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BSI Standards Publication

Water quality — Determination of selected polybrominated diphenly ether (PBDE) in whole water samples — Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography — mass spectrometry (GC-MS)

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Water quality - Determination of selected polybrominated diphenly ether (PBDE) in whole water samples - Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography - mass spectrometry (GC-MS)

Qualité de l'eau - Dosage du pentabromodiphényléther (PBDE) dans des échantillons d'eau totale - Méthode par extraction en phase solide (SPE) avec disques SPE, avec couplage chromatographie en phase gazeuse-spectrométrie de masse (CG-SM)

Wasserbeschaffenheitt - Bestimmung von ausgewählten polybromierten Diphenylethern (PBDE) in Gesamtwasserproben - Verfahren mittels Festphasenextraktion (SPE) mit SPE-Disks in Verbindung mit Gaschromatographie - Massenspektrometrie (GC-MS)

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European foreword

This document (EN 16694:2015) has been prepared by Technical Committee CEN/TC 230 “Water analysis”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

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Introduction

WARNING — Persons using this European Standard should be familiar with usual laboratory practice. This European 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.

IMPORTANT — It is absolutely essential that tests conducted according to this European Standard be carried out by suitably trained staff.

Polybrominated diphenyl ethers (PBDE) are priority substances listed in Annex X of the EU Water Framework Directive (WFD, Directive 2000/60/EC) for which environmental quality standards (EQS) have been set at EU level for inland waters as well as other surface waters to protect the aquatic environment against chemical pollution (Directive 2008/105/EC). With the exception of metals, the EQS are expressed as total concentrations in the whole water sample. Furthermore, analytical methods used in WFD monitoring need to meet certain requirements as regards the minimum limit of quantification and the maximum tolerable measurement uncertainty (Directive 2009/90/EC). So far, there is no standardized method available for the determination of PBDE in whole water samples fulfilling those requirements. Hence, the European Commission mandated CEN to develop or improve standards in support of the implementation of the monitoring requirements of WFD.

Directive 2008/105/EC has been amended by Directive 2013/39/EU, however this standard has been developed for the analysis of PBDE as listed in Annex A of Directive 2008/105/EC.

The priority substances list in Annex X of the WFD includes technical pentabromodiphenyl ether, which is regarded as a mixture of the congeners BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154. The annual average environmental quality standard (AA-EQS) for pentabromodiphenyl ether in inland surface waters is 0,5 ng/l and is defined for the whole water sample including suspended particulate matter (SPM) present in the sample. Compounds such as PBDE strongly adsorb to environmental solids resulting in a fraction bound to particles, which may be substantial. The aim of the method is to extract whole water samples in one single step to determine the dissolved as well as the particle bound PBDE fraction. Identification and quantification of BDE congeners at trace level concentrations require both highly sensitive chromatographic equipment and effective enrichment steps and awareness of the potential impact of blanks.

1 Scope

This European Standard specifies a method for the determination of six selected polybrominated diphenyl ethers (PBDE) listed in Table 1, representative for technical brominated diphenyl ethers (BDE) in water samples in mass concentrations ≥ 0,025 ng/l for each individual congener. The method uses solid-phase extraction with SPE-disks in combination with gas chromatography-mass spectrometry (GC-MS). It is applicable to the analysis of PBDE in surface water containing suspended particulate matter (SPM) up to 500 mg/l (whole water samples), drinking water and groundwater. The limit of quantification (LOQ) was determined according to ISO/TS 13530, on the basis of replicate determinations of the procedural blank, carried out under reproducibility conditions.

This method may be used for the analysis of other BDE congeners not listed in Table 1 or other types of water. However, it is important to verify its applicability before use.

Table 1 — Polybrominated diphenyl ethers (PBDE) determined by this method

Congener	Abbreviation[a]	Formula	Molar mass g/mol	CAS RN[b]
2,4,4'-Tribromodiphenyl ether	BDE-28	$C_{12}H_7Br_3O$	406,8954	41318–75–6
2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	$C_{12}H_6Br_4O$	485,7950	5436–43–1
2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	$C_{12}H_5Br_5O$	564,6911	60348–60–9
2,2',4,4',6-Pentabromodiphenyl ether	BDE-100	$C_{12}H_5Br_5O$	564,6911	189084–64–8
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	$C_{12}H_4Br_6O$	643,5872	68631–49–2
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE-153	$C_{12}H_4Br_6O$	643,5872	207122–15–4

NOTE EC numbers are not applicable for PBDE congeners.

[a] Numbering analog to IUPAC nomenclature for PCB

[b] CAS RN: Chemical Abstracts Service Registry Number

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.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

EN ISO 5667-1, *Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1)*

EN ISO 5667-3, *Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3)*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Principle

A mixture of suitable internal standards ($^{13}C_{12}$-labelled BDE or fluorinated BDE) is added to a 1 l water sample, which is then extracted using a solid-phase extraction disk (SPE-disk). The disk is eluted with a

suitable solvent (5.4) or solvent mixture and the resulting extract is concentrated for analysis or further clean-up.

Prior to injection, an injection standard is added to each extract, and an aliquot is injected into the gas chromatograph. The analytes are separated by capillary gas chromatography and detected and quantified by electron ionization high-resolution mass spectrometry (EI-HRMS) or alternatively, by low resolution negative chemical ionization mass spectrometry (NCI-MS) or low resolution tandem mass spectrometry (MS/MS). In the latter cases a clean-up step using e. g. a multilayer-silica column, and/or removal of sulfur, e. g. by gel permeation chromatography, may be necessary.

4 Interferences

4.1 Interferences with extraction and clean up

To avoid interference, collect samples as specified in Clause 7.

Commercially available SPE-disks can differ frequently in quality. Variations in the selectivity of the materials can occur from batch to batch, and therefore might cause significant deviations in extraction yield. This does not basically impair their suitability, apart from a resulting higher detection limit of individual substances. To ensure that the analytical results have a high accuracy and precision, use materials from one batch for both measurement and calibration. Avoid major fluctuations in the extraction times and elution procedures within one sample sequence when analysing the samples.

4.2 Interferences with GC-MS

Interferences may be caused, e. g. by the injection system used or by inadequate separation of the analytes. Experienced operators might be able to minimize this type of interference. Regular checking of the chromatographic and spectrometric system is required to maintain adequate performance. Required system stability should be checked regularly using a GC standard.

5 Reagents

The reagents shall be free from impurities possibly interfering with the GC-MS analysis.

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents use, as far as available “residual grade” or better in order to obtain low blanks. Verify by blank determinations and, if necessary, apply additional cleaning steps.

5.1 Water, complying to grade 1 according to EN ISO 3696, or equivalent.

5.2 Operating gases for the gas chromatography mass spectrometry, of high purity and according to the manufacturer's specifications.

5.3 Nitrogen of high purity, i.e. minimum 99,996 % by volume, for concentration by evaporation.

5.4 Solvents for extraction, chromatography and preparation of reference solutions.

A variety of solvents may be used depending on the procedural step and the availability of commercial stock solutions, e. g.

