of the statistical tests for the determination of octaBDE isomers in ABS.

Statistical test	**See Chapter**	**Result**
Mandel's h statistic	5.6.1.1	No outlier
Mandel's k statistic	5.6.1.2	L003 outlier
Cochran's test	5.6.1.3	L003 outlier
Grubbs' test	5.6.1.4	No outlier

Based on these results Laboratory 003 will be expunged.

Figure 22 gives a graphical representation of the laboratory means, general means and standard deviation.

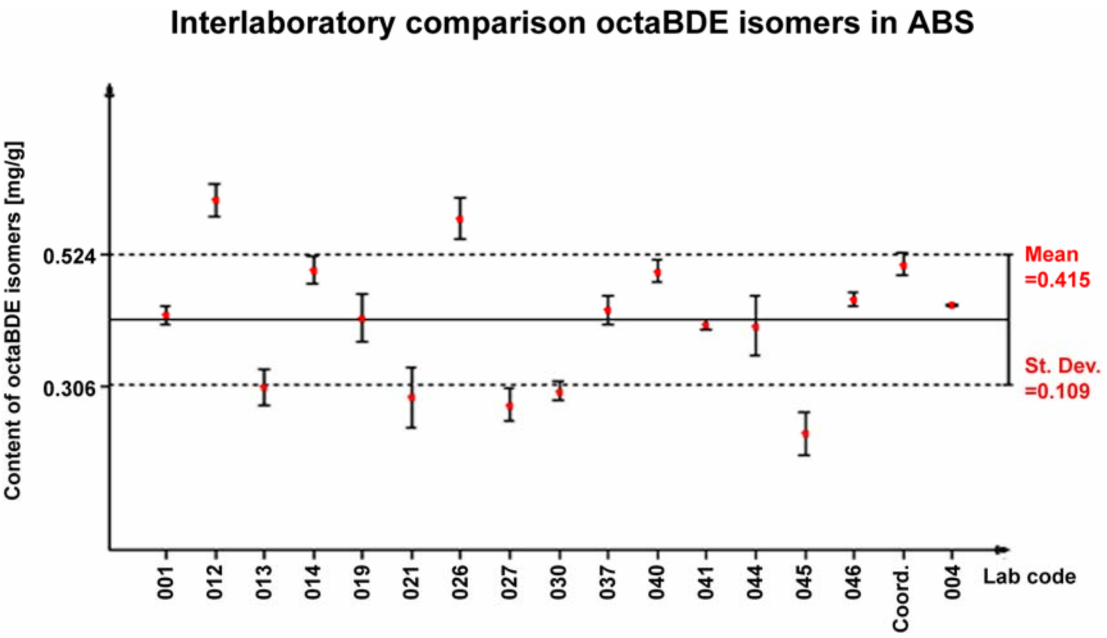

Figure 22: Graphical representation of the laboratory means as a sum of octaBDE isomers [mg g^{-1}] in ABS with OCTA-BDE flame retardant (Mean: general mean; St. Dev: standard deviation); 17 laboratories (outliers expunged).

0.415 ± 0.11 mg g^{-1} has been obtained for the general mean of the tested sample as a sum of octaBDE isomers in ABS. The relative standard deviation is 26.2 %.

5.7. Precision under repeatability and reproducibility conditions of the standard measurement method

Table 29 displays the general mean m_j, the repeatability standard deviation s_{rj} and the reproducibility standard deviation s_{Rj} of the samples tested using the standard measurement method (Annex 1) (see Chapter 3.5.2).

Table 29: Summary of the results of the interlaboratory comparison.

Polymer	**Sum isomers**	**p_j**	**m_j [mg g^{-1}]**	**s_{rj} [mg g^{-1}]**	**s_{Rj} [mg g^{-1}]**
Epoxy resin	PentaBDE	15	1.09	0.044	0.167
Polyurethane	PentaBDE	15	1.3	0.038	0.195
Polystyrene	OctaBDE	18	0.99	0.043	0.255
ABS	OctaBDE	17	0.42	0.029	0.114

p_j: number of laboratories; m_j: general mean; s_{rj}: repeatability standard deviation; s_{Rj}: reproducibility standard deviation.

5.8. Determination of PBDE in real samples using the standard measurement method

5.8.1. Mini silica gel column

In addition to the desired flame retardants, different matrix components are also extracted by the soxhlet extraction from the polymers. They may lead to a rapid contamination of the GS/MS system and an impairment of the resolutions of the peaks in the chromatogram and thus to a worsening of the detection limit.

For the separation of impurities, various chromatographic columns can be used. Since only a filtration and a separation of the polar substances are necessary, a mini silica gel column can be used (see Section 8.5).

The silica gel column may cause losses or other systematic deviations. To determine this error an analyte recovery function with the technical products PENTA- and OCTA-BDE has been determined as an example for BDE99 and BDE197 (calibration range for BDE99: 20 to 180 ng mL^{-1} and BDE197: 12 to 106 ng mL^{-1}, 5 equidistant calibration levels).

The parameters of the analyte recovery functions obtained are displayed in Table 30 (also see Section 4.4).

Table 30: Axis intercept b_f, slope a_f and residual standard deviation s_{yf} of the analyte recovery functions.

	a_f	b_f	s_{yf}
BDE99	0.9303	4.3978	13.15
BDE197	0.9515	4.4827	4.85

A test for constant or proportional systematic deviations (similar to Chapter 4.4) shows that the treatment using the mini silica gel column for the tested isomers causes no errors within the concentration range applied at a confidence level of 95 %.

5.8.2. Investigation of real samples

The analytical procedure developed was tested on various products from plastic. It was difficult to find sample material with PBDE content.

Table 31 shows a few real samples, in which pentaBDE isomers were detected using the standard measurement method (Annex 1) (industry samples, which were available in ground state).

Table 31: Results of the standard measurement method for real samples as a sum of pentaBDE isomers

Product	**Sum of pentaBDE isomers [mg g^{-1}]**
Acrylonitrile-butadiene-styrene-copolymer (ABS)	0.28
High-Impact Polystyrene (HIPS)	0.1
Polybutylene terephthalate (PBT)	0.08
Polycarbonate (PC)	0.11

The analysis of real samples indicates that it is probably necessary to perform a clean-up after sample extraction. Since the sample extracts are highly clouded or coloured, these impurities may cause rapid contamination of the GC/MS system.

Some of the sample extracts were tested without a clean-up, some following the clean-up using the mini silica gel column (Chapter 8.5, Section 5.8.1) (see Table 32).

Table 32: Results of the standard measurement method for real samples with regard to the pentaBDE isomer BDE99.

Product	**BDE99 [mg g^{-1}]** **without clean-up**	**BDE99 [mg g^{-1}]** **with clean-up**
ABS	0.130	0.105
HIPS	0.098	0.105
PBT	0.081	0.065

The turbidity and discolouring in some samples, in particular in ABS, could be removed by using the mini silica gel column.

6 Recapitulatory discussion

6.1. Results of the interlaboratory comparison

For the quality assurance of a standardised measuring method, the measurement results determined by the method must be tested for accuracy defined by trueness and precision of the method. The determination of the extent of accuracy requires relevant reference materials on whose basis the trueness of a standard measurement method can be investigated using interlaboratory comparisons. Since relevant reference materials were not available, testing of the standard measurement method "Determination of penta- and octabrominated diphenylethers in polymers" (Annex 1) was limited to the determination of the repeatability standard deviation s_{rj} and the reproducibility standard deviation s_{Rj} as statistical parameters of precision of a standardised measuring method according to DIN ISO 5725-2:2002-12 /12/.

The statistical parameters were determined by an interlaboratory comparison. Both national and international laboratories from the industry and public and private laboratories were involved in the interlaboratory test with altogether 18 participants. The preparation and execution of the interlaboratory test and the evaluation of the test results were based on /12/.

As a preparation, two polymer materials were manufactured with PENTA-BDE and OCTA-BDE flame retardants. As base polymers epoxy resin and polyurethane were selected for the analytic determination of the pentaBDE isomers and polystyrene and acrylonitrile butadiene styrene (ABS) for the determination of the octaBDE isomers. The polymers containing flame retardants were comminuted, ground and homogenized using the cross-riffling scheme /11/. The statistical testing of sample homogeneity took place applying the standard measurement method on eight systematically selected sub-samples with four or three parallel measurements. The homogeneity of the tested polymer materials is guaranteed at a significance of 99 % under the given conditions.

In agreement with the Directive 2003/11/EC, the sum of pentaBDE isomers and octaBDE isomers were determined /15/. The following isomers were selected as target substances: 2,2',4,4',6-pentaBDE (BDE100), 2,2',4,4',5-pentaBDE (BDE99), 2,2',3,4,4'-pentaBDE (BDE85), 2,2',3,4,4',5,5',6-octaBDE (BDE203), 2,2',3,3',4,4',5,6'-octaBDE (BDE196), 2,2',3,3',4,4',6,6'-octaBDE (BDE197).

The evaluation of the test results of the interlaboratory comparison took place based on /12/ by means of graphical outlier tests (Mandel’s h statistic: testing the laboratory average values; Mandel’s k statistic: testing the standard deviation of the test results on a characteristic level) and numeric outliers tests (Grubbs' test: testing the laboratory average values; Cochran's test: testing the laboratory variances).

An analysis of PENTA-BDE in ABS on a voluntarily basis with 11 participants prior to the interlaboratory test provided 0.90 ± 0.134 mg g^{-1} for the general mean of the sum of pentaBDE isomers. This preliminary test was meant to help the participants gain practice in the standard measurement method and discover gross errors in the guidelines and test execution. The evaluation of the test results using Grubbs' and Cochran's tests has not shown any outliers of the laboratory average values and laboratory variances. Based on these results the standard measurement method was released for the interlaboratory comparison.

The results of the interlaboratory comparison will be discussed below.

Based on the outlier tests performed for the epoxy resin polymer with PENTA-BDE flame retardant, the test results of laboratories 003, 045 and 046 were expunged. Laboratory 003 exceeded the limiting indicator lines both in terms of Mandel’s h statistic (extreme deviation from the general mean) and Mandel’s k statistic (high or low standard deviation of the test results from a characteristic level). The numerical outlier test using Grubbs' test and Cochran's test confirmed this result. Laboratory 045 dropped out in Mandel’s h statistic as a straggler and in Grubbs' test as an outlier. Laboratory 046 showed strong dispersion of the test results and was identified as an outlier by Cochran's test.

After expunging the outliers, 1.09 ± 0.163 mg g^{-1} was obtained for the general mean of the sum pentaBDE isomers in epoxy resin.

The test results of the polyurethane polymer with PENTA-BDE flame retardant were tested for outliers. Laboratory 003 was clearly identified as an outlier with the help of Mandel's k statistic and Cochran's test. Mandel's h statistic and Grubbs' test proved Laboratory 045 to be an outlier. Laboratory 045 and laboratory 046 showed large dispersions of the test results and were identified as outliers by Cochran's test. After expunging the outliers, 1.30 ± 0.19 mg $g^{–1}$ was obtained for the general mean for the sum PentaBDE isomers in polyurethane.

The Grubbs and Cochran test on the results for polystyrene with OCTA-BDE flame retardant has not indicated any outliers. The general mean for the sum of octaBDE isomers in polystyrene was found to be 0.99±0.270 mg g^{-1}.

For the ABS polymer with OCTA-BDE flame retardant the test results of Laboratory 003 were expunged as a result of the outlier tests. Both Mandel's k statistic and Cochran's test has proved Laboratory 003 an outlier. After expunging the outliers, 0.42 ± 0.110 mg g^{-1} was obtained for the general mean for the sum of octaBDE isomers in ABS. It could not be clarified why the sum of octaBDE isomers in ABS did not correspond to the expected approx. 1 mg g^{-1}. An error during mixing (see Section 3.5.2) cannot be excluded.

The laboratories whose results were identified as outliers, were requested to check and, if necessary, correct their test results within a set period. Laboratory 003 showed a strong dispersion of the test results for the epoxy resin, ABS and polyurethane samples. After consultation with the responsible person in the laboratory, the cause of the instability of the GC/MS system was found: the repeated injection of samples provided results with a large dispersion. This measurement error could not be eliminated during the period of the execution of the interlaboratory comparison.

Laboratory 045 showed outliers for the sum of pentaBDE isomers in epoxy resin and polyurethane. After consultation with the responsible person for the laboratory, the high temperature in the laboratory (> 28°C) during the extraction of the polymer samples and a lack of temperature control in the heating system of the soxhlet apparatus were identified as potential causes.

Cochran's test indicated outliers for Laboratory 046 for the sum of pentaBDE in polyurethane and epoxy resin. The cause could not be clarified by the responsible person for the laboratory.

6.2. Participants comments and remarks concerning the standard measurement method

The participants of the interlaboratory comparison were asked to report on their experience and possible difficulties during the execution of the analyses. The intention was to record whether the standard analysis guidelines have a clear structure and contain clear, understandable instructions. The table in Annex 10 gives an overview of the data to be recorded with extracts. In the following, the comments and remarks made by the participants on the standard measurement method will be discussed.

The recommended addition of 1 mL of methanol to the sample extract in order to dissolve the potential turbidity observed in ABS in particular did not lead to the desired result in every case. However, turbidity did not impair the results of the analysis.

It was reported that in one case there was no correlation between the standard substance DBOFB specified in the guidelines to control the analyte recovery rate and the PBDE. DBOFB is specified in the standard measurement method to control the analyte recovery rate so that gross errors during sample preparation can be detected. A correction of the analyte recovery rate does not take place since it is assumed that DBOFB added before the extraction does not behave in a similar way to PBDEs directly available in the polymer in an additive form so a correction may result in a larger analytical error. Since the laboratory making this comment was expunged as an outlier, the lack of correlation between DBOFB and PBDEs could also be due to the dispersion of the test results.

The procurement of the DBOFB standard was difficult in some cases and led to time delays. In such cases another suitable standard substance can generally be used as an alternative Thus, for instance, decachlorobiphenyl, which is specified in the standard measurement method as a standard for the correction for injection error, can be used instead of DBOFB to control the analyte recovery rate. In this case a new standard must be selected for the correction for the injection error (e.g. $^{13}C_{12}$-3,3',4,4'-tetrabromodiphenylether).

The remark was made by one of the participants that the volumetric flasks used for the execution of the analyses were not annealed at 450°C as specified for calibration reasons in the standard measurement method to achieve decontamination. When PBDE blank values occur, it is generally recommended to anneal the volumetric flasks and other glass devices at the specified temperature of 450 °C and to calculate the PBDE concentration in the solutions through the weighed portion and density of toluene.

Isolated problems arose in the analysis of the selected octaBDE isomers: unsatisfactory resolution and tailing of the peaks in the chromatogram were reported under actual conditions. In particular the lowest concentration in the calibration range of 50 to 500 ng mL^{-1} specified in the standard measurement method could only be poorly evaluated in certain cases since the peaks were very small and were below or close of the detection limit with regard to the signal-noise ratio.

Reducing the extract volume of the samples from 100 mL to 50 mL to ensure adequate analysis of the octaBDE isomers has also been suggested. The decision must be taken in each individual case, depending on the GC/MS configuration (type of injector, type of column) which leads to different results depending upon manufacturer and thus has an influence on the analytical sensitivity of the method. Intensified matrix problems may be an issue due to the decreased extract volume at the same weighed portion. Also, the increase of the weighed portion, as recommended in one case, might lead to an increase of matrix problems whose prerequisite is relevant sample cleaning to achieve the analytical quality. In particular real samples may clearly exhibit a higher load due to further additives compared to the polymer samples tested in the interlaboratory comparison.

A comparison of the chromatograms of the smallest measured calibration solution indicates only a moderate peak resolution and superposition of the peaks of the octaBDE isomers for the majority of the participants. The calibration range used by the participants deviates from that of the standard measurement method and varies widely (the smallest selected concentration is between 0.2 ng mL^{-1} and 550 ng mL^{-1} quantified by technical PENTA-BDE). A remedy could be obtained by resorting to a longer GC column and/or a further optimisation of the temperature programme of the gas chromatograph and the injector. Evaluation of the participants' calibrations, attached in copy, also indicated an increasing quadratic trend for the octaBDE isomers in particular. Since the comment was made that the selection of the injector type and its optimisation has a substantial influence on the resolution and separation and thus on the peak height of the isomers, selection of the optimum conditions by testing different available injectors is recommended. In particular PTV systems require such an optimisation. An on-column feed system or a split/splitless injection system possibly gives better results when peak resolution is insufficient. This must be decided by the analyst on a case-by-case basis.

