BS EN 62321-6:2015

BSI Standards Publication

Determination of certain substances in electrotechnical products

Part 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography–mass spectrometry (GC-MS)

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National foreword

This British Standard is the UK implementation of EN 62321-6:2015. It is identical to IEC 62321-6:2015. Together with BS EN 62321-1:2013, BS EN 62321-2:2014, BS EN 62321-3-1:2014, BS EN 62321-3-2:2014, BS EN 62321-4:2014, BS EN 62321-5:2014, BS EN 62321-7-1, BS EN 62321-7-2 and BS EN 62321-8 it supersedes BS EN 62321:2009, which will be withdrawn upon publication of all parts of the BS EN 62321 series.

The UK participation in its preparation was entrusted to Technical Committee GEL/111, Electrotechnical environment committee.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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Verfahren zur Bestimmung von bestimmten Substanzen in Produkten der Elektrotechnik - Teil 6: Polybromierte Biphenyl- und Diphenylether in Polymeren durch Gaschromatographie-Massenspektrometrie (GC-MS) (IEC 62321-6:2015)

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European Committee for Electrotechnical Standardization
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European foreword

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Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

NOTE 1 When an International Publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

NOTE 2 Up-to-date information on the latest versions of the European Standards listed in this annex is available here: www.cenelec.eu

Publication	Year	Title	EN/HD	Year
IEC 62321	2008	Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)	EN 62321	2009
IEC 62321-1	2013	Determination of certain substances in electrotechnical products - Part 1: Introduction and overview	EN 62321-1	2013
IEC 62321-2	2013	Determination of certain substances in electrotechnical products - Part 2: Disassembly, disjunction and mechanical sample preparation	EN 62321-2	2014

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography–mass spectrometry (GC-MS)

FOREWORD

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International Standard IEC 62321-6 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems.

The first edition of IEC 62321:2008 was a 'stand-alone' standard that included an introduction, an overview of test methods, a mechanical sample preparation as well as various test method clauses.

This first edition of IEC 62321-6 is a partial replacement of IEC 62321:2008, forming a structural revision and generally replacing Annex A.

Future parts in the IEC 62321 series will gradually replace the corresponding clauses in IEC 62321:2008. Until such time as all parts are published, however, IEC 62321:2008 remains valid for those clauses not yet re-published as a separate part.

The text of this standard is based on the following documents:

FDIS	Report on voting
111/368/FDIS	111/379/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 62321 series, published under the general title: *Determination of certain substances in electrotechnical products,* can be found on the IEC website

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

The widespread use of electrotechnical products has drawn increased attention to their impact on the environment. In many countries this has resulted in the adoption of regulations affecting wastes, substances and energy use of electrotechnical products.

The use of certain substances (e.g. lead (Pb), cadmium (Cd) and polybrominated diphenyl ethers (PBDE's)) in electrotechnical products is a source of concern in current and proposed regional legislation.

The purpose of the IEC 62321 series is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of certain substances of concern in electrotechnical products on a consistent global basis.

WARNING – Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography–mass spectrometry (GC-MS)

1 Scope

This Part of IEC 62321 specifies one normative and two informative techniques for the determination of polybrominated biphenyls (PBB) and diphenyl ethers (PBDE) in polymers of electrotechnical products.

The gas chromatography–mass spectrometry (GC-MS) test method is suitable for the determination of monobrominated to decabrominated biphenyls (PBB) and monobrominated to decabrominated diphenyl ethers (PBDE).

Annexes A and C contain methods using ion attachment mass spectrometry (IAMS) coupled with direct injection probe (DIP) and high-pressure liquid chromatography coupled to photo diode array ultra violet detector (HPLC-PDA/UV). These techniques have utility as fast, qualitative or semi-quantitative type methods but are subject to limitations including interferences or the number or type of PBB and PBDE compounds within their scope.

The ion attachment mass spectrometry (IAMS) technique is limited to the determination of decabromo biphenyl and technical mixtures of decabromodiphenyl ether, octabromodiphenyl ether, and pentabromo diphenyl ether flame retardant compounds. The determination of other PBBs or PBDEs by this method has not been evaluated.

The high-pressure liquid chromatography technique is limited to the determination of technical mixtures of decabromodiphenyl ether, octabromo diphenyl ether, decabromo biphenyl and octabromo biphenyl technical flame retardants. The determination of other PBBs or PBDEs by this method has not been evaluated.

These test methods have been evaluated for use with PS-HI (polystyrene, high-impact) and PC/ABS (a blend of polycarbonate and acrylonitrile butadiene styrene) containing individual PBDEs between 20 mg/kg to 2 000 mg/kg and total PBDEs between 1 300 mg/kg to 5 000 mg/kg as depicted in this standard including in Annex F. The use of these methods for other polymer types, PBBs or other PBDE compounds or concentration ranges other than those specified above has not been specifically evaluated.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 62321:2008, *Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)*

IEC 62321-1:2013, *Determination of certain substances in electrotechnical products – Part 1: Introduction and overview*

IEC 62321-2:2013, *Determination of certain substances in electrotechnical products – Part 2: Disassembly, disjointment and mechanical sample preparation*

3 Terms, definitions and abbreviations

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
semi-quantitative
level of accuracy in a measurement amount where the relative uncertainty of the result is typically 30 % or better at a defined level of confidence of 68 %

3.1.2
technical mixture
commercial product (e.g. flame retardants) manufactured for industrial use whose purity is not as clearly defined as an individual high purity calibration standard

3.2 Abbreviations

BDE	brominated diphenyl ether
BFR	brominated flame retardant
Br	bromine
CIC	combustion – ion chromatography
DIP	direct injection probe
GC-MS	gas chromatography-mass spectrometry
HPLC-UV	high-performance liquid chromatography-ultra violet
IAMS	ion attachment mass spectrometry
IS	internal standard
MDL	method detection limit
LOD	limit of detection
LOQ	limit of quantification
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PDA	photodiode array (UV) detector
PS-HI (or HIPS)	high impact polystyrene
PTV	programmed temperature vaporising
QC	quality control
SIM	single (or “selected”) ion monitoring
XRF	X-ray fluorescence spectroscopy
TICS	tentatively identified compounds
RSD	relative standard deviation
CCC	continuing calibration check standard
BSA	bis(trimethylsilyl)acetamide
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
BCR 681	Bureau Communautaire de Référence

NOTE BCR 681 contains 7 trace elements in a polyethylene matrix. The certified value for Br is 98 mg/kg ± 5 mg/kg

GC	gas chromatography
ABS	acrylonitrile-butadiene-styrene plastic
PDA/UV	photo diode array ultra violet detector
OFP	octafluoro pentanol
PTFE	polytetrafluoroethylene

4 Principle

PBB and PBDE compounds are quantitatively determined using Soxhlet extraction of the polymers with separation by gas chromatography – mass spectrometry (GC-MS) qualitatively and quantitatively using single (or “selected”) ion monitoring (SIM).

5 Reagents and materials

All reagent chemicals shall be tested for contamination and blank values prior to application as follows:

a) toluene (GC grade or higher);
b) helium (purity of greater than a volume fraction of 99,999 %);
c) technical BDE-209 with BDE-209 ~ 96,9 % and BDE-206 ~ 1,5 % solution;
d) calibrants: refer to 8.4;
e) surrogate and internal standards
   – surrogate standard used to monitor analyte recovery according to 8.2.1 a), 8.2.3 c), 8.2.4 e), 8.5.2 and 8.5.3, e.g. DBOFB (4, 4’-dibromooctafluorobiphenyl) (n),
   – internal standard used to correct for injection errors, according to 8.2.1 b), 8.2.5 and 8.5.3, e.g. CB209 (2,2’,3,3’,4,4’,5,5’,6,6’-decachlorobiphenyl).

The standards are acceptable when using a quadrupole-type mass spectrometer. A high-resolution mass spectrometer will require the use of other suitable standard substances having a mass and elution time similar to that of the analyte. ^{13}C-labelled nonaBDE and ^{13}C-labelled decaBDE are recommended for the high-mass PBDEs.

NOTE The standards suggested are adequate for measuring the concentrations of mono- through octaBDE. Due to their low mass and “high” volatility, these standards can be inadequate for measuring decaBDE and nonaBDE concentrations. By far the best calibration standard for these specific analytes would be ^{13}C-labelled decaBDE or one of the ^{13}C-labelled nonaBDEs. Some laboratories, operating on the principal of high volume/low price, can find these labelled materials too expensive for their business plan. A potential low-cost substitute is decaBB (BB 209). BB 209 has a high mass (943,1 g/mol versus 959,1g/mol for decaBDE or 864,2 g/mol for nonaBDE), which elutes just before the three nonaBDEs on a typical DB-5 column. The presence of significant quantities of decaBB in the sample itself can readily be determined by monitoring the peak area of this standard, and comparing it to what is expected from the added quantity of decaBB. The use of the suggested labelled standards or decaBB can be limited to those analyses where the only analytes of interest are decaBDE and/or the nonaBDEs. With additional experimentation it can be possible to identify alternate standards that have the high mass and low volatility necessary for the quantification of the nonaBDEs and decaBDE.

6 Apparatus

The following items shall be used for the analysis:

a) analytical balance capable of measuring accurately to 0,000 1 g;
b) 1 ml, 5 ml, 10 ml, 100 ml volumetric flasks;
c) Soxhlet extractors
   – 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);

d) extraction thimble (cellulose, 30 ml, ID 22 mm, height 80 mm);

e) glass wool (for extraction thimble);

f) deactivated injector liner (for GC-MS);

g) heating jackets;

h) funnel;

i) aluminium foil;

NOTE Brown or amber vessels as indicated in the text of the procedure can also be used.

j) Microlitre syringe or automatic pipettes;

k) Pasteur pipette;

l) 1,5 ml sample vials with 100 μl glass insert and a screw cap with polytetrafluoroethylene (PTFE) gasket or, depending on the analytical system, a comparable sample receptacle. Brown or amber vessels shall used as indicated in the text of the procedure.

m) mini-shaker (also known as vortexer or vortex mixer);

n) a gas chromatograph with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) is used for the analysis. The mass spectrometric detector shall be able to perform selective ion monitoring and have an upper mass range of at least 1 000 m/z. The high-range mass is required to unambiguously identify decaBDE and nonaBDE. The use of an autosampler is strongly recommended to ensure repeatability;

o) a column length of approximately 15 m has sufficient separation efficiency for PBB and PBDE compounds (see 8.3 a) for example of suitable column);

p) 0,45 μm PTFE filter membrane.

7 Sampling

As described in IEC 62321-2 unless indicated otherwise (e.g. “..using a nipper.”), cryogenic grinding with liquid nitrogen cooling is recommended. The samples shall be ground to pass through a 500 μm sieve before extraction.

8 Procedure

8.1 General instructions for the analysis

The following general instructions shall be followed:

a) In order to reduce blank values, ensure the cleanliness of all glass equipment (excluding volumetric flasks) and deactivate glass wool (see Clause 6 e)) by subjecting it to 450 °C for at least 30 min. To avoid decomposition and/or debromination of PBDEs by UV light during extraction and analysis, glass equipment made from brown or amber glass shall be used.

NOTE If no brown or amber glass is available, aluminium foil can be used for protection from light.

b) If the amount of Br in the sample (determined by XRF, CIC or other means) is considerably above the 0,1 % range, it will be necessary to carry out the analysis using an adjusted sample size or by repeating the analysis using an extract that has been appropriately diluted prior to internal standard addition.

8.2 Sample preparation

8.2.1 Stock solution

The following stock solutions shall be prepared:

a) surrogate standard (to monitor analyte recovery): 50 μg/ml in toluene (e.g. DBOFB);

b) internal standard (to correct for injection error): 10 μg/ml in toluene (e.g. CB209);

c) polybrominated biphenyl (PBB) solution: 50 μg/ml in an organic solvent;

d) polybrominated diphenyl ether (PBDE) solution: 50 μg/ml in an organic solvent; all brominated species from mono- to decabrominated biphenyl (PBB) and mono- to decabrominated diphenyl ether (PBDE) shall be included in the PBB and PBDE stock solutions (see 8.4). Other stock solution concentrations can be utilized providing the standard solution concentrations given in 8.5.3 can be achieved.

e) matrix spiking solution; containing a total of four calibration congener standards in toluene as indicated in Table 1. The addition of 1 ml of a matrix spiking solution containing each of the four congeners in a concentration of 10 μg/ml is suitable for delivery of the required 10 μg (see 11.2 b)) in the matrix spike sample.

Table 1 – Matrix spiking solution

Level of bromination	Number of PBDE congeners	Number of PBB congeners
Mono to penta	1	1
Hexa- to deca-	1	1

8.2.2 Pre-extraction of the Soxhlet extractors

To clean the Soxhlet extractors (see Clause 6 c)), a 2 h pre-extraction is carried out with 70 ml of toluene. The washing solvent is discarded.

8.2.3 Extraction

The following steps shall be followed for sample extraction:

a) Quantitatively transfer 100 mg ± 10 mg of the sample into the extraction thimble (see Clause 6 d)) through a funnel (see Clause 6 h)). In order to ensure a quantitative transfer, the funnel is rinsed with approximately 10 ml of toluene extraction solvent. Record the sample mass to the nearest 0,1 mg.

b) 200 μl of the surrogate standard (see 8.2.1 a)) (50 μg/ml) is added (in accordance with 8.2.1).

c) In order to prevent the sample from floating, the extraction thimble is closed with glass wool (see Clause 6 e)). Approximately 60 ml of solvent is placed in the 100 ml round-bottomed flask, the equipment is covered with aluminium foil to exclude light and the sample is extracted for at least 2 h with each cycle being approximately 2 min to 3 min. Shorter extraction times may result in lower recoveries of the analytes, particularly for the higher molecular mass PBDEs.

d) The extract is placed in a 100 ml volumetric flask and the round-bottomed flask is rinsed with approximately 5 ml of solvent.

NOTE 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 disregarded in this case in the calculation.

e) The volumetric flask is filled with 100 ml of solvent. For a soluble polymer sample, the alternative extraction procedure may be applied as described in 8.2.4.

8.2.4 Alternative extraction procedures for soluble polymers

For a soluble polymer sample, especially PS-HI (or HIPS), the following alternative extraction procedure may be applied:

a) Weigh 100 mg of sample to the nearest 0,1 mg in a brown or amber vial (see Clause 6 l)) (at least 20 ml in volume).

NOTE 1 Other sample amounts can be used for samples with potentially very low or very high PBB or PBDE concentrations.

b) Transfer 9,8 ml of the appropriate solvent to the vial, and record the mass of the mixture.

NOTE 2 The solvent volume can be adjusted accordingly for samples with potentially very low or very high PBB or PBDE concentrations.

c) Add 200 µl of the surrogate standard (see 8.2.1 a)) (50 µg/ml) to the vial and record the new mass. Record the total mass of the sample, solvent, vial and cap.

d) Tightly cap the sample vial. Place it in an ultra sonic bath and sonicate for 30 min until the sample has been dissolved. A small piece of adhesive tape may be used to prevent the cap from vibrating loose. After the sample has dissolved, allow the vial to cool and record the mass. Verify that the mass is the same as recorded in step c) above.

e) Transfer 1,0 ml of the solution to a brown or amber vial (at least 12 ml in volume) and weigh the aliquot to the nearest 0,1 mg.

f) Choose a non-solvent for the polymer that is a good solvent for PBB/PBDE. Transfer 9,0 ml of the non-solvent to the vial and record the mass of vial and contents to the nearest 0,1 mg.

g) Allow the polymer to settle out or filter the mixture through a 0,45 µm PTFE membrane. Alternatively, transfer a 1,0 ml aliquot of solution to a 10 ml volumetric flask and weigh the aliquot accurately to 0,1 mg. Bring the volume up to the mark with fresh solvent, record the final mass and mix well.

NOTE 3 For example, dissolve a sample of PS-HI in toluene, then dilute a 1,0 ml aliquot of the solution with 9,0 ml of isooctane.

h) If the polymer precipitation step was followed, prepare a 10 % solution of the solvent in the non-solvent and use a calibrated volumetric flask to determine the density of the mixture. Use this density in later calculations.

i) Prepare a blank extraction and dilution by the same procedure.

j) Follow the analytical procedures and parameters described in 8.2.5, 8.3, 8.4 and 8.5. Calculate the PBB or PBDE concentration in the sample according to Clause 9.

8.2.5 Addition of the internal standard (IS)

Prepare a 1 ml aliquot of each sample and standard to be analysed and place it in a appropriate sample vial. Add 20 µl of internal standard solution (see 8.2.1 b)) to the vial and cap the vial. Invert the vial two times to mix.