— toluene, C_7H_8 (boiling point: 111 °C),

— acetone, C_3H_6O (boiling point: 56 °C),

— *iso*- or n-hexane, C_6H_{14}, (boiling point: 60 °C),

— *iso*-octane (2,2,4-trimethylpentane), C_8H_{18} (boiling point: 99 °C),

— nonane, C_9H_{20} (boiling point: 151 °C),

— dichloromethane, CH_2Cl_2, (boiling point: 39,7 °C),

— ethyl acetate, $C_4H_8O_2$ (boiling point: 77 °C),

— *iso*-propanol, C_3H_8O (boiling point: 82 °C)

for residual analysis. A suitable keeper is recommended (e. g. toluene), when reducing the volume of the extract to less than 0,5 ml. For large volume injection a more volatile solvent, e. g. hexane, should be used.

5.5 Clean up material, according to Annex C.

5.6 Sodium sulfate, anhydrous, Na_2SO_4, powdered.

5.7 Standards

5.7.1 Reference substances

PBDE listed in Table 1 are used for calibration. Solutions of the reference substances are commercially available.

5.7.2 Internal standards

Solutions of reference substances for use as internal standards for electron impact ionization (see Table 2) are commercially available.

Table 2 — Examples of internal standards for GC-EI-MS analysis

Standard	Abbreviation	Formula	Molar mass g/mol
2,4,4'-Tribromo[$^{13}C_{12}$]diphenyl ether	^{13}C-BDE-28	$^{13}C_{12}H_7Br_3O$	418,8038
2,2',4,4'-Tetrabromo[$^{13}C_{12}$]diphenyl ether	^{13}C-BDE-47	$^{13}C_{12}H_6Br_4O$	497,7035
2,2',4,4',5-Pentabromo[$^{13}C_{12}$]diphenyl ether	^{13}C-BDE-99	$^{13}C_{12}H_5Br_5O$	576,5995
2,2',4,4',5,5'-Hexabromo[$^{13}C_{12}$]diphenyl ether	^{13}C-BDE-153	$^{13}C_{12}H_4Br_6O$	655,4955

Solutions of reference substances for use as internal standards for negative ion chemical ionization (see Table 3) are commercially available.

Table 3 — Examples of internal standards for GC-NCI-MS analysis

Standard	Abbreviation	Formula	Molar mass g/mol
2-Fluoro-2,4,4'-tribromodiphenyl ether	F-BDE-28	$C_{12}H_6Br_3OF$	424,8858
6-Fluoro-2,2',4,4'-tetrabromodiphenyl ether	F-BDE-47	$C_{12}H_5Br_4OF$	503,7819
3-Fluoro-2,2',4,4',6-pentabromodiphenyl ether	F-BDE-100	$C_{12}H_4Br_5OF$	582,6779
4'-Fluoro-2,3,3',4,5,6-hexabromodiphenyl ether	F-BDE-160	$C_{12}H_3Br_6OF$	661,5740

5.7.3 Injection standard

To determine recovery rates for the internal standards in each sample e. g. dibromooctafluorobiphenyl ($C_{12}Br_2F_8$) is used as an injection standard.

5.7.4 Preparation of standard stock solutions

5.7.4.1 Stock solutions of the single reference substances/internal standards

Use either commercially available solutions or prepare stock solutions by dissolving e. g. 10 mg of each of the reference substances in toluene (5.4) in a 100 ml volumetric amber flask and bring to volume, resulting in a final concentration of 100 µg/ml. Correct the concentration for purity if this is < 99 %. Store stock solutions at temperatures between 1°C and 5°C according to EN ISO 5667-3, protected from light. They are stable for at least 12 months.

5.7.4.2 Stock solution of the injection standard

Use a commercially available solution or prepare a stock solution by dissolving e. g. 10 mg of the reference substance in toluene (5.4) in a 100 ml volumetric amber flask and bring to volume, resulting in a final concentration of 100 µg/ml. Make appropriate dilutions in hexane or toluene allowing to spike e. g. 100 pg accurately to the final extract of a water sample. Store stock solutions at temperatures between 1°C and 5°C according to EN ISO 5667-3, protected from light. They are stable for at least 12 months.

5.7.4.3 Multicomponent stock solution of reference substances

Accurately transfer between 100 µl to 500 µl of each single standard solution (5.7.4.1) into a 10 ml volumetric amber flask and bring to volume, resulting in final concentrations between 1 µg/ml and 5 µg/ml per substance. Store multicomponent stock solutions at temperatures between 1 °C and 5 °C, protected from light. They are stable for at least 6 months.

5.7.4.4 Multicomponent stock solution of internal standards

Prepare a stock solution of the internal standards (5.7.4.1) at an appropriate concentration in hexane or toluene (e. g. 1 ng/ml). Store multicomponent stock solutions at temperatures between 1°C and 5°C, protected from light. They are stable for at least 6 months.

5.7.4.5 Calibration control standard solution

Use a commercially available standard solution of reference substances from an independent supplier or prepare an independent standard solution from the pure reference substances. Store the calibration control standard solution at temperatures between 1°C and 5°C, protected from light. It is stable for at least 6 months.

6 Apparatus

Equipment or parts of it which have contact with the water sample or its extract shall be free from residues causing interferences. The use of vessels made of glass, stainless steel or polytetrafluoroethylene (PTFE) is recommended. To minimize the blank contribution the vessels shall be rinsed with organic solvent prior to use.

6.1 Sample flasks, e. g. brown glass, flat bottomed, with glass or PTFE coated stoppers, e. g. 1 000 ml or 2 000 ml.

6.2 One-mark volumetric flasks, capacity e. g. 10 ml, 25 ml, 50 ml and 100 ml.

6.3 Single volume pipettes, capacities between 1 ml and 50 ml.

6.4 Capillary gas chromatograph with high resolution mass spectrometric detector using electron ionization **(GC-HRMS)**, or **capillary gas chromatograph** with mass spectrometric detector using chemical ionization in negative mode **(GC-NCI-MS)**.

The gas supplies shall be in accordance with the respective manufacturer's instructions.

6.5 Non-discriminating GC injector, e. g. splitless mode of a split/splitless injection system or programmable temperature vaporizer (PTV), programmable for large volume injection (LVI).

A cold injection technique is recommended; depending on the sensitivity of the instrument large volume injection may be necessary.

6.6 Automatic sampler with option for large volume injection (LVI), including syringes for normal injection (e. g. 1 µl and 2 µl) and for LVI (e. g. 10 µl, 50 µl and 100 µl).

6.7 Capillary columns, for gas chromatography (example chromatograms are given in Annex A). It is advantageous to use non-polar columns (e. g. low-bleed 5 %-phenylsiloxane column), providing thermal stability up to 400 °C; e. g. inner diameter ≤ 0,25 mm, length 15 m, film thickness of 0,1 µm is recommended.

6.8 Solid-phase extraction disks (SPE-disks), wide inner diameter: e. g. 40 mm to 60 mm, packed with an appropriate reversed phase adsorbent material, e. g. C_{18}-based or SDB-based adsorbent (for examples, see Annex C).

6.9 Vacuum device for solid-phase extraction, e. g. extraction box or automated workstation for solid-phase extraction procedure capable for processing SPE-disks.

6.10 Evaporation device, such as rotary evaporator, turboevaporator or vacuum concentration device.

6.11 Syringes, 2 µl, 5 µl, 10 µl and 50 µl, volume precision ± 2 %.

6.12 Sample vials; amber glass with fluoropolymer-lined screw-cap is most suitable.

6.13 Glass columns for chromatographic clean-up.

6.14 Pasteur pipettes, made of glass.

7 Sampling

Collect samples as specified in EN ISO 5667-1 and EN ISO 5667-3.