The quantification of the octaBDE isomers by calibration using a technical product (Laboratory 021) gave comparable results to quantifications with single substances. Four participants quantified the sum of the three selected octaBDE isomers over one or two existing individual octaBDE standards (Laboratories 004, 012, 045, 046). One of the participants quantified the target analyte by response factors using a standard marked by $^{13}C_{12}$ isotopes (Laboratory 026). A control of the test results shows relatively strong deviations to the general mean for these laboratories for the octaBDE sample in polystyrene in particular compared to the remaining laboratory average values.

In principle, to do the quantification by calibration with single standards is recommended since the quantification presupposes the knowledge of the accurate percentage composition of the technical product (e.g. previous quantification of the technical product with individual PBDEs). Also, a broader concentration range than specified in the standard measurement method (Annex 1) must be selected as a calibration range in order to include the analyte contents of all isomers that are present in clearly different contents in the technical products.

In addition, it was pointed out that the determination of blank values in the quantification of PBDEs in samples is not taken into account in the standard measurement method. The standard measurement method (Annex 1) was provided with a relevant instruction.

Reducing the number of calibration standards (ten) in order to increase the efficiency was suggested by one of the participants. Generally, the decision about the selected number of calibration points to guarantee the quality assurance of the analytical results is within the discretion of the responsible person of the laboratory. For the evaluation of the analytical results, the number of calibration points was already reduced by certain participants within the interlaboratory comparison. To what extent this decrease or the different number of calibration points among the participants influences the quality of the test results and thus the overall result of the interlaboratory comparison, remains open.

Furthermore, one of the participants has recommended adding to the standard measurement method that the individual isomers should be evaluated over retention times and SIM masses to be selected for the individual target substances prior to the interlaboratory comparison.

6.3. Result and evaluation of the standard measurement method

Altogether the results show that the developed standard measurement method supplies precise test results in particular for the quantitative analysis in the range of the limiting value 0.1 % by mass for the sum of pentaBDE isomers and octaBDE isomers [1 mg g^{-1}] under the specified conditions. The standard deviation under repeatability conditions s_{rj} results in a value of 0.044 mg g^{-1} for the sum of pentaBDE isomers related to the general mean of 1.09 mg g^{-1} of the epoxy resin sample and 0.038 mg g^{-1} related to the general mean of 1.3 mg g^{-1} of the polyurethane sample. The analysis of the sum of octaBDE isomers has provided 0.043 mg g^{-1} for the repeatability standard deviation for polystyrene related to the general mean of 0.99 mg g^{-1} and 0.029 mg g^{-1} for ABS related to the general mean of 0.42 mg g^{-1}. A comparison of the repeatability standard deviation shows a good agreement under the given conditions, i.e. the standard measurement method provides reproducible analytical results under repeatability conditions irrespective of the polymer types tested here.

0.167 mg g^{-1} was obtained for the determined reproducibility standard deviation s_{Rj} for the sum of pentaBDE isomers in the epoxy resin polymer related to the general mean of 1.09 mg g^{-1}. 0.195 mg g^{-1} was obtained for s_{Rj} for polyurethane for the sum of pentaBDE isomers related to the general mean of 1.3 mg g^{-1}. s_{Rj} was 0.255 mg g^{-1} for polystyrene related to the general mean of 0.99 mg g^{-1}. For ABS the sum of octaBDE isomers was 0.114 mg g^{-1} for s_{Rj} related to the general mean of 0.042 mg g^{-1}. The polymers tested under the given conditions provided comparable values for s_{Rj} also here.

A comparison of the values for s_{rj} and s_{Rj} shows that the standard measurement method provides a value for the standard deviation under reproducibility conditions s_{Rj} by a factor 4 to 6 higher than for the standard deviation under repeatability conditions s_{rj}. The larger dispersion of the analytical results under reproducibility conditions can have different causes, such as the influence of differently configured GC/MS systems of the participants or the influence of different analysts on the analytical results etc.

The investigation of matrix influences on the standard measurement method using the analyte recovery function in Section 4.4 shows that there is no constant-systematic deviation for the selected PBDEs at a level of significance of 95 %. The investigation of proportional-systematic deviations exhibits a small proportional-systematic deviation for three of the four tested PBDEs at a confidence level of 95 %. There is no deviation for BDE99 and BDE197 at a confidence level of 99 %. However, it is only at a confidence level of 99.9 % where BDE203 does not exhibit any deviation. Proportional-systematic deviations lead to a change in the slope of the matrix calibration straight lines. These deviations from the true value may be due to individual process steps or matrix effects. In particular the strong deviation observed for BDE203 might be caused by inaccurate quantification using technical OCTA-BDE since only a small amount of BDE203 is present in the technical OCTA-BDE. The use of the technical PENTA-BDE and OCTA-BDE respectively for the determination of the analyte recovery function was necessary since large weighed portions had to be used. For an exclusively proportional-systematic deviation, the analyte recovery rate can be specified. It can be calculated from the slope of the analyte recovery calibration straight lines and is 131 % for BDE203. For further validation of the analytical results the procedure of the standard addition can be used when proportional-systematic deviations are there /9/.

The results of the interlaboratory comparison indicate that the extraction time of 2 hours using a soxhlet and toluene as solvents, as specified in the instructions of the standard measurement method, proved to be sufficient for the quantitative determination of octaBDE and pentaBDE isomers. Individual participants, e.g. Laboratory 030, had used longer extraction times of up to 10 hours in contrast to the specified instructions. The determined contents failed to exhibit any significant or recognizable difference compared to other test results.

The predominant majority of the participants worked as specified with 20 to 30 extraction cycles. In certain cases a larger number, up to 100 cycles, were used due to slightly varying extraction times.

The weighed portion of the sample material to be tested is specified as 0.1 g by the instruction of the standard measurement method. This instruction was adhered to by the participants with a few exceptions (the originally weighed portion varied depending upon polymer between 0.06 and 0.2 g). Laboratory 037 used 0.01 g as a weighed portion and worked with a nominal volume of the sample extract of 10 mL, in contrast to 100 mL specified in the standard analytical instruction.

Laboratory 019 indicated a volume deviation of 0.3 % for the measuring flasks and therefore corrected the weighed portion of the sample extract not against the density of toluene as specified, but recorded the measured solvent volume with the measuring flask. Laboratory 021 used 50 mL as the nominal volume of the sample extract not 100 mL as specified. However these laboratories did not show any significant difference for the determined contents compared to other laboratories.

Based on these results it is recommended to adhere to the specified extraction time of a minimum 2 hours. The volume of the solvent (toluene in this case) can be reduced, if necessary, to 50 mL as previously discussed. However, as already mentioned, an increased impurity by the increasing sample concentration must be considered.

A weighed portion of < 0.1 g can only conditionally be recommended since apart from the increased weighed portion error, small weighed portions increase the influence of inhomogeneities of the tested sample material on the analytical result.

To increase the sensitivity of the standard measurement method several participants used increased injection volumes > 1 µL. In particular the quantification of octaBDE isomers, which was considered difficult by the participants, can be improved. In this instance the responsible person of the laboratory must decide in individual cases whether the detection sensitivity can be regarded as sufficient. The increase of the injection volume can again lead to an increase of matrix influences.

For characterisation and comparison of the results z-scores were calculated. They show the deviation of the laboratory average value from the general mean as a multiple of the standard deviation. A z-score of 1 means that the result is at a distant of 1 × s_{Rj} from the general mean.

Table 33 illustrates the z-scores calculated as

$$z-score=\frac{x_i-\overline{x}}{s_{Ri}}$$

with

x_i: laboratory mean [mg g^{-1}]
$\overline{x}$: general mean [mg g^{-1}]
$s_{Rj:}$ reproducibility standard deviation [mg g^{-1}] .

The results indicate that Laboratory 003 supplies an increased value for z (between 2 and 3) (sum octaBDE isomers in polystyrene) compared to the other laboratories. Laboratory 013 also shows a value greater than 2 for z (sum of pentaBDE isomers in PUR). These results exceed s_{Rj} by a factor 2 and are thus to be regarded as questionable. All remaining laboratories supplied satisfactory results for z.

Table 33: Calculated z-scores of the participants of the interlaboratory comparison.

	z-score[1]			
Laboratory	**OctaBDE in ABS**	**OctaBDE in polystyrene**	**PentaBDE in PUR**	**PentaBDE in epoxy resin**
001	0.08	-0.15	-1.19	-1.07
003	*	2.28	*	*
012	1.74	1.36	0.77	0.46
013	-0.98	-0.61	-2.21	-0.75
014	0.73	-0.31	0.51	0.13
019	0.03	0.25	0.72	0.39
021	-1.12	-1.50	-0.81	-0.49
026	1.47	-0.62	0.07	0.05
027	-1.24	0.03	0.35	0.22
030	-1.03	-1.11	1.81	0.39
037	0.14	0.04	-0.62	-0.64
040	0.71	-0.34	0.11	0.50
041	-0.08	-0.53	-0.41	-0.05
044	-0.09	0.02	0.35	0.08
045	-1.65	-1.74	*	*
046	0.29	0.44	*	*
Coord	0.82	0.55	1.02	0.10
004	0.22	1.94	-0.50	0.04

[1] $|z| < 2$ = satisfactory analysis; $2 < |z| < 3$ = result/analysis is questionable; $|z| > 3$ = non-satisfactory result; *expunged outliers

6.4. Comparison of the results of the standard measurement method and the results of the laboratory methods

The possibility was given optionally to the participants of the interlaboratory comparison to use the internal laboratory method to determine the contents of the sum of pentaBDE isomers and octaBDE isomers in addition to the prescribed standard measurement method. Table 34 summarises the results of four laboratory methods.

Table 34: Test results of the voluntary analyses performed using laboratory methods.

Laboratory	Method	Sum octaBDE-isomers [mg g^{-1}] in		Sum pentaBDE-Isomers [mg g^{-1}] in	
		ABS	Polystyrene	PUR	Epoxy resin
L012	Microwave, 50 mL acetone/toluene, 10 min at 90°C, GC-ECD	0.43	0.69	1.58	1.19
L014	Vial extraction, static, 5 - 20 mL toluene, 2 h	0.48	1.06	1.13	1.15
L021	Ultrasonic, 5 mL toluene, 2h	0.25	0.61	1.21	1.03
L044	ASE[1] , 30 - 35 mL toluene, 10 - 15 min	0.22	0.36	1.44	1.19
General mean of the interlaboratory comparison m_j		0.42	0.99	1.3	1.09
Reproducibility standard deviation s_{Rj}		0.114	0.255	0.195	0.167

[1]Accelerated solvent extraction;

Table 35 displays the z-scores of the results of the laboratory methods calculated as $\frac{x_i - \overline{x}}{s_{Rj}}$.

Table 35: Calculated z-scores of the results of the laboratory methods.

	z-score*			
Laboratory	OctaBDE in ABS	OctaBDE in polystyrene	PentaBDE in PUR	PentaBDE in epoxy resin
L012	0.09	-1.18	1.44	0.60
L014	0.53	0.27	-0.87	0.36
L021	-1.49	-1.49	-0.46	-0.36
L044	-1.75	-2.4	0.72	0.60

* $|z| < 2$ = satisfactory; $2 < |z| < 3$ = result is questionable; $|z| > 3$ = non-satisfactory

Using the respective analytical methods, Laboratory 012 and Laboratory 014 provided z-scores $|z| < 2$ and thus can be regarded as satisfactory.

Laboratory 021 shows increased z-scores in particular for the sum of octaBDE isomers, the values are however below 2. Laboratory 044 supplied a z-score of –2.4 for the sum of octaBDE isomers in polystyrene. Here the result has to be regarded as questionable. In particular the results for the sum of octaBDE isomers show higher z-scores compared to the results for the sum of pentaBDE isomers.

In the evaluation of the laboratory methods it must be considered that these are individual test results. These data do not provide any information about the precision of the applied laboratory methods since the method should be tested in an interlaboratory comparison in order to determine the precision.

6.5. Result discussion for real samples

The standard measurement method has been tested on real samples with unknown contents of octaBDE and pentaBDE isomers. The tested samples, in which the technical PENTA-BDE was proven, showed discolouration of the sample extracts and light turbidity in the case of the ABS material. Turbidity and discolouration could be removed by a clean-up of the sample extracts using a mini silica gel column (see Section 8.5).

As an example the analysis of the selected BDE99 pentaBDE isomer using GC/MS indicated that turbidity and discolouration did not have any effect on the quantitative result of the isomer. Depending on the sample matrix, which can vary widely, it must be decided whether a clean up using a mini silica gel column must be used.

6.6. Final discussion

Based on the overall results, the developed standard measurement method is considered suitable to control the specified threshold value of 0.1 % by mass for the sum of pentaBDE isomers or octaBDE isomers [1 mg g^{-1}] in polymers taking into account the measurement uncertainty which is defined by the repeatability standard deviation s_{rj} and the reproducibility standard deviation s_{Rj}.

The influence of the matrix of the materials to be tested must be considered under real conditions since the statistical parameters s_{Rj} and s_{rj} of the standard measurement method have been determined based on specified model polymers. In certain cases the application of the standard measurement method to real samples requires additional sample clean-up.

To check the accuracy of the method and to determine the measurement uncertainty (repeatability and reproducibility standard deviation) further interlaboratory comparisons should be carried out when testing real samples.

In this case the testing would be recommended on not only one but several characteristic levels.

7 Summary

Within the framework of the research project a standard measurement method was developed to determine penta- and octabrominated diphenylethers in polymers. This serves the control of the threshold value of 0.1 % by mass required by the Directive 2003/11/EC for the sum of pentaBDE or octaBDE isomers in products /15/.

The sample preparation was performed by soxhlet extraction using toluene as an extraction agent. Identification and quantitative determination of the components took place with the help of the gas chromatography and mass spectrometry (GC/MS). The analysis of PBDEs was made in the single ion monitoring (SIM) mode using three characteristic ion traces per isomer.
The selection of penta- and octabrominated diphenylether isomers to be tested was made by taking into account the composition of the PENTA and OCTA-BDE technical products and the commercially available standards: 2,2',4,4',6-pentaBDE (BDE100), 2,2',4,4',5-pentaBDE (BDE99), 2,2',3,4,4'-pentaBDE (BDE85), 2,2',3,4,4',5,5',6-octaBDE (BDE203), 2,2',3,3',4,4',5,6'-octaBDE (BDE196) and 2,2',3,3',4,4',6,6'-octaBDE (BDE197). Decachlorobiphenyl (CB209) and dibromo octafluorobiphenyl (DBOFB) were used as internal standards.

For the purposes of quality assurance and method validation of the analytical method, various statistical parameters were determined. To determine the repeatability and reproducibility standard deviation an international interlaboratory comparison was carried out with 18 participants based on DIN ISO 5725-2 /12/.
The interlaboratory comparison was performed using specified model polymers and provided the results summarized in Table 36.

Table 36: Results of the interlaboratory comparison.

Polymer	**Sum isomers**	**p_j**	**m_j [mg g^{-1}]**	**s_{rj} [mg g^{-1}]**	**s_{Rj} [mg g^{-1}]**
Epoxy resin	PentaBDE	15	1.09	0.044	0.167
Polyurethane	PentaBDE	15	1.3	0.038	0.195
Polystyrene	OctaBDE	18	0.99	0.043	0.255
ABS	OctaBDE	17	0.42	0.029	0.114

p_j: number of laboratories; m_j: general mean; s_{rj}: repeatability standard deviation; s_{Rj}: reproducibility standard deviation;

Problems arose in certain cases in the analysis of octaBDE isomers: unsatisfactory resolution of the peaks and tailing of the peaks in the chromatogram. In particular the lowest concentration (50 ng mL^{-1}) either could not or were only poorly evaluated since the peaks were very small and in certain cases, below or close to the detection limit with regard to the signal-to-noise ratio.