Inject 1 µl of the sample solution into the GC-MS and analyse it according to the parameters described in 8.3.

8.3 Instrumental parameters

Different conditions might be necessary to optimize a specific GC-MS system to achieve effective separation of all calibration congeners and meet the QC and limits of detection (LOD) requirements. The following parameters have been found suitable and are provided as an example:

a) GC column: non-polar (phenyl-arylene-polymer equivalent to 5 % phenyl-methyl-polysiloxane), length 15 m; internal diameter 0,25 mm; film thickness 0,1 µm. A high-temperature column (maximum = 400 °C) shall be used for the stated GC conditions in the method.

b) PTV (programmed temperature vaporising), cool on-column, split/splitless injector or comparable injections systems can be used. The following parameters are recommended/ optional:

1) PTV programme: 50 °C to 90 °C (0 min) at 300 °C/min to 350 °C (15 min); modus: split purge time 1 min; purge flow 50 ml/min.

NOTE 1 The initial temperature can be adjusted by the operator, depending on the boiling point of the solvent used.

The use of an on-column injector can also be suggested as another means of introducing the sample. This is particularly beneficial for the sensitivity of heavier

congeners like octaBDE and nonaBDE. However, caution is advised due to sensitivity to matrix effects.

2) Split/splitless programme: injection temperature 280 °C, 1,0 µl splitless injection for 0,5 min duration. Split vent flow ~ 50,0 ml/min.

c) Injector liner: 4 mm single bottom taper glass liner with glass wool at bottom (deactivated).

NOTE 2 Additional deactivation of a purchased deactivated injector liner can be performed. This is especially useful if the "PR-206" quality control requirements in 11.3 cannot be achieved. An example of a chemical deactivation procedure is as follows: take a commercially available, factory-deactivated liner (split/splitless single-taper with glass wool at the bottom) and immerse it in 5 % dimethyldichlorosilane (DMDCS) in dichloromethane or toluene for 15 min. Pick it up with forceps and drain and immerse it three times in the DMDCS to make sure the glass wool has been thoroughly covered and flushed. Drain once more and blot the residue solution onto a clean wiper. Immerse the liner in methanol for 10 min to 15 min, and again drain/immerse three times. Rinse it inside and out with methanol from a squeeze bottle, followed by dichloromethane from a squeeze bottle. Transfer the liner to a vacuum oven purged with nitrogen and dry it at 110 °C for at least 15 min. Once dry it is ready for use.

d) Carrier: helium (see Clause 5, b)), 1,0 ml/min, constant flow.

e) Oven: 110 °C for 2 min, 40 °C/min ramp to 200 °C; 10 °C/min ramp to 260 °C; 20 °C/min ramp to 340 °C for 2 min.

f) Transfer line: 300 °C, direct.

g) Ion source temperature: 230 °C.

h) Ionization method: electron ionization (EI), 70 eV.

i) Dwell time: 80 ms.

NOTE 3 To achieve the required data quality for a PBB or PBDE GC peak, 3 to 4 scans of the quantification ions selected can be acquired per second. This will give the appropriate dwell time for each ion (m/z) to be monitored. The scan rate will result in a dwell time in the range of 80 ms per ion. It is noted that by default some software sets the dwell time as a function of the scan rate. The analysis of PBBs and PBDEs is carried out in SIM (single ion monitoring) modus with the mass traces (the bold mass traces have been used for quantification) given in Tables 2 and 3. These have been found suitable and are provided as examples.

Table 2 – Reference masses for the quantification of PBBs

Type of PBB	**Ions (m/z) monitored in the extract**		
Mono	**231,9**[a]	233,9	
Di	309,8	**311,8**	313,8[b]
Tri	387,8	**389,8**	391,8
Tetra	307,8	**309,8**	467,7
Penta	385,7	**387,7**	545,6
Hexa	465,6	**467,6**	627,5
Hepta	543,6	**545,6**	705,4
Octa	623,5	**625,5**	627,5
Nona	701,4	**703,4**	705,4 (863,4) [c]
Deca	781,3	**783,3**	785,3 (943,1;215,8, 382,6; 384,5)

[a] Bold = quantification ions.

[b] Underlined = identification ions.

[c] Brackets ( ) = optional ions.

Table 3 – Reference masses for the quantification of PBDEs

Type of PBDE	Ions (m/z) monitored in the extract		
Mono	**247,9**[a]	249,9	
Di	325,8	**327,8**	329,8[b]
Tri	403,8	**405,8**	407,8
Tetra	323,8	**325,8**	483,7
Penta	401,7	**403,7**	561,6
Hexa	481,6	**483,6**	643,5
Hepta	559,6	**561,6**	721,4
Octa	639,5	**641,5**	643,5 (801,3)[c]
Nona	717,4	**719,4**	721,4 (879,2)
Deca	797,3	**799,3**	959,1

[a] Bold = quantification ions.

[b] Underlined = identification ions.

[c] Brackets ( ) = optional ions.

A full scan run using a total ion current (“full scan”) MS method for each sample is also recommended for checking for the existence of peaks/congeners not present in the calibration (tentatively identified compounds or “TICS”) or not seen in the SIM window. If present, identify the peak and determine the class of compound (e.g. octabromobiphenyl, pentabromodiphenyl ether, etc.) by evaluation of the total ion spectra.

8.4 Calibrants

All brominated species from mono- to decabrominated biphenyl (PBB) and mono- to decabrominated diphenyl ether (PBDE) shall be included in the calibration. The availability of congener standards for a particular PBB or PBDE (e.g. pentaBDE) may vary from region to region. The following Table 4 is an example list of typically available calibration congeners that have been found suitable for this analysis.

Table 4 – Example list of commercially available calibration congeners considered suitable for this analysis

PBB[a]	Compound name
BB-003	4-Bromo biphenyl
BB-015	4,4'-Dibromo biphenyl
BB-029	2,4,5-Tribromo biphenyl
BB-049	2,2',4,5'-Tetrabromo biphenyl
BB-077	3,3',4,4'-Tetrabromo biphenyl
BB-103	2,2',4,5',6-Pentabromo biphenyl
BB-153	2,2',4,4',5,5'-Hexabromo biphenyl
BB-169	3,3',4,4',5,5'-Hexabromo biphenyl
FR-250	Technical mixture of nonabromo biphenyl, octabromo biphenyl (80 %) and heptabromo biphenyl
BB-209	Decabromo biphenyl
PBDE[a]	Compound name
BDE-003	4-Bromo diphenyl ether
BDE-015	4,4'-Dibromo diphenyl ether
BDE-033	2',3,4-Tribromo diphenyl ether
BDE-028	2,4,4'-Tribromo diphenyl ether
BDE-047	2,2',4,4'-Tetrabromo diphenyl ether
BDE-099	2,2',4,4',5-Pentabromo diphenyl ether
BDE-100	2,2',4,4',6-Pentabromo diphenyl ether
BDE-153	2,2',4,4',5,5'-Hexabromo diphenyl ether
BDE-154	2,2',4,4',5,6'-Hexabromo diphenyl ether
BDE-183	2,2',3,4,4',5',6-Heptabromo diphenyl ether
BDE-203	2,2',3,4,4',5,5',6-Octabromo diphenyl ether
BDE-206	2,2',3,3',4,4',5,5',6-Nonabromo diphenyl ether
BDE-209	Decabromo diphenyl ether
[a] Ballschmiter and Zell classification numbers have been used for PBBs and PBDEs.	

8.5 Calibration

8.5.1 General

Wherever possible, the solvent used for the sample and standard solutions shall be the same to avoid any potential solvent effects. A calibration curve shall be developed for quantitative analysis. At least five calibration solutions shall be prepared in equidistant concentration steps. Quantification is made on the basis of the measurement of the peak areas. The linear regression fit of each calibration curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of the linear calibration function.

NOTE Linear regression calibration is most desirable. In the event that the linear regression fit requirement (a relative standard deviation (RSD) of less than or equal to 15 %) cannot be achieved, the use of a polynomial calibration is suitable if another statistical treatment (e.g. coefficient of correlation or curve fit of 0.995 or better) can demonstrate acceptability.

8.5.2 PBB (1 μg/ml for each congener), PBDE (1 μg/ml for each congener) and surrogate standard (1 μg/ml) stock solution

100 μl of each PBB (see 8.2.1 c)) and each PBDE (see 8.2.1 d)) stock solution (50 μg/ml) and 100 μl of the surrogate stock solution (see 8.2.1 a)) (50 μg/ml) is placed in a 5 ml volumetric flask and filled up with extraction solvent up to the mark.

8.5.3 Standard solutions

The following calibration solutions are produced from the stock solution of the PBB (1 μg/ml for each congener), PBDE (1 μg/ml for each congener) and surrogate standard (1 μg/ml) (8.5.2). The volumes indicated in Table 5 are placed in a 1 ml volumetric flask with a pipette and filled with extraction solvent up to the mark. 20 μl of 10 μg/ml internal standard solution (see 8.2.1 b)) is then added.

For decaBDE, the calibration range suggested in Table 5 may have to be modified. When establishing a calibration curve for decaBDE, the lower range should be set according to the instrument's sensitivity. A higher concentration may be used for the upper range to account for the generally high (a mass fraction of 10 % to 12 %) levels of decaBDE normally found in samples.

Table 5 – Calibration solutions of PBBs and PBDEs

No.	Volume PBB+PBDE+surrogate μl (see 8.5.2)	Volume internal standard μl (see 8.2.1 b))	*c*(PBB) *c*(PBDE) ng/ml per congener	*c*(Surrogate) ng/ml
1	50	20	50	50
2	150	20	150	150
3	250	20	250	250
4	350	20	350	350
5	450	20	450	450

The internal standard is used for the correction of the injection error. Therefore the evaluation of the response factor or ratio is carried out by A/A_{IS}.

To produce the calibration straight lines, the response A/A_{IS} is plotted against the concentration ratio c/c_{IS}.

A linear regression is carried out using Equation (1):

$$\frac{A}{A_{IS}} = a \times \frac{c}{c_{IS}} + b \quad (1)$$

where

A is the peak area of PBB, PBDE or the surrogate in the calibration solution;

A_{IS} is the peak area of the internal standard;

c is the concentration of PBB, PBDE or the surrogate per congener (ng/ml);

c_{IS} is the concentration of the internal standard (ng/ml).

NOTE 1 It is common practice to set the internal standard concentration to 1 ng/ml for the internal standard methods when the amount and concentration of the internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

NOTE 2 A polynomial (e.g. second-order) regression can be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

9 Calculation of PBB and PBDE concentration

9.1 General

Only detected PBB and PBDE compounds shall be included in a total summation.

In the event that there are no PBDEs or no PBBs detected in the sample, the total PBDE (or PBB) shall be reported as a function of the congener(s) with the highest method detection limits. For example, if the method detection limit is 20 mg/kg for decaBB and 10 mg/kg for all other PBBs, and no PBBs are found in the sample, the total PBB shall be reported as <20 mg/kg.

Analytes detected below the limit of quantification (and above the limit of detection) shall be summed using the limit of quantification for the analyte detected. For example, if decaBB is found above the limit of detection but below the limit of quanitification, and if the limit of quantification is 60 mg/kg for decaBB and no other PBBs were found above the limit of detection in the sample, the total PBB shall be reported as 60 mg/kg.

9.2 Calculation

Quantify the samples using the calibration curve. The instrument software usually performs the quantification. Normally, the calibration level of the internal standard for all five calibration levels are set to 1 in the instrument method, but it can also be performed manually using the equation of the fit from the calibration.

For a linear fit, the equation takes the form of

$$y = ax + b \tag{2}$$

where

y is the response factor or ratio (A/A_{IS}) for the congener in the sample;

a is the slope of the line that best fits the calibration obtained in Equation (1);

x is the instrumental result (c/c_{IS} where c_{IS} is commonly = 1) in ng/ml (the concentration of the congener in the extract);

b is the intercept on the y-axis of the calibration curve.

For a quadratic fit the equation takes the form of:

$$y = ax^2 + bx + c \tag{3}$$

where

y is the response factor or ratio (A/A_{IS}) for the congener in the sample;

a and *b* are constants that correspond to the curve that best fits the calibration;

x is the instrumental result in ng/ml (the concentration of the congener in the extract);

c is the *y* intercept or the concentration when the response factor equals 0.

Equation (2), which is in the form of a linear equation, can be rewritten in the form of Equation (4):

$$c = \left(\frac{A}{A_{IS}} - b \right) \left(\frac{c_{IS}}{a} \right) \quad (4)$$

where

A is the peak area of PBB, PBDE or the surrogate;

A_{IS} is the peak area of the internal standard;

c is the (intermediate) concentration of PBB, PBDE or the surrogate per congener in ng/ml;

c_{IS} is the concentration of the internal standard in ng/ml.

NOTE 1 It is common practice to set the internal standard concentration to 1ng/ml for the internal standard methods when the amount and concentration of internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

NOTE 2 A polynomial (e.g. second-order) regression may be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

If the concentration of each congener in a sample does not fall within the range of its respective calibrants, prepare a serial sample dilution that will bring the concentration of the congener to the midpoint of the calibration. Analyse the dilution and use the dilution factor to quantify the concentration of those congeners that were not within the calibration range in the original analysis. The dilution factor (D) can be calculated by dividing the final volume of the dilution by the volume of the aliquot:

$$D = \frac{V_f}{V_a} \quad (5)$$

where

D is the dilution factor;

V_f is the final volume in ml;

V_a is the volume of the aliquot in ml.

Equation (4) does not give the final concentration as the volume of the organic solvent, the mass of the sample and the volume of the extract and any dilution factor needs to be taken into account. A conversion factor (F) to convert the units from ng to μg is also needed. The final concentration of PBB, PBDE or the surrogate per congener in the sample can be calculated by using Equation (6):

$$c_{final} = \left(\frac{A}{A_{IS}} - b \right) \times \frac{c_{IS}}{a} \times \frac{V}{m} \times F \quad (6)$$

where

c_{final} is the concentration of PBB, PBDE or the surrogate per congener in the sample in μg/g;

V is the final extraction volume (100 ml);

m is the mass of the sample in grams;

F is a conversion factor for ng to μg (1×10^{-3}).

The calculation example shown above is for linear regression calibration only. A separate calculation is required if polynomial regression calibration is utilized.

The total results are the sum of the concentration of each PBB (total PBBs) and the sum of the concentrations of each PBDE (total PBDEs).

The total PBDEs or the total PBBs can be calculated by summing the measured concentrations of all of the signals identified as a PBDE or PBB. The PBBs and the PBDEs that are included in the total results shall include all the signals with appropriate mass, retention time and ion ratios for a PBB or a PBDE. The PBBs and PBDEs included in the totals shall not be limited only to those used in the calibration solutions since most entities are interested in the concentration of the total PBBs and total PBDEs, not specific isomers.

The calibration solutions can be used to establish an average response factor for each degree of bromination within the PBDEs and PBBs. The average response factors can then be used in the calculation of the measured concentration of detected congeners in the sample that are not included in the calibration (e.g. tentatively identified compounds or “TICS”, see also 8.3). Automatic integration of signals meeting the criteria for a PBB or a PBDE is a common function of software used in GC-MS trace analysis.

The PBDEs isolated from the sample extraction (see 8.2.3) are quantified by adding the internal standard (CB 209) (see 8.2.1 b)) to an extract aliquot, injecting the solution into the GC-MS, measuring the area of the analyte peak(s) and the area of the CB 209 peak and calculating the concentration of the analyte according to Equations (4) and (6). Data on the surrogate standard (DBOFB) (see 8.2.1 a)) are used for quality control purposes (see 11.2 d)) and are not used in the calculation of the analyte concentration(s) in the sample.

10 Precision

10.1 Threshold judgement

The overall threshold judgement with respect to compliance with a maximum allowable concentration limit of <1 000 mg/kg total PBB or PBDE from interlaboratory study 4B (IIS 4B) results is shown in Table 6.

Table 6 – IIS4B threshold judgement

Sample ID/ Compound type	Expected threshold judgement P or F [a]	Number of laboratories submitting threshold judgement results	Number of laboratories submitting correct threshold judgement results	Number of laboratories submitting incorrect threshold judgement results
IIS4B-K01 / Total PBB	P	11	11	0
IIS4B-K01 / Total PBDE	F	11	10	1
IIS4B-L02 / Total PBB	P	11	11	0
IIS4B-L02 / Total PBDE	P	11	11	0
IIS4B-M03 / Total PBB	P	11	11	0
IIS4B-M03 / Total PBDE	F	11	11	0

[a] An expected threshold judgement of “P” refers to a result <1 000 mg/kg and an expected threshold judgement of “F” refers to a result >1 000 mg/kg.