For sampling, use thoroughly cleaned, flat bottomed glass flasks (6.1). Fill the bottles completely with the water to be examined.

Treat and analyze the samples after sample collection as specified in EN ISO 5667-3.

Store the samples at temperatures between 1°C and 5°C, protected from light. Carry out the extraction procedure within 3 weeks.

8 Procedure

8.1 Sample preparation

In general, samples are examined without pre-treatment, e. g. suspended particulate matter is not removed prior to analysis. Do not filter the sample.

Large particles (e. g. leaves, little branches) should be removed using a sieve (screening gap 1 mm).

Add a precisely defined amount of the internal standard stock solution (5.7.4.4) to e. g. 1 000 ml of whole water sample; typically the concentration of the internal standards in the water sample is ca. 100 pg/l. Calculate the exact volume of the water sample by accurately weighing the sample container before extraction and after emptying the sample container.

It is recommended to add the internal standard stock solution (5.7.4.4) first to a water miscible solvent, e. g. 10 ml isopropanol, which is subsequently added to the water sample.

8.2 Extraction by solid-phase extraction disks (SPE-disks)

For conditioning of SPE-disks add an amount of acetone (6 ml to10 ml) and let it pass through the disk in about 20 s, e. g. using a vacuum device. Ensure that the adsorbent does not run dry.

Repeat this step once.

Add an amount of water (6 ml to10 ml) and let it pass through the disk in about 20 s, e. g. using a vacuum device. Ensure that the adsorbent does not run dry.

Repeat this step once.

For sample loading and extraction of analytes dissolved in the water phase take, for example, 1 000 ml of the sample to be examined (8.1) and pass it through the disk conditioned as described above at a flow rate of about 50 ml/min.

For transferring particulate matter on the disk that might have remained in the bottle, rinse the sample reservoir (e. g. the sample bottle) twice with approximately 9 ml of water and pass it through the disk as described above. Dry the disk using a vacuum device (6.9) or by a gentle stream of nitrogen (5.3) for about 10 min to 15 min.

Perform the extraction and elution as follows.

Add an amount of acetone (6 ml to 10 ml), allowing 5 min for the solvent to soak. Collect the eluate by passing it through the disk in about 20 s.

Add an amount of acetone (4 ml to 8 ml), allowing 5 min for the solvent to soak. Collect the eluate by passing it through the disk in about 20 s.

Repeat this step twice.

Collect the combined eluates in a glass vessel. Carefully evaporate the solvent and concentrate the eluate as specified in 8.3.

Other solvents may be used for extraction and elution. However, their suitability should be established in preliminary tests with blank water samples spiked with certified sediment up to 500 mg/l and processed according to Clause 8. Recoveries for each substance under investigation should be > 70 % and ≤ 120 %.

To obtain sufficiently high absolute recoveries it is essential to dry the disk completely prior to elution or to use a water removing solvent in the first elution step.

8.3 Solvent concentration

Add a defined amount of injection standard (e. g. dibromooctafluorobiphenyl) dissolved in solvent, e. g. hexane or toluene (5.4), and concentrate the SPE eluate (see 8.2) carefully to a final volume of about 0,5 ml to 1,0 ml (e. g. in a gentle stream of nitrogen (5.3) or on a rotary evaporator under reduced pressure). To achieve a higher sensitivity, solvent evaporation can be continued to smaller final volumes (e.g. 0,1 ml).The temperature of the eluate during concentration shall be kept below 30 °C.

In some cases and especially when using GC-NCI-MS or GC-MS/MS detection a clean-up step might be necessary to remove interfering compounds as follows. Concentrate the SPE eluate (see 8.2) carefully to 1 ml to 2 ml, add 20 ml of hexane (5.4) and continue to concentrate. Repeat this step once in order to remove as much acetone as possible. If necessary dry the extract with Na_2SO_4. Proceed with a clean-up (see Annex D for an example) and concentrate the eluate obtained in the clean-up step to a final volume as described above.

8.4 Gas chromatrography and mass spectrometry

Optimize the operating conditions of the GC-MS system e. g. according to the manufacturer's instructions. Examples of suitable gas chromatographic conditions are given in Annex A.

Prior to analysis, establish the operating conditions and verify the GC-MS system performance and the calibration for all analytes and their internal standards by analysis of a calibration standard.

For separation, use appropriate capillary columns (6.7) and adjust chromatographic conditions for maximum selectivity and sensitivity (see Annex A for examples).

NOTE When using GC-HRMS (with mass resolution of at least 5 000), GC-MS/MS or GC-NCI-MS as detection technique and operating at optimal instrumental conditions an enrichment factor of at least 10 000 is needed for the detection of the BDE congeners at the required LOQ level. As an example 1 l whole water sample is extracted and concentrated to a final volume of 0,5 ml followed by a 10 µl injection into the GC-MS system.

8.5 Identification of individual compounds by means of GC-MS

Identify the sample component by matching both retention times and relative intensities of the diagnostic ions (see Table 4) of sample components and reference substances (5.7).

The target compound in the sample shall be regarded as identified if:

— the relative or the absolute sample component retention time (*RT*) measured in the selected ion current chromatogram matches the relative or absolute retention time of the authentic compound within ± 0,2 % in the chromatogram of the latest calibration standard solution (e. g. multi-component reference solutions of reference substances; see 5.7.4.3), measured under identical conditions;

— two selected diagnostic ions (see Table 4) are present at the substance-specific retention time;

— relative intensities of all selected diagnostic ions measured in the sample do not deviate by more than ± (0,1 × *I* + 10) % from the relative intensities determined in the calibration standard solution, where *I* is the relative intensity of the diagnostic ion of the individual reference substance.

EXAMPLE Three selected diagnostic ions have the following relative intensities: 100 %, 50 % and 15 %. The maximum allowed deviation for I_2 and I_3 in the sample is (I_1 is by definition 100 % in both the sample and reference standard):

— I_2: ± (0,1 × 50 + 10) % = ± 15 %; the relative intensity in the sample shall be between 35 % and 65 %;

— I_3: ± (0,1 × 15 + 10) % = ± 11,5 %; the relative intensity in the sample shall be between 3,5 % and 26,5 %.

NOTE 1 Further guidance on identification is given in EN ISO 22892 [3] or in the guideline SANCO/12571/2013 [10].

NOTE 2 Deviating relative abundances are due to interferences. It is possible to remove interferences by applying a clean-up step (see e. g. Annex D).