Relying on DIN 32 645, for BDE99 as an example, 0.02 mg g^{-1} was determined as the detection limit and 0.06 mg g^{-1} for the limit of quantitation. For BDE197 used as an example for octaBDE isomers, the detection limit was 0.04 mg g^{-1} and the determination limit 0.12 mg g^{-1}.

The standard measurement method developed was additionally tested on some real samples. A clean-up was necessary in certain cases due to the higher matrix load by other additives. A mini silica gel column proved to be useful and sufficient.

Altogether the test results show that the standard measurement method developed is suitable to control the specified threshold value of 0.1 % by mass [1 mg g^{-1}] for the sum of pentaBDE isomers or octaBDE isomers in polymers taking into account the measurement uncertainty which is defined by the repeatability standard deviation s_{rj} and the reproducibility standard deviation s_{Rj}. The influence of the matrix of the materials to be tested must be considered under real conditions since the statistical parameters s_{Rj} and s_{rj} of the standard measurement method have been determined based on specified model polymers. In certain cases the application of the standard measurement method to real samples requires additional sample clean-up.

8 Chemicals and methods used

8.1. Chemicals and devices

Substance	Manufacturer/marketing
Toluene, Suprasolv, for org. trace analysis	Merck
2,2',3,4,4'-pentaBDE (BDE85) 50 µg/mL in n-nonane	CIL/Promochem
2,2',4,4',5-pentaBDE (BDE99) 50 µg/mL in n-nonane	CIL/Promochem
2,2',4,4',6-pentaBDE (BDE100) 50 µg/mL in n-nonane	CIL/Promochem
2,2',3,3',4,4',5,6'-octaBDE (BDE196) 50 µg/mL in n-nonane	Wellington/Campro Scientific
2,2',3,3',4,4',6,6'-octaBDE (BDE197) 50 µg/mL in n-nonane	Wellington/Campro Scientific
2,2',3,4,4',5,5'6-octaBDE (BDE203) 50 µg/mL in n-nonane	Wellington/Campro Scientific
Techn. pentabromo diphenylether (PENTA-BDE) DE-71	Great Lakes Chemical Corporation
Techn. octabromo diphenylether (OCTA-BDE) DE-79	Great Lakes Chemical Corporation
Decachloro biphenyl (CB209)	CIL/Promochem
4,4'-dibromo octafluoro biphenyl	Sigma-Aldrich
Acrylonitrile-butadiene-styrene-copolymer (with 0.97 % DE-71)	Grafe Color Batch GmbH
Acrylonitrile-butadiene-styrene-copolymer (with 2.95 % DE-79)	Grafe Color Batch GmbH
Polystyrene (with 2.96 % DE-7-9)	Grafe Color Batch GmbH
Polyurethane hard foam sample (with 1 % DE-71)	Rühl Puromer GmbH

Substance	Manufacturer/marketing
Viscacid epoxy building resin	Remmers
Extractions thimbles (cellulose, 30 mL, ID 22 mm, height 80 mm)	Schleicher & Schuell MicroScience
Glass wool, extra fine	Hecht/Th. Geyer
Raschig rings, soda-lime glass	Hilgenberg/Th.Geyer
Heating bonnet (HRS 100 mL, 150 W)	Horst GmbH
Minishaker MS 2	IKA
Analytical balance LA 230 S, d = 0.1 mg	Sartorius
GC Series 6890	Agilent
Kodiak 1200	Bear Instruments
(Mass range 10 – 1500 amu)	

8.2. Preparation of epoxy resin (see Annex 4)

20.2 g of Great Lakes DE-71 are thoroughly stirred into component A under light heating (30 °C). After complete dissolution of the FR in component A (no more schlieren images visible), component B is added, thoroughly stirred again and the polymer is poured in a thin layer onto a polystyrene foil. After cooling, the polymer can be cut into pieces and kept in a glass container.

8.3. Pulverisation of the polymers

PUR H and EP must first be cut up by hand with the help of a pair of scissors or pliers to a maximum size of 1 cm^2. The other polymers (ABS and PS) have already been supplied as granules.

After being embrittled by liquid nitrogen, the polymers are pulverised and homogenized in a centrifugal mill (Retsch ZM 1000, see Figure 23) through a filter inset of 0.5 mm. In order to avoid contamination between the individual grinding processes, the mill is thoroughly cleaned and "rinsed" with approx. 100 g of polymer before each grinding.

The ground polymers are dried in crystallising shells in the drying oven at 22 °C up to mass constancy to remove potential condensation moisture.

Figure 23: Centrifugal mill, Retsch ZM 1000.

8.4. Statistical homogenisation (cross-riffling) of polymer materials

The ground polymers were mixed in an overhead shaker before the application of the method for about 12 h. For "cross-riffling" /11/ first a sample divider with 10 portions, then a sample divider with eight portions were used (Retsch DR 100 and Fritsch Laborette 27, see Figure 24).

Figure 24: Sample divider with eight portions (Retsch DR 100, left) and sample divider with ten portions (Fritsch Laborette 27, right).

8.5. Mini silica gel column

The mini silica gel column has been manufactured by us using a Pasteur's pipette (see schematic illustration in Figure 25). Siloxane-free glass wool serves to seal the syringe and prevent the silica gel from floating.

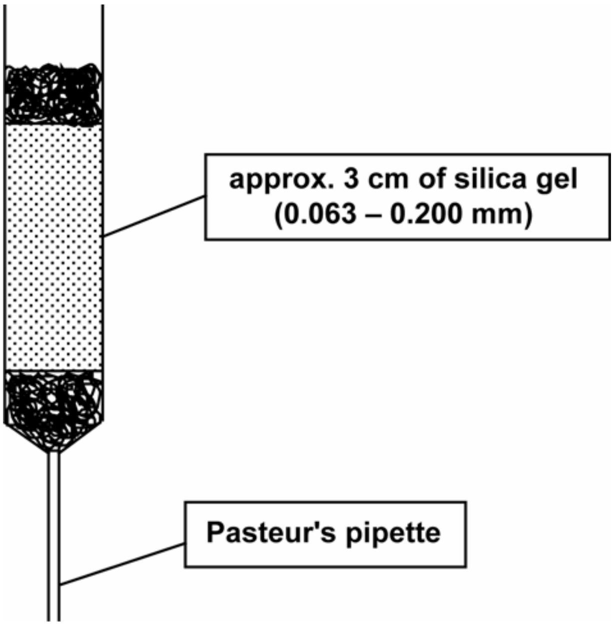

Figure 25: Schematic illustration of a mini silica gel column.

10 mL of the polymer extract is removed. The extract is placed on the dry silica gel column and the first 1 to 2 mL of filtrate is rejected. The filtrate is collected in a vial, mixed with the internal standard as per Section 1.5.5 in Annex 1 and measured using GC/MS.

For security reasons a blank value is taken using toluene.

9 Literature

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14. Kemmlein, S. Polybromierte Flammschutzmittel: Entwicklung eines Analyseverfahrens und Untersuchung und Bewertung der Belastungssituation ausgewählter Umweltkompartimente. (Polybrominated flame retardants: a new analytical method and investigation and evaluation of contamination of selected environmental compartments.) Thesis, Technische Universität Berlin, ISBN 3-89820-128-7, 2000

15. Richtlinie 2003/11/EG des Europäischen Parlaments und des Rates vom 06.02.2003 zur Änderung der Richtlinie 76/769/EWG des Rates über Beschränkungen des Inverkehrbringens und der Verwendung gewisser gefährlicher Stoffe und Zubereitungen (Pentabromdiphenylether, Octabromdiphenylether), [Directive 2003/11/EC of the European Parliament and Council of 06.02.2003 as an amendment of Directive 76/769/ECC of the Council on the restriction of marketing and use of certain hazardous materials and preparations (octabromo diphenylether, pentabromo diphenylether)] Amtsblatt der Europäischen Union vom 15.02.2003, L 042, 45 – 46

16. Verordnung über Verbote und Beschränkungen des Inverkehrbringens gefährlicher Stoffe, Zubereitungen und Erzeugnisse nach dem Chemikaliengesetz (Chemikalienverbotsverordnung) vom 14.10.1993 (BGBl. I S 1720), zuletzt geändert durch Artikel 1 der Verordnung vom 23.12.2004 (BGBl. I S 3855). [Ordinance on prohibition and restriction of marketing of hazardous materials, preparations and products in accordance with the Chemicals Act (Chemicals Prohibition Ordinance)

of 14.10.1993 (BGBl. I S 1720), last amended by Article 1 of the Ordinance of 23.12.2004 (BGBl. I S 3855)]

17. Verordnung zum Schutz vor Gefahrstoffen (Gefahrstoffverordnung), vom 23.12.2004 (BGBl. I S 3758), geändert durch Artikel 2 der Verordnung vom 23.12.2004 (BGBl. I S 3855). [Ordinance on Protection from Hazardous Materials (Hazardous Materials Ordinance), of 23.12.2004 (BGBl. I S 3758), amended by Article 2 of the Ordinance of 23.12.2004 (BGBl. I S 3855)].

Annex 1 Standard measurement method

Federal Institute for Materials Research and Testing,
IV.2 Emissions from materials

STANDARD MEASUREMENT METHOD FOR THE DETERMINATION OF PENTABROMINATED AND OCTABROMINATED DIPHENYLETHERS IN POLYMERS

1 Abstract

This method describes an analytical method for the determination of selected pentabrominated diphenylethers (pentaBDE isomers) and octabrominated diphenylethers (octaBDE isomers) in polymers. The sum of pentaBDE isomers and the sum of octaBDE isomers are determined using soxhlet extraction of the polymers with separation by gas chromatography and mass spectrometric detection (GC/MS) qualitatively and quantitatively.

2 Chemicals and standards

All chemicals must be tested for contamination and blank values prior to application.

- Toluene, pro analysis
- Standard substances

BDE85 (2,2’,3,4,4’-pentaBDE)	50 µg/ml in organic solvent
BDE99 (2,2’,4,4’,5-pentaBDE)	50 µg/ml in organic solvent
BDE100 (2,2’,4,4’,6-pentaBDE)	50 µg/ml in organic solvent
BDE203 (2,2’,3,4,4’,5,5’,6-octaBDE)	50 µg/ml in organic solvent
BDE196 (2,2’,3,3’,4,4’,5,6’-octaBDE)	50 µg/ml in organic solvent
BDE197 (2,2’,3,3’,4,4’,6,6’-octaBDE)	50 µg/ml in organic solvent
CB209 (2,2’,3,3’,4,4’,5,5’,6,6’-decachlorobiphenyl)	
DBOFB (4,4’-dibromoctafluorobiphenyl)	

3 Devices and auxiliary materials

- Analytical balance, accuracy 0.1 mg
- 1 ml, 5ml, 10 ml, 100 ml measuring flask
- <u>Soxhlet extractors</u>
  - 30 ml soxhlet extractors,
  - 100 ml round-bottomed flask,
  - Ground-in stopper NS 29/32,
  - Dimroth condenser NS 29/32,
  - Boiling stones (e.g. glass pearls or Raschig rings);
- Extraction thimble (cellulose, 30 ml, ID 22 mm, height 80 mm)
- Glass wool

- Heating jackets
- Funnel
- Aluminium foil
- Cork rings
- Microlitre syringe or transferpettor®
- Pasteur's pipette
- 1.5 ml sample vials with 100 µl glass inset and a screw cap with teflon gasket or, depending on the analytical system, a comparable sample receptacle
- Minishaker (vortexer)

4 General instructions on the analysis

- In order to reduce blank values, it is reasonable to anneal all glass devices at 450 °C. In order to avoid decomposition (debromination) of PBDEs by UV light during extraction and analysis, glass devices made from brown glass should be used so far possible. If no brown glass is available, aluminium foil can be used for protection from light.

- In order to determine the concentrations of all standard solutions and sample extracts, differential weighing is carried out and converted with the help of the density of toluene (0.87 g/ml).

- The GC method must be optimised and validated on the concentration range mentioned in Chapter 6.

- Peculiarities or difficulties during the analysis must be recorded.

STANDARD MEASUREMENT METHOD FOR THE DETERMINATION OF PENTABROMINATED AND OCTABROMINATED DIPHENYLETHERS IN POLYMERS

5 Sample preparation

5.1. Stock solutions

The following stock solutions were needed:

Internal standard (to control analyte recovery)	DBOFB:	50 µg/ml in toluene
Internal standard (to correct for injection error)	CB209:	0.2 µg/ml in toluene 1 µg/ml in toluene
Polybrominated diphenylether	PBDE:	50 µg/ml in an organic solvent

Additional note based on the experience of the interlaboratory comparison:

- *DBOFB used as a check of analyte recovery may also be replaced by another suitable standard substance.*

5.2. Pre-extraction of the soxhlet extractors

To clean the soxhlet extractors, a two-hour pre-extraction is carried out with 70 ml toluene. The washing solvent is rejected.

5.3. Weighing in the polymers

Approx. 100 mg of the polymer is weighed on a piece of aluminium foil with an accuracy of 1 mg. The weighing process is recorded. After transfer into the extraction thimbles (Section 5.4), the remainder of the polymer on the aluminium foil is determined by differential weighing and is taken into account when calculating the weighed portion.

5.4. Sample extraction

The sample is transferred through a funnel into the extraction thimble. In order to ensure a quantitative transfer, the funnel is rinsed with approx. 10 ml of toluene.
200 µl of the internal standard DBOFB [50 µg/ml] is added (in accordance with Section 5.1).

In order to prevent the sample from floating, the thimble is closed with fibre glass. Approx. 60 ml of toluene is put in the 100-ml round-bottomed flask, the equipment is covered with aluminium foil to exclude light and the sample is extracted for about 2 hours (20 extraction cycles).

The extract is put in a weighed 100-ml measuring flask and the round-bottomed flask rinsed with approx. 5 ml of toluene.

Remark: If the solution exhibits turbidity due to the matrix, this can be reduced by adding 1 ml of methanol. The difference between the density of methanol and toluene can be neglected in this case in the calculation.

The measuring flask is filled up with 100 ml of toluene and weighed. The precise volume of solvent is calculated by the density.

5.5. Addition of the CB209 internal standard

50 µl of the extract is transferred into the glass inset of the sample vial with a microlitre pipette or a transferpettor® and 50 µl of the CB209 internal standard [0.2 µg/ml] is added in accordance with Section 5.1. The sample vials are homogenised before the analysis by shaking or vortexes.

6 Calibration

The calibration takes place in the linear range of the GC/MS system. To establish this, ten calibration solutions are needed in equidistant concentration steps. Quantification is made based on the peak areas.

6.1 PBDE [1 µg/ml for each congener] and DBOFB [0.2 µg/ml] stock solution

100 µl of each PBDE stock solution (50 µg/ml) and 20 µl of the DBOFB stock solution (50 µg/ml) is put in a 5-ml measuring flask in accordance with Section 5.1 and filled up with toluene up to the mark. The solvent volume is determined by differential weighing with the help of the density of toluene.

6.2. Calibration

For the external calibration the following calibration solutions are produced from the PBDE stock solution [1 µg/ml for each congener] and DBOFB internal standard [0.2 µg/ml] (Section 6.1) and the stock solution of the CB209 internal standard [1 µg/ml] (Section 5.1).
The volumes indicated in Table 37 are put into a 1-ml measuring flask by a pipette and filled up with toluene up to the mark.

Table 37: Calibration solutions of PBDEs.

	Volume *PBDE+DBOFB*[1] (Section 6.1)	**Volume *CB209*[2] (Section 5.1)**	**c(PBDE) [ng/ml per congener]**	**c(DBOFB) [ng/ml]**	**c(CB209) [ng/ml]**
PBDE 1	50	100	50	10	100
PBDE 2	100	100	100	20	100
PBDE 3	150	100	150	30	100
PBDE 4	200	100	200	40	100
PBDE 5	250	100	250	50	100
PBDE 6	300	100	300	60	100
PBDE 7	350	100	350	70	100
PBDE 8	400	100	400	80	100
PBDE 9	450	100	450	90	100
PBDE 10	500	100	500	100	100

[1] Internal standard to control the analyte recovery rate,
[2] Internal standard to correct injection error

Additional note based on the experience of the interlaboratory comparison:

- *If necessary the number of calibration points can be reduced after internal validation of the method.*

The CB209 internal standard is used for the correction of the injection error. Therefore the evaluation of the response is carried out by $\frac{A_{PBDE}}{A_{CB209}}$.