10.2 Repeatability and reproducibility

When the values of two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table 7 below, the absolute difference between the two test results obtained will not exceed the repeatability limit *r* deduced by statistical analysis of the international interlaboratory study 4B (IIS 4B) results in more than 5 % of cases.

When the values of two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table 7 below, the absolute difference between the two results will not be greater than the reproducibility limit *R* by statistical analysis of interlaboratory study 4B (IIS 4B) results in more than 5 % of cases.

Table 7 – IIS4B repeatability and reproducibility

Parameter	Mean value mg/kg	*r* mg/kg	*R* mg/kg
Total PBDE	1 298	203,4	429,1
Total PBDE	4 620	586,1	2 490,5
HexaBDE	94	9,3	47,2
HexaBDE	306	52,5	206,8
HeptaBDE	519	129,8	304,7
HeptaBDE	1 748	318,4	939,7
OctaBDE	484	75,1	124,2
OctaBDE	1 688	203,4	741,1
NonaBDE	211	43,9	131,8
NonaBDE	696	177,7	499,1
DecaBDE	12	10,1	37,0
DecaBDE	81	26,3	73,7

See Annex F for supporting data.

11 Quality assurance and control

11.1 Resolution

At least annually (or any time instrumental parameters are changed), a 5 μg/ml solution of technical decaBDE (BDE-209, e.g. Wellington Laboratories[1] Cat. # TBDE-83R or equivalent with BDE-209 ~ 96,9 % and BDE-206 ~ 1,5 %) with internal standard shall be analysed to confirm that the GC-MS system and parameters are suitable for the accurate determination of nonaBDEs in the presence of BDE-209 and to demonstrate that congener degradation is not occurring. After the concentration (in μg/ml) of BDEs 206 and 209 measured in the injection solution is measured, the 206/(206 + 209) per cent ratio (“PR – 206”) is calculated as shown below.

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1 Wellington Laboratories Cat. N°. TDE-83R is an example of a suitable product supplied available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of this product.

$$PR = \frac{c_A}{c_A + c_B} \times 100 \quad (7)$$

where

PR is the per cent ratio, “PR-206”;

c_A is the measured concentration of BDE-206 in μg/ml;

c_B is the measured concentration of BDE-209 in μg/ml.

Table 8 gives an example calculation.

Table 8 – Example calculation

BDE congener	Theoretical injection concentration μg/ml	Measured concentration μg/ml	PR-206 %
BDE-209	4,845	5,200	(0,107 / 5,307) × 100 = 2,01
BDE-206	0,076	0,107	
Total		5,307	

A calculated PR-206 in the injection <4,0 is acceptable and samples can be tested. A calculated PR-206 >4,0 is unacceptable and samples shall not be tested until this condition is corrected. Effective corrections include replacement of the injection liner, reduction of the injection temperature, reduction of oven temperature or times, etc. New limits of detection (LOD) studies are required if the instrumental parameters are changed.

11.2 Performance

The following steps are taken for the quality control:

a) One reagent blank shall be extracted with each sequence of samples. The reagent blank is 60 ml of only solvent taken through the entire extraction procedure according to 8.2.3 or 8.2.4. The concentration of any PBB or PBDE compounds found in the method blank shall be less than the method detection limits (see 11.3) for each compound.

b) One sample per sequence or one every ten samples, depending on the sample load, shall be spiked with 10 μg of each congener in the matrix spiking solution (see 8.2.1 e). The following formula shall be used for calculation:

$$R = \frac{C_m - C}{C_s} \times 100 \quad (8)$$

where

R is the recovery of each PBB or PBDE congener in %;

C_m is the concentration of each PBB or PBDE congener in the matrix spike in ng/ml;

C is the concentration of each PBB or PBDE congener in the original sample in ng/ml;

C_s is the concentration of PBB or PBDE spike solution in ng/ml.

The per cent recovery for each congener shall be between 50 % and 150 %. The per cent recovery for each matrix spike shall be recorded and tracked in a spreadsheet to determine possible matrix effects in the analysis.

c) After every tenth sample run and at the end of each sample set, analyse a continuing calibration check standard (CCC). A CCC is an unextracted mid-range calibrant that is analysed as a sample. The per cent recovery for each congener shall be between 70 % and 130 %. If the per cent recovery for any congener in the CCC standard falls outside of

this range, the CCC standard should be reinjected within 12 h. If the recovery is still out of range after re-injection of the CCC standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples injected before the last successful CCC standard may be reported, but all samples after the failing CCC standard shall be re-analysed with a new calibration.

d) The surrogate recovery shall be monitored for each sample. Per cent (%) surrogate recovery shall be calculated by the following formula:

$$SR = \frac{ms}{10\ \mu g} \times 100 \quad (9)$$

where

SR is the surrogate recovery, as a percentage (%);

ms is the total mass (μg) of surrogate measured in the final sample solution.

Acceptable surrogate recovery shall be between 70 % and 130 %. If the surrogate recovery for any sample is outside of these limits, the sample shall be re-analysed. If, after re-analysis, the surrogate recovery is not within these limits, the sample shall be re-extracted and re-analysed.

e) From the results of the five calibrants (according to Table 5), calculate the average response (peak area) for the internal standard. The internal standard (IS) response for each sample shall be monitored throughout the analysis and compared to the average. If, at any point in the analysis, the IS response fluctuates below 50 % or above 150 % of the average, the sample is deemed out of control and shall be re-analysed. If the IS response is still out of range, check the results of the duplicate extract. If both are out of range and biased in the same direction, report data as suspect due to matrix effects.

f) A solvent blank run between each injection is recommended in order to be certain that there is no analyte carry-over from sample to sample. This is particularly important when samples containing high levels of decaBDE and/or potentially interfering brominated flame retardants are analysed. Failure to determine that the instrument is free of contaminating analytes may result in falsely elevated results. It is recommended that the solvent shall contain a small amount of silylating agent (BSA, BSTFA) to maintain the inertness of the injector liner.

g) The retention time of analytes having an identification mass corresponding to BDE-209 and BDE-206 shall be within ±20 s of the BDE-209 and BDE-206 standards used in the calibration solutions and the corresponding retention time difference between BDE-209 and BDE-206 shall be less than 130 % of the difference between BDE-209 and BDE-206 standards used in the calibration solutions in order to be confirmed as being BDE-209 and/or BDE-206. Peaks eluting outside this range cannot be identified as BDE-209 and/or BDE-206. (Samples containing decaBDE will have BDE-206 as the dominant nonaBDE.) The use of retention times as a confirmation criterion is a widely accepted practice.

11.3 Limit of detection (LOD) or method detection limit (MDL) and limit of quantification (LOQ)

A limit of detection (LOD) or method detection limit (MDL) study shall be completed before conducting testing and each time there is a significant change in the method or instrument type. The LOD or MDL is most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated LOD or MDL shall be performed for this analysis. The complete LOD or MDL for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. IUPAC recommends a factor of 3 for a minimum of six replicates, whilst EPA utilizes a one-sided confidence interval with the multiplier equal to Student's *t* value chosen for the number of replicates and the level of confidence (e.g. $t = 3{,}36$ for six replicates for 99 % confidence).

a) Mill approximately 2 g of suitable polymer from a pure source known not to contain brominated flame retardants or other compounds that may interfere with the analysis (e.g. polyethylene material BCR-681 or other).

b) Weigh out 100 mg of the milled polymer and place it in a new extraction thimble. Repeat this step six more times.

c) Place the extraction thimble in the Soxhlet extraction apparatus.

d) Spike the thimble with 5 μg of each calibration congener approximating the concentration of the lowest concentration calibrant.

e) Use the procedure (extraction according to 8.2.3 or 8.2.4) to extract each of the samples. Analyse accordingly.

f) The per cent recovery of each congener shall be between 70 % and 130 %. If the recovery is above or below these limits, the analysis shall be repeated. If the recovery is outside of these limits a second time, the entire extraction and analysis procedure shall be repeated.

g) Each congener shall have a calculated LOD or MDL of less than or equal to 100 mg/kg. If the calculated LOD or MDL for any of the congeners is above these limits, the procedure, extraction and analysis shall be repeated for that/those congener(s).

h) The limits of quantification (LOQ) for each congener shall be, at a minimum, three times the respective LOD or MDL. Unlike the LOD or MDL, which relates to detection only, the limit of quantification (LOQ) is a concentration that can be accurately quantified for a given compound.

If the required LOD or MDL cannot be met, a concentration step can be added to the extraction procedure. Since the concentration step will also increase the resin concentration in the extract, a clean-up step is also recommended for each sample. This will extend the life of the column and reduce the frequency of instrument maintenance. If the concentration and clean-up steps are used in the analysis, they should also be used for the LOD or MDL samples.

12 Test report

For the purpose of this part of IEC 62321, IEC 62321-1:2013, 4.8 (Test report) applies in addition to the following:

- identification of technical mixtures (if any) used for calibration.

Annex A
(informative)

Determination of PBB and PBDE in polymers by ion attachment mass spectrometry (IAMS)

A.1 Principle

The ion attachment mass spectrometry (IAMS) method is suitable to identify brominated flame retardants (BFRs) based on their different mass number and isotope distribution pattern. This method allows the direct analysis of a polymer sample without prior pre-treatment process.

NOTE While not specifically evaluated by this method, IAMS can be similarly used for the determination of tribrominated to decabrominated biphenyls (PBB) and tribrominated to decabrominated diphenyl ethers (PBDE) compounds. Mono- and di-brominated PBB and PBDE compounds cannot be accurately measured by this technique due to their volatility profile.

The IAMS method is suitable for the fast qualitative and semi-quantitative analysis of decabromobiphenyl and technical mixtures of decabromodiphenyl ether, octabromodiphenyl ether and pentabromodiphenylether flame retardant compounds in the range of 100 mg/kg to 2 000 mg/kg and as high as 100 000 mg/kg for decaBDE. Since isomers cannot be identified, only the PBBs and PBDEs with the same number of bromine attached are distinguished. For single congener analysis GC-MS should be used.

A.2 Reagents and materials

a) Tetrahydrofuran (GC grade or higher).

b) Dry air (a dew point is less than –50 °C , grade 3).

c) Calibrants: refer to A.5.4 and 8.4.

d) PBDE response factor standard: refer to Table A.3.

e) Internal standard (IS) in a polymer matrix (for correcting recovery ratio and instrumental fluctuation). The internal standard shall be present in the polymeric matrix at ~0,2 % by weight, with a mass number up to 500 and a boiling point in the range of DecaBDE. An ABS or polystyrene resin containing IRGANOX259, (1,6-Hexamethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]),CAS: 35074-77-2, Formula: $C_{40}H_{62}O_6$) has been found suitable.

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

A.3 Apparatus

The following items shall be used for the analysis:

a) Analytical balance capable of measuring accurately to 0,000 01 g (0,01 mg).

b) Cryogenic grinding with liquid N2 cooling.

c) Sample pan (made of stainless steel, diameter 4 mm).

d) Nipper (a kind of hand tool to cut a sample).

e) Medicine spoon.

f) Tweezers.

g) Metallic rod (~4 mm diameter).

h) Mass spectrometer equipped with an ion attachment ion source (“IAMS”). The IAMS equipment consists of the Li^+ attachment reaction chamber with Li^+ emitter. Additionally, the IAMS coupled with direct injection probe (DIP) which has capability of programmed heating up to 350 °C. The thermal desorbed sample molecules (M) form adducts ($(M + Li)^+$)

with Li^+ in the reaction chamber. Nitrogen gas of around 50 Pa is introduced into the reaction chamber which has the function to decelerate Li^+ and to remove excess energies of Li^+ adducts. In the polymer analysis, since irreducible gas from the matrix decreases the sensitivity of Li^+, it is desirable to use dry air instead of nitrogen to oxidize the sample. The mass spectrometric detector shall be able to perform selective ion monitoring and have an upper mass range of at least 1 000 m/z. See Annex B for an informative diagram of an IAMS instrument.

A.4 Sampling

A.4.1 General

Sampling shall be performed as described in IEC 62321-2. Unless indicated otherwise (e.g. "..using a nipper."), cryogenic grinding with liquid nitrogen cooling is recommended to achieve the particle size reduction specified.

A.4.2 Qualitative stage

The sample is cut into pieces using a nipper.

A.4.3 Semi-quantitative stage

a) The sample shall be ground as small as 500 μm in diameter.

b) PBB/PBDE calibrants shall be also ground in the same way.

A.5 Procedure

A.5.1 General instructions for the analysis

a) Prior to the sample measurement, the IAMS equipment should be optimized to clearly observe an intensity of calibrant containing approximately 300 mg/kg of DecaBDE above background noise.

b) A signal-background ratio (S/B) at m/z 966 of more than 10 is required.

A.5.2 Sample preparation

A.5.2.1 General

A two-stage measurement is performed. The first stage is qualitative for identifying PBB/PBDE using a full scan mode. Samples that have detectable PBBs/PBDEs in the first stage continue to the second stage quantitative analysis using the SIM mode.

A.5.2.2 Qualitative stage

a) Approximately 0,5 mg to 1,5 mg of sample is pressed on the sample pan using a metallic rod in such manner that thermal conductivity is secured.

b) Place the sample pan into the DIP and insert it to the instrument.

A.5.2.3 Semi-quantitative stage

a) Approximately 0,5 mg of internal standard with the matrix A.2 e) is weighed precisely into the sample pan.

b) Approximately 0,5 mg to 1,5 mg of ground sample is weighed precisely into the sample pan.

c) Place the sample pan into the DIP and insert it into the instrument.

NOTE Refer to the flow chart (see Annex E) for an example of qualitative and semi-quantitative applicability.

A.5.3 Instrumental parameters

Different conditions might be necessary to optimize a specific IAMS system to achieve effective determination of PBBs and PBDEs and meet the QC and MDL requirements. The following parameters (see Table A.1) have been found suitable and are provided as an example:

a) In case of interference existence in qualitative (SCAN-mode) analysis, other relative isomer-ion of PBBs/PBDEs shall be applicable for quantification using a SIM-mode measurement.

b) 1 μg of DecaBDE reagent should be measured in profile mode for checking whether the mass axis has shifted. If the central axis is within ±0,15 m/z at 966,17 m/z, analysis can be continued. If it is more than ±0,15, the analysis shall be stopped and mass tuning should be carried out using perfluorokerocene with EI mode.

NOTE To achieve the required data quality for a PBB or PBDE mass spectrum, the minimum mass resolution is 1 500 minimum (m/z 966) in order to identify ambiguous samples.

c) In the analysis, the detector response of the octafluoropentanol (OFP) introduced into the instrument as a standard gas should be carefully monitored. If the OFP ion intensity (m/z 239) decreases below 50 % of the expected normal value during heating of the sample, the analysis shall be repeated changing the sample amount and heating ratio (e.g. the sample amount is 0,5 mg, the temperature program starts at 30 °C with 64 °C/min up to 300 °C (hold time 2,5 min)). If the intensity is still below 50 %, this method cannot be used and the GC-MS method shall be applied.

Table A.1 – Measurement condition of IAMS

Ion source temperature	220 °C					
DIP temperature	For resin	30 °C (128 °C/min) 180 °C (64 °C/min) 300 °C (3min)				
	For reagent	30 °C (128 °C/min) 130 °C (32 °C/min) 180 °C (64 °C/min) 300 °C (1 min)				
Ionization method	Ion attachment (Li^+)					
Ionization pressure	50 Pa with dry air (dew point <70°C)					
Qualitative analysis (SCAN)	Mass range: 200 m/z –1 000 m/z Cycle time: 2,5 s/scan					
Quantitative analysis (Selected ion monitoring)		Monitored ion (m/z)				
	OFP [a]	239,0				
	Tri-BB	**412,8** [b]	414,8 [c]	Tri-BDE	**396,8**	398,8
	Tetra-BB	**492,7**	490,7	Tetra-BDE	**476,7**	474,7
	Penta-BB	**570,6**	572,6	Penta-BDE	**554,6**	556,6
	Hexa-BB	**650,5**	648,5	Hexa-BDE	**634,5**	632,5
	Hepta-BB	**730,4**	728,4	Hepta-BDE	**714,4**	712,4
	Octa-BB	**808,4**	806,4	Octa-BDE	**792,3**	794,3
	Nona-BB	**886,3**	888,3	Nona-BDE	**870,3**	872,3
	Deca-BB	**966,2**	964,2	Deca-BDE	**950,2**	948,2
Dwell time	150 ms					

[a] Octafluoropentanol gas is used in order to monitor the variation of Li^+ intensity.