Table 4 — Selected diagnostic ions for mass spectrometric detection and relative abundances

Congener	Ion 1 *m/z*	Ion 2 *m/z*
	Diagnostic ions for GC-HRMS	
BDE-28	405,8026 (100)	407,8006 (97)
BDE-47	483,7131 (68)	485,7111 (100)
BDE-99	563,6215 (100)	565,6195 (98)
BDE-100	563,6215 (100)	565,6195 (98)
BDE-153	481,6975 (68)	483,6955 (100)
BDE-154	481,6975 (68)	483,6955 (100)
^{13}C-BDE-28	417,8428 (100)	419,8408 (97)
^{13}C-BDE-47	495,7533 (68)	497,7513 (100)
^{13}C-BDE-99	575,6619 (100)	577,6599 (98)
^{13}C-BDE-153	493,7378 (68)	495,7357 (100)
^{13}C-PCB-209	509,7229 (100)	511,7199 (86)
	Diagnostic ions for GC-NCI-MS	
all BDE	79 (100)	81 (98)
all F-BDE	79 (100)	81 (98)
	Diagnostic ions for GC-MS/MS	
BDE-28	405,80 > 245,97 (100)	407,80 > 247,97 (97)
BDE-47	483,71 > 325,88 (68)	485,71 > 325,88 (100)
BDE-99	563,62 > 403,79 (100)	565,62 > 405,78 (98)
BDE-100	563,62 > 403,79 (100)	565,62 > 405,78 (98)
BDE-153	643,57 > 483,70 (100)	645,53 > 485,69 (73)
BDE-154	643,57 > 483,70 (100)	645,53 > 485,69 (73)
^{13}C-BDE-28	417,84 > 258,01 (100)	419,84 > 260,01 (97)
^{13}C-BDE-47	495,75 > 335,92 (68)	497,75 > 337,92 (100)
^{13}C-BDE-99	575,66 > 415,83 (100)	577,66 > 417,83 (98)
^{13}C-BDE-153	653,57 > 493,74 (100)	655,57 > 493,74 (73)
^{13}C-PCB-209	509,72 > 439,80 (100)	511,72 > 439,80 (86)

8.6 Blank value measurements

Use periodic blank value measurements (at least one measurement per sequence) to ensure the instruments and chemicals are free from contamination. Blank measurements shall comprise all steps of the analytical procedure. If blank values are unusually high (over 50 % of the lowest reporting level), review every step in the procedure and determine the cause by systematic checks so as to be able to eliminate the contamination source. Try to reduce the blank values as much as possible by applying various measures, such as avoiding contamination by ambient air and using suitable solvents (5.4) as well as checking the analytical instrumentation.

9 Calibration

9.1 Calibration with internal standards

The use of an internal standard for the determination of the concentration minimizes possible errors made during injection and by sample losses during sample pretreatment, and corrects for differences in the final sample extract volumes and changes in recoveries caused by matrix effects. This calculation is usually available as an option in the quantification programs of most manufacturers' data analysis software.

Additionally, it is possible to measure the recovery for the total procedure for each sample, if the values of the internal standard in the calibration solutions are compared to the values obtained for the extract. To achieve this, it is essential that the final volumes are identical. Alternatively, an injection standard can be used for the calculation of recoveries of internal standards (see 10.2).

9.2 Procedure

9.2.1 Evaluation of the range of linear relationship

See Table 5 for typical concentrations of reference compounds and internal standards in solutions to evaluate the linear range. Adjust the concentrations according to the sensitivity of the used equipment and the required range of determinations.

The linear relationship should be ensured with the concentration-response relationships as used in internal standardization. Plot for each substance *i* the ratio values $y_i/y_{\mathrm{is},i}$ (peak areas or peak heights of BDE compound *i* and corresponding internal standard *is*; use either the response of the diagnostic ion of highest intensity or the sum of the responses of both diagnostic ions) on the ordinate and the associated ratio of mass concentrations $\rho_i/\rho_{\mathrm{is},i}$ on the abscissa. Check the linear relationship by a graphical representation and statistical evaluation of the calibration data according to ISO 8466-1.

9.2.2 Two point calibration over the total linear range

Carry out a two-point calibration, using calibration solutions with concentrations corresponding to e.g. 20 % and 80 % of the linear range. Check the validity of this calibration function which is dependent on the stability of the GC-MS system at least with each batch of samples.

Use the mean values of multi-injections e. g. $y_{i(1)}/y_{\mathrm{is},i(1)}$, $y_{i(2)}/y_{\mathrm{is},i(2)}$, $y_{i(3)}/y_{\mathrm{is},i(3)}$ at two concentration levels.

Establish the linear function of the two pairs of values $y_i/y_{\mathrm{is},i}$ and $\rho_i/\rho_{\mathrm{is},i}$ of the measured series using the following Formula (1):

$$\frac{y_i}{y_{\mathrm{is},i}} = a_i \frac{\rho_i}{\rho_{\mathrm{is},i}} + b_i \quad (1)$$

where

y_i is the measured response of substance *i*; the unit depends on the evaluation, e.g. area value;

ρ_i is the mass concentration of substance *i*, in the working standard solution, in picograms per millilitre, (pg/ml);

a_i is the slope of the calibration function of substance *i*, the unit depends on the evaluation;

b_i is the ordinate intercept of the calibration curve, the unit depends on the evaluation;

$y_{is,i}$ is the measured response of the corresponding internal standard for the substance *i*, the unit depends on the evaluation;

$\rho_{\mathrm{is},i}$ is the mass concentration of the corresponding internal standard for the substance *i*, in picograms per millilitre, (pg/ml).

Estimate the accuracy of the calibration as described in 9.2.3.

9.2.3 Estimation of the accuracy of the calibration for the concentration of interest

For example, analyze, as a minimum in triplicate, an independent standard solution (5.7.4.5) and calculate the results in accordance with the above calibration method. For each substance *i* the standard deviation between the single results ρ_{ij} and the known value q_i of the concentration in the standard is then calculated according to Formula (1):

$$s_{\rho_i} = \sqrt{\frac{\sum_{j=1}^{N} \left(\rho_{ij} - q_i\right)^2}{N-1}} \quad (2)$$

where

s_{ρ_i} is a measure of the accuracy of the calibration;

ρ_{ij} is the measured mass concentration of substance *i*;

q_i is the known mass concentration of substance *i*;

N is the number of measurements.

Table 5 — Example concentrations in solutions for evaluating the linear range (GC-HRMS, 1 µl injection)

Congener	Solution 1 pg/ml	Solution 2 pg/ml	Solution 3 pg/ml	Solution4 pg/ml	Solution 5 pg/ml	Solution 6 pg/ml	Solution 7 pg/ml
BDE-28	75	150	300	600	1 200	2 400	4 800
BDE-47	75	150	300	600	1 200	2 400	4 800
BDE-99	75	150	300	600	1 200	2 400	4 800
BDE-100	75	150	300	600	1 200	2 400	4 800
BDE-153	75	150	300	600	1 200	2 400	4 800
BDE-154	75	150	300	600	1 200	2 400	4 800
Internal standards for EI							
^{13}C-BDE-28	600	600	600	600	600	600	600
^{13}C-BDE-47	600	600	600	600	600	600	600
^{13}C-BDE-99	600	600	600	600	600	600	600
^{13}C-BDE-153	600	600	600	600	600	600	600

10 Quantification

10.1 Determination of the BDE concentrations in whole water samples

The mass concentrations of the internal standards ρ_{is} in the final volume of extract shall be the same for calibration and sample measurement. Use the same solvent composition for the working standard solutions and the extracts. Inject identical volumes of the sample extracts as injected as calibration solutions.

