

Water quality — Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge — Method using extraction and gas chromatography/mass spectrometry

ICS 13.060.50

National foreword

This British Standard is the UK implementation of EN ISO 22032:2009. It is identical with ISO 22032:2006. It supersedes BS ISO 22032:2006 which is withdrawn.

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

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30 June 2009	This corrigendum renumbers BS ISO 22032:2006 as BS EN ISO 22032:2009

English Version

Water quality - Determination of selected polybrominated
diphenyl ethers in sediment and sewage sludge - Method using
extraction and gas chromatography/mass spectrometry (ISO
22032:2006)

Qualité de l'eau - Dosage d'une sélection d'éthers
diphényles polybromés dans des sédiments et des
boues d'épuration - Méthode par extraction et
chromatographie en phase gazeuse/spectrométrie de
masse (ISO 22032:2006)

Wasserbeschaffenheit - Bestimmung ausgewählter
polybromierter Diphenylether in Sediment und Klärschlamm
- Verfahren mittels Extraktion und
Gaschromatographie/Massenspektrometrie (ISO
22032:2006)

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Foreword

The text of ISO 22032:2006 has been prepared by Technical Committee ISO/TC 147 “Water quality” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 22032:2009 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of an identical text or by endorsement, at the latest by August 2009, and conflicting national standards shall be withdrawn at the latest by August 2009.

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Endorsement notice

The text of ISO 22032:2006 has been approved by CEN as a EN ISO 22032:2009 without any modification.

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Introduction

The user should be aware that particular problems could require the specification of additional marginal conditions.

Water quality — Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge — Method using extraction and gas chromatography/mass spectrometry

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.

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

1 Scope

This International Standard specifies a method for the determination of selected polybrominated diphenyl ethers (PBDE) (see Figure 1 and Table 1) in sediment and sludge using gas chromatography/mass spectrometry (GC-MS) in the electron impact (EI) or negative ion chemical ionization (NCI) mode.

When using GC-EI-MS, the method is applicable to samples containing 0,05 µg/kg to 25 µg/kg of tetra- to octabromo congeners and 0,3 µg/kg to 100 µg/kg of decabromo diphenyl ether (BDE-209), respectively. Approximately ten times lower concentrations can be quantified when using GC-NCI-MS. The risk of misinterpretation of interfering substances is smaller with EI due to its higher specificity. It is also possible to analyse other brominated diphenyl ethers according to this International Standard, after verifying its applicability in each case.

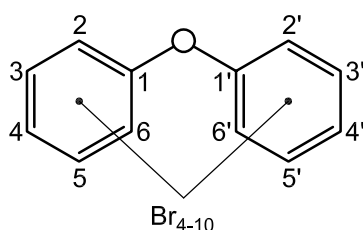


Figure 1 — Chemical formula of polybrominated diphenyl ethers

Table 1 — PBDE congeners determined by this method

No.	Congener	Formula	Abbreviation ^a	Molar mass g/mol
1	2,2',4,4'-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	BDE-47	485,795 0
2	2,2',4,4',5-Pentabromodiphenyl ether	C ₁₂ H ₅ Br ₅ O	BDE-99	564,691 1
3	2,2',4,4',6-Pentabromodiphenyl ether	C ₁₂ H ₅ Br ₅ O	BDE-100	564,691 1
4	2,2',4,4',5,6'-Hexabromodiphenyl ether	C ₁₂ H ₄ Br ₆ O	BDE-154	643,587 2
5	2,2',4,4',5,5'-Hexabromodiphenyl ether	C ₁₂ H ₄ Br ₆ O	BDE-153	643,587 2
6	2,2',3,4,4',5',6-Heptabromodiphenyl ether	C ₁₂ H ₃ Br ₇ O	BDE-183	722,483 2
7	Decabromodiphenyl ether	C ₁₂ Br ₁₀ O	BDE-209	959,171 4

^a Numbering analogous to IUPAC nomenclature for PCB.

2 Normative references

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

ISO 5667-13, *Water quality — Sampling — Part 13: Guidance on sampling of sludges from sewage and water-treatment works*

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

Extraction of brominated diphenyl ethers from the dried sample by an organic solvent. Clean-up of the extract by, e.g. preparative multi-layer silica gel column chromatography. After concentration, separation of the brominated diphenyl ethers by capillary gas chromatography and detection by either mass spectrometry in the selected ion monitoring mode using electron impact (EI), or negative ion chemical ionization (NCI). For determination of the concentration in the sample, an internal standard calibration over the total procedure is used.