[b] Bold = Quantification ions.

[c] Underlined = Identification ions.

A.5.4 Calibrants

Tables A.2 and A.3 show the commercially available reference materials used as calibrants (and to correct for polymer matrix interferences) and PBDE response factor standards considered suitable for this analysis.

Table A.2 – Example list of commercially available calibrant reference materials considered suitable for this analysis

PBB – PBDE Mixture	Compound name(s)
NMIJ CRM8108-b, CRM8110-a	Decabromo diphenyl ether
IRMM ERM590, ERM591	Technical mixture of pentabromo diphenyl ether, octabromo diphenyl ether, decabromo diphenyl ether and decabromo biphenyl.

Table A.3 – Example PBDE response factor standards (i.e. BDE-WD (Wellington), solution/ mixture of polybrominated diphenyl ether congeners(PBDE))

Common name	Commercial name	Chemical name	Concentration μg/ml
Mono-BDE	BDE-1	2-Bromodiphenyl ether	1,0
	BDE-3	4- Bromodiphenyl ether	
Di-BDE	BDE-10	2,6- Dibromodiphenyl ether	1,0
	BDE-15	4,4’- Dibromodiphenyl ether	
Tri-BDE	BDE-30	2,4,6- Tribromodiphenyl ether	1,0
	BDE-37	3,4,4’- Tribromodiphenyl ether	
Tetra-BDE	BDE-54	2,2’,6,6’- Tetrabromodiphenyl ether	1,0
	BDE-60	2,3,4,4’- Tetrabromodiphenyl ether	
Penta-BDE	BDE-82	2,2’,3,3’,4- Pentabromodiphenyl ether	1,0
	BDE-104	2,2’,4,6,6’- Pentabromodiphenyl ether	
Hexa-BDE	BDE-128	2,2’,3,3’,4,4’- Hexabromodiphenyl ether	2,0
	BDE-155	2,2’,4,4’,6,6’- Hexabromodiphenyl ether	
Hepta-BDE	BDE-170	2,2’,3,3’,4,4’,5- Heptabromodiphenyl ether	2,0
	BDE-188	2,2’,3,4’,5,6,6’- Heptabromodiphenyl ether	
Octa-BDE	BDE-195	2,2’,3,3’,4,4’,5,6- Octabromodiphenyl ether	2,0
	BDE-202	2,2’,3,3’,5,5’,6,6’- Octabromodiphenyl ether	
Nona-BDE	BDE-206	2,2’,3,3’,4,4’,5,5’,6- Nonabromodiphenyl ether	5,0
	BDE-208	2,2’,3,3’,4,5,5’,6,6’- Nonabromodiphenyl ether	
Deca-BDE	BDE-209	Decabromodiphenyl ether	5,0

A.5.5 Calibration

A.5.5.1 General

Wherever possible, the solvent used for sample and standard solutions shall be the same to avoid any potential solvent effects.

A.5.5.2 Standard materials

The use of internal standards (A.2.e) with melting points that are higher than the target analytes (PBB, PBDE) are required to avoid interference caused by vaporization of the sample matrix (e.g. resin) or analytes.

To have the same matrix effect as the actual sample, standard reference materials are considered more suitable to make calibration curve (calibrant). Standard reference materials (Table A.2)) are used for calibration.

Adequate amounts of calibrants are weighed into the each sample pan. Calibrant reference materials (see Table A.2) in the concentrations as given in Table A.4 are used for calibration.

Table A.4 – Calibrant amounts

	Calibrant reference materials	**Amount IS with material** mg	**Concentration calibrant** mg/kg	**Amount calibrant** mg	**Absolute amount** (PBDE) ng
1	CRM-8108-b	0,2	312	0,25	78
2	CRM-8108-b	0,2	312	0,5	156
3	CRM-8110-a	0,2	886	0,35	310
4	CRM-8110-a	0,2	886	0,7	620
5	CRM-8110-a	0,2	886	1,5	1 330

The internal standard is used for the correction of the injection error. Therefore, the evaluation of the response factor or ratio is carried out by the quotient A/A_{IS}.

To produce the calibration straight lines the response $A/A_{IS} \times m_{IS}$ is plotted against the concentration c

A linear regression is carried out using Equation (A.1):

$$\frac{A}{A_{IS}} \times m_{IS} = ac + b \quad \text{(A.1)}$$

where

A is the peak area of PBB, PBDE in the calibration solution;

A_{IS} is the peak area of the internal standard;

c is the concentration of PBB, PBDE in ng;

m_{IS} is the mass of the internal standard in milligrams;

NOTE It is common practice to set the internal standard mass to 1 for the internal standard methods when the amount and concentration of internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

A.6 Calculation of PBB and PBDE concentration

A.6.1 General

Only detected PBB and PBDE values shall be included in a total summation. It is pointless to include limits of detection in the summation for non-detected analytes.

NOTE If large amounts of Tetrabromobisphenol A (2,3-dibromopropylether) are found together with small amounts of DecaBDE, 500 mg/kg of DecaBDE can be distinguished from 1 % or less of tetrabromobisphenolA (2,3-dibromopropylether) by summing the mass profile from 1 min to 1min and 16 s. If 1 % or more of Tetrabromobisphenol A (2,3-dibromopropylether) is present, move to the GC-MS method (see 8.2).

In the event that there are no PBDEs or no PBBs detected in the sample, the total PBDE (or PBB) shall be reported as a function of the congener(s) with the highest method detection limits. For example, if the method detection limit was 20 mg/kg for decaBB and 10 mg/kg for all other PBBs, and no PBBs were found in the sample, the total PBB shall be reported as <20 mg/kg.

Analytes detected below the limit of quantification (and above the limit of detection) shall be summed using the limit of quantification for the analyte detected. For example, if decaBB was found above the limit of detection but below the limit of quantification, and if the limit of quantification was 60 mg/kg for decaBB, and no other PBBs were found above the limit of detection in the sample, the total PBB shall be reported as 60 mg/kg.

A.6.2 Calculation

For a linear fit, the equation takes the following form:

$$y = ax + b \tag{A.2}$$

where

y is the response factor or ratio ($A/A_{IS} \times m_{IS}$) for the congener in the sample;

a is the slope of the line that best fits the calibration obtained in Equation (A.1);

x is the instrumental result (the mass in ng of the congener in the extract);

b is the intercept on the y-axis of the calibration.

For a quadratic fit the equation takes the following form:

$$y = ax^2 + bx + c \tag{A.3}$$

where

y is the response factor or ratio ($A/A_{IS} \times m_{IS}$) for the congener in the sample;

a and b are constants that correspond to the curve that best fits the calibration;

x is the absolute amount of the analyte in ng;

c is the y intercept or the concentration when the response factor equals 0.

The calibration solution or calibrant (e.g. ERM EC-590) can be used to establish an average response factor for each degree of bromination for PBBs and PBDEs.

The average response factor for each congener can then be used in the calculation of the measured concentration of detected congeners in the sample that are not included.

The response factor of deca-BDE for example that is calculated from the BDE-WD (Wellington) is displayed in Table A 5. The final concentration of PBB, PBDE per congener in the sample can be calculated by using Equation (A.4):

$$c_{final} = \left(\frac{A}{A_{IS}} \times m_{IS} - b \right) \times \left(\frac{1}{a} \right) \times \frac{1\,000}{m} \times S \tag{A.4}$$

where

c_{final} is the concentration of PBB, PBDE or the surrogate per congener in the sample in μg/g;

A is the peak area of DecaBDE in the standard;

A_{IS} is the peak area of the internal standard;

m_{IS} is the mass of the internal standard in milligrams;

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

m is the mass of the sample in milligrams;

S is the response factor of each congener (refer to Table A.5).

Table A.5 – Response factor of each PBDE congener[a]

PBDE congener	Monitored ion m/z	Injection amount μg	Response factor VS DecaBDE
Tri-BDE	412,8	0,2	0,14
Tetra-BDE	492,7	0,2	0,11
Penta-BDE	570,6	0,2	0,21
Hexa-BDE	650,5	0,4	0,32
Hepta-BDE	730,4	0,4	0,56
Octa-BDE	808,4	0,4	0,62
Nona-BDE	886,3	1,0	0,93
Deca-BDE	966,2	0,5	1,00
NOTE The response factor VS DecaBDE for Decabromo biphenyl (DecaBB) is 0,70 which can be determined using CRM（ERM590, ERM591）.			
[a] Reference standard: BDE-WD (Wellington), solution/mixture of polybrominated dipenyl ether congeners (PBDE)			

A.6.3 Judgement of ambiguous spectrum

When the nominal mass of m/z = 950 is detected, it has the ambiguity to be DecaBB (m/z = 950,17) or tetrabromobisphenol A (2,3-dibromopropylether) (CAS:21850-44-2, m/z = 950,50) (voir la Figure A.1). The following procedure should be performed for clear identification:

a) measure an ambiguous sample near m/z = 950 profile using a profile mode method;

b) judgement can be performed by the difference of the isotopic pattern and the accurate mass number of the two compounds;

c) the accurate mass number is the intersection obtained by extending a perpendicular line from the center of highest peak to the mass (X) axis.

NOTE If large amounts of Tetrabromobisphenol A (2,3-dibromopropylether) are found together with small amounts of DecaBB, 500 mg/kg of DecaBB can be distinguished from 1 % or less of TetrabromobisphenolA (2,3-dibromopropylether) by summing the mass profile from 1 min to 1 min and 16 s. If 1 % or more of Tetrabromobisphenol A (2,3-dibromopropylether) is present, move to the GC-MS method (see 8.2).

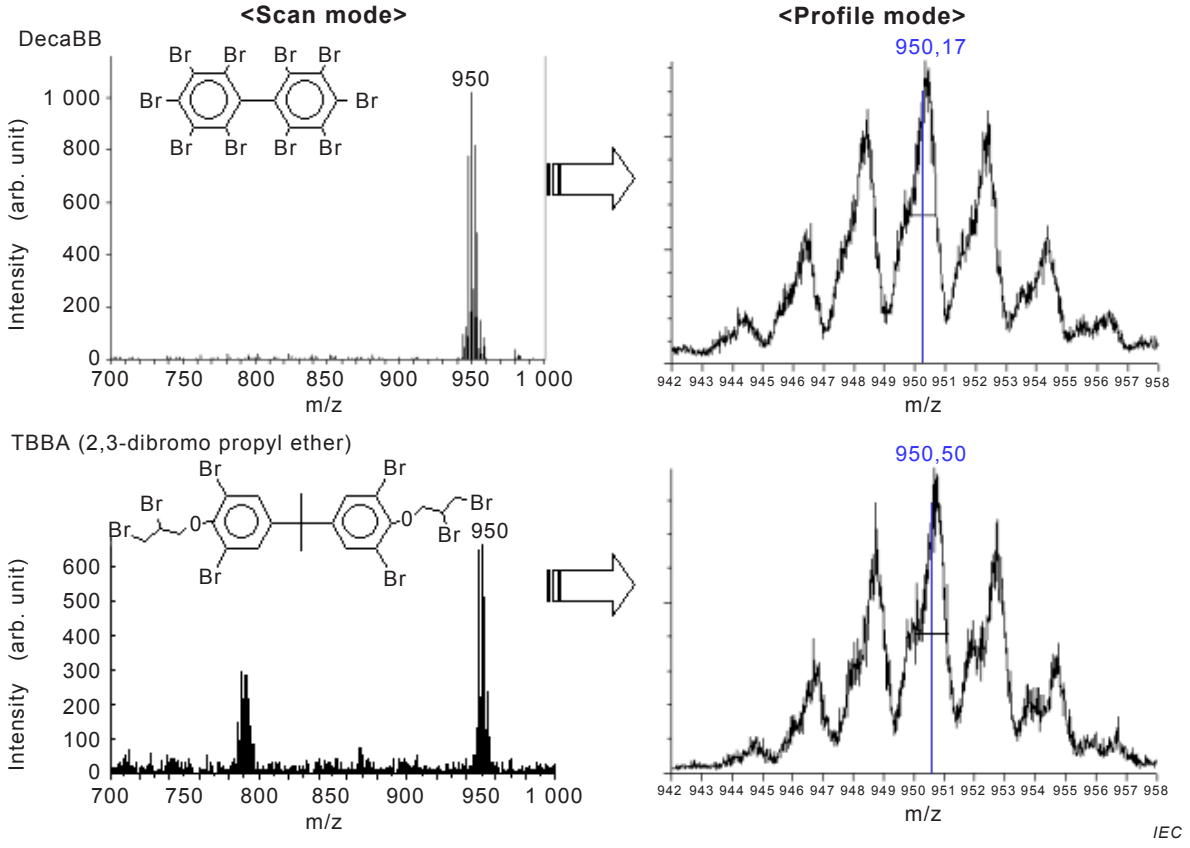


Figure A.1 – Mass spectra of Deca BB and TBBA obtained in scan mode and profile mode

In the event that paraffin wax is interfering with the quantification ion for Tetra-, Penta- and Hexa-BDE, especially in the presence of polypropylene or polystyrene, the identification can be ensured by the isotope pattern recognition of each congener as shown below (see Figure A.2).

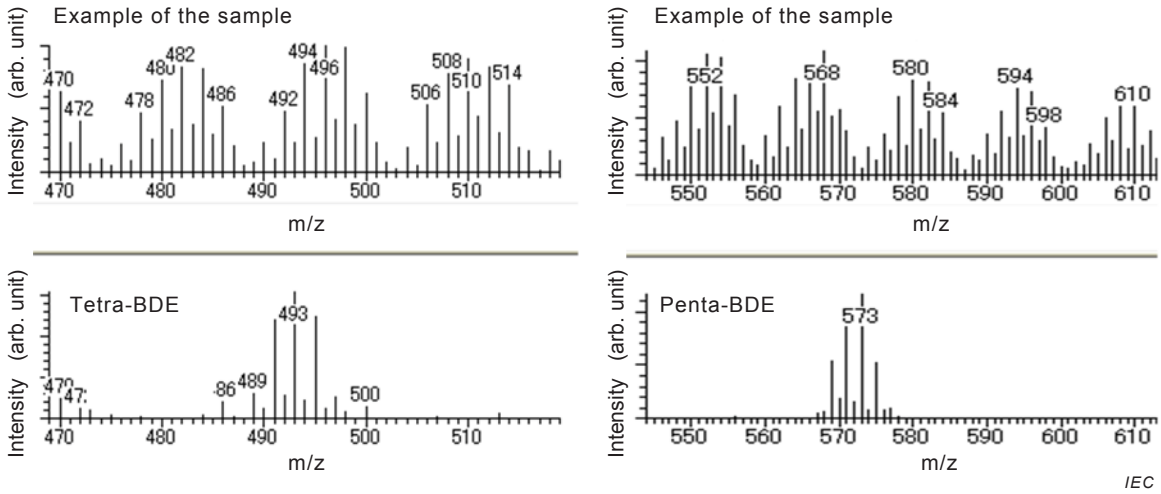


Figure A.2 – Identification of Tetra-BDE and Penta-BDE by isotope pattern recognition

A.7 Precision

A.7.1 Threshold judgement

The overall threshold judgement with respect to compliance with a maximum allowable concentration limit of < 1 000 mg/kg total PBB or PBDE from interlaboratory study 4B (IIS 4B) results is shown in Table A.6.

Table A.6 – IIS4B threshold judgement

Sample ID/ compound type	Expected threshold judgement P or F[a]	Number of laboratories submitting threshold judgement results	Number of laboratories submitting correct threshold judgement results	Number of laboratories submitting incorrect threshold judgement results
IIS4B-K01 / Total PBB	P	7	6	1
IIS4B-K01 / Total PBDE	F	7	5	2
IIS4B-L02 / Total PBB	P	7	7	0
IIS4B-L02 / Total PBDE	P	7	6	1
IIS4B-M03 / Total PBB	P	7	6	1
IIS4B-M03 / Total PBDE	F	7	5	2

[a] An expected threshold judgement of “P” refers to a result < 1 000 mg/kg and an expected threshold judgement of “F” refers to a result > 1 000 mg/kg.

A.7.2 Repeatability and reproducibility

When the values of two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator, using the same equipment within a short interval of time, lie within the range of the mean values cited in Table A.7 below, the absolute difference between the two test results obtained will not exceed the repeatability limit *r* deduced by statistical analysis of the international interlaboratory study 4B (IIS 4B) results in more than 5 % of cases.