Calculate the mass concentration ρ_i of the substance using Formula (3).

$$\rho_i = \frac{\frac{y_i}{y_{\mathrm{is},i}} - b_i}{a_i} \cdot \frac{m_{\mathrm{is},i}}{V} = \frac{\rho_i}{\rho_{\mathrm{is},i}} \cdot \frac{m_{\mathrm{is},i}}{V} \qquad (3)$$

where

ρ_i is the mass concentration of the substance *i* in the water sample in picograms per litre (pg/l);

y_i is the measured response, e.g. peak area, of the substance *i* in the sample extract;

$y_{is,i}$ is the measured response, e.g. peak area, of the corresponding internal standard of substance *i* in the sample extract;

$\rho_{is,i}$ is the mass concentration of the corresponding internal standard of substance *i* in the sample extract, in picograms per millilitre, (pg/ml);

$m_{is,i}$ is the mass of the added internal standard of substance *i* in picograms (pg);

V is the sample volume in litre (l);

a_i see Formula (1);

b_i see Formula (1).

10.2 Determination of the recoveries of the internal standards

It is possible to measure the recoveries of the internal standards for single samples by comparing the values of the internal and the injection standards obtained in the calibration with those obtained for sample extracts. Provided the relationship between the concentration and the response of the internal standard is linear and the intercept of this curve is negligible, the recovery of each internal standard is calculated according to Formula (4).

$$A_{\mathrm{is}} = \frac{y_{\mathrm{is,E}} \cdot y_{\mathrm{inj,C}}}{y_{\mathrm{is,C}} \cdot y_{\mathrm{inj,E}}} \cdot 100 \qquad (4)$$

where

A_{is} is the recovery of the internal standard in percent (%);

$y_{is,E}$ is the measured response, e.g. peak area, of the internal standard in the sample extract;

$y_{is,C}$ is the measured response, e.g. peak area, of the internal standard in the calibration solution;

$y_{inj,E}$ is the measured response, e.g. peak area, of the injection standard in the sample extract;

$y_{inj,C}$ is the measured response, e.g. peak area, of the injection standard in the calibration solution.

For a reliable quantification of the BDE congeners in the sample the recoveries of the internal standards should be between 70 % and 120 %. If this criterion is not met, it should be indicated in the test report. Re-analysis of the sample after dilution can help to improve the recoveries.

11 Expression of results

Substract from the calculated mass concentrations (see 10.1) the concentrations which were obtained for the blank determinations.

The mass concentration, in nanograms per litre (ng/l), of the congeners listed in Table 1 shall be reported to two significant figures.

EXAMPLES	2,4,4'-Tribromodiphenyl ether, BDE-28	11 ng/l
	2,2',4,4'-Tetrabromodiphenyl ether, BDE-47	1,2 ng/l
	2,2',4,4',5-Pentabromodiphenyl ether, BDE-99	0,14 ng/l
	2,2',4,4',6-Pentabromodiphenyl ether, BDE-100	0,021 ng/l

12 Test report

The test report shall contain at least the following information:

a) the applied test method, with a reference to this European Standard (EN 16694);

b) all information necessary for the complete identification of the water sample;

c) sample preparation and extraction;

d) expression of the results, according to Clause 11;

e) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the results.

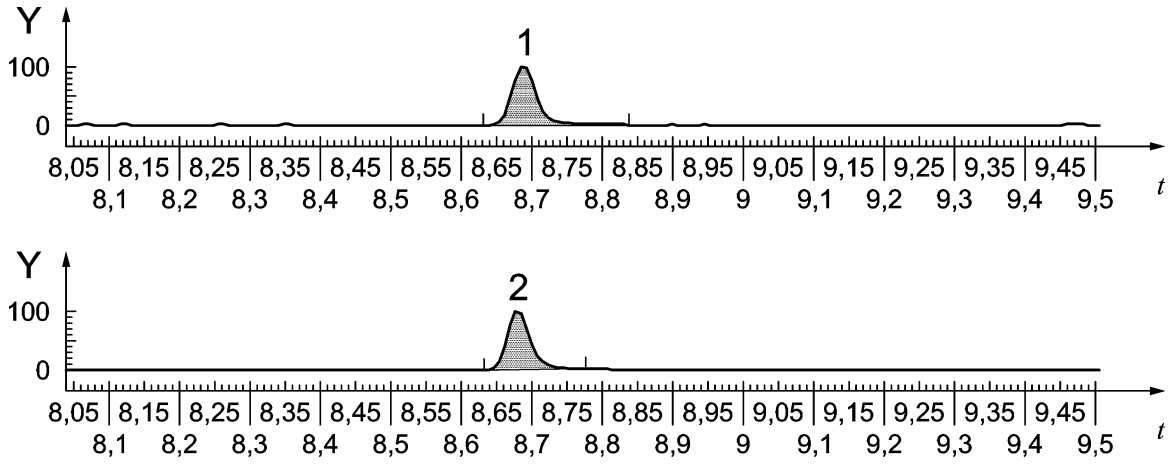
Annex A
(informative)

Suitable gas chromatographic conditions and example chromatograms

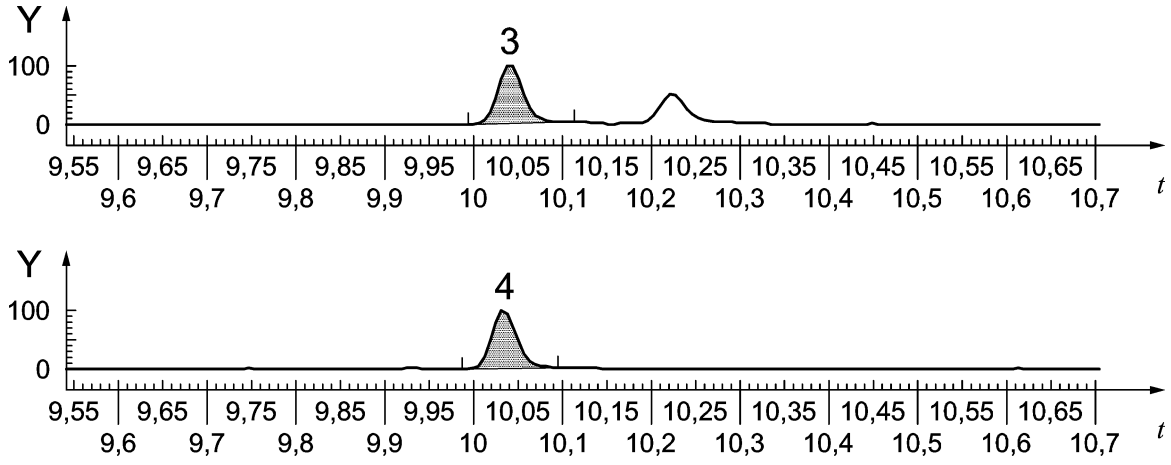
A.1 GC-HRMS conditions for the chromatograms in Figure A.1

GC equipment:	Agilent 7890A [1)]
Injection:	1 µl, glass-liner (baffled, Siltek® [1)] deactivated), I.D: 1,0 mm, Gerstel CIS 4 [1)], 100 °C; 40 °C/min to 110°C (hold 0,1 min), 300 °C/min to 250 °C (hold 1,08 min), 40°C/min to 350°C (hold 12,5 min), 10 min; pulsed splitless *or* large volume injection e. g. 10 µl, glass-liner (baffled, Siltek® [1)] deactivated), I.D: 1,0 mm, Gerstel CIS 4 [1)];105 °C, venting 12 kPA during 0,17min, 300°C/min to 250 °C (hold 2 min), 40 °C/min to 350 °C (hold 12 min)
Capillary column:	Restek Rtx-1614 [1)]: 15 m x 0,25 mm x 0,1 µm
Carrier gas:	helium (5.0); 1 ml/min
Temperature programme:	90°C (1 min); 15°C/min to 275°C (hold 0,67 min); 60°C/min to 350°C (hold 1,75 min)
MS detector:	Waters Autospec Premier [1)], magnetic sector MS, EI 70 eV, SIM, resolution 5 000