STANDARD MEASUREMENT METHOD FOR THE DETERMINATION OF PENTABROMINATED AND OCTABROMINATED DIPHENYLETHERS IN POLYMERS

To produce the calibration straight lines the response $\frac{A_{PBDE}}{A_{CB209}}$ is plotted against the concentration $\frac{c_{PBDE}}{c_{CB209}}$.

A linear regression is carried out using the equation

$$\frac{A_{PBDE}}{A_{CB209}} = a * \frac{c_{PBDE}}{c_{CB209}} + b$$

with
A_{PBDE}: PBDE peak area
A_{CB209}: CB209 peak area
c_{PBDE}: PBDE concentration per congener in the calibration [ng/ml]
c_{CB209}: internal standard CB209 concentration in the calibration [ng/ml]
a: slope
b: axis intercept

6.3. Calculation of PBDE concentration

The concentrations of PBDEs in the samples [mg/g] will be calculated by the following formula:

$$C_{PBDE}\ [\mathrm{mg\ g^{-1}}] = \frac{\left[\frac{\left(\frac{A_{PBDE}}{A_{CB209}} - b\right) * c_{CB209}}{a}\right] * G * D[ml]}{F * E[g]}$$

with D [ml]: volume of toluene, calculated from the weighed amount of extract [g] and the density of toluene (0.87 g/ml) according to the formula:

$$D\ [\mathrm{ml}] = \frac{T[g]}{0.87[g]} * [ml]$$

F: conversion factor of the units (from ng to mg) = 10^6
E [g]: weighed portion
G: dilution factor (Section 5.5) = 2

Additional note based on the experience of the interlaboratory comparison:

- *When calculating the PBDE concentrations in the sample, a potential blank value (according to Section 6.4) must be taken into account.*

The DBOFB internal standard serves as a control of sample preparation for serious errors (e.g. dilution errors). If the analyte recovery rate is less than 60 % or greater than 115 %, the extraction should be repeated. The results are not corrected over the analyte recovery rate.

6.4. Blank values

The blank value is determined for each extraction unit. In order to determine the blank value, the standard measurement method is performed without any sample material.

7 GC/MS

Capillary gas chromatography coupled to a mass spectrometric detector is used for the analysis.
The GC column for the determination of highly brominated PBDEs should not be too long, since PBDEs are inclined to debromination when they are exposed to high temperatures for long periods.
A column length of approx. 15 m exhibits a sufficient separation efficacy for pentaBDE and octaBDE isomers.

The following parameters are suggested depending on the GC/MS system:

GC column:	phenyl-arylene-polymer equivalent to (5% phenyl)-methyl-polysiloxane length 15 m; internal diameter 0.25 mm; film thickness 0.1 µm
PTV programme:	90 °C (0 min) – 300 °C/min – 350 °C (15 min) modus: splitless purge time 1 min; purge flow 50 ml/min
GC oven programme:	70 °C (2 min) - 20 °C/min - 300 °C (15 min)
Constant flow	1.2 ml/min
Carrier gas	helium
Restriction capillary	deactivated, fused silica, length 3 m, internal diameter 0.18 mm
Transfer line	310 °C
Ion source T	200 °C
Ionisation method	EI; 70 eV

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The analysis of PBDEs is carried out in SIM (Single Ion Monitoring) Modus (EI: Electron Impact Ionisation) with the following mass traces (the underlined mass traces have been used for quantification):

PentaBDE	$(M^+\text{-2Br})+2$, $(M^+\text{-2Br})+4$, M^++4	403.7, 405.7, 563.6
OctaBDE	$(M^+\text{-2Br})+6$, $(M^+\text{-2Br})+8$, M^++8	641.6, 643.6, 801.5
CB209	M^++4, M^++6, $(M^+\text{-2Cl})+4$	497.5, 499.6, 427.6
DBOFB	M^++3, M^++2, $(M^+\text{-FBr})+2$	455.8, 454.4, 357.5

In addition to the SIM–masses, the retention times of the standard substances are used for the analytic determination.

Annex 2 Characterisation of the technical PBDEs

2.1 Characterisation of the technical PENTA-BDE (DE-71-Great-Lakes)

<u>Manufacturer</u> Great Lakes Chemical Corporation[1]
500 E. 96th Street, Suite 500, Indiana 46240; USA

Table 38: Mass percentage composition of technical PENTA-BDEs.

No. (see Figure 26)	Ballschmitter No.		% by mass /14/
1	17	2,2',4-triBDE	0.067
2	28	2,4,4'-triBDE	0.22
3	47	2,2',4,4'-tetraBDE	32.96
4	66	2,3',4,4'-tetraBDE	0.77
5	100	2,2',4,4',6-pentaBDE	9.96
6	99	2,2',4,4',5-pentaBDE	42.03
7	85	2,2',3,4,4'-pentaBDE	1.82
8	154	2,2',4,4',5,6'-hexaBDE	4.15
9	153	2,2',4,4',5,5'-hexaBDE	4.77
10	138	2,2',3,4,4',5'-hexaBDE	0.46

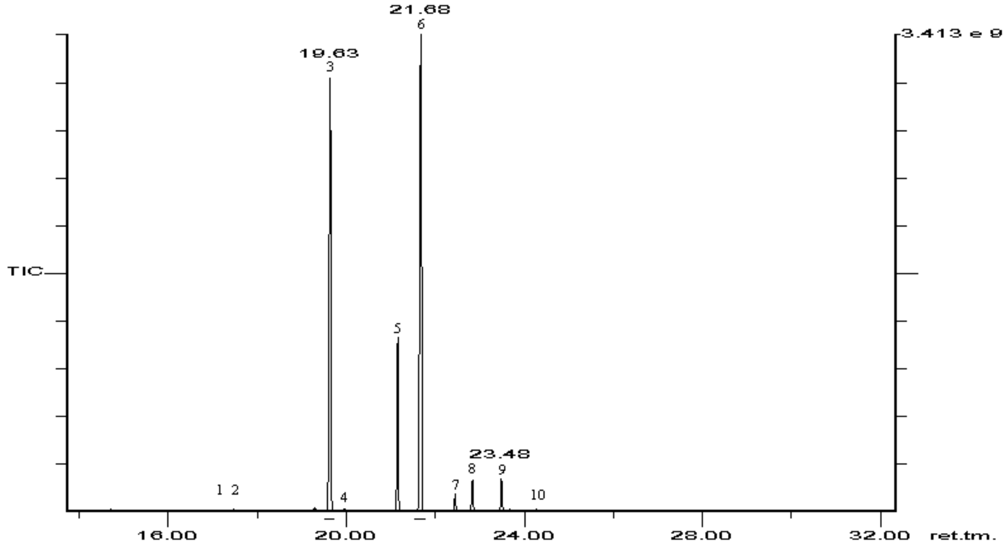

Figure 26: Chromatogram of technical PENTA-BDE;
DB5-ms, 15 m, 0.25 mm ID, 0.1 µm df; 1 µL (50 ng/µL);
70°C (2 min) - 10°C/min - 300°C (15 min).

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[1] Great Lakes Company's generosity in providing the DE-71 and DE-79 flame retardants is appreciated.

2.2 Characterisation of technical OCTA-BDE (DE-79-Great-Lakes)

Manufacturer	Great Lakes Chemical Corporation 500 E. 96th Street, Suite 500, Indiana 46240; USA

Table 39: Mass percentage composition of technical OCTA-BDE.

No. (see Figure 27)	Ballschmitter No.		% by mass /14/
1	154	2,2’,4,4’,5,6’-hexaBDE	1.19
2	153	2,2’,4,4’,5,5’-hexaBDE	8.10
3	183	2,2’,3,4,4’,5’,6-heptaBDE	40.17
4	u	HeptaBDE	2.01
5	190	2,3,3’,4,4’,5,6-heptaBDE	0.84
6	197*	2,2’,3,3’,4,4’,6,6’-octaBDE	21.42
7	203*	2,2’,3,4,4’,5,5’,6-octaBDE	5.51
8	196*	2,2’,3,3’,4,4’,5,6’-octaBDE	8.27
9	u	NonaBDE	12.49

u: unknown isomer; *these isomers have been identified using retention comparison with available standards.

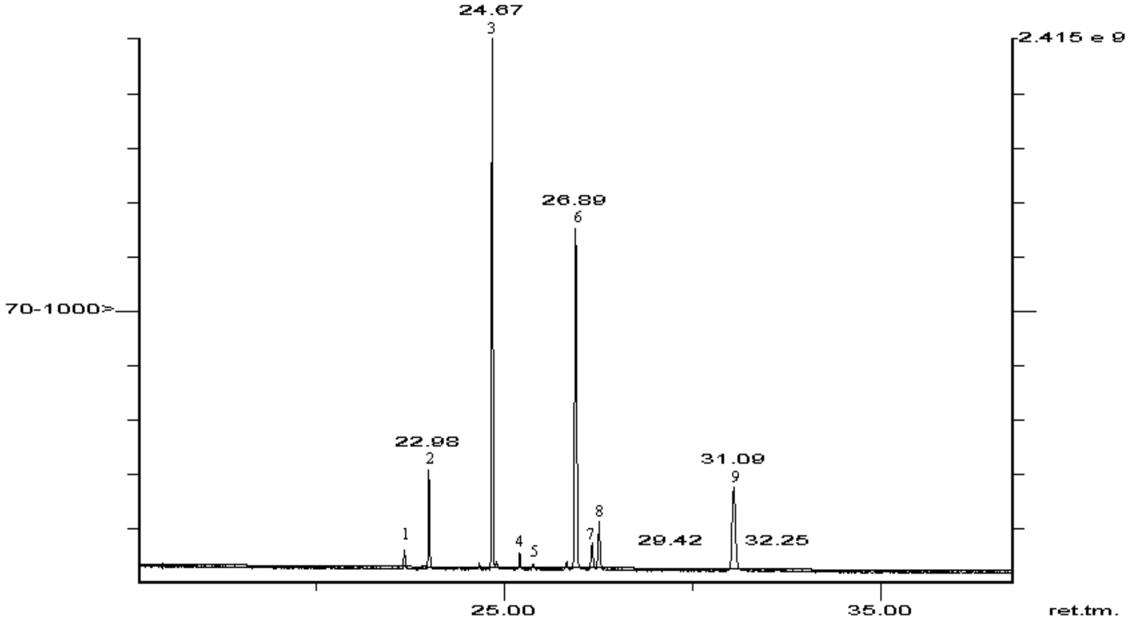

Figure 27: Chromatogram of technical OCTA-BDE;
DB5-ms, 15 m, 0.25 mm ID, 0.1 µm df; 1 µL (50 ng/µL);
70°C (2 min) - 10°C/min - 300°C (15 min).

Annex 3 Method validation (calibration function, variance homogeneity)

3.1 Calibration function and process parameters

The calibration solutions (according to Annex 1, Table 37) have been tested three times (see Table 40) and the preliminary calibration functions of 1st and 2nd degree calculated from the determined measurement values, whose process parameters are needed for further statistical tests.

Table 40: Average values of three repeat analyses of the calibration solutions.

	Response (A_{PBDE}/A_{CB209})						
	BDE100	**BDE99**	**BDE85**	**BDE197**	**BDE203**	**BDE196**	**DBOFB**
PBDE 1	0.242	0.233	0.216	0.034	0.022	0.033	0.129
PBDE 2	0.565	0.519	0.431	0.051	0.035	0.060	0.246
PBDE 3	0.939	0.826	0.702	0.092	0.058	0.103	0.364
PBDE 4	1.388	1.174	1.011	0.117	0.084	0.142	0.500
PBDE 5	1.804	1.499	1.170	0.149	0.105	0.173	0.620
PBDE 6	2.314	1.872	1.490	0.180	0.132	0.205	0.748
PBDE 7	2.983	2.381	1.955	0.241	0.166	0.264	0.900
PBDE 8	3.523	2.742	2.254	0.250	0.174	0.272	1.033
PBDE 9	4.113	3.170	2.456	0.300	0.201	0.325	1.132
PBDE 10	4.236	3.477	2.546	0.358	0.204	0.359	1.320

Calibration function of 1st degree /9/

The regression analysis provides the linear calibration function with the process parameters (slope b, axis intercept a, residual standard deviation s_{y1}, process standard deviation s_{xo}, relative process standard deviation V_{xo}) displayed in Table 41.

Table 41: Linear calibration function and process parameters.

	BDE100	**BDE99**	**BDE85**	**BDE197**	**BDE203**	**BDE196**	**DBOFB**
b	0.0096	0.0074	0.0056	0.0007	0.0004	0.0007	0.0131
a [ng mL^{-1}]	-0.4227	-0.2549	-0.1120	-0.0181	-0.0036	-0.0074	-0.0209
s_{y1} [ng mL^{-1}]	0.1512	0.0781	0.0953	0.0138	0.0079	0.0081	0.0182
s_{xo} [ng mL^{-1}]	15.785	10.512	17.074	19.383	17.796	11.123	1.389
V_{xo} [%]	5.74	3.82	6.21	7.05	6.47	4.04	2.52

Calibration function of 2nd degree /9/

The regression analysis provides the quadratic calibration function with its process parameters (function coefficients a, b, c; residual standard deviation s_{y2}, process standard deviation s_{xo}, relative process standard deviation V_{xo}) displayed Table 42.

Table 42: Calibration function of 2nd degree and process parameters.

	BDE100	**BDE99**	**BDE85**	**BDE197**	**BDE203**	**BDE196**	**DBOFB**
a [ng mL^{-1}]	3×10^{-6}	3×10^{-6}	-2×10^{-7}	5×10^{-7}	-2×10^{-7}	2×10^{-8}	1.4×10^{-5}
B	0.0078	0.0058	0.0057	0.0004	0.0005	0.0007	0.0115
C	-0.2411	-0.0949	-0.1245	0.0091	-0.0123	-0.0061	0.0107
s_{y2} [ng mL^{-1}]	0.1482	0.0548	0.1018	0.0167	0.0186	0.0112	0.0149
s_{xo} [ng mL^{-1}]	15.678	7.351	18.208	24.691	47.731	15.778	1.140
V_{xo} [%]	5.70	2.67	6.62	8.98	17.36	5.74	2.07

Testing linearity

If possible, a linear calibration function should be used. Calibration of 2nd degree should only be applied in justified exceptional cases.

Mandel's smooth test /9/:

Mandel's smooth test is recommended for the numerical linearity test. For this purpose the linear calibration function and the calibration function of 2nd degree, including the respective residual standard deviation, should be used. The difference of the variances DS^2 is calculated from the residual standard deviations s_{y1} and s_{y2}

$$DS^2 = (N-2)s_{y1}^2 - (N-3)s_{y2}^2$$

with *f: degree of freedom = 1*

N: number of the selected concentration steps = 10

Test value TV can be calculated for the F test as $TV = \frac{DS^2}{s_{y2}^2}$

and compared with the table value F ($f_1 = 1$, $f_2 = N-3$, P = 99 %).

When TV is less than or equal to F, no significantly better adjustment will be achieved by the calibration function of 2nd degree. The calibration function is linear.

Table 43: Results of Mandel's smooth test.

	BDE100	**BDE99**	**BDE85**	**BDE197**	**BDE203**	**BDE196**	**DBOFB**
s_{y1}	0.1512	0.0781	0.0953	0.0138	0.0079	0.0081	0.0182
s_{y2}	0.1482	0.0548	0.1018	0.0167	0.0186	0.0112	0.0149
N	10	10	10	10	10	10	10
DS^2	0.0291	0.0279	0.0002	-0.0004	-0.0019	-0.0004	0.0011
TV	1.3	9.3	0.0	-1.5	-5.6	-2.8	4.9
F (1; 7; 99%)	12.25						

All tested calibrations (see Figure 28 to Figure 34) are linear.