When the values of two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited Table A.7 below, the absolute difference between the two results will not be greater than the reproducibility limit *R* by statistical analysis of interlaboratory study 4B (IIS 4B) results in more than 5 % of cases.

Table A.7 – IIS4B repeatability and reproducibility

Parameter	**Mean value** [mg/kg]	***r*** mg/kg	***R*** mg/kg
Total PBDE	1 026	303,5	421,4
Total PBDE	4 844	519,8	2 010,0
HexaBDE	66	76,7	431,7
HexaBDE	333	53,9	75,6
HeptaBDE	390	129,8	222,3
HeptaBDE	1 869	512,6	818,7
OctaBDE	457	124,7	316,6
OctaBDE	1 921	295,5	1 205,9
NonaBDE	165	39,3	254,4
NonaBDE	518	261,0	964,1
DecaBDE	2	2,9	16,6
DecaBDE	109	25,2	75,9

Refer also to Annex Ffor supporting data.

NOTE Use of the internal standard (e.g. described in Clause A.2 and in A.5.2.3, A.5.5 and A.6.2) was not included in the IIS4B. Although not used in the IIS4B, the inclusion of internal standard as described in this Annex A is expected to improve the repeatability and reproducibility of the IAMS method.

A.8 Quality assurance and control

A.8.1 Sensitivity

Instrumental sensitivity shall be confirmed by the S/N ratio of 1 μg deca-BDE(S/B≧30).

A high concentration (500 μg/ml) of deca-BDE (BDE-209) is needed.

NOTE Such a concentration can be made by dissolving decaBDE reagent (>98 %) in tetrahydrofuran, because a commercial solution with high concentration is not available.

A.8.2 Recovery

a) 2 μl of deca-BDE solution (500 μg/ml) is measured with each sequence according to the instrumental test conditions listed in Table A.1.

b) Around 1 mg of certified reference material (e.g. NMIJ CRM8108-a) is measured with each sequence according to the instrumental test conditions listed in Table A.1.

c) Recovery is carried out by means of the following formulae:

$$C_{\mathrm{m}} = \frac{A_{\mathrm{RM}}}{A_{\mathrm{S}}} \times \frac{1000}{m} \tag{A.5}$$

$$R = \frac{C_{\mathrm{m}}}{C} \times 100 \tag{A.6}$$

where

C_{m} is the concentration of deca-BDE carried out by CRM measurement in mg/kg;

A_{RM} is the peak area of DecaBDE in the CRM;

A_{S} is the peak area of DecaBDE in the solution;

m is the mass of the CRM in milligrams;

R is the recovery of deca-BDE in %;

C is the concentration of deca-BDE in the CRM certified value in mg/kg.

The per cent recovery for each congener shall be between 50 % and 150 %. The per cent recovery for each matrix spike shall be recorded and tracked in a spreadsheet to determine possible matrix effects in the analysis.

After every tenth sample run and at the end of each sample set, analyse a continuing calibration check standard (CCC). A CCC is a mid-range calibrant that is analysed as a sample. The per cent recovery shall be between 70 % and 130 %. If the per cent recovery for any congener in the CCC standard falls outside of this range, the CCC standard should be re-injected within 12 h. If the recovery is still out of range after re-injection of the CCC standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples injected before the last successful CCC standard may be reported, but all samples after the failing CCC standard shall be re-analysed with a new calibration.

A.8.3 Blank test

A blank cup shall be measured according to the instrumental test conditions listed in Table A.1. If the result is more than 30 mg/kg, appropriate maintenance (cleaning) of the equipment should be performed and the blank cup remeasured with acceptable results prior to collecting sample data.

A.8.4 Limits of detection (LOD) and limits of quantification (LOQ)

A limits of detection (LOD) study shall be completed before conducting this testing and each time there is a significant change in the method or instrument type. MDLs are defined as the minimum concentration of a substance that can be measured and reported with 99 % confidence from which a qualitative detection of a sample is permissible in a given matrix concerning the analyte. The MDL is obtained by calculating the standard deviation for a minimum of seven replicate analyses. The standard deviation is then multiplied by the Student's *t* value for the total number of replicates (*n*) for *n*-1 degrees of freedom.

All analyses used to calculate an MDL should be consecutive.

a) Mill approximately 2 g of suitable polymer from a pure source known not to contain brominated flame retardants or other compounds that may interfere with the analysis (e.g. polystyrene material CRM8108-a or other).
b) Analyse each of the samples according to the instrumental test conditions listed in Table A.1. The per cent recovery of each congener shall be between 70 % and 130 %. If the recovery is above or below these limits, the analysis shall be repeated.
c) Deca-BDE congener shall have a calculated MDL of less than or equal to 100 mg/kg. If the calculated LOD is above these limits, the procedure shall be repeated.

A.9 Test report

For the purpose of this part of IEC 62321, IEC 62321-1:2013, 4.8 (Test report) applies, in addition to the following:

- identification of technical mixtures (if any) used for calibration.

Annex B
(informative)

Diagram of an IAMS instrument

Figure B.1 is a basic diagram of an IAMS instrument arrangement. It is presented for information purposes. Other suitable arrangements may be possible providing the quality control assurance and control requirements can be achieved.

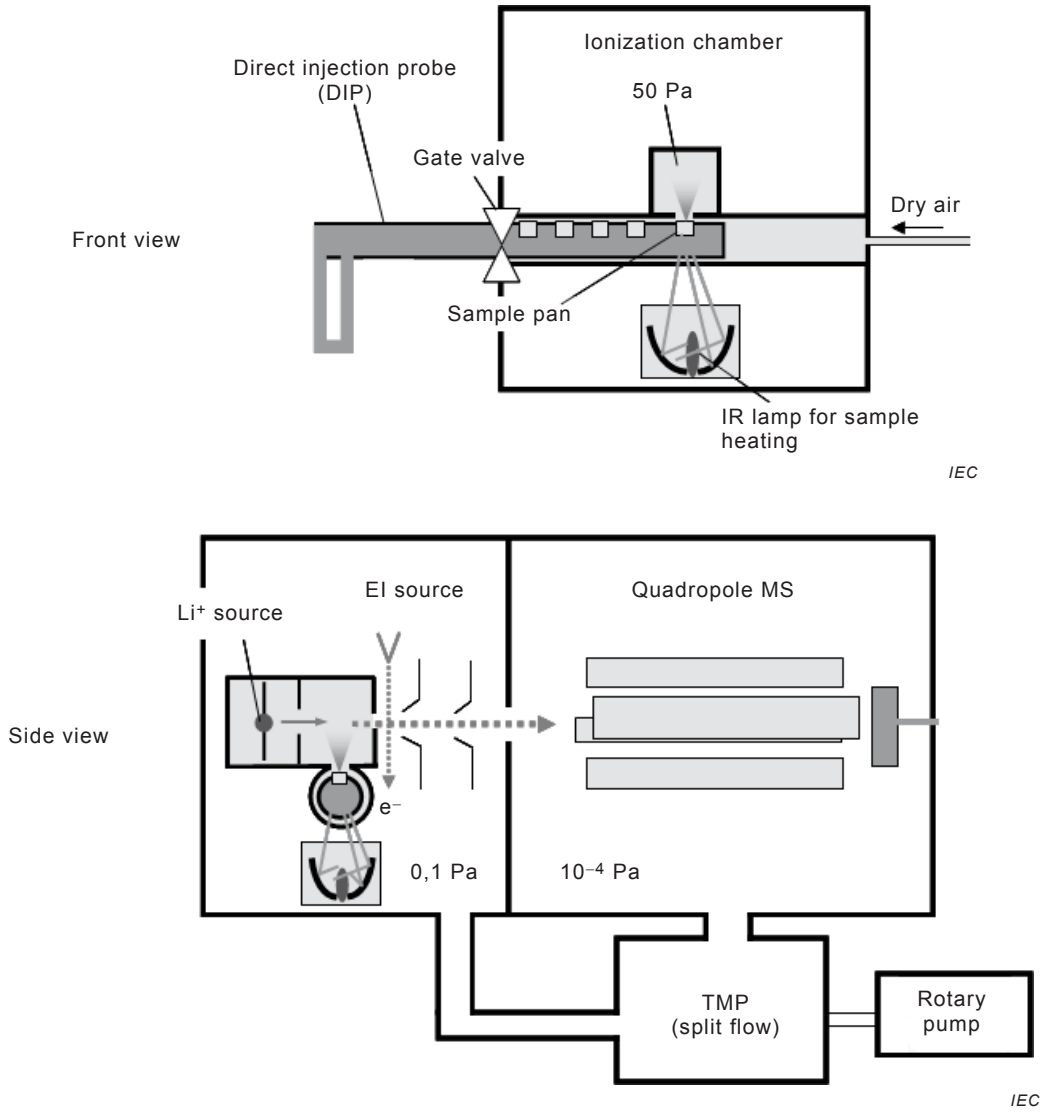


Figure B.1 – Diagram of an IAMS instrument

Annex C
(informative)

Determination of PBB and PBDE in polymers by high-pressure liquid chromatography – Ultra violet detection (HPLC-UV)

C.1 Principle

In the HPLC-UV method, technical octabromo biphenyl (octaBB), decabromo biphenyl (decaBB), octabromo diphenylether (octaBDE) and decabromo diphenylether (decaBDE) flame retardant compounds are determined using ultra sonic (qualitative analysis) or Soxhlet (for quantitative analysis) extraction followed by high-pressure, liquid chromatography separation and photo diode array ultra violet detection. The qualitative or semi-quantitative limitations of this method are dictated by the presence of interferences between octaBDE, decaBB and octaBB, octaBDE and other polymer additives. The HPLC-UV method is suitable for the qualitative analysis of octaBB, decaBB, decaBDE and octaBDE compounds in the range of >50 mg/kg to 2 000 mg/kg and as high as 2 000 mg/kg for decaBDE and semi-quantitative analysis of octaBB, decaBB, decaBDE and octaBDE compounds in the same respective range. This method is mainly targeted for analysis of commercial flame retardant products (e.g. technical mixtures) rather than single flame retardant congeners. For single congener analysis, GC-MS should be used.

C.2 Reagents and materials

a) Methanol (HPLC grade);

b) Acetic acid (HAc) (p.A. analytical grade >99,5 %);

c) n-Propanol (HPLC grade);

d) Calibrants: refer to Table C.1.

C.3 Apparatus

The following items shall be used for the analysis:

a) Analytical balance capable of measuring accurately to 0,000 1 g;

b) Extraction unit;

c) Ultra sonic bath;

d) High-performance liquid chromatograph (HPLC) system equipped with a PDA/UV detector, autosampler, pump and column oven;

e) Volumetric flasks;

f) Adjustable pipettes;

g) 12 mm × 32 mm vials;

h) Paper filters, medium-fast filtration, general laboratory use;

i) Column: C18 250/4 100-7 (C18 stationary phase, 250 mm in length and 4 mm in diameter, 10 μm pore size with 7 μm particle size) configured with an C18 8/4 100-5 pre-column (C18 stationary phase, 8 mm in length and 4 mm in diameter, 100 μm pore size with 5 μm particle size) or suitable equivalent;

j) Extraction vessels;

k) Soxhlet extractors:

   – 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 (for extraction thimble).

C.4 Sampling

As described in IEC 62321-2, unless indicated otherwise (e.g. "..using a nipper."), cryogenic grinding with liquid nitrogen cooling is recommended to achieve a particle size of ~1 mm.

C.5 Procedure

C.5.1 General instructions for the analysis

The method is capable of qualitatively identifying technical flame retardants by comparison of the typical fingerprint peak sequence in the retention time chromatogram as well as by comparison of UV-spectra of the peaks with the data base entries of the reference standards of the same composition. Any flame retardants of the PBB/PBDE family will result in detectable peaks. Due to the above mentioned combination of both parameters, the identification of the relevant compounds is easy. Usually unambiguous identification is possible. Quantification is facilitated by integration over all peaks and using mg/l units rather than molar expressions. If peak sequences with the required retention time pattern are detected but under interference with other peaks, or if more than one flame retardant is detected in a sample with overlay in the retention time, GC-MS analysis is recommended as the verification method for both identification and quantification. The method is not primarily designed for single congener detection as required for testing of biological samples. Due to low chromatographic resolution compared to GC-MS, the differentiation of the single congeners is not possible in every case.

The detector used is a PDA wavelength scanning detector. It is used in the scan mode to record complete UV spectra.

The sample preparation requires clean glassware (e.g. single use items) to avoid cross contamination. The validation of the instrumentation should include testing of potential cross contaminations between sequent samples. Additional blanks or inverted sequence of testing will help to exclude that issue.

Qualitative identification of the BFRs of interest is achieved utilizing both retention times and UV spectra. UV data from the largest peak of the technical flame retardant mixtures as well as retention times are compared between the sample and reference chromatogram. In the event that the difference in retention times or correlation of UV spectra between sample and standard chromatograms are found to be greater than those observed between two standard chromatograms of the same BFR, the qualitative identification is suspect and GC-MS should be used as the reference method.

C.5.2 Sample preparation

C.5.2.1 Qualitative extraction

a) 100 ± 20 mg of the sample is extracted in 2 ml of n-Propanol for 15 min in an ultra sonic bath at 50 °C of water temperature. The exact weight is recorded to the nearest 1 mg.

b) The sample extract solution is then cooled for 1 h (< 8 °C) and filtered through a paper filter.

c) The extract is transferred into a 2 ml HPLC testing vial with PTFE coated seal.

C.5.2.2 Semi-quantitative extraction

C.5.2.2.1 Pre-extraction of the Soxhlet extractors

To clean the Soxhlet extractors (C3 k), a 2 h pre-extraction is carried out with 70 ml of toluene. The washing solvent is discarded.

C.5.2.2.2 Extraction

a) Approximately (20 ± 5) mg of the sample is weighed into cellulose extraction thimbles for Soxhlet extraction. The exact weight is noted.

b) Approximately 70 ml of n-Propanol is used for extraction under reflux. In order to prevent the sample from floating, the thimble is closed with glass wool. The equipment is covered with aluminium foil to exclude light and the sample is extracted for at least 2 h with each cycle being approximately 2 min to 3 min. Shorter extraction times may result in lower recoveries of the analytes, particularly for the higher molecular mass PBDEs.

c) After 2 h of reflux followed by cooling for 1 h (<8 °C), the solvent is filtered through a paper filter and filled to 100 ml in a volumetric flask at ambient temperature.

d) The extract is transferred into a 2 ml HPLC sample or autosampler vial with PTFE coated seal. If the sample is stored and not measured directly it should be stored in brown or amber glass.

NOTE The flow chart in Annex E gives an example of qualitative and semi-quantitative applicability.

C.5.3 Instrumental parameters

C.5.3.1 General

Different conditions might be necessary to optimize a specific HPLC-PDA system to achieve effective determination of PBBs and PBDEs and meet the QC and limits of detection (LOQ) requirements. The following parameters have been found suitable and are provided as an example:

C.5.3.2 Liquid (mobile) phase

The liquid phase used is 99,90 % methanol/0,10 % acetic acid (volume fraction). n-Propanol is used as the solvent for the dissolution of pure standards and for the extraction of samples.

C.5.3.3 Stationary (column) phase

C18 250/4 100-7 (C18 stationary phase, 250 mm in length and 4 mm in diameter, 100 μm pore size with 7 μm particle size) configured with an C18 8/4 100-5 pre-column (C18 stationary phase, 8 mm in length and 4 mm in diameter, 100 μm pore size with 5 μm particle size) (see C 3 i)).

C.5.3.4 Measurement conditions

The run time is 10 min at a flow rate of 1,2 ml/min. The liquid phase is methanol with a volume fraction of 0,1 % HAc. Data are collected in the scan mode between 400 nm and 200 nm. The injection volume used is 10 μl and the column temperature is (23 ± 2) °C.

C.5.4 Calibrants

Technical calibration mixtures are used as calibrants. Table C.1 shows technical calibration mixtures considered suitable for this analysis.

Table C.1 – Example list of commercially available technical calibration mixtures considered suitable for this analysis

PBB – PBDE CAS# / Trade name	Compound name(s)
13654-09-6	Decabromo biphenyl
FR-250	Octabromo biphenyl (technical grade)
DE-79	Octabromo diphenyl ether (technical grade)
DE-83R	Decabromo diphenyl ether (technical grade)

C.6 Calibration

C.6.1 General

Wherever possible, the solvent used for HPLC and GC-MS sample and standard solutions shall be the same to avoid any potential solvent effects.