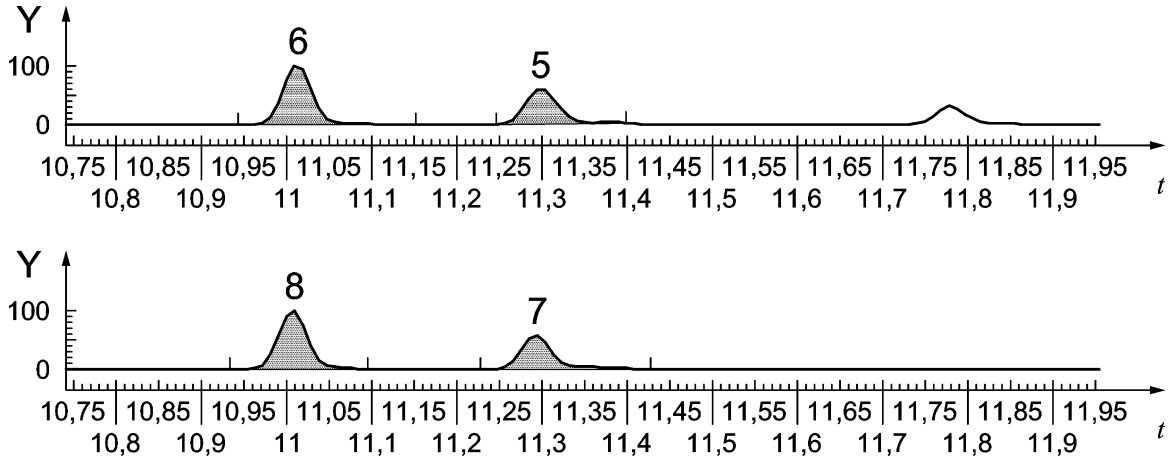
1) Agilent 7890A, Siltek®, Gerstel CIS 4, Restek RTX-1614 and Waters Autospec Premier are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.



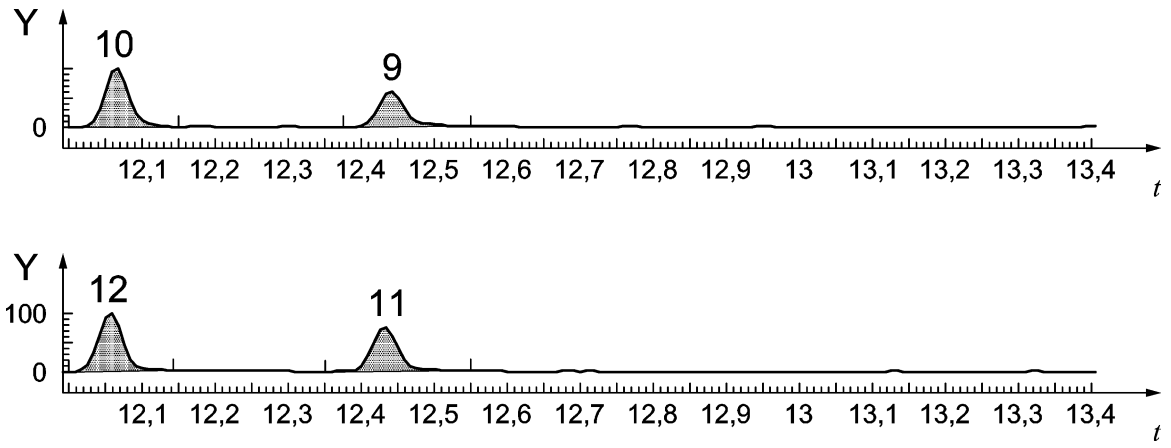
a) ion 405,80



b) ion 483,71



c) ion 563,62



d) ion 481,69

Key

t time in minutes (min)