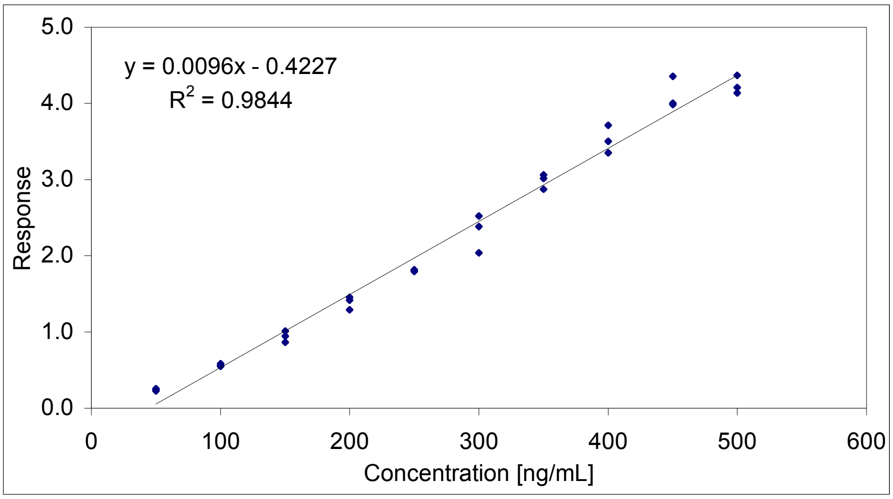

Figure 28: Calibration BDE100.

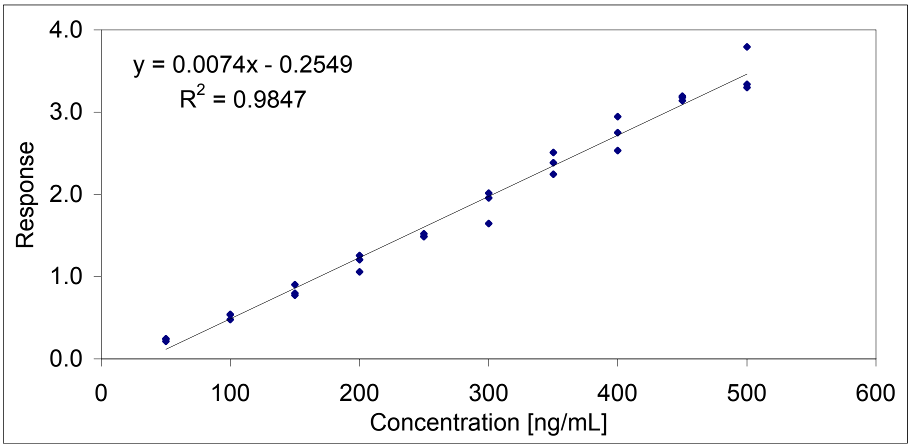

Figure 29: Calibration BDE99.

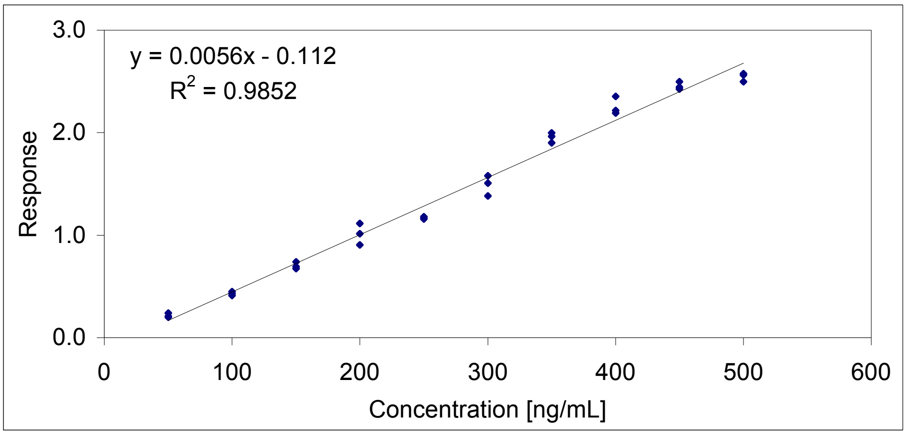

Figure 30: Calibration BDE85.

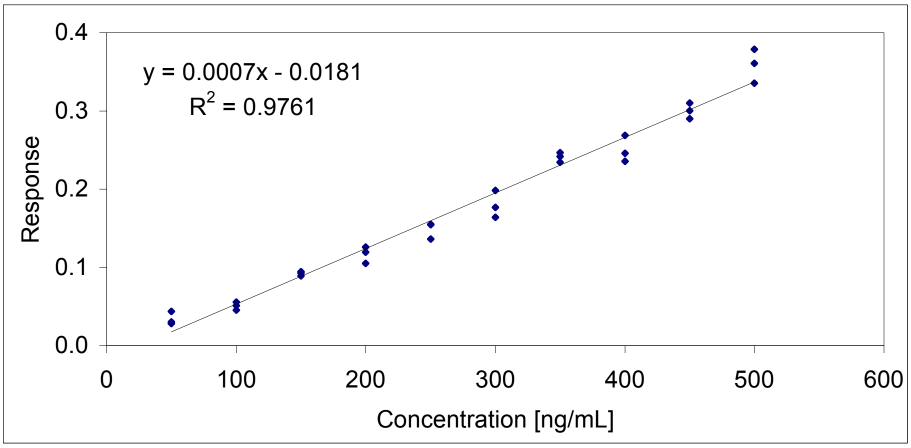

Figure 31: Calibration BDE197.

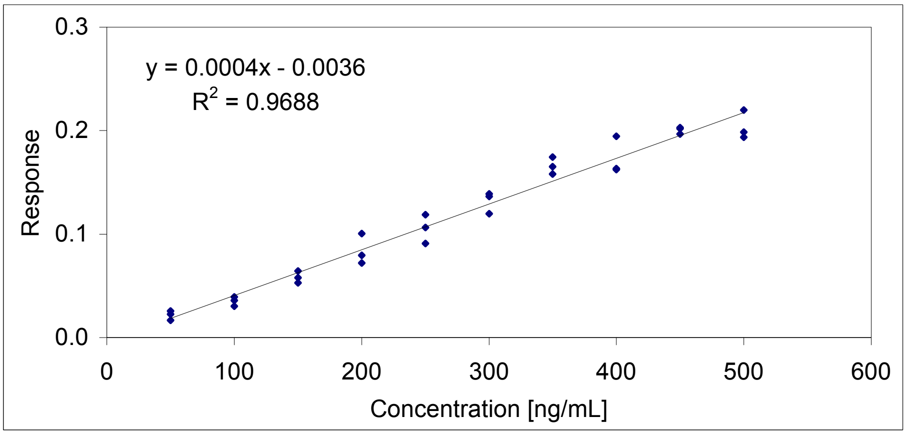

Figure 32: Calibration BDE203.

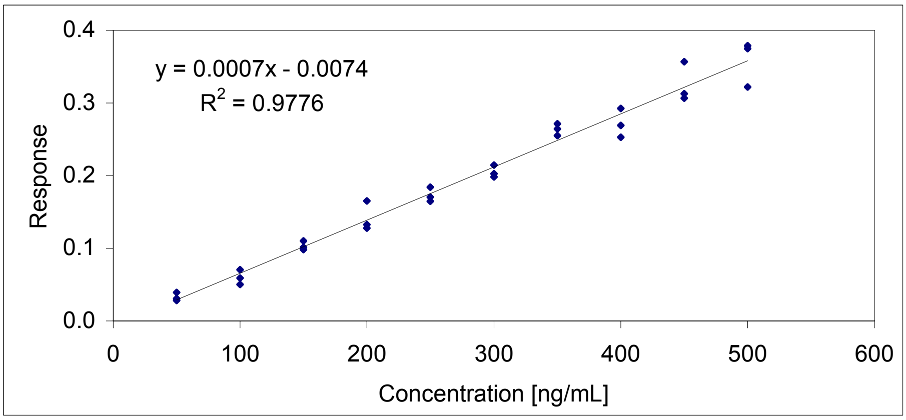

Figure 33: Calibration BDE196.

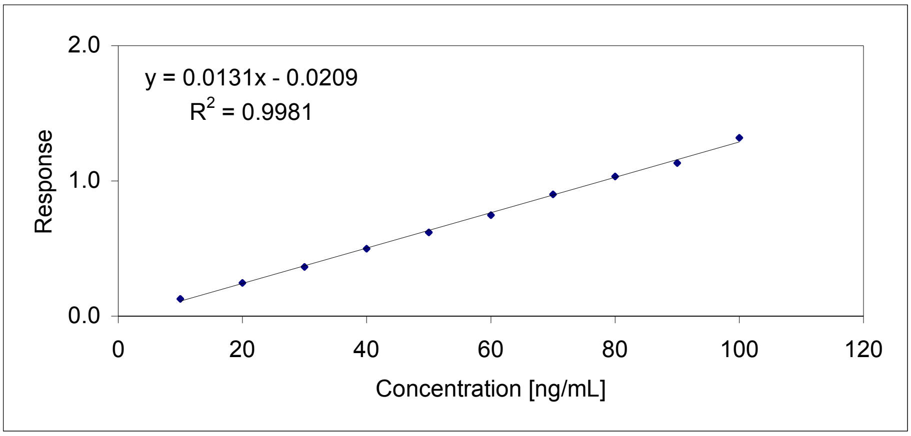

Figure 34: Calibration DBOFB.

3.2 Testing variance homogeneity

The lowest (x_1) and the highest (x_N) concentration of calibration (PBDE and DBOFB) have been analysed separately ten times (see Table 44 to Table 46). Each data set obtained has been tested for outliers using Grubbs´ outlier test. The tenth test of the high PBDE concentration has been identified as an outlier and not included in the evaluation. The measured values are starred (*).

Table 44: Series of measured values (response: A/A_{CB209}) for BDE100, BDE99, BDE85 of the lowest (x_1) and highest (x_N) concentration.

	BDE100		**BDE99**		**BDE85**	
	50 ng mL^{-1}	**500 ng mL^{-1}**	**50 ng mL^{-1}**	**500 ng mL^{-1}**	**50 ng mL^{-1}**	**500 ng mL^{-1}**
Test 1	0.3544	6.1359	0.3416	5.0415	0.2851	4.0520
Test 2	0.3496	6.1801	0.3242	5.0882	0.2872	4.0934
Test 3	0.3610	6.1719	0.3189	5.0118	0.2897	4.0128
Test 4	0.3595	6.1608	0.3233	5.0329	0.2707	4.0355
Test 5	0.3318	6.1523	0.3139	5.0207	0.2797	4.0140
Test 6	0.3767	6.1213	0.3261	5.0743	0.2849	4.0211
Test 7	0.3381	6.1735	0.2808	5.0789	0.2757	4.0645
Test 8	0.3504	6.1380	0.3064	5.0177	0.2878	4.0125
Test 9	0.3540	6.1064	0.2808	5.0342	0.2531	4.0225
Test 1	0.3351	7.2114*	0.3186	5.6515*	0.2520	4.9159*
Mean $\bar{y}$	0.3511	6.1489	0.3135	5.0445	0.2766	4.0365
Variance s^2	0.000183	0.000640	0.000378	0.000823	0.000195	0.000792
TV	3.50		2.18		4.06	
F (0.99; 9; 8)	5.47					

Table 45: Series of measured values (response: A/A_{CB209}) for BDE197, BDE203, BDE196 of the lowest (x_1) and highest (x_N) concentration.

	BDE197		**BDE203**		**BDE196**	
	50 ng mL^{-1}	**500 ng mL^{-1}**	**50 ng mL^{-1}**	**500 ng mL^{-1}**	**50 ng mL^{-1}**	**500 ng mL^{-1}**
Test 1	0.0532	0.5988	0.0382	0.4361	0.0497	0.6311
Test 2	0.0510	0.5967	0.0388	0.4337	0.0530	0.6366
Test 3	0.0503	0.5968	0.0398	0.4381	0.0560	0.6338
Test 4	0.0591	0.5915	0.0392	0.4305	0.0575	0.6358
Test 5	0.0521	0.5910	0.0383	0.4303	0.0550	0.6311
Test 6	0.0535	0.5964	0.0309	0.4376	0.0505	0.6312
Test 7	0.0505	0.5943	0.0323	0.4396	0.0494	0.6319
Test 8	0.0504	0.5916	0.0326	0.4312	0.0498	0.6381
Test 9	0.0498	0.5972	0.0329	0.4323	0.0477	0.6368
Test 10	0.0505	0.7069*	0.0339	0.5550*	0.0458	0.7875*
Mean $\bar{y}$	0.0520	0.5949	0.0357	0.4344	0.0514	0.6340
Variance s^2	7.78E-06	8.47E-06	1.19E-05	1.26E-05	1.44E-05	7.95E-06
TV	1.09		1.06		1.81	
F (0.99; 9; 8)	5.47					

Table 46: Series of measured values (response: A/A_{IS}) for DBOFB of the lowest (x_1) and highest (x_N) concentration.

	10 ng mL^{-1}	**100 ng mL^{-1}**
Test 1	1.9233*	6.5102
Test 2	0.7716	6.5881
Test 3	0.7370	6.5043
Test 4	0.7735	6.5876
Test 5	0.7079	6.5509
Test 6	0.7910	6.5495
Test 7	0.7146	6.5565
Test 8	0.7189	6.5635
Test 9	0.7020	6.5911
Test 10	0.7126	5.1636*
Mean $\bar{y}$	0.7366	6.5557
Variance s^2	1.12E-03	1.02E-03
TV	1.10 < F(0.99; 9, 9) = 5.35	

Annex 4 Specification of the polymers used

Support by the companies Grafe Color Batch and Rühl PUROMER in manufacturing the polymer materials is appreciated.

Annex 4.1 Acrylonitrile-butadiene-styrene-copolymer (ABS)

Manufacturer	Grafe Color Batch GmbH Waldecker Straße 21 99444 Blankenhain
Formulation	Magnum 8391 (Dow Chemical Company)
Main application	Household products, consume goods, toys

Table 47: ABS general parameters.

	Test methode	Value
Physical properties		
Density	ISO 1183	1050 kg/m^3
Bulk density		650 kg/m^3
Thermal properties		
Vicat softening temperature, 49N/50 °C	ISO 306B	95 °C
Form stability temperature, 1.82 MPa	ISO 75-1	95 °C

FR addition in % by mass:

0.97 % Great Lakes DE-71 or

2.95 % Great Lakes DE-79

In addition, ABS has been delivered without any additive.

Delivery form white cylinder granules

Annex 4.2 Polystyrene (PS)

Manufacturer	Grafe Color Batch GmbH Waldecker Straße 21 99444 Blankenhain
Formulation	Lacqrene® PS-HI 6631 (Atofina S.A.)
Main applications	Toys, computers, keyboards, office equipment, television casing

Table 48: PS general parameters.

	Test methode	**Value**
Physical properties		
Density	ISO 1183	1040 kg/m^3
Process shrinkage		0.4 – 0.7 %
Thermal properties		
Vicat softening temperature, 50N/50 °C	ISO 306B50	82 °C
Form stability temperature, 1.82 MPa	ISO 75-2A	78 °C

FR additive in % by mass:

2.96 % Great Lakes DE-79

In addition, PS has been delivered without any additive.

Delivery form white cylinder granules

Annex 4.3 Polyurethane hard foam (PUR-H)

Manufacturer	Rühl PUROMER GmbH Hugenottenstraße 105 61381 Friedrichsdorf
Formulation	Component A PUR 460BS-85 (Polyether polyole) Component B PUR 900/1 (Diphenylmethane-diisocyanate, MDI)
Main applications	Block foam components, back-fill foam

Table 49: PUR-H general parameters.