C.6.2 Standard solutions

Standard stock solutions from technical grades of flame-retardants as referred to in Tables C.1, in the concentrations as given in Table C.2, are used for calibration. The concentrations are given in mg/100 ml because of the technical mixtures of different compounds.

Table C.2 – Standard stock solution concentrations (mg/100 ml)

Compound	DecaBDE	OctaBDE	DecaBB	OctaBB
Concentration in mg/100 ml	1	2	2	2
	0,75	1	1	1
	0,50	0,75	0,75	0,75
	0,25	0,50	0,50	0,50
	0,1	0,25	0,25	0,25
	0,05	0,1	0,1	0,1
		0,05	0,05	0,05

To produce the calibration straight lines, the signal area of DecaBDE is plotted against the absolute amount ng.

A linear regression is carried out using Equation (C.1):

$$y = ax + b \tag{C.1}$$

where

y is the peak area of the calibrant;

x is the absolute amount of the calibrant;

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

C.7 Calculation of PBB and PBDE concentration

C.7.1 General

Only detected PBB and PBDE values shall be included in a total summation. It is pointless to include limits of detection in the summation for non-detected analytes.

NOTE If large amounts of tetrabromobisphenol A (2,3-dibromopropylether) are found together with small amounts of decaBDE, 500 mg/kg of decaBDE can be distinguished from 1 % or less of tetrabromobisphenol A (2,3-dibromopropylether) by summing the mass profile from 1 min, to 1 min and 16 s. If 1% or more of tetrabromobisphenol A (2,3-dibromopropylether) is present, move to the GC-MS method (see 8.2).

In the event that there are no PBDEs or no PBBs detected in the sample, the total PBDE (or PBB) shall be reported as a function of the congener(s) with the highest method detection limits. For example, if the method detection limit was 20 mg/kg for decaBB and 10 mg/kg for all other PBBs, and no PBBs were found in the sample, the total PBB shall be reported as $<$20 mg/kg.

Analytes detected below the limit of quantification (and above the limit of detection) shall be summed using the limit of quantification for the analyte detected. For example, if decaBB is found above the limit of detection but below the limit of quantification, and if the limit of quantification was 60 mg/kg for decaBB, and no other PBBs are found above the limit of detection in the sample, the total PBB shall be reported as 60 mg/kg.

C.7.2 Calculation

For the HPLC-UV measurement and data evaluation, the instrument supplier instructions are followed.

Basically, the principles for calculating the concentration manually is similar to the GC-MS method as described in Clause 9.

Technical decaBDE mixtures can precipitate from extraction solutions. This is not an issue for testing after qualitative extraction (see C.5.2.1). For testing after semi-quantitative extraction (see C.5.2.2) it is important to make sure that the found concentration is well within the calibration range. It might become necessary to repeat the extraction with a lower amount of sample in the same volume for the semi-quantitative measurement.

For a linear fit, the equation takes the following form:

$$y = ax + b \tag{C.2}$$

where

y is the signal area for the analyte in the sample; either single peaks or peak groups can be used, assuming that for calibration and calculation of concentration the same parameters for integration are used;

a is the slope of the line that best fits the calibration obtained in Equation (2);

x is the calibrated concentration in mg/100 ml;

b is the intercept on the y-axis of the calibration curve.

For a quadratic fit, the equation takes the following form:

$$y = ax^2 + bx + c \tag{C.3}$$

where

y is the signal area for the analyte in the sample; either single peaks or peak groups can be used, assuming that for calibration and calculation of concentration the same parameters for integration are used;

a and *b* are constants that correspond to the curve that best fits the calibration;

x is the calibrated concentration in mg/ml;

c is the intercept on the y-axis of the calibration curve.

Dilutions are calculated in exactly the same way as for GC-MS.

C.8 Precision

C.8.1 Threshold judgement

The overall threshold judgement with respect to compliance with a maximum allowable concentration limit of <1 000 mg/kg total PBB or PBDE from interlaboratory study 4B (IIS 4B) results is shown in Table C.3.

Table C.3 – IIS4B threshold judgement

Sample ID / compound type	Expected Threshold Judgement P or F[a]	Number of laboratories submitting threshold judgement results	Number of laboratories submitting correct threshold judgement results	Number of laboratories submitting incorrect threshold judgement results
IIS4B-K01 / Total PBB	P	6	6	0
IIS4B-K01 / Total PBDE	F	6	2	4
IIS4B-L02 / Total PBB	P	6	6	0
IIS4B-L02 / Total PBDE	P	6	6	0
IIS4B-M03 / Total PBB	P	6	6	0
IIS4B-M03 / Total PBDE	F	6	6	0

a An expected threshold judgement of "P" refers to a result <1 000 mg/kg and an expected threshold judgement of "F" refers to a result >1 000 mg/kg.

C.8.2 Repeatability and reproducibility

When the values of two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table C.4 below, the absolute difference between the two test results obtained will not exceed the repeatability limit *r* deduced by statistical analysis of the international interlaboratory study 4B (IIS 4B) results in more than 5 % of cases.

When the values of two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited Table C.4 below, the absolute difference between the two results will not be greater than the reproducibility limit *R* by statistical analysis of interlaboratory study 4B (IIS 4B) results in more than 5 % of cases.

Table C.4 – IIS4B Repeatability and reproducibility

Parameter	Mean value mg/kg	*r* mg/kg	*R* mg/kg
Total PBDE	1 136	159,3	985,3
Total PBDE	3 563	638,5	2 133,5
HexaBDE	Not reported	0,0	0,0
HexaBDE	Not reported	0,0	0,0
HeptaBDE	Not reported	0,0	0,0
HeptaBDE	Not reported	0,0	0,0
OctaBDE	587	181,6	378,6
OctaBDE	2 344	384,2	1 960,5
NonaBDE	Not reported	0,0	0,0
NonaBDE	Not reported	0,0	0,0
DecaBDE	Below detection limit	Not applicable	Not applicable
DecaBDE	Below detection limit	Not applicable	Not applicable
NOTE Only small amounts (18 mg/kg) of DecaBDE were expected for the samples evaluated in the last two rows of Table C.4. Two laboratories reported detection of DecaBDE, while four laboratories reported “below detection limit”. The expected value is at or near the lower end of the limit of quantification for this method. Therefore repeatability and reproducibility values are not applicable.			

Refer also to Annex F for supporting data.

C.9 Quality assurance and control

C.9.1 Standards spike recovery

In order to determine the accuracy trueness and recovery, the following spike recovery experiments should be carried out:

- spike the extract of a sample with independent flame retardant standards;
- determine the recoveries for independent standards.

For both sets of experiments, the recovery to the given value shall be in the range of 90 % to 110 %.

C.9.2 Internal control samples and blanks

Frequent recalibration including measurements of internal control samples and blank values are measured to make sure the instrument is running properly.

The quality of the measurement is ensured by limiting the validity of the liquid standard solutions to 6 months.

Each month a full recalibration is required.

Independent quality control standards are used to maintain the peak areas of, for example a DecaBDE standard as a quality control card. Acceptable recovery rates for the independent validation standard are 70 % to 130 % for qualitative and 90 % to 110 % for quantitative samples.

C.9.3 Limits of detection (LOD) and limits of quantification (LOQ)

A limits of detection (LOD) study shall be completed before conducting this test and each time there is a significant change in the method or instrument type. Limits of detection (LOQ) are defined as the minimum concentration of a substance that can be measured and reported with 99 % confidence from which a qualitative detection of a sample is permissible in a given matrix concerning the analyte. The limits of detection (LOQ) is obtained by calculating the standard deviation for a minimum of seven replicate analyses. The standard deviation is then multiplied by the Student's *t* value for the total number of replicates (*n*) for *n*-1 degrees of freedom.

All analysis used to calculate an MDL should be consecutive.

a) Mill approximately 2 g of suitable polymer from a pure source known not to contain brominated flame retardants or other compounds that may interfere with the analysis (e.g. polyethylene material BCR-681 or other).

b) Weigh out 100 mg of the milled polymer and place it in a new extraction thimble. Repeat this step six more times.

c) Place the extraction thimble in the Soxhlet extraction apparatus.

d) Spike the thimble with 5 μg of each calibration congener approximating the concentration of the lowest concentration calibrant.

e) Use the procedure (according to 8.2.3 or 8.2.4) to extract each of the samples. Analyse accordingly.

f) The per cent recovery of each congener shall be between 70 % and 130 %. If the recovery is above or below these limits, the analysis shall be repeated. If the recovery is outside of these limits a second time, the entire extraction and analysis procedure shall be repeated.

g) Each technical flame retardant shall have a calculated MDL of less than or equal to 100 mg/kg.

If the required MDL cannot be met, a concentration step can be added to the extraction procedure. Since the concentration step will also increase the resin concentration in the extract, a clean-up step is also recommended for each sample. This will extend the life of the column and reduce the frequency of instrument maintenance. If the concentration and clean-up steps are used in the analysis, they should also be used for the MDL samples.

C.10 Test report

For the purpose of this part of IEC 62321, IEC 62321-1:2013, 4.8 (Test report) applies, in addition to that shown below.

- identification of technical mixtures (if any) used for calibration.

Annex D
(informative)

Examples of chromatograms at suggested conditions

D.1 GC-MS method

Table D.1 shows PBB and PBDE congeners in the mixture used for the examples of chromatograms shown in Figures D.1 to D.3.

Table D.1 – PBB and PBDE congeners in the mixture

PBB congeners	PBDE congeners
B-2 = 3-Bromo biphenyl	BDE-1 = 2-Bromo diphenyl ether
B-10 = 2,6-Dibromo biphenyl	BDE-7 = 2,4-Dibromo diphenyl ether
B-30 = 2,4,6-Tribromo biphenyl	BDE-28 = 2,4,4'-Tribromo diphenyl ether
B-80 = 3,3',5,5'-Tetrabromo biphenyl	BDE-47 = 2,2',4,4'-Tetrabromo diphenyl ether
B-103 = 2,2',4,5',6-Pentabromo biphenyl	BDE-99 = 2,2',4,4',5-Pentabromo diphenyl ether
B-169 = 3,3',4,4',5,5'-Hexabromo biphenyl	BDE-100 = 2,2',4,4',6-Pentabromo diphenyl ether
B-194 = 2,2’,3,3’,4,4’,5,5’-Octabromo biphenyl	BDE-154 = 2,2',4,4',5,6'-Hexabromo diphenyl ether
B-206 = 2,2’,3,3’,4,4’,5,5’,6-Nonabromo biphenyl	BDE-183 = 2,2',3,4,4',5',6-Heptabromo diphenyl ether
B-209 = Decabromo biphenyl	BDE-203 = 2,2',3,4,4',5,5',6-Octabromo diphenyl ether
–	BDE-206 = 2,2',3,3',4,4',5,5',6-Nonabromo diphenyl ether
–	BDE-209 = Decabromo diphenyl ether

The following chromatograms were obtained by using the GC parameters described in 8.3.

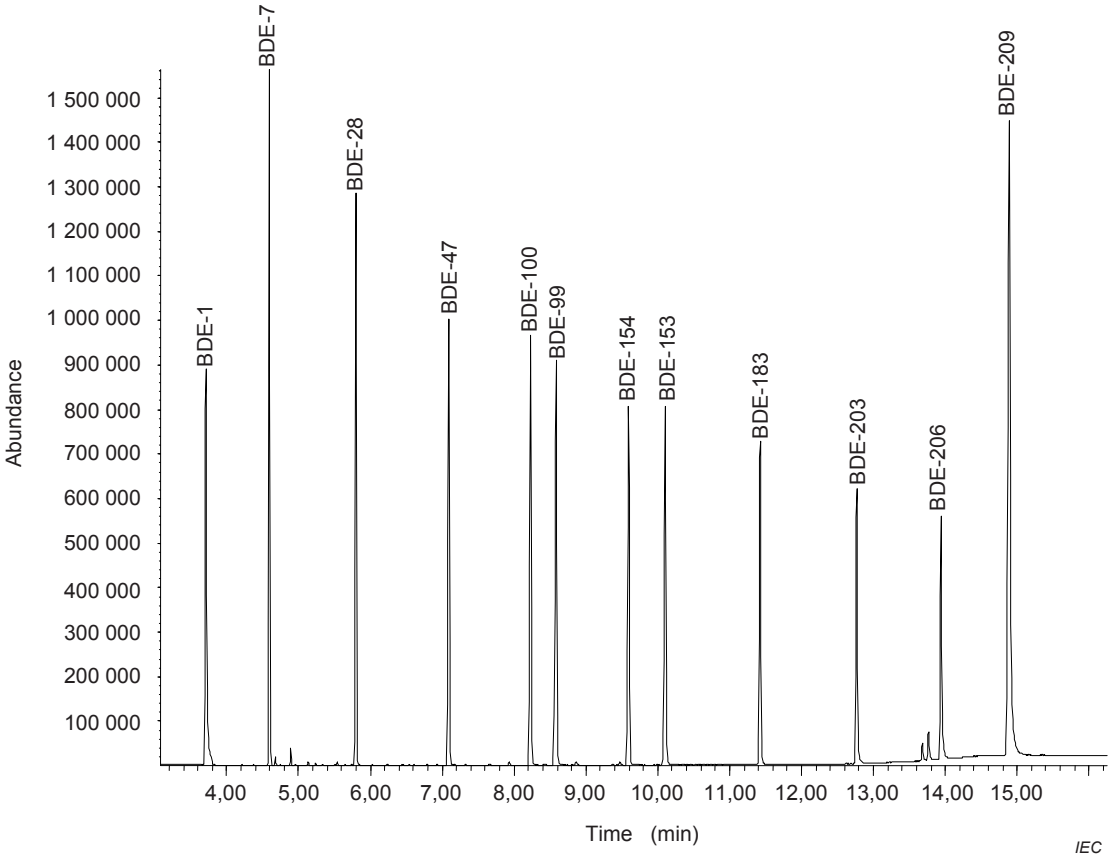


Figure D.1 – Total ion chromatogram of PBDE mixture, BDE-1 to BDE-206 (5 μg/ml), BDE-209 (50 μg/ml)

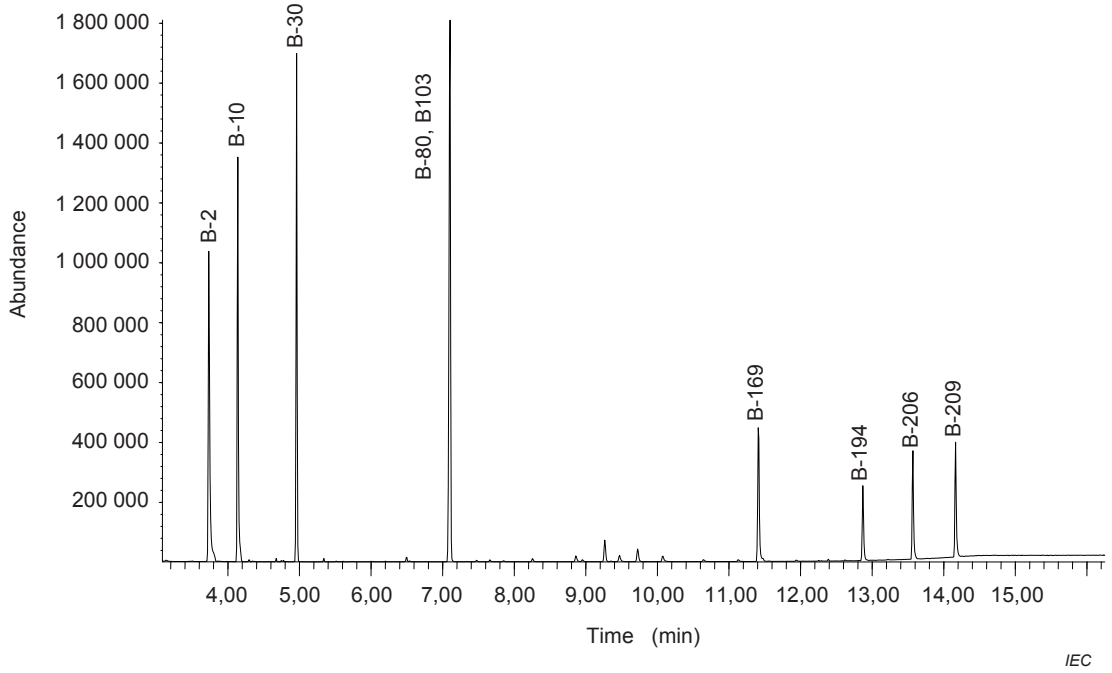


Figure D.2 – Total ion chromatogram of PBB mixture (3,5 μg/ml)