Y abundance, signal intensity

1 BDE-28

2 ^{13}C-BDE-28

3 BDE-47

4 ^{13}C-BDE-47

5 BDE-99

6 BDE-100

7 ^{13}C-BDE-99

8 ^{13}C-BDE-100

9 BDE-153

10 BDE-154

11 ^{13}C-BDE-153

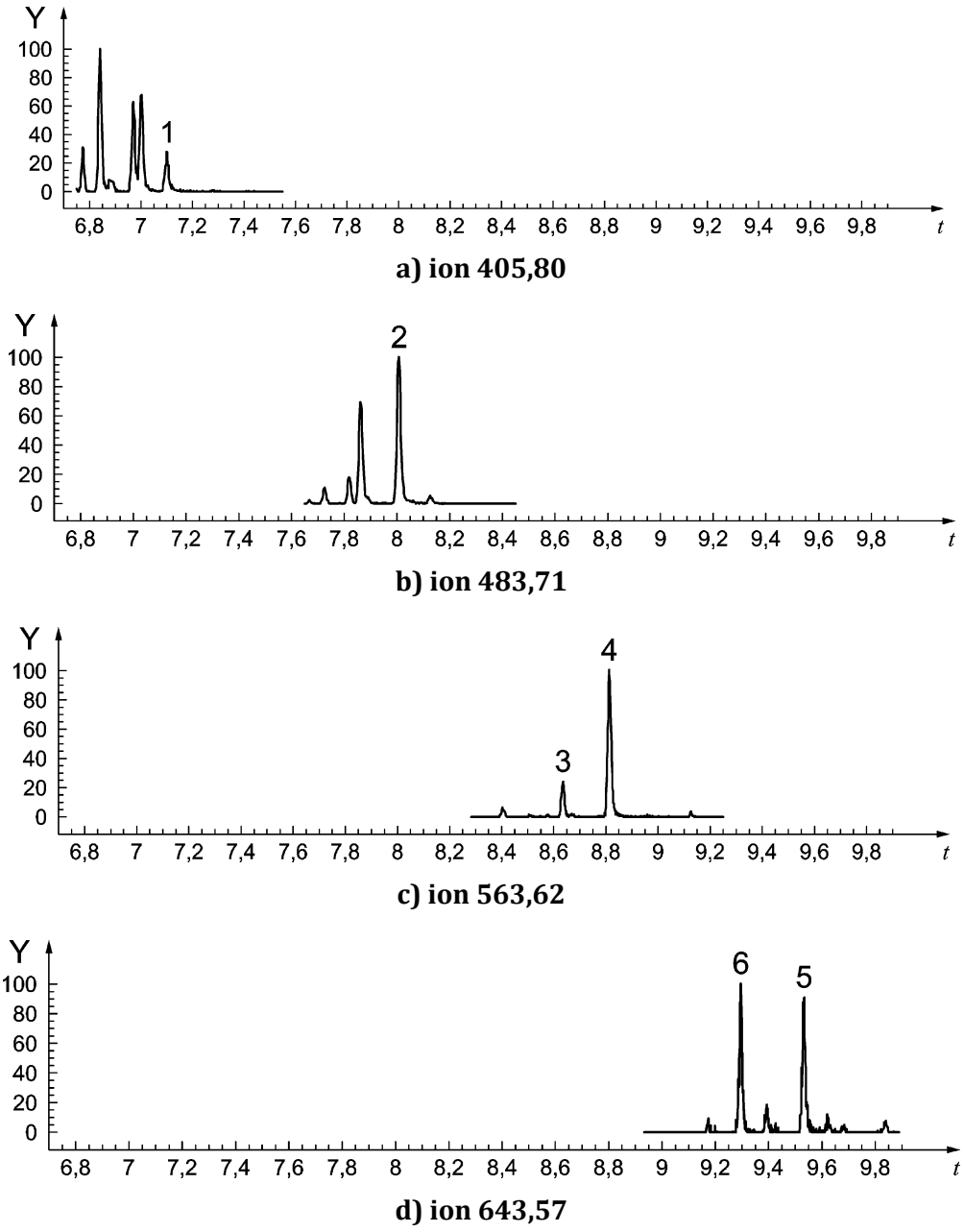
12 ^{13}C-BDE-154

Figure A.1 — Example of GC-HRMS ion chromatograms for PBDE congeners

A.2 GC-MS/MS conditions for the chromatograms in Figure A.2

GC equipment:	Thermo Trace 1300 [2)]
Injection:	50 µl PTV, 45 °C, splitless time 3 min, split flow 50 ml/min, inject time 0,25 min, transfer 5 °C/min to 280 °C (6 min), glass-liner (sintered, deactivated)
Capillary column:	Restek RTX-1614 [2)] 15 m x 0,25 mm ID × 0,1 µm FT
Carrier gas:	helium (5.0); 1,5 ml/min
Temperature programme:	60 °C (1 min); 25 °C/min to 320 °C (hold 4 min)
MS detector:	Thermo TSQuantum XLS Ultra MS/MS [2)]
Collison gas:	Argon, 1,3 mm Torr

2) Thermo Trace 1300, Restek RTX-1614 and Thermo TSQuantum XLS Ultra MS/MS are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.



Key

t time in minutes (min)

Y abundance, signal intensity

1 BDE-28

2 BDE-47

3 BDE-100

4 BDE-99

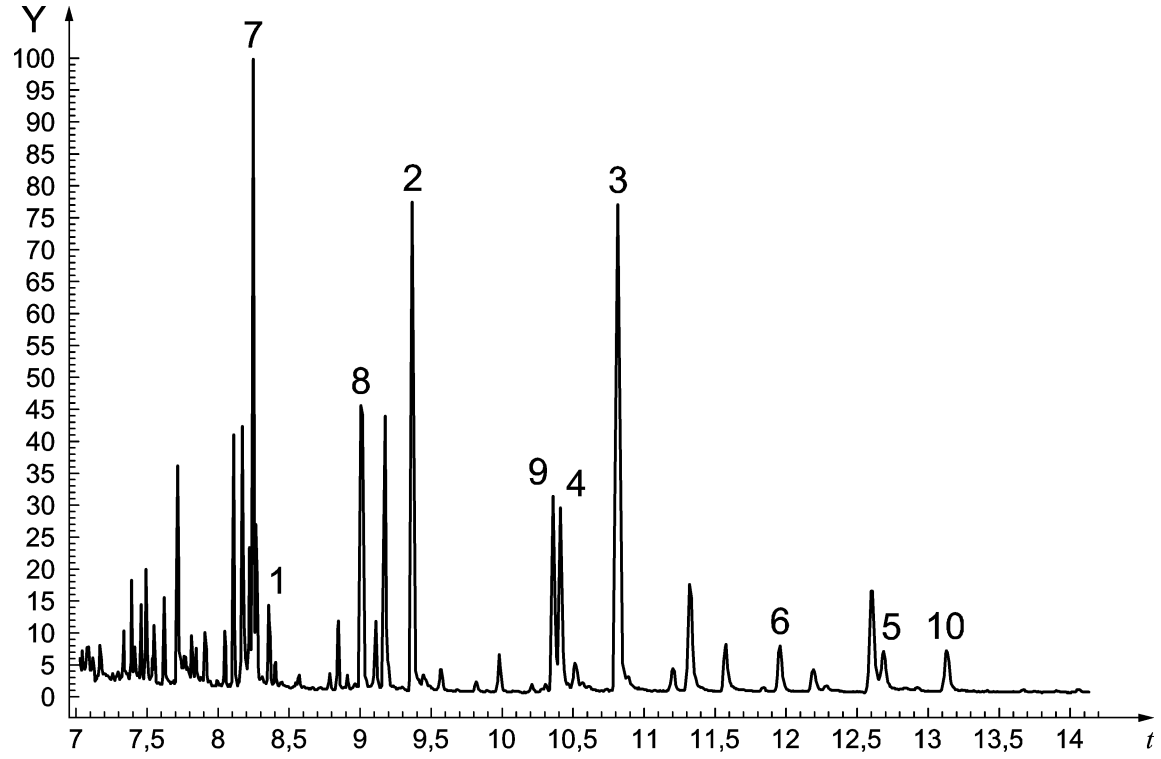
5 BDE-153

6 BDE-154

Figure A.2 — Example of LV-GC-MS/MS ion chromatograms for native PBDE congeners (extract of whole water sample)

A.3 GC-NCI-MS conditions for the chromatograms in Figure A.3

GC equipment:	Agilent 6890A [3)]
Injection:	1 µl, pulsed splitless, 300°C, pulse time 1,25 min, glass-liner (double taper, deactivated), I.D: 4,0 mm
Capillary column:	DB5-MS [3)], 20 m x 0,18 mm x 0,18 µm
Carrier gas:	helium (5.0); 1 ml/min
Temperature programme:	100°C (2 min); 20°C/min to 320°C (hold 10 min)
MS detector:	Agilent 5975C inert XL EI/CI MSD [3)], quadrupole MS, CI (methane), SIM



Key

t	time in minutes (min)				
Y	abundance, signal intensity				
1	BDE-28	(RT 8,36 min)	6	BDE-154	(RT 11,96 min)
2	BDE-47	(RT 9,37 min)	7	F-BDE-28	(RT 8,25 min)
3	BDE-99	(RT 10,82 min)	8	F-BDE-47	(RT 9,01 min)
4	BDE-100	(RT 10,41 min)	9	F-BDE-100	(RT 10,36 min)
5	BDE-153	(RT 12,69 min)	10	F-BDE-160	(RT 13,13 min)

Figure A.3 — Example of a GC-NCI-MS total ion chromatogram for native BDE and F-BDE congeners (standard solution)

3) Agilent 6890A, DB5-MS and Agilent 5975C inert XL EI/CI MSD are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.

Annex B
(informative)

Repeatability and reproducibility data

The performance data on repeatability and reproducibility given in Tables B.1, B.2 and B.3 were determined in a European interlaboratory trial for validation carried out in June 2014 on surface water.

Sample 1 and 2 were natural mineral water samples additionally spiked with different amounts of suspended particulate matter (SPM). The SPM material used was a synthetic PBDE-containing SPM derived from a PBDE model SPM [11, 12]. Homogeneous SPM containing slurries were prepared by adding an appropriate amount of PBDE-SPM to Milli-Q water. Under constant mixing defined aliquots of the slurries were taken and added reproducibly to the Sample 1 and Sample 2 bottles.