	PUR 460BS-85	PUR 900/1
Density (25 °C)	1.04 g/cm^3	1.23 g/cm^3
Viscosity (25 °C)	550 ± 100 mPas	210 ± 50 mPas
Foaming performance (25 °C, standard values)		
Mix ratio	100 g	120 g
Rest period	50 ± 5 s	
Rise time	230 ± 20 s	
Volumetric mass	80 ± 5 kg/m^3	

FR additive in % by mass

approx. 2 % Great Lakes DE-71

In addition, PUR-H has been delivered without any additives.

Delivery form foamed in two cups

Annex 4.4 Epoxy resin (EP)

Resin has been manufactured as described in Section 8.2.

Manufacturer	Remmers Bauchemie GmbH Am Priggenbusch 13 49624 Löningen Mixing of the components: BAM IV.2
Formulation	Viscacid® epoxy building resin Component A: Bisphenol-A-epichlorohydrin resins MG<700, Glycidyl ester of neodecane acid Component B: Polyoxy propylene diamine, nonylphenol, m-xylylene diamine, isophorone diamine
Main applications	screed, floor coverings, binders for antiskid coverings

Table 50: EP general parameters

	Component A	**Component B**	**Mix**
Viscosity at 25 °C	1800 mPas	80 mPas	730 mPas
Density	1.12 g/cm^3	0.97 g/cm^3	1.08 g/cm^3
Mix ratio	3 parts component A + 1 part component B		
Process time (1 kg, 20 – 50 °C)	50 min		
Pot life (100 g, 20 – 50 °C)	55 min		

FR additive in % by mass

2.0 % Great Lakes DE-71

In addition, EP has been cast without any additives.

Delivery form: two packages à 1 kg

Annex 5 Formulae to calculate homogeneity of polymeric materials

Abbreviations:

f_1 = *degree of freedom between the sub-samples*

f_2 = *degree of freedom within the sub-samples*

i = *sub-sample*

j = *repeat test*

p=: *number of sub-samples*

$\overset{=}{n}$ =: *mean of the number of repeat tests*

n_i = *number of repeat tests of sub-sample i*

$MV_{general}$ = *mean of* MV_i *of all sub-samples in mg* g^{-1}

MV_i = *mean of repeat tests of sub-sample i in mg* g^{-1}

SQ_1 = *sum of squares between the sub-samples*

SQ_2 = *sum of squares inside the sub-samples*

$s_{general}$ = *mean of* s_i *of all sub-samples in mg* g^{-1}

s_i = *standard deviation of sub-sample i in mg* g^{-1}

s_L = *standard deviation due to the influence of sub-samples*

s_r^2 = *repeat variance*

s_v^2 = *variance between the sub-samples*

$V_{general}$ = *mean of the relative standard deviations of all sub-samples in %*

V_i = *relative standard deviation of the sub-sample i in %*

x_{ij} = *result of the repeat test j of sub-sample i in mg* g^{-1}

Equations to determine the analytical data

	Example (ABS with OCTA-BDE)
Equation 1 $MV_i = \frac{1}{n_i}\sum_{j=1}^{n_i} x_{ij}$	Sub-sample 4: (n_1 = 3) $MV_4 = \frac{1}{3}(0.570 + 0.568 + 0.542) = 0.560$
Equation 2 $s_i = \sqrt{\frac{1}{n_i - 1}\sum_{j=1}^{n_i}\left(x_{ij} - MW_i\right)^2}$	$s_4 = \sqrt{\frac{1}{2}\left[(0.570-0.560)^2 + (0.568-0.560)^2 + (0.542-0.560)^2\right]}$ $= 0.0156$
Equation 3 $V_i = \frac{s_i \cdot 100\%}{MW_i}$	$V_4 = \frac{0.0156 \cdot 100\%}{0.560} = 2.8\%$
	All sub-samples (p = 8)
Equation 4 $MV_{general} = \frac{1}{p}\sum_{i=1}^{p} MV_i$	$MV_{general} = \frac{1}{8}(0.508 + 0.549 + 0.539 + 0.560 + 0.513$ $+ 0.504 + 0.473 + 0.578) = 0.528$
Equation 5 $s_{general} = \frac{1}{p}\sum_{i=1}^{p} s_i$	$s_{general} = \frac{1}{8}(0.0193 + 0.0413 + 0.0462 + 0.0156$ $+ 0.0281 + 0.0526 + 0.0280 + 0.0317)$ $= 0.0329$
Equation 6 $V_{general} = \frac{s_{general} \cdot 100\%}{MV_{general}}$	$V_{general} = \frac{0.0329 \cdot 100\%}{0.528} = 6.2\%$

Equations to the ANOVA table

	Example (ABS with OCTA-BDE)
Equation 7 $SQ_1 = \sum_{i=1}^{p} n_i \left(MV_i - MV_{general}\right)^2$	$\begin{aligned} &SQ_1 = 4(0.508-0.528)^2 + 4(0.549-0.528)^2 + 3(0.539-0.528)^2 \\ &+ 3(0.560-0.528)^2 + 3(0.513-0.528)^2 + 3(0.504-0.528)^2 \\ &+ 3(0.473-0.528)^2 + 3(0.578-0.528)^2 = 0.026 \end{aligned}$
Equation 8 $SQ_2 = \sum_{i=1}^{p} \sum_{j=1}^{n_i} (x_{ij} - MV_i)^2$	$\begin{aligned} &SQ_2 = (0.524 - 0.528)^2 + (0.524 - 0.528)^2 + (0.495 - 0.528)^2 \\ &+ (0.487 - 0.528)^2 + (0.504 - 0.528)^2 + (0.547 - 0.528)^2 \\ &+ (0.540 - 0.528)^2 + (0.604 - 0.528)^2 + (0.502 - 0.528)^2 \\ &+ (0.591 - 0.528)^2 + (0.525 - 0.528)^2 + (0.570 - 0.528)^2 \\ &+ (0.568 - 0.528)^2 + (0.542 - 0.528)^2 + (0.527 - 0.528)^2 \\ &+ (0.481 - 0.528)^2 + (0.532 - 0.528)^2 + (0.532 - 0.528)^2 \\ &+ (0.536 - 0.528)^2 + (0.443 - 0.528)^2 + (0.458 - 0.528)^2 \\ &+ (0.505 - 0.528)^2 + (0.455 - 0.528)^2 + (0.542 - 0.528)^2 \\ &+ (0.593 - 0.528)^2 + (0.600 - 0.528)^2 = 0.022 \end{aligned}$ $f_1 = 7$
Equation 9 $f_1 = p - 1$	
Equation 10 $f_2 = \left(\sum_{i=1}^{p} n_i\right) - p$	$f_2 = 4 + 4 + 3 + 3 + 3 + 3 + 3 + 3 - 8 = 18$
Equation 11 $s_v^2 = \frac{SQ_1}{f_1}$	$s_v^2 = \frac{0.026}{7} = 0.0037$
Equation 12 $s_r^2 = \frac{SQ_2}{f_2}$	$s_r^2 = \frac{0.022}{18} = 0.0012$
Equation 13 $\overset{=}{n} = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_i - \frac{\sum_{i=1}^{p} n_i^2}{\sum_{i=1}^{p} n_i}\right]$	$\begin{aligned} &\overset{=}{n} = \frac{1}{7}\left[26 - \frac{4^2 + 4^2 + 3^2 + 3^2 + 3^2 + 3^2 + 3^2 + 3^2}{26}\right] \\ &= 3.24 \end{aligned}$
Equation 14 $s_L = \sqrt{\frac{s_v^2 - s_r^2}{\overset{=}{n}}}$	$s_L = \sqrt{\frac{0.0037 - 0.0012}{3.24}} = 0.0278$

Annex 6 Mass spectra of the tested PBDE, DBOFB, CB209

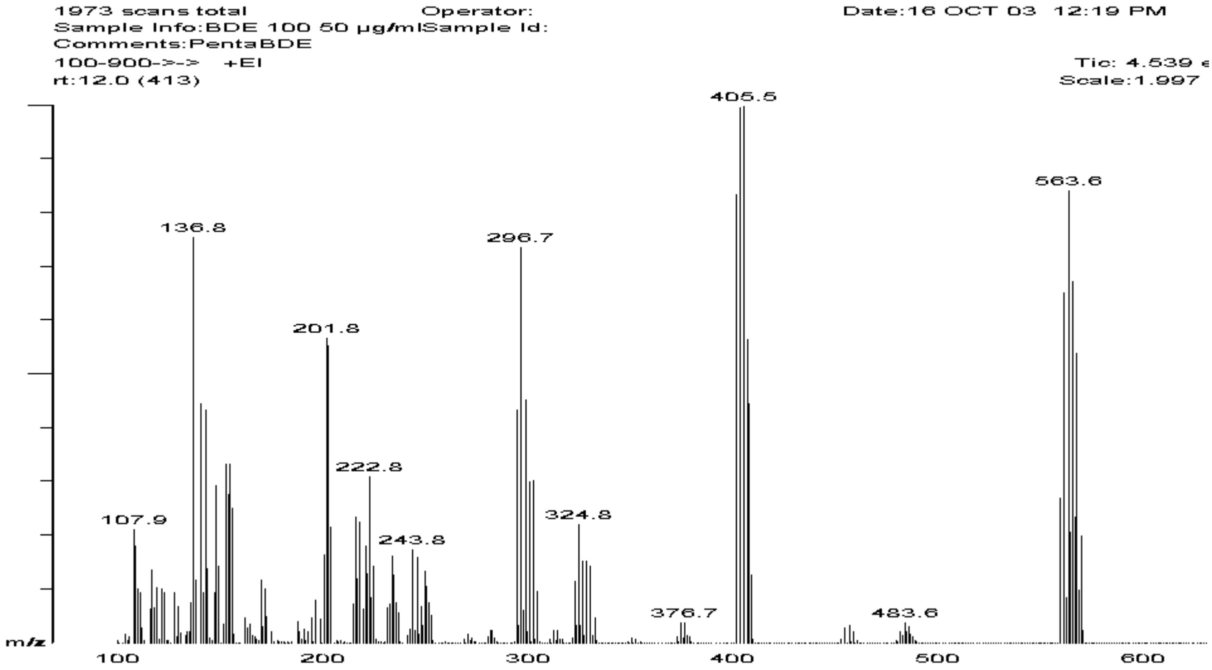

Figure 35: EI mass spectrum of 2,2’,4,4’,6-pentaBDE (BDE100).

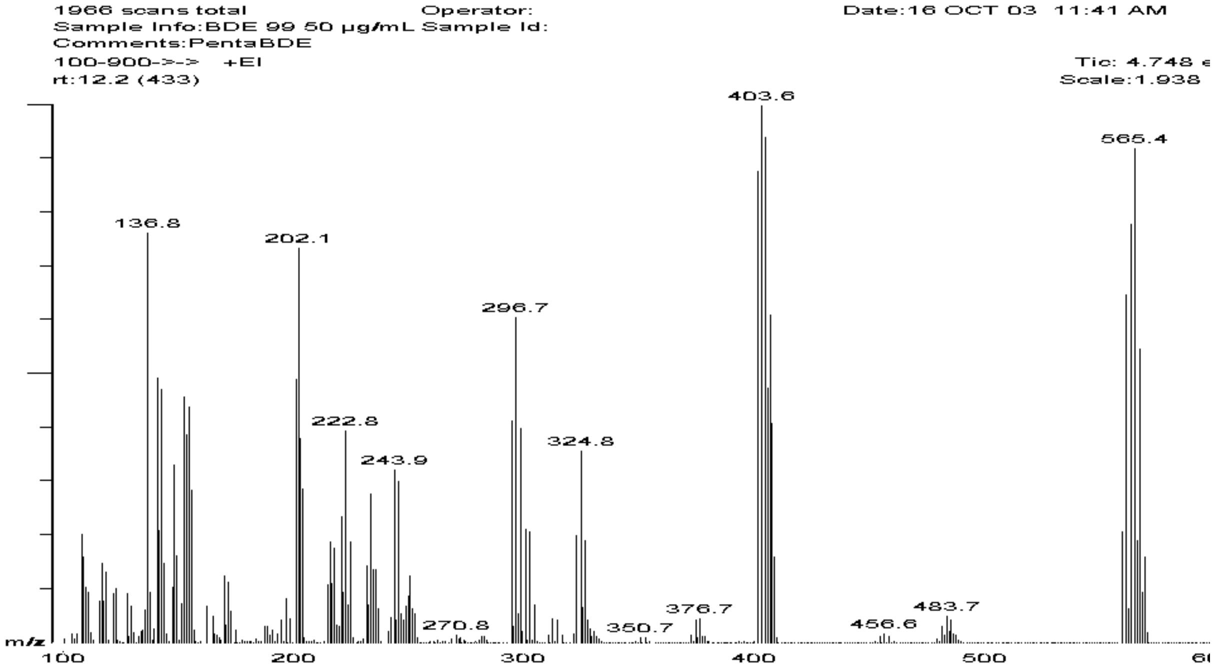

Figure 36: EI mass spectrum of 2,2’,4,4’,5-pentaBDE (BDE99).

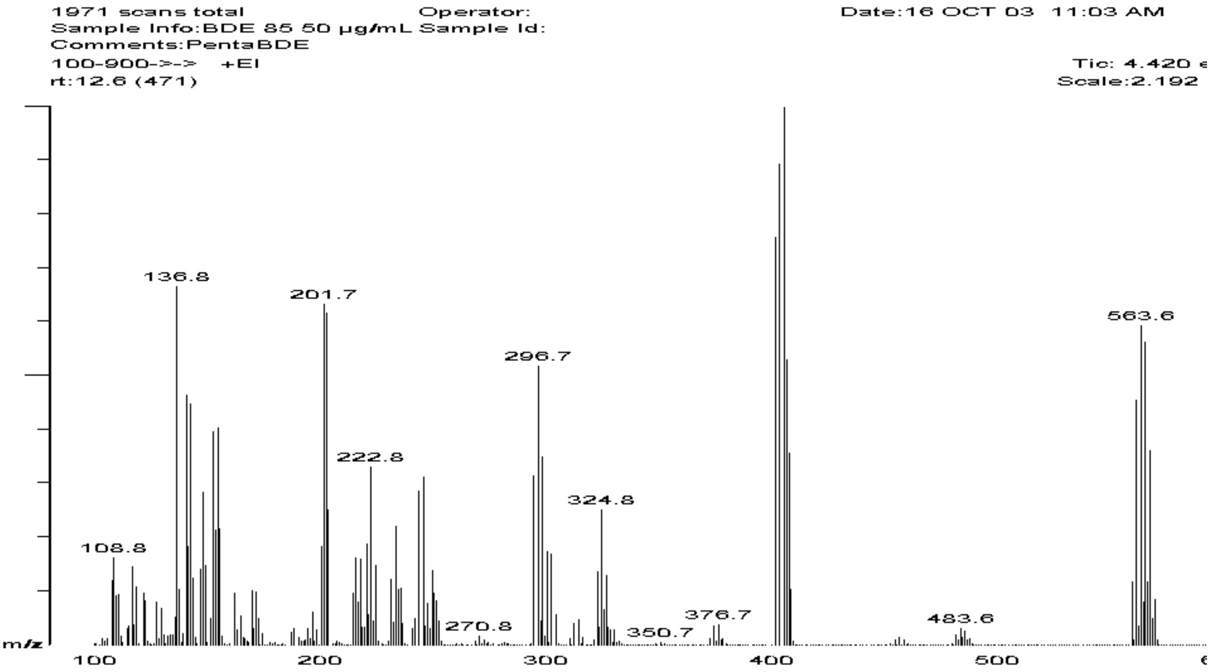

Figure 37: EI mass spectrum of 2,2',3,4,4'-pentaBDE (BDE85).