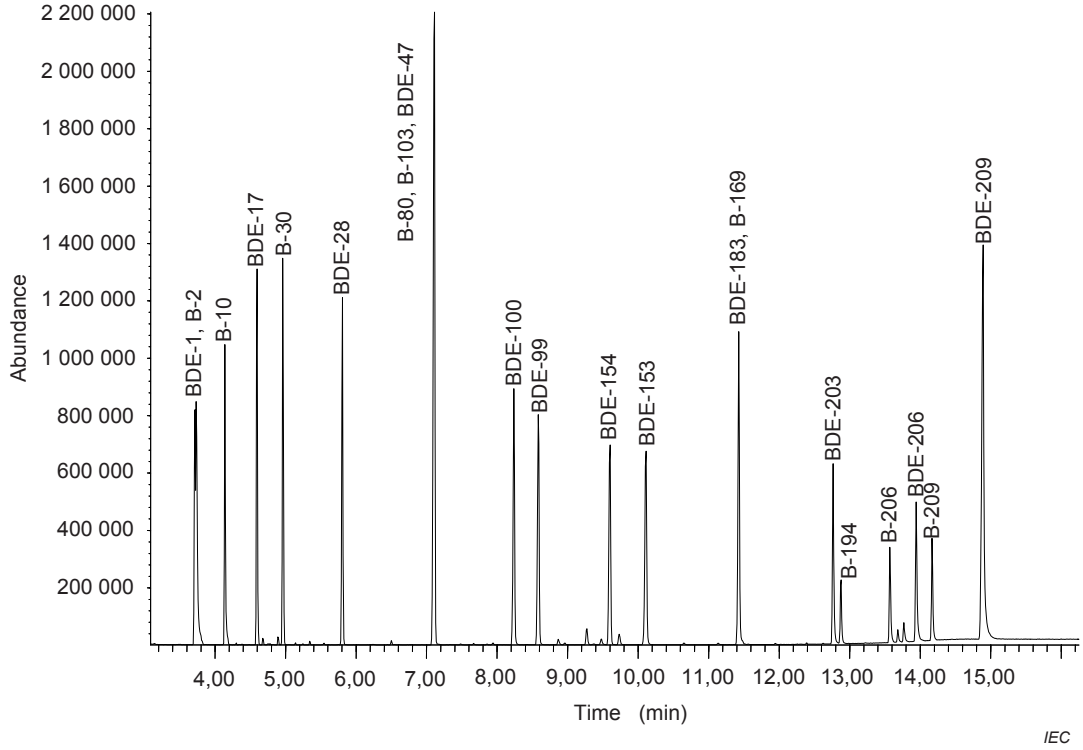


Figure D.3 – Total ion chromatogram of PBB and PBDE mixtures (BDE-1 to BDE-206 5 μg/ml, BDE-209 50 μg/ml, PBBs 3,5 μg/ml)

D.2 IAMS method

Example IAMS PBDE mass spectrum chromatograms are illustrated in Figures D.4 to D.7.

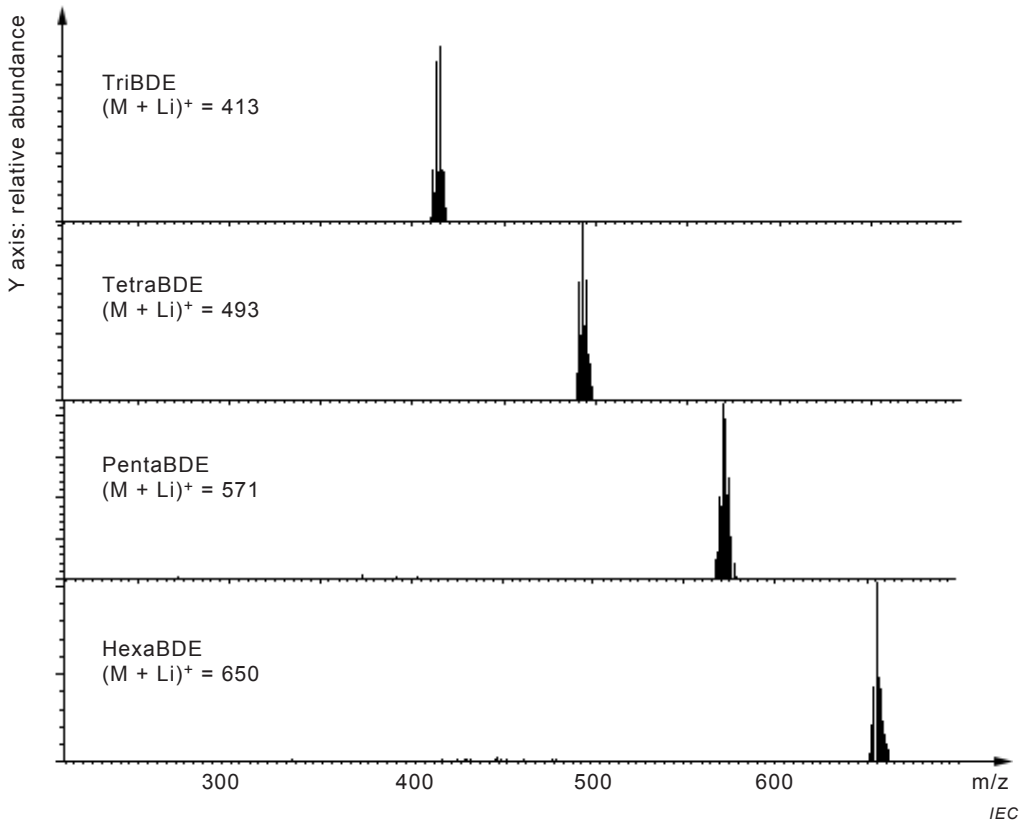


Figure D.4 – Mass spectrum of each PBDE congener by IAMS-1 (TriBDE to HexaBDE)

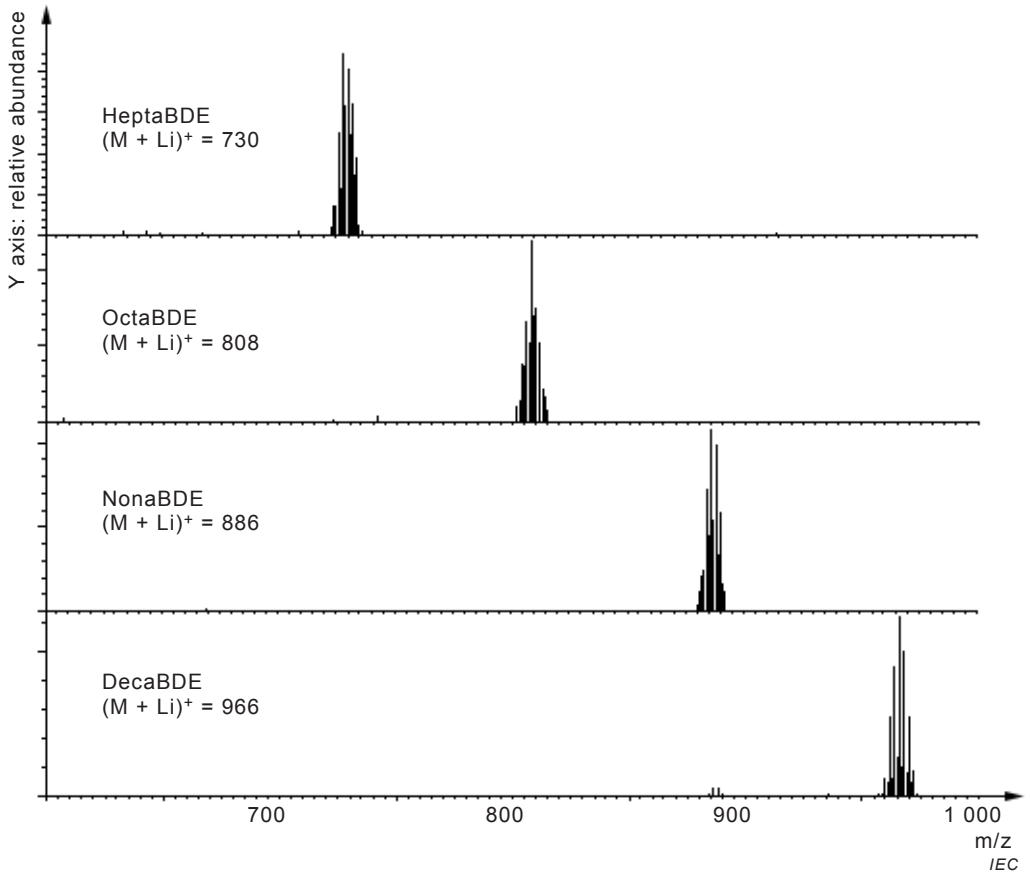


Figure D.5 – Mass spectrum of each PBDE congener by IAMS-2 (HeptaBDE to DecaBDE)

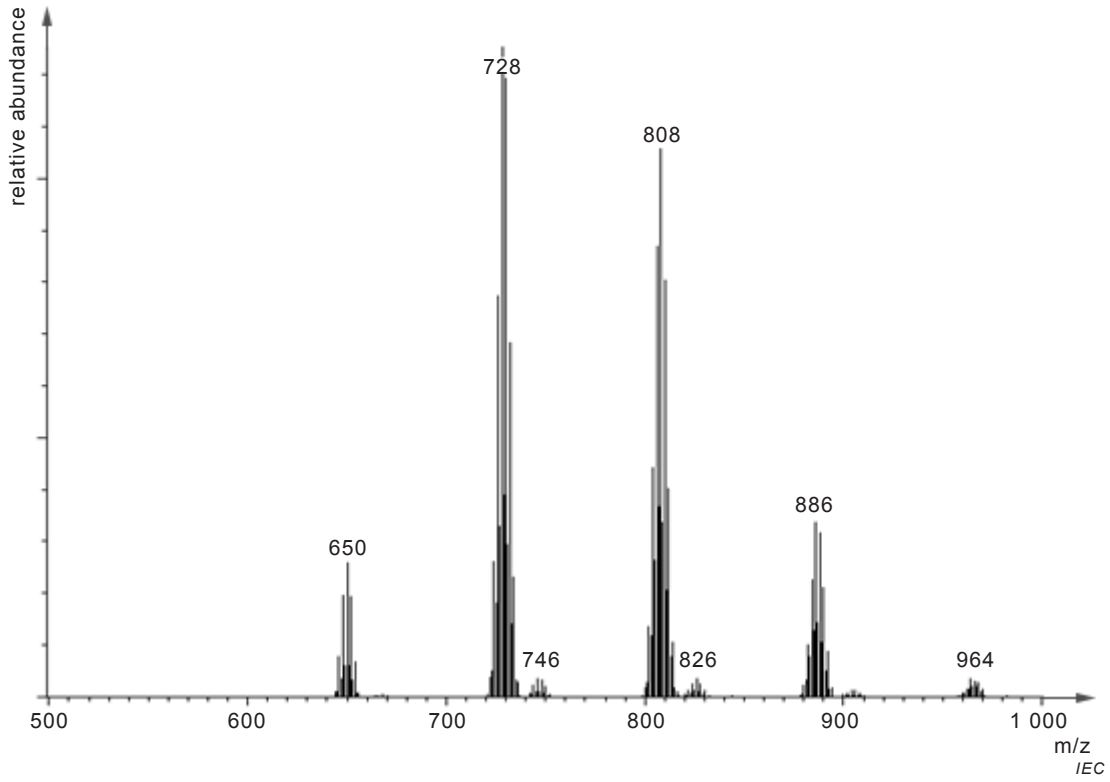


Figure D.6 – Mass spectra of technical OctaBDE(a) as mixture

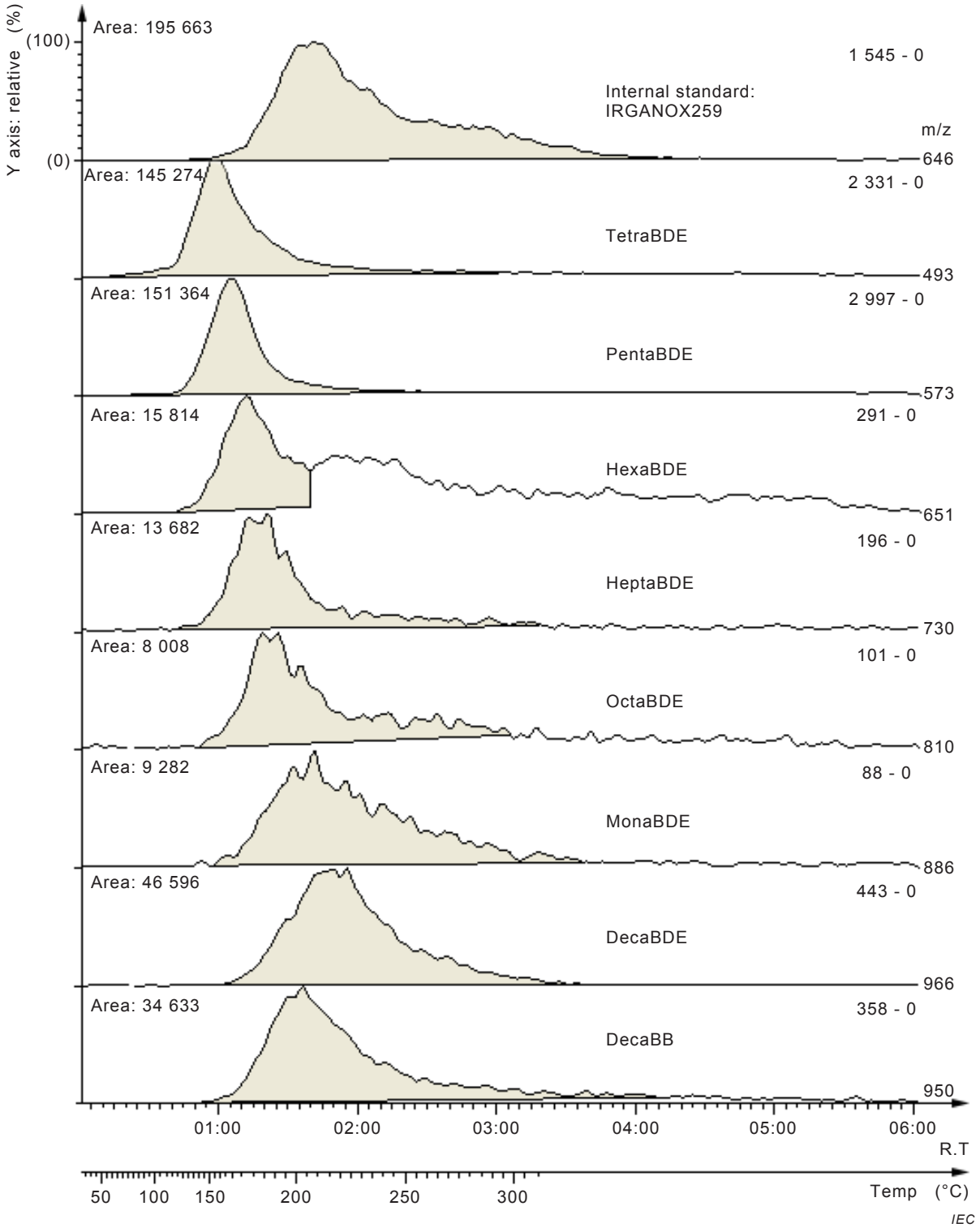


Figure D.7 – Temperature-programmed chromatography of each PBDE congener in the quantitative analysis of the reference material (ERM EC-590)

D.3 HPLC-UV method

Example HPLC-UV PBDE and PBB chromatograms are illustrated in Figures D.8 to D.11.