Sample 3 was spiked with a technical pentaBDE mixture (Wellington Laboratories, cat n° TBDE-71).

Evaluation of data was carried out according to ISO 5725-2.

The physico-chemical interactions taking place when adding model SPM to pre-filled water bottles are not known in detail. Therefore all concentrations in the final water samples based on slurry addition are estimated.

Table B.1 — Performance data for PBDE in mineral water, spiked with 20 mg/l of suspended particulate matter (SPM), sample 1

Compound	l	n	o %	X ng/l	$\bar{\bar{x}}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
BDE-28	-	-	-	< 0,025	-	-	-	-	-	-
BDE-47	9	18	10,0	0,328	0,365	111,3	0,0562	15,4	0,0422	11,6
BDE-99	9	18	10,0	0,761	0,849	111,6	0,115	13,5	0,0878	10,3
BDE-100	9	18	10,0	0,113	0,133	117,7	0,0251	18,9	0,0168	12,7
BDE-153	10	20	0,0	0,155	0,164	105,8	0,0488	29,7	0,0250	15,3
BDE-154	9	18	0,0	0,072	0,094	130,6	0,0334	35,5	0,0110	11,7
Sum 6 BDE	9	18	10,0	1,454	1,609	110,7	0,222	13,8	0,173	10,7

l number of laboratories after outlier rejection
n number of individual test results after outlier rejection
o percentage of outliers
X assigned value
$\bar{\bar{x}}$ overall mean of results (without outliers)
η recovery rate
s_R reproducibility standard deviation
$C_{V,R}$ coefficient of variation of reproducibility
s_r repeatability standard deviation
$C_{V,r}$ coefficient of variation of repeatability

Table B.2 — Performance data for PBDE in mineral water, spiked with 200 mg/l of suspended particulate matter (SPM), sample 2

Compound	l	n	o %	X ng/l	$\bar{\bar{x}}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
BDE-28	8	16	20,0	0,032	0,0296	92,5	0,0076	25,7	0,0032	10,8
BDE-47	11	22	0,0	2,51	2,65	105,7	0,775	29,2	0,273	10,3
BDE-99	11	22	0,0	5,82	6,13	105,3	2,09	34,1	0,625	10,2
BDE-100	11	22	0,0	0,86	0,965	112,2	0,338	35,0	0,068	7,0
BDE-153	11	22	0,0	1,19	1,12	94,2	0,419	37,4	0,156	13,9
BDE-154	9	18	18,2	0,55	0,528	96,0	0,168	31,8	0,021	4,0
Sum 6 BDE	11	22	0,0	10,96	11,74	107,1	3,27	27,8	1,282	10,9
NOTE For explanation of symbols see Table B.1.										

Table B.3 — Performance data for PBDE in mineral water, spiked with a technical pentaBDE mix, sample 3

Compound	l	n	o %	X ng/l	$\bar{\bar{x}}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
BDE-28	-	-	-	< 0,025	-	-	-	-	-	-
BDE-47	10	18	0,0	0,173	0,178	102,9	0,046	25,8	0,016	9,0
BDE-99	10	18	0,0	0,235	0,213	90,6	0,067	31,5	0,030	14,3
BDE-100	9	16	0,0	0,048	0,049	102,1	0,013	26,5	0,0041	8,2
BDE-153	-	-	-	< 0,025	-	-	-	-	-	-
BDE-154	-	-	-	< 0,025	-	-	-	-	-	-
Sum 6 BDE	10	18	0,0	0,531	0,514	96,8	0,121	23,5	0,038	7,4
Including BDE-153 and BDE-154										
BDE-153	8	14	0,0	0,021	0,019	90,5	0,0071	36,8	0,0036	18,9
BDE-154	8	14	0,0	0,018	0,021	116,7	0,0092	42,9	0,0017	7,9
Sum 6 BDE	10	18	0,0	0,520	0,505	97,1	0,124	24,6	0,036	7,1
NOTE For explanation of symbols see Table B.1										

Annex C
(informative)

Examples of suitable solid phase extraction disks

Table C.1 lists some examples of solid-phase extraction disks (SPE-disks), that have been tested within standardization work and which have proved to be suitable for the purpose. Other disks can be used as well if their suitability has been established in preliminary test.

Table C.1 — Examples of suitable SPE-disks

Sorbent (disk type)	Product name (supplier) [4)]
Silica based monolithic sorbent, C_{18} (disk, 50 mm)	SPEC Disk SPEC18 AR (Agilent)
Silica based sorbent, C_{18} (cartridge type, 47 mm)	BAKERBOND Speedisk C18 (J.T.Baker)
Silica based sorbent, C_{18} (cartridge type, 47 mm)	BAKERBOND Speedisk C18 high capacity (J.T.Baker)
Styrene-divinyl benzene (SDB) copolymer (cartridge type, 47 mm)	BAKERBOND Speedisk H_2O-phobic DVB (J.T.Baker)
Styrene-divinyl benzene (SDB) copolymer (cartridge type, 47 mm)	BAKERBOND Speedisk H_2O-phobic DVB high capacity (J.T.Baker)
Styrene-divinyl benzene copolymer (disk, 47 mm)	Empore Styrene DVB (3M)
N-vinylpyrrolidone-divinyl benzene copolymer (disk, 47 mm)	Oasis HLB (Waters)
N-vinylpyrrolidone-divinyl benzene copolymer (disk, 47 mm)	Atlantic DVB-D (Horizon)

4) The listed names are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.

Annex D
(informative)

Clean up procedure

D.1 Reagents

D.1.1 Silica 60, 63 µm to 200 µm, baked at 250°C for 12 h.

D.1.2 Silica treated with sulfuric acid.

56 g of silica, 44 g of sulfuric acid (H_2SO_4, 95 % to 97 %). Add the sulfuric acid drop by drop and shake the mixture for 8 h. Store in amber glass bottles. The mixture is stable for approximately 1 month.

D.1.3 Silica treated with sodium hydroxide.

33 g of silica, 17 g of sodium hydroxide (NaOH, 1 mol/l). Add the sodium hydroxide solution drop by drop and shake the mixture for 8 h. Store in amber glass bottles. The mixture is stable for approximately 1 month.

D.2 Procedure

The whole clean up procedure should be executed with clean glassware (cleaned by heating and rinsing with solvents), with maximum protection from light and possible laboratory contamination.

Prepare a multilayer silica column by bringing consecutively in a small chromatography column 1 g of silica containing 33 % NaOH 1N and 5 g of silica containing 44 % of concentrated sulfuric acid.

Wash the multilayer column with hexane.

Evaporate the extract of the water sample to a volume < 1 ml, using a gentle stream of nitrogen.

Rinse the wall of the container with a small volume of hexane and evaporate again to a volume < 1 ml.

Repeat this step twice and bring to a final volume of approximately 1 ml.

Bring this volume on top of the multilayer silica column.

Elute the PBDE with 30 ml of hexane, leaving the non-acid-resistant interferences in the column.

Concentrate the cleaned extract to a volume of < 1 ml.

Rinse the wall of the container with a small volume of hexane and concentrate to the desired volume.

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[1] EN 16377, *Characterization of waste - Determination of brominated flame retardants (BFR) in solid waste*

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