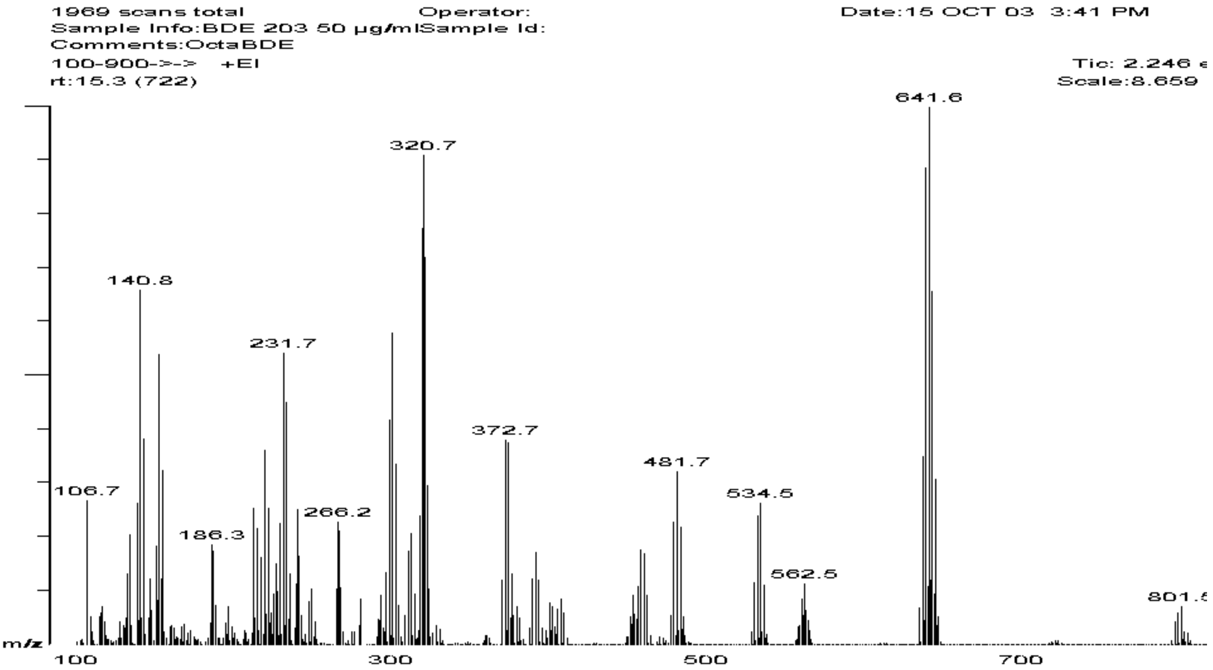

Figure 38: EI mass spectrum of 2,2',3,4,4',5,5',6-octaBDE (BDE203).

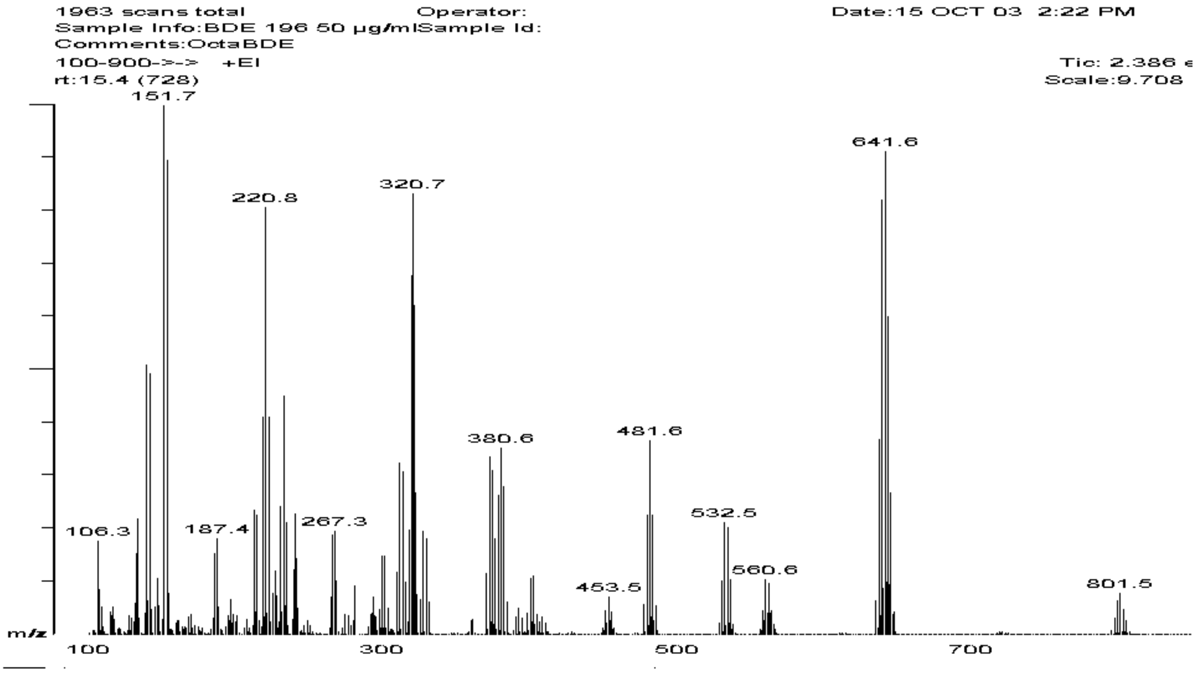

Figure 39: EI mass spectrum of 2,2’,3,3’,4,4’,5,6’-octaBDE (BDE196).

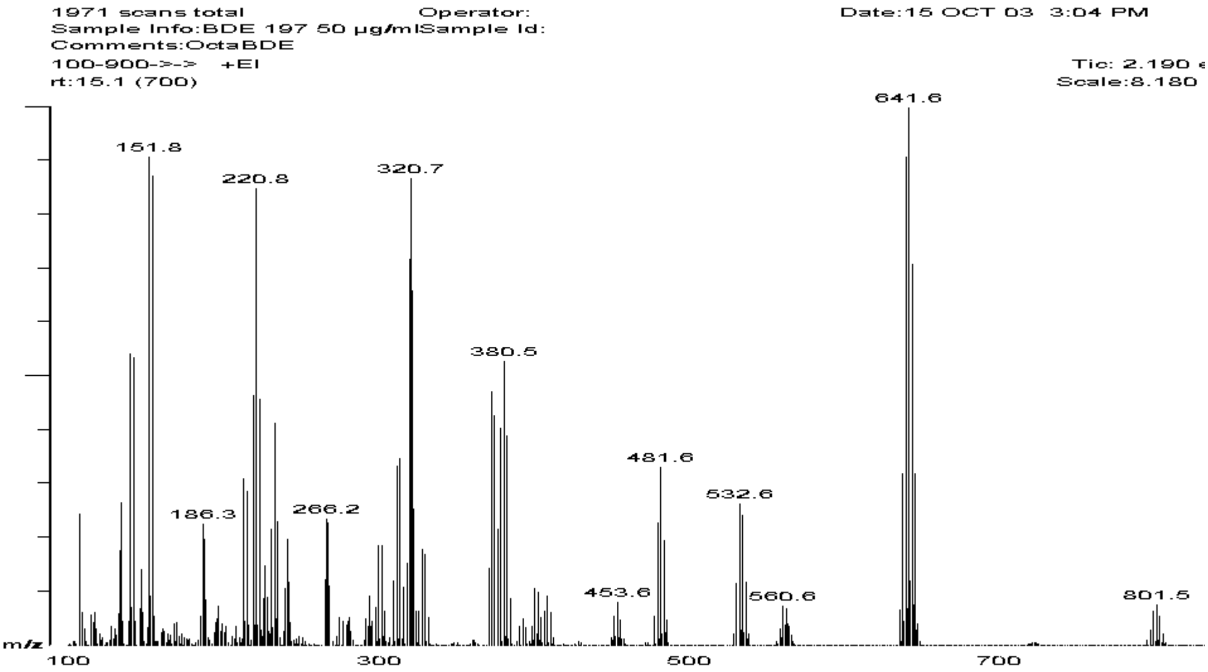

Figure 40: EI mass spectrum of 2,2’,3,3’,4,4’,6,6’-octaBDE (BDE197).

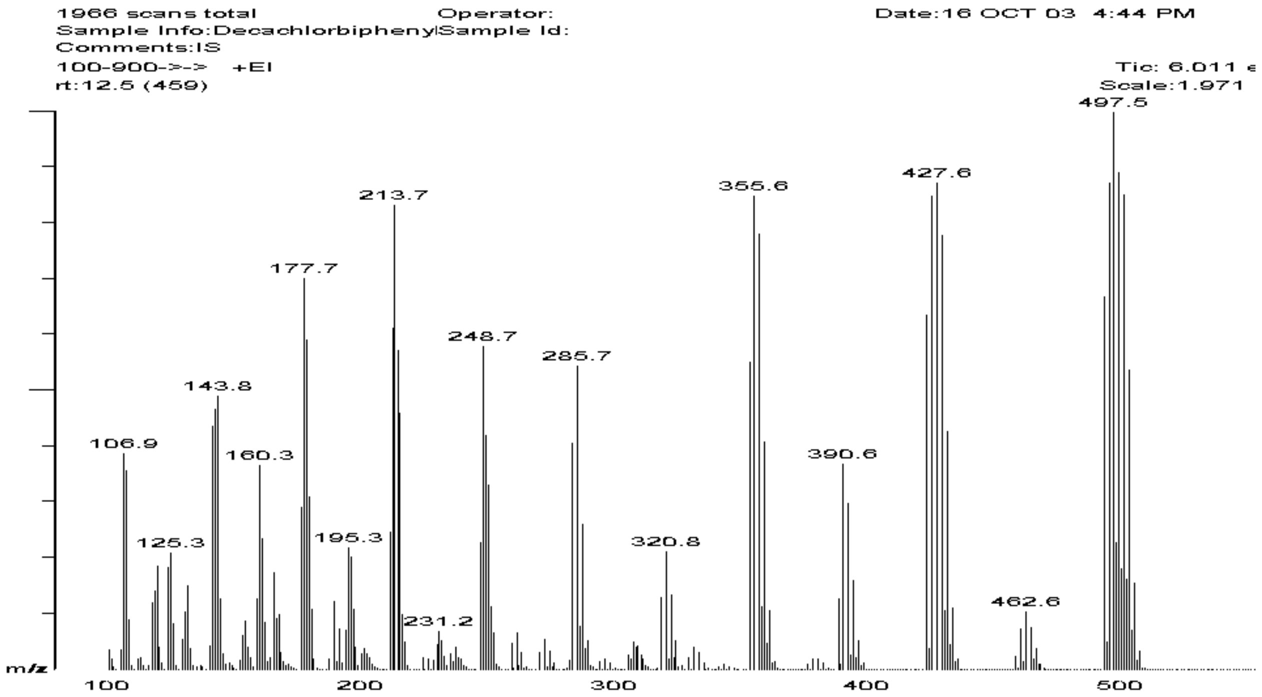

Figure 41: EI mass spectrum of decachlorobiphenyl (CB209).

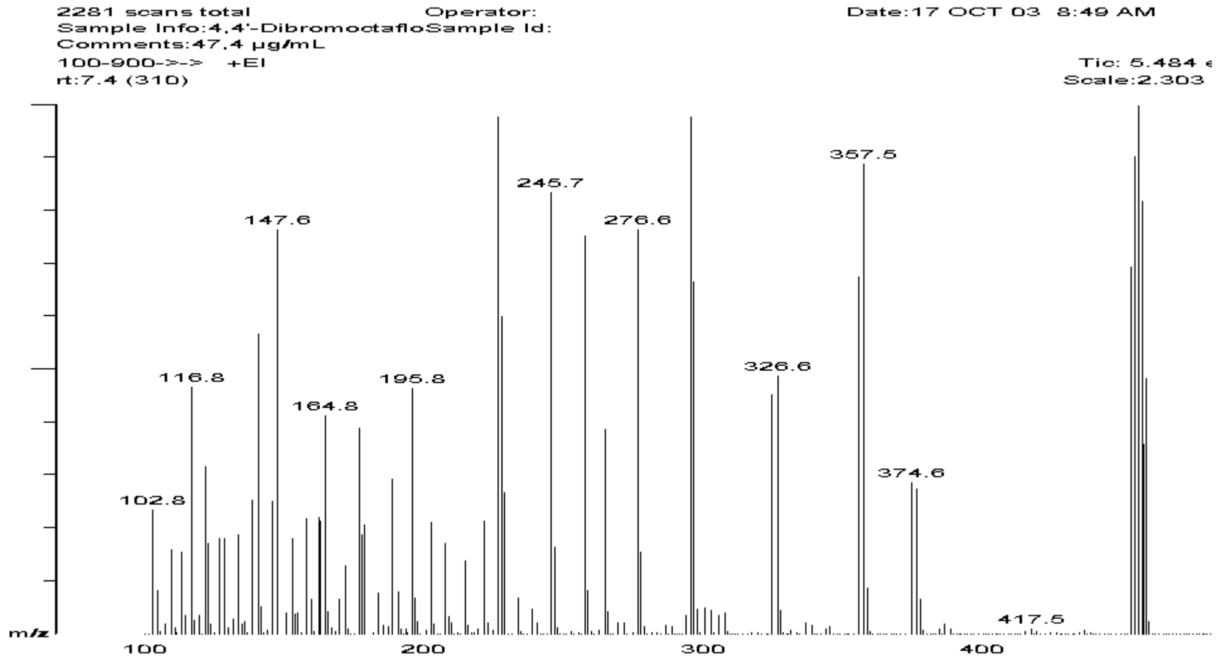

Figure 42: EI mass spectrum of 4,4’-dibromooctafluorobiphenyl (DBOFB).

Annex 7 Calculation of the indicators of Mandel's h and k statistic

Annex 7.1 Mandel’s h statistic

Mandel's h statistic serves to calculate the compatibility parameter between the laboratories, h, and can be calculated as follows:

$$h_{ij} = \frac{\overline{y}_{ij} - \overline{\overline{y}}_j}{\sqrt{\frac{1}{(p_j - 1)} \sum_{i=1}^{p_j} (\overline{y}_{ij} - \overline{\overline{y}}_j)^2}}$$

with

$\overline{y}_{ij}$: *arithmetical laboratory mean*

$\overline{\overline{y}}_j$: *arithmetical general mean*

p_j : *number of laboratories*

Annex 7.2 Mandel’s k statistic

The compatibility parameter within the laboratory, k, can be calculated as follows:

$$k_{ij} = \frac{s_{ij}\sqrt{p_j}}{\sqrt{\sum s_{ij}^2}}$$

with

s_{ij} : *standard deviation of the test results of a laboratory*

Annex 7.3 Results for h and k in individual polymers

Annex 7.3.1 PentaBDE isomers in epoxy resin

Table 51: Calculated values for h (Σ pentaBDE isomers in epoxy resin).

Laboratory	**Arithmetical mean [mg g^{-1}]**	**General mean [mg g^{-1}]**	**Standard deviation between the cells [mg g^{-1}]**	h_{ij}
001	0.914	1.177	0.281	*-0.937*
003	1.868	1.177	0.281	*2.458*
004	1.107	1.177	0.281	*-0.250*
012	1.279	1.177	0.281	*0.362*
013	0.786	1.177	0.281	*-1.392*
014	1.145	1.177	0.281	*-0.114*
019	1.25	1.177	0.281	*0.259*
021	0.893	1.177	0.281	*-1.011*
026	1.113	1.177	0.281	*-0.228*
027	1.181	1.177	0.281	*0.014*
030	1.25	1.177	0.281	*0.259*
037	0.832	1.177	0.281	*-1.228*
040	1.297	1.177	0.281	*0.426*
041	1.07	1.177	0.281	*-0.381*
044	1.125	1.177	0.281	*-0.186*
045	1.795	1.177	0.281	*2.199*
046	1.152	1.177	0.281	*-0.090*
Coord	1.132	1.177	0.281	*-0.161*

Coord: Coordinator (BAM IV.2)

Table 52: Calculated values for k (Σ pentaBDE isomers in epoxy resin).