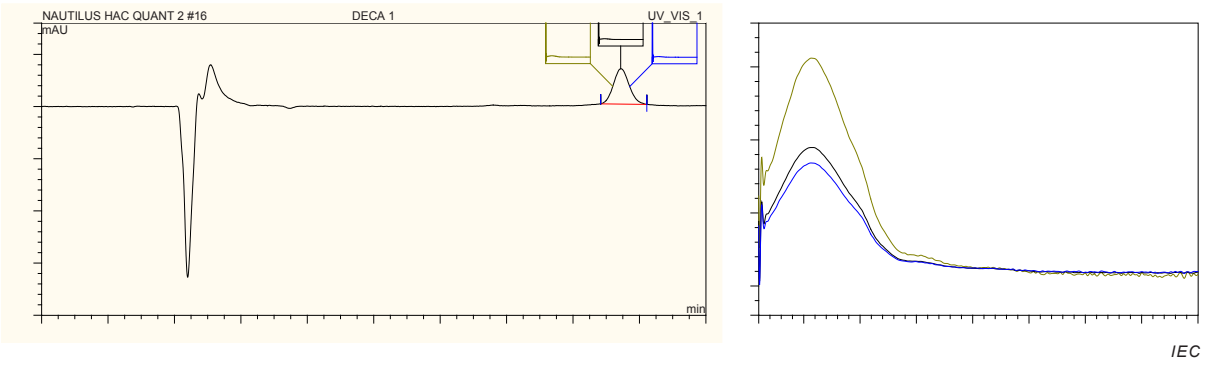


Figure D.8 – Chromatogram and UV spectrum of DecaBDE

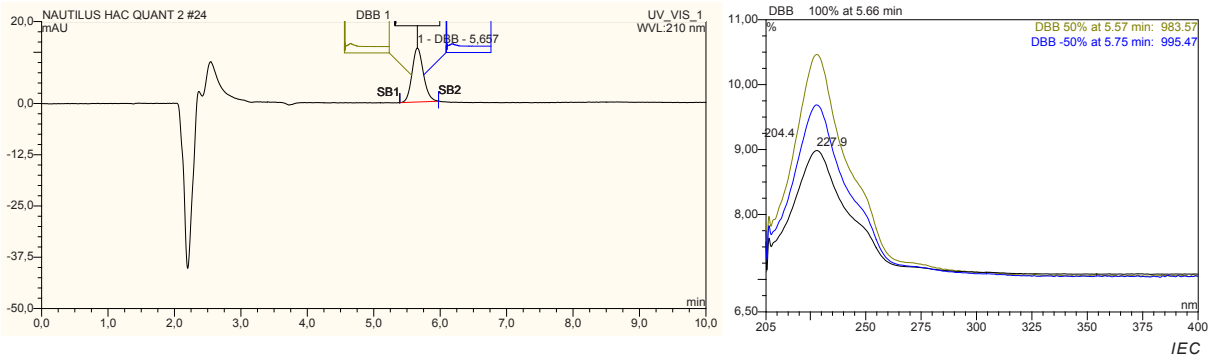


Figure D.9 – Chromatogram and UV spectrum of decaBB

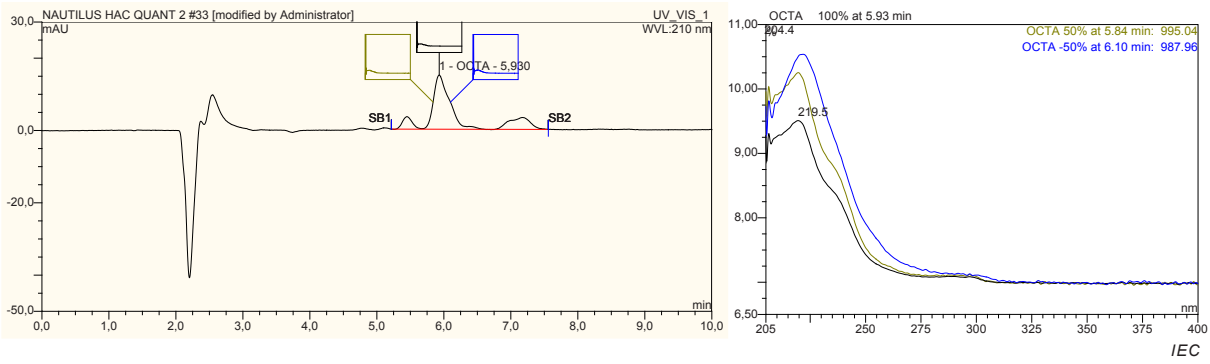


Figure D.10 – Chromatogram and UV Spectrum of OctaBDE

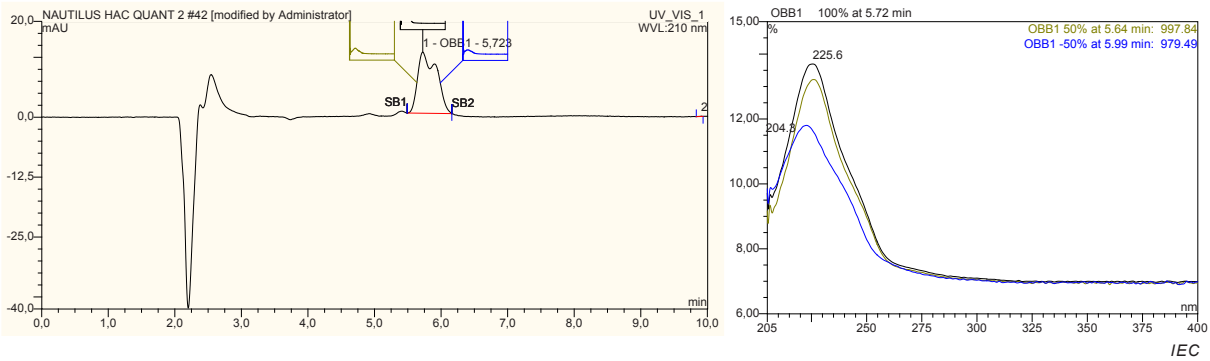
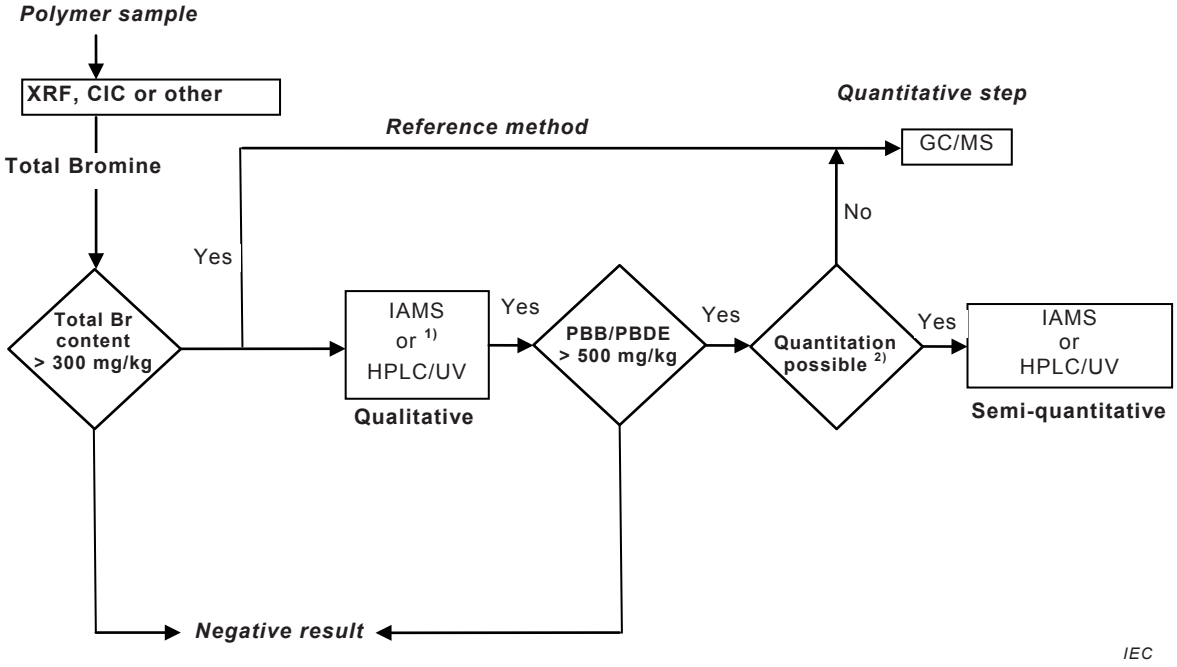


Figure D.11 – Chromatogram and UV spectrum of octaBB

Annex E
(informative)

Example applicability of the IAMS, HPLC and GC-MS test methods

Figure E.1 provides an informative flow chart example of the qualitative and semi-quantitative applicability of the IAMS, HPLC and GC-MS test methods for the determination of PBB and PBDE in polymers .



1) IAMS: Technical grade mixtures
HPLC: Technical grade mixtures

2) Quantitation is possible if:

a) interference free (no additional peaks from other compounds than the target compounds) and,

b) full peak sequence (all peaks of the technical compounds mixture present)

If a) or b) is not the case, GC/MS will be the only method to use.

Figure E.1 – Flow chart, example applicability of the IAMS, HPLC and GC-MS test methods

Annex F
(informative)

Results of international interlaboratory study 4B (IIS4B)

See Tables F.1 to F.3.

Table F.1 – Statistical Data for GC-MS

Technique	Sample	Parameter	m[a] mg/kg	v[b] mg/kg	n[c]	$s(r)$[d] mg/kg	r[e] mg/kg	$s(R)$[f] mg/kg	R[g] mg/kg	p[h]	Outlier labs
GC-MS	IIS4B-K01	PBB	0	0	33	0,0	0,0	0,0	0,0	11	0
	IIS4B-L02	PBB	0	0	33	0,0	0,0	0,0	0,0	11	0
	IIS4B-M03	PBB	0	0	33	0,0	0,0	0,0	0,0	11	0
	IIS4B-K01	PBDE	1 298	1 272	27	72,6	203,4	153,3	429,1	9	2
	IIS4B-L02	PBDE	1	0	33	1,5	4,3	2,1	5,8	11	0
	IIS4B-M03	PBDE	4 620	5 000	30	209,3	586,1	889,5	2 490,5	10	1
	IIS4B-K01	HexaBDE	94	93	27	3,3	9,3	16,9	47,2	9	2
	IIS4B-L02	HexaBDE	0	0	29	0,0	0,0	0,0	0,0	10	0
	IIS4B-M03	HexaBDE	306	450	30	18,7	52,5	73,8	206,8	10	1
	IIS4B-K01	HeptaBDE	519	489	33	46,4	129,8	108,8	304,7	11	0
	IIS4B-L02	HeptaBDE	0	0	30	0,0	0,0	0,0	0,0	10	0
	IIS4B-M03	HeptaBDE	1 748	2 050	30	113,7	318,4	335,6	939,7	10	1
	IIS4B-K01	OctaBDE	484	426	27	26,8	75,1	44,4	124,2	9	2
	IIS4B-L02	OctaBDE	0	0	30	0,0	0,0	0,0	0,0	10	0
	IIS4B-M03	OctaBDE	1 688	1 800	27	72,6	203,4	264,7	741,1	9	2
	IIS4B-K01	NonaBDE	211	247	27	15,7	43,9	47,1	131,8	9	2
	IIS4B-L02	NonaBDE	0	0	30	0,0	0,0	0,0	0,0	10	0
	IIS4B-M03	NonaBDE	696	650	27	63,5	177,7	178,2	499,1	9	2
	IIS4B-K01	DecaBDE	12	18	33	3,6	10,1	13,2	37,0	11	0
	IIS4B-L02	DecaBDE	1	0	30	1,6	4,5	2,2	6,1	10	0
	IIS4B-M03	DecaBDE	81	50	24	9,4	26,3	26,3	73,7	8	3

[a] m general mean of the test property in mg/kg
[b] v expected value in mg/kg
[c] n number of test results taken into calculation
[d] $s(r)$ repeatability standard deviation
[e] r repeatability
[f] $s(R)$ reproduciblity standard deviation
[g] R reproducibility
[h] p number of laboratories taken into calculation

Table F.2 – Statistical data for IAMS

Technique	Sample	Parameter	m[a] mg/kg	v[b] mg/kg	n[c]	$s(r)$[d] mg/kg	r[e] mg/kg	$s(R)$[f] mg/kg	R[g] mg/kg	p[h]	Outlier labs
IAMS	IIS4B-K01	PBB	0	0	18	0,0	0,0	0,0	0,0	6	1
	IIS4B-L02	PBB	0	0	21	0,0	0,0	0,0	0,0	7	0
	IIS4B-M03	PBB	0	0	18	0,0	0,0	0,0	0,0	6	1
	IIS4B-K01	PBDE	1 026	1 272	18	108,4	303,5	150,5	421,4	6	1
	IIS4B-L02	PBDE	0	0	18	0,0	0,0	0,0	0,0	6	1
	IIS4B-M03	PBDE	4 844	5 000	15	185,6	519,8	717,9	2 010,0	5	2
	IIS4B-K01	HexaBDE	66	93	21	27,4	76,7	154,2	431,7	7	5
	IIS4B-L02	HexaBDE	0	0	21	0,0	0,0	0,0	0,0	7	0
	IIS4B-M03	HexaBDE	333	450	9	19,2	53,9	27,0	75,6	3	4
	IIS4B-K01	HeptaBDE	390	489	15	46,4	129,8	79,4	222,3	5	2
	IIS4B-L02	HeptaBDE	0	0	18	0,0	0,0	0,0	0,0	6	1
	IIS4B-M03	HeptaBDE	1 869	2 050	15	183,1	512,6	292,4	818,7	5	2
	IIS4B-K01	OctaBDE	457	426	18	44,5	124,7	113,1	316,6	6	1
	IIS4B-L02	OctaBDE	0	0	21	0,0	0,0	0,0	0,0	7	0
	IIS4B-M03	OctaBDE	1 921	1 800	15	105,5	295,5	430,7	1 205,9	5	2
	IIS4B-K01	NonaBDE	165	247	15	14,0	39,3	90,9	254,4	5	2
	IIS4B-L02	NonaBDE	0	0	18	0,0	0,0	0,0	0,0	6	1
	IIS4B-M03	NonaBDE	518	650	15	93,2	261,0	344,3	964,1	5	2
	IIS4B-K01	DecaBDE	2	18	18	1,0	2,9	5,9	16,6	6	1
	IIS4B-L02	DecaBDE	0	0	21	0,0	0,0	0,0	0,0	7	0
	IIS4B-M03	DecaBDE	109	50	15	9,0	25,2	27,1	75,9	5	2

[a] m general mean of the test property in mg/kg
[b] v expected value in mg/kg
[c] n number of test results taken into calculation
[d] $s(r)$ repeatability standard deviation
[e] r repeatability
[f] $s(R)$ reproduciblity standard deviation
[g] R reproducibility
[h] p number of laboratories taken into calculation

Table F.3 – Statistical data for HPLC-UV

Technique	Sample	Parameter	m[a] mg/kg	v[b] mg/kg	n[c]	$s(r)$[d] mg/kg	r[e] mg/kg	$s(R)$[f] mg/kg	R[g] mg/kg	p[h]	Outlier labs
HPLC	IIS4B-K01	PBB	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-L02	PBB	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	PBB	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-K01	PBDE	1 136	1 272	9	56,9	159,3	351,9	985,3	3	3
	IIS4B-L02	PBDE	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	PBDE	3 563	5 000	12	228,1	638,5	762,0	2 133,5	4	2
	IIS4B-K01	HexaBDE	not reported	93	18	0,0	0,0	0,0	0,0	6	6
	IIS4B-L02	HexaBDE	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	HexaBDE	not reported	450	18	0,0	0,0	0,0	0,0	6	6
	IIS4B-K01	HeptaBDE	not reported	489	18	0,0	0,0	0,0	0,0	6	6
	IIS4B-L02	HeptaBDE	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	HeptaBDE	not reported	2 050	18	0,0	0,0	0,0	0,0	6	6
	IIS4B-K01	OctaBDE	587	426	12	64,8	181,6	135,2	378,6	4	2
	IIS4B-L02	OctaBDE	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	OctaBDE	2 344	1 800	12	137,2	384,2	700,2	1 960,5	4	2
	IIS4B-K01	NonaBDE	not reported	247	18	0,0	0,0	0,0	0,0	6	6
	IIS4B-L02	NonaBDE	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	NonaBDE	not reported	650	18	0,0	0,0	0,0	0,0	6	6
	IIS4B-K01	DecaBDE	below detection	18	18	0,3	0,7	8,3	23,3	6	0
	IIS4B-L02	DecaBDE	0	0	18	0,0	0,0	0,0	0,0	6	0
	IIS4B-M03	DecaBDE	below detection	50	18	0,4	1,1	19,6	54,8	6	0

[a] m general mean of the test property in mg/kg
[b] v expected value in mg/kg
[c] n number of test results taken into calculation
[d] $s(r)$ repeatability standard deviation
[e] r repeatability
[f] $s(R)$ reproduciblity standard deviation
[g] R reproducibility
[h] p number of laboratories taken into calculation

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