

# SVENSK STANDARD

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**Vattenundersökningar – Bestämning av några utvalda polybromerade difenyletrar (PBDE) i vattenprover – Gaskromatografisk och masspektrometrisk metod (GC-MS) efter fastfasextraktion (SPE diskar)**

**Water quality – Determination of selected polybrominated diphenyl 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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EUROPEAN STANDARD

EN 16694

NORME EUROPÉENNE

EUROPÄISCHE NORM

September 2015

ICS 13.060.50

English Version

Water quality - Determination of selected polybrominated diphenyl 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)

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

This European Standard was approved by CEN on 27 June 2015.

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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of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.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  $\geq 0,025$  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 <sup>a</sup>	Formula	Molar mass g/mol	CAS RN <sup>b</sup>
2,4,4'-Tribromodiphenyl ether	BDE-28	C <sub>12</sub> H <sub>7</sub> Br <sub>3</sub> O	406,8954	41318-75-6
2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	485,7950	5436-43-1
2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	564,6911	60348-60-9
2,2',4,4',6-Pentabromodiphenyl ether	BDE-100	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	564,6911	189084-64-8
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	643,5872	68631-49-2
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE-153	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	643,5872	207122-15-4

NOTE EC numbers are not applicable for PBDE congeners.

<sup>a</sup> Numbering analog to IUPAC nomenclature for PCB

<sup>b</sup> 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 (<sup>13</sup>C<sub>12</sub>-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<sub>7</sub>H<sub>8</sub> (boiling point: 111 °C),
- acetone, C<sub>3</sub>H<sub>6</sub>O (boiling point: 56 °C),
- *iso*- or *n*-hexane, C<sub>6</sub>H<sub>14</sub>, (boiling point: 60 °C),