BS EN 16694:2015

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)

bsi.

...making excellence a habit.™

Document Sharing Hub

Full document details: BS EN 16694:2015

National foreword

This British Standard is the UK implementation of EN 16694:2015.

The UK participation in its preparation was entrusted to Technical Committee EH/3/2, Physical chemical and biochemical methods.

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.

© The British Standards Institution 2015. Published by BSI Standards Limited 2015

ISBN 978 0 580 84520 8

ICS 13.060.50

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 September 2015.

Amendments issued since publication

Date	Text affected

Documents
Document Sharing Hub

Full document details: BS EN 16694:2015

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16694

September 2015

ICS 13.060.50

English Version

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)

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

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

© 2015 CEN All rights of exploitation in any form and by any means reserved worldwide for CEN national Members.

Ref. No. EN 16694:2015 E

Documents
Document Sharing Hub

Full document details: BS EN 16694:2015

Contents

Page

European foreword ... 4

Introduction ... 5

1 Scope ... 6

2 Normative references ... 6

3 Principle ... 6

4 Interferences ... 7
4.1 Interferences with extraction and clean up ... 7
4.2 Interferences with GC-MS ... 7

5 Reagents ... 7

6 Apparatus ... 10

7 Sampling ... 11

8 Procedure ... 11
8.1 Sample preparation ... 11
8.2 Extraction by solid-phase extraction disks (SPE-disks) ... 11
8.3 Solvent concentration ... 12
8.4 Gas chromatrography and mass spectrometry ... 12
8.5 Identification of individual compounds by means of GC-MS ... 12
8.6 Blank value measurements ... 14

9 Calibration ... 15
9.1 Calibration with internal standards ... 15
9.2 Procedure ... 15
9.2.1 Evaluation of the range of linear relationship ... 15
9.2.2 Two point calibration over the total linear range ... 15
9.2.3 Estimation of the accuracy of the calibration for the concentration of interest ... 16

10 Quantification ... 17
10.1 Determination of the BDE concentrations in whole water samples ... 17
10.2 Determination of the recoveries of the internal standards ... 18

11 Expression of results ... 18

12 Test report ... 19

Annex A (informative) Suitable gas chromatographic conditions and example chromatograms ... 20

A.1 GC-HRMS conditions for the chromatograms in Figure A.1 ... 20

A.2 GC-MS/MS conditions for the chromatograms in Figure A.2 ... 23

A.3 GC-NCI-MS conditions for the chromatograms in Figure A.3 ... 25

Annex B (informative) Repeatability and reproducibility data ... 26

Annex C (informative) Examples of suitable solid phase extraction disks ... 29

Annex D (informative) Clean up procedure ... 30

D.1 Reagents ... 30

Documents
Document Sharing Hub

Full document details: BS EN 16694:2015

D.2 Procedure **30**
Bibliography **31**

Documents
Document Sharing Hub
Full document details: BS EN 16694:2015

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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Documents
Document Sharing Hub
Full document details: BS EN 16694:2015

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.

Documents
Document Sharing Hub
Full document details: BS EN 16694:2015

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

Documents
Document Sharing Hub
Full document details: BS EN 16694:2015

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),

Documents
Document Sharing Hub
Full document details: BS EN 16694:2015

— *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.

Documents
Document Sharing Hub
Full document details: BS EN 16694:2015

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.

AVA Documents
Document Sharing Hub

Full document details: BS EN 16694:2015