Laboratory	s_{ij} [mg g^{-1}]	s_{ij}^2	$\sqrt{p_j}$	$\sum s_{ij}^2$	$\sqrt{\sum s_{ij}^2}$	k_{ij}
001	0.040	0.0016	4.24	0.1476	0.38	0.44
003	0.265	0.0702	4.24	0.1476	0.38	2.93
004	0.046	0.0021	4.24	0.1476	0.38	0.51
012	0.023	0.0005	4.24	0.1476	0.38	0.25
013	0.040	0.0016	4.24	0.1476	0.38	0.44
014	0.037	0.0014	4.24	0.1476	0.38	0.41
019	0.045	0.0020	4.24	0.1476	0.38	0.50
021	0.051	0.0026	4.24	0.1476	0.38	0.56
026	0.046	0.0021	4.24	0.1476	0.38	0.51
027	0.024	0.0006	4.24	0.1476	0.38	0.27
030	0.044	0.0019	4.24	0.1476	0.38	0.49
037	0.092	0.0085	4.24	0.1476	0.38	1.02
040	0.041	0.0017	4.24	0.1476	0.38	0.45
041	0.024	0.0006	4.24	0.1476	0.38	0.27
044	0.053	0.0028	4.24	0.1476	0.38	0.59
045	0.099	0.0098	4.24	0.1476	0.38	1.09
046	0.19	0.0361	4.24	0.1476	0.38	2.10
Coord	0.038	0.0014	4.24	0.1476	0.38	0.42

p_j: number of laboratories (= 18), s_{ij}: standard deviation of the arithmetical mean of a cell, Coord: Coordinator (BAM IV.2)

Annex 7.3.2 PentaBDE isomers in polyurethane

Table 53: Calculated values for h (Σ pentaBDE isomers in polyurethane).

Laboratory	**Arithmetical mean [mg g^{-1}]**	**General mean [mg g^{-1}]**	**Standard deviation between the cells [mg g^{-1}]**	**h_{ij}**
001	1.069	1.365	0.285	-1.039
003	1.848	1.365	0.285	1.695
004	1.202	1.365	0.285	-0.572
012	1.450	1.365	0.285	0.298
013	0.870	1.365	0.285	-1.737
014	1.400	1.365	0.285	0.123
019	1.441	1.365	0.285	0.267
021	1.143	1.365	0.285	-0.779
026	1.313	1.365	0.285	-0.182
027	1.368	1.365	0.285	0.011
030	1.653	1.365	0.285	1.011
037	1.180	1.365	0.285	-0.649
040	1.322	1.365	0.285	-0.151
041	1.220	1.365	0.285	-0.509
044	1.369	1.365	0.285	0.014
045	2.082	1.365	0.285	2.516
046	1.148	1.365	0.285	-0.761
Coord	1.498	1.365	0.285	0.467

Coord: Coordinator (BAM IV.2)

Table 54: Calculated values for k (pentaBDE isomers in polyurethane).

Laboratory	s_{ij} [mg g^{-1}]	s_{ij}^2	$\sqrt{p_j}$	$\sum s_{ij}^2$	$\sqrt{\sum s_{ij}^2}$	k_{ij}
001	0.009	0.0001	4.24	0.6718	0.82	0.05
003	0.776	0.6022	4.24	0.67	0.82	4.02
004	0.058	0.0034	4.24	0.67	0.82	0.30
012	0.042	0.0018	4.24	0.67	0.82	0.22
013	0.028	0.0008	4.24	0.67	0.82	0.14
014	0.008	0.0001	4.24	0.67	0.82	0.04
019	0.043	0.0018	4.24	0.67	0.82	0.22
021	0.021	0.0004	4.24	0.67	0.82	0.11
026	0.026	0.0007	4.24	0.67	0.82	0.13
027	0.034	0.0012	4.24	0.67	0.82	0.18
030	0.013	0.0002	4.24	0.67	0.82	0.07
037	0.056	0.0031	4.24	0.67	0.82	0.29
040	0.057	0.0032	4.24	0.67	0.82	0.30
041	0.043	0.0018	4.24	0.67	0.82	0.22
044	0.029	0.0008	4.24	0.67	0.82	0.15
045	0.152	0.0231	4.24	0.67	0.82	0.79
046	0.150	0.0225	4.24	0.67	0.82	0.78
Coord	0.068	0.0046	4.24	0.67	0.82	0.35

p_j: number of laboratories (= 18), s_{ij}: standard deviation of the arithmetical mean of a cell, Coord: Coordinator (BAM IV.2)

Annex 7.3.3 OctaBDE isomers in polystyrene

Table 55: Calculated values for h (Σ octaBDE isomers in polystyrene).

Laboratory	Arithmetical mean [mg g^{-1}]	General mean [mg g^{-1}]	Standard deviation between the cells [mg g^{-1}]	h_{ij}
001	1.069	1.365	0.285	-1.039
003	1.848	1.365	0.285	1.695
004	1.202	1.365	0.285	-0.572
012	1.45	1.365	0.285	0.298
013	0.87	1.365	0.285	-1.737
014	1.4	1.365	0.285	0.123
019	1.441	1.365	0.285	0.267
021	1.143	1.365	0.285	-0.779
026	1.313	1.365	0.285	-0.182
027	1.368	1.365	0.285	0.011
030	1.653	1.365	0.285	1.011
037	1.18	1.365	0.285	-0.649
040	1.322	1.365	0.285	-0.151
041	1.22	1.365	0.285	-0.509
044	1.369	1.365	0.285	0.014
045	2.082	1.365	0.285	2.516
046	1.148	1.365	0.285	-0.761
Coord	1.498	1.365	0.285	0.467

Coord: Coordinator (BAM IV.2)

Table 56: Calculated values for k (Σ octaBDE isomers in polystyrene).

Laboratory	s_{ij} [mg g^{-1}]	s_{ij}^2	$\sqrt{p_j}$	$\sum s_{ij}^2$	$\sqrt{\sum s_{ij}^2}$	k_{ij}
001	0.046	0.0021	4.24	0.0348	0.19	1.05
003	0.042	0.0018	4.24	0.0348	0.19	0.96
004	0.058	0.0034	4.24	0.0348	0.19	1.32
012	0.067	0.0045	4.24	0.0348	0.19	1.52
013	0.021	0.0004	4.24	0.0348	0.19	0.48
014	0.010	0.0001	4.24	0.0348	0.19	0.23
019	0.046	0.0021	4.24	0.0348	0.19	1.05
021	0.000	0.0000	4.24	0.0348	0.19	0.00
026	0.031	0.0010	4.24	0.0348	0.19	0.71
027	0.067	0.0045	4.24	0.0348	0.19	1.52
030	0.022	0.0005	4.24	0.0348	0.19	0.50
037	0.049	0.0024	4.24	0.0348	0.19	1.11
040	0.012	0.0001	4.24	0.0348	0.19	0.27
041	0.009	0.0001	4.24	0.0348	0.19	0.20
044	0.056	0.0031	4.24	0.0348	0.19	1.27
045	0.062	0.0038	4.24	0.0348	0.19	1.41
046	0.030	0.0009	4.24	0.0348	0.19	0.68
Coord	0.063	0.0040	4.24	0.0348	0.19	1.43

p_j: number of laboratories (= 18), s_{ij}: standard deviation of the arithmetical mean of a cell, Coord: Coordinator (BAM IV.2)

Annex 7.3.4 OctaBDE isomers in ABS

Table 57: Calculated values for h (Σ octaBDE isomers in ABS).

Laboratory	Arithmetical mean [mg g^{-1}]	General mean [mg g^{-1}]	Standard deviation between the cells [mg g^{-1}]	h_{ij}
001	0.424	0.4180	0.106	0.057
003	0.47	0.4180	0.106	0.491
004	0.44	0.4180	0.106	0.208
012	0.613	0.4180	0.106	1.840
013	0.303	0.4180	0.106	-1.085
014	0.498	0.4180	0.106	0.755
019	0.418	0.4180	0.106	0.000
021	0.287	0.4180	0.106	-1.236
026	0.583	0.4180	0.106	1.557
027	0.274	0.4180	0.106	-1.358
030	0.298	0.4180	0.106	-1.132
037	0.431	0.4180	0.106	0.123
040	0.496	0.4180	0.106	0.736
041	0.406	0.4180	0.106	-0.113
044	0.405	0.4180	0.106	-0.123
045	0.227	0.4180	0.106	-1.802
046	0.448	0.4180	0.106	0.283
Coord	0.508	0.4180	0.106	0.849

Coord: Coordinator (BAM IV.2)

Table 58: Calculated values for k (Σ octaBDE isomers in ABS).

Laboratory	s_{ij} [mg g^{-1}]	s_{ij}^2	$\sqrt{p_j}$	$\sum s_{ij}^2$	$\sqrt{\sum s_{ij}^2}$	k_{ij}
001	0.016	0.0003	4.24	0.0534	0.23	0.29
004	0.002	0.0000	4.24	0.0534	0.23	0.04
003	0.199	0.0396	4.24	0.0534	0.23	3.65
012	0.028	0.0008	4.24	0.0534	0.23	0.51
013	0.029	0.0008	4.24	0.0534	0.23	0.53
014	0.023	0.0005	4.24	0.0534	0.23	0.42
019	0.04	0.0016	4.24	0.0534	0.23	0.73
021	0.049	0.0024	4.24	0.0534	0.23	0.90
026	0.033	0.0011	4.24	0.0534	0.23	0.61
027	0.026	0.0007	4.24	0.0534	0.23	0.48
030	0.015	0.0002	4.24	0.0534	0.23	0.28
037	0.024	0.0006	4.24	0.0534	0.23	0.44
040	0.018	0.0003	4.24	0.0534	0.23	0.33
041	0.009	0.0001	4.24	0.0534	0.23	0.17
044	0.051	0.0026	4.24	0.0534	0.23	0.94
045	0.036	0.0013	4.24	0.0534	0.23	0.66
046	0.012	0.0001	4.24	0.0534	0.23	0.22
Coord	0.019	0.0004	4.24	0.0534	0.23	0.35

p_j: number of laboratories (= 18), s_{ij}: standard deviation of the arithmetical mean of a cell, Coord: Coordinator (BAM IV.2)

Annex 8 Testing the variances of the laboratory means (Cochran's test)

Cochran's test serves to identify outliers within laboratory variances /12/. The variances of laboratories s_i^2 are ordered in decreasing order. The highest value s_{max}^2 will be tested using Cochran's test:

$$C_{TV} = \frac{s_{max}^2}{\sum_{i=1}^{p} s_i^2}$$

The calculated test value C_{TV} was compared to the critical value of Cochran's statistic C-crit (at a specified level of significance of 1% or 5%). The critical values at a specified number of laboratories and number of samples, which were mainly analysed, can be found in the table of Cochran's statistic /12/.

It holds:

Case 1: $C \leq$ C-crit (level of significance 5%)
The tested unit can be considered as correct.

Case 2: C-crit (level of significance 5%)$<C \leq$ C-crit (level of significance 1%). The tested unit is considered as a „straggler“.

Case 3: $C >$ C-crit (level of significance 1%)
The tested unit is considered as a „statistical outlier“.

Annex 9 Testing the laboratory means (Grubbs' test)

Grubbs' test serves to identify single outliers (the lowest and highest value) or two outliers (the two lowest or two highest values) /12/. The laboratory means are ordered in an increasing order.

Annex 9.1 Single outliers

In accordance with /12/ Grubbs' test is initially used to identify single outliers. If a single laboratory mean (e.g. the highest) is identified as an outlier, this value is expunged and the test repeated for the other (e.g. the lowest) extreme arithmetic mean.

The highest value is tested using:

$$T_n = \frac{x_p - \bar{x}}{s}$$

The smallest value is tested using:

$$T_1 = \frac{\bar{x} - x_1}{s}$$

with $\bar{x}$: *general mean*

x_p: *highest value*

x_1: *smallest value*

s: standard deviation to general mean

The calculated test value T is compared to the critical value of Grubbs' statistic T-crit (at a specified level of significance of 1% or 5%). The critical values, at a specified number of laboratories can be found in the table of Grubbs' test, e.g. /12/.

It holds:

Case 1: T ≤ T-crit (level of significance 5%)
The tested unit can be considered as correct.

Case 2: T-crit (level of significance 5%)< T ≤ T-crit (level of significance 1%). The tested unit is considered as a „straggler“.

Case 3: T > T-crit (level of significance 1%)
The tested unit is considered as a „statistical outlier“.

Annex 9.2 Two outliers

Grubbs' test for two outliers should only be used when Grubbs' test for single outliers fails to identify any arithmetic mean as an outlier. The calculation formulae are listed in /12/.

The calculated test value G is compared to the critical value of Grubbs' statistic G-crit (at a specified level of significance of 1% or 5%). The critical values at a specified number of laboratory can be found in the table of Grubbs' test, e.g. /12/.

Case 1: G ≥ G-crit (level of significance 5%)
The tested unit can be considered as correct.

Case 2: G-crit (level of significance 5%) > G ≥ G-crit (level of significance 1%). The tested unit is considered as a „straggler“.

Case 3: G < G-crit (level of significance 1%)
The tested unit is considered as a „statistical outlier“.

Lab Code	Weighed polymer [g]	Extraction period [h]	Weighed toluene [g]	Injection system	Injection volume [µL]	Type of column	Calibration solution		Standard deviation of calibration [%]					
							Low concentration [ng mL^{-1}]	High concentration [ng mL^{-1}]	BDE85	BDE99	BDE100	BDE196	BDE197	BDE203
L001	0.1	2.5	100	PTV	2	RTX-CLP, 30 m, 0.25 mm. 0.25 µm	50	500	1.88	1.41	2.19	3.62	3.76	3.98
L003	0.1	2	87	PTV	2	Rtx-5ms, 15 m, 0.25 mm; 0.25 µm	50	500	21	20	19	20	16	19
L004	0.05-0.1	2	86	Splitless	2	ZB-5, 15 m; 0.25 mm; 0.1 µm, pre-column: 1.5 m ZB5, 0.25 mm, 0.25 µm; restriction: 5 m, 0.25 mm ID	50	500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L012	0.1	2	86	PTV	1	DB5ms, 15 m; 0.25 mm; 0.1 µm	10	100	2	2	2	n.d.	n.d.	1
L013	0.1	3	-	PTV	1	DB-5ht, 15 m; 0.25 mm; 0.1 µm	25	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L014	0.08-0.2	2	81	PTV	2	HP-5ms 30m+7m pre-column 0.25mm; 0.25µm	51	915	2.81	1.97	1.84	12.2	7.94	14.0
L019	0.1	2	100 mL	PTV	1	Phenomenex ZB5, 12 m; 0.25 mm; 0.25 µm	50	500	5.94	6.05	3.04	5.91	4.79	6.70
L021	0.1	2	43	Splitless	1	HP-5MS, 30m; 0.25 mm; 0.25 µm, pre-column 1m DPT MDS, 2.5 mm	16 – 550 *	700 – 5550*	10	1.9	5.2	OctaBDE 1[1]: 13 OctaBDE 2[1]: 21 OctaBDE 3[1]: 22		
L026	0.1	2	100	Splitless	1	RTX-5MS. 20m; 0.25 mm; 0.25µm, pre-column 1m de-activated, 0.25 mm	Determined via response factors of $^{13}C_{12}$ standard	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L027	0.1	2	85	PTV	1	Agilent 112-5511, 15m; 0.25mm; 0.25µm	100	500	2.4	3.5	3.5	6.2	7.4	9.6
L030	0.06-0.1	10	92	Splitless	1	SGE BPX 5, 12m; 0.22mm; 25µm	50	1000	4.39	3.56	2.63	0.24	8.25	12.60
L037	0.01	2	10 mL	Splitless	1-2	HP-5MS, 30m; 0.25 µm; restriction 1m	50	500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L040	0.1	2	-	Spitless split	1	Factor four, 30m; 0.25mm; 0.25µm	8.0	40,000.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L041	0.1	2	87	Splitless	1	DB 5 ms; 15 m; 0.25 mm; 0.25 µm	50	500	2.08	2.99	2.49	5.18	4.12	3.70
L044	0.1	2		PTV	5	DB-5, 15 m; 0.25 mm; 0.1 µm, pre-column 1 m	50	500	7.65	5.47	3.72	23.01	15.13	21.78
L045	0.1	2 – 2.5	85	Splitless	1	DB-XLB 30 m; 0.25 mm; 0.10 µm	50	500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
L046	0.1	3	96	Splitless	1	DB-5-HT, 15m; 0.25mm; 0.1µm	0.2	800	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: no data

[1] The isomers were not attributed as quantification was performed via the technical product.

*Quantification via the technical products PENTA- and OCTA-BDE