4 Interferences

When applying GC-NCI-MS, 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) and tetrabromobisphenol A can co-elute with BDE-154 and BDE-153, respectively, when using non-polar capillary columns and hence, interfere with the determination of the corresponding BDE congeners when monitoring the bromide ions $m/z = 79$ and $m/z = 81$. Moreover, naturally produced brominated compounds, such as halogenated bipyrrols and brominated phenoxyanisols, can be considered as potential interferences.

Sources of contamination are the following: brominated diphenyl ethers used as flame-retardants in organic polymers. Therefore, contact of the sample or the reagents with these organic polymers shall be avoided. Transportation paths include airborne dust, vial covers, pasteur pipette fillers and recycled paper.

5 Reagents and standards

Only use reagents with negligibly low concentrations of brominated diphenyl ethers compared with the concentration to be determined and verify by blank determinations. To prevent degradation, store standards in the dark at temperatures recommended by the manufacturer (calibration solutions should preferably be stored at approximately -18°C).

5.1 Solvents for extraction, clean-up and preparation of stock solutions.

A variety of solvents may be used depending on the particular sample matrix to be analysed and the availability of commercial standard solution, e.g. toluene (C_7H_8), or acetone (propanone, $\text{C}_3\text{H}_6\text{O}$), or a mixture of acetone (propanone, $\text{C}_3\text{H}_6\text{O}$) and hexane (C_6H_{14}), or heptane (C_7H_{16}), or iso-octane (2,2,4-trimethylpentane, C_8H_{18}), or nonane (C_9H_{20}), or dichloromethane (CH_2Cl_2) for residual analysis.

5.2 Reference substances.

See Table 1. Solutions of reference substances are commercially available.

5.3 Internal standard substances.

Solutions of reference substances for use as internal standards for electron impact ionization (Table 2, substances 1 to 5) and for negative ion chemical ionization (Table 2, substances 6, 7 and 8) are commercially available.

Table 2 — Examples of internal standards

No	Name	Formula	Abbreviation	Molar mass g/mol
Internal standards for GCMS with electron impact ionization				
1	2,2',4,4'-Tetrabromo[$^{13}\text{C}_{12}$]diphenyl ether	$^{13}\text{C}_{12}\text{H}_6\text{Br}_4\text{O}$	^{13}C -BDE-47	497,703 5
2	2,2',4,4',5-Pentabromo[$^{13}\text{C}_{12}$]diphenyl ether	$^{13}\text{C}_{12}\text{H}_5\text{Br}_5\text{O}$	^{13}C -BDE-99	576,599 5
3	2,2',4,4',5,5'-Hexabromo[$^{13}\text{C}_{12}$]diphenyl ether	$^{13}\text{C}_{12}\text{H}_4\text{Br}_6\text{O}$	^{13}C -BDE-153	655,495 5
4	2,2',3,4,4',5,6-Heptabromo[$^{13}\text{C}_{12}$]diphenyl ether	$^{13}\text{C}_{12}\text{H}_3\text{Br}_7\text{O}$	^{13}C -BDE-183	734,391 6
5	Decabromo[$^{13}\text{C}_{12}$]diphenyl ether	$^{13}\text{C}_{12}\text{Br}_{10}\text{O}$	^{13}C -BDE-209	971,079 7
Internal standards for GCMS with negative ion chemical ionization ^a				
6	3,3',4,4'-Tetrabromodiphenyl ether	$\text{C}_{12}\text{H}_6\text{Br}_4\text{O}$	BDE-77	485,795 0
7	2,2',3,4,4',5,6-Heptabromodiphenyl ether	$\text{C}_{12}\text{H}_3\text{Br}_7\text{O}$	BDE-181	722,483 2
8	Decabromo[$^{13}\text{C}_{12}$]diphenyl ether	$^{13}\text{C}_{12}\text{Br}_{10}\text{O}$	^{13}C -BDE-209	971,079 7
^a Check for interferences when non-labelled PBDE is used as an internal standard. Other BDE congeners are suitable as internal standards, e.g. BDE-140.				

5.4 Sodium sulfate, anhydrous, Na_2SO_4 , powdered.

5.5 Operating gases, for gas chromatography/mass spectrometry, of high purity and in accordance with manufacturer's specifications.

5.6 Nitrogen, of high purity, at least 99,999 % by volume, for drying and for concentration by evaporation.