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

Qualité de l'eau — Dosage d'une sélection d'éthers diphényliques polybromés dans des sédiments et des boues d'épuration — Méthode par extraction et chromatographie en phase gazeuse/spectrométrie de masse

Reference number
ISO 22032:2006(E)

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 22032 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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.

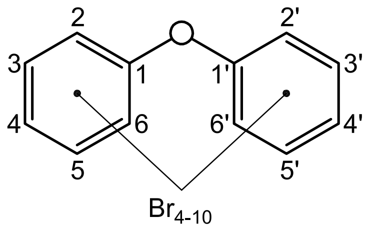

Figure 1 — Chemical formula of polybrominated diphenyl ethers

Table 1 — PBDE congeners determined by this method

No.	Congener	Formula	Abbreviation [a]	Molar mass g/mol
1	2,2',4,4'-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	BDE-47	485,795 0
2	2,2',4,4',5-Pentabromodiphenyl ether	$C_{12}H_5Br_5O$	BDE-99	564,691 1
3	2,2',4,4',6-Pentabromodiphenyl ether	$C_{12}H_5Br_5O$	BDE-100	564,691 1
4	2,2',4,4',5,6'-Hexabromodiphenyl ether	$C_{12}H_4Br_6O$	BDE-154	643,587 2
5	2,2',4,4',5,5'-Hexabromodiphenyl ether	$C_{12}H_4Br_6O$	BDE-153	643,587 2
6	2,2',3,4,4',5',6-Heptabromodiphenyl ether	$C_{12}H_3Br_7O$	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, C_3H_6O), or a mixture of acetone (propanone, C_3H_6O) 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[$^{13}C_{12}$]diphenyl ether	$^{13}C_{12}H_6Br_4O$	^{13}C-BDE-47	497,703 5
2	2,2',4,4',5-Pentabromo[$^{13}C_{12}$]diphenyl ether	$^{13}C_{12}H_5Br_5O$	^{13}C-BDE-99	576,599 5
3	2,2',4,4',5,5'-Hexabromo[$^{13}C_{12}$]diphenyl ether	$^{13}C_{12}H_4Br_6O$	^{13}C-BDE-153	655,495 5
4	2,2',3,4,4',5',6-Heptabromo[$^{13}C_{12}$]diphenyl ether	$^{13}C_{12}H_3Br_7O$	^{13}C-BDE-183	734,391 6
5	Decabromo[$^{13}C_{12}$]diphenyl ether	$^{13}C_{12}Br_{10}O$	^{13}C-BDE-209	971,079 7
Internal standards for GCMS with negative ion chemical ionization [a]				
6	3,3',4,4'-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	BDE-77	485,795 0
7	2,2',3,4,4',5,6-Heptabromodiphenyl ether	$C_{12}H_3Br_7O$	BDE-181	722,483 2
8	Decabromo[$^{13}C_{12}$]diphenyl ether	$^{13}C_{12}Br_{10}O$	^{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.

5.7 Solutions of the single reference substances / internal standards.

Use commercially available solutions (may be in nonane, toluene or iso-octane) or prepare stock solutions, e.g. by dissolving 10 mg of each of the reference substances (5.2, 5.3) in toluene (5.1) in an amber, 10-ml volumetric flask and bring to volume (concentration: 1 mg/ml). Store at approximately –18 °C in the dark.

5.8 Multicomponent stock solution of reference substances.

Accurately transfer between 100 µl to 500 µl of each single standard solution (5.7) into an amber, 10-ml volumetric flask and bring to volume with the appropriate solvent, e.g. toluene, or nonane, or iso-octane (5.1). (Concentrations are between 10 µg/ml and 50 µg/ml per substance.)

5.9 Calibration solutions for multicomponent-multilevel calibration.

Prepare, e.g. seven calibration solutions with concentrations according to the detection capacity of the mass spectrometer. Combine the multicomponent stock solutions of reference substances (5.8), internal standards (5.10) and, if necessary, injection standard (5.12) to produce the solutions (e.g. shown in Table 5) by appropriate dilution with the appropriate solvent, e.g. toluene, or nonane, or iso-octane (5.1).

In order to avoid potential photodegradation, store the solutions in the dark. Check the concentrations of calibration solutions before use.

Use one of the calibration solutions to optimize the GC-MS system and to determine the retention times. As an alternative, determine and use relative retention times.

5.10 Stock solution of the internal standards.

Prepare a stock solution of the internal standards at an appropriate concentration in, e.g. toluene or iso-octane (2,2,4-trimethylpentane). Dilute this stock solution. See Table 5 for suggested concentrations of calibration solutions and sample extracts.

5.11 Clean-up material.

See Annex A.

5.12 Injection standard.

Use an injection standard, e.g. dibromooctafluorobiphenyl ($C_{12}Br_2F_8$), to determine recovery rates for the internal standard in each sample.

5.13 Baked sand.

Bake sand for at least 8 h at 400 °C.

6 Apparatus

Clean all glassware by rinsing with acetone (propanone) (5.1). Heating the glassware to 400 °C will reduce blanks. Recalibrate volumetric apparatus prior to use if heated.

6.1 Wide-necked bottle, 1 000 ml up to 5 000 ml capacity, for wet sediment or sludge.

6.2 Freeze drying apparatus.

6.3 Deep freezer.

6.4 Mortar and pestle, or **a grinding mill**.

6.5 Drying ovens, capable of maintaining temperatures in the ranges of 100 °C to 400 °C for baking and storage of clean-up materials, for baking of glassware and for dry residue determination of samples.

6.6 Sieve shaker with appropriate sieve meshes (aperture size), e.g. 2 mm.

6.7 Desiccator.

6.8 Soxhlet extraction apparatus, consisting of round bottom flasks (e.g. 250 ml), Soxhlet extractors and Soxhlet thimbles (e.g. 27 mm × 100 mm), vertical condensers (e.g. 300 mm) and heating apparatus.

6.9 Evaporation device, e.g. rotary evaporator, turbo evaporator or vacuum concentration device.

6.10 Glass columns for chromatographic clean-up.

6.11 Volumetric cylinders, 250 ml and 500 ml.

6.12 Volumetric flasks, 1 ml, 2 ml, 10 ml, and 25 ml.

6.13 Pasteur pipettes, e.g. 2 ml.

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

6.15 Sample vials.

Amber glass with fluoropolymer-lined screw-cap is most suitable.

6.16 Gas chromatograph, with either a splitless injection port or an on-column injection port coupled to a mass spectrometer (GC-MS) with electron impact or chemical ionization and appropriate reactant gas (e.g. CH_4).

6.17 Analytical column.

Fused silica column with non-polar low bleed separating phase (see Annex B for examples), e.g. inner diameter < 0,25 mm, length 15 m to at maximum 30 m (shorter columns for higher brominated congeners). A film thickness of 0,1 µm is recommended.

7 Sampling and sample pre-treatment

Take samples as specified in ISO 5667-13 in a bottle (6.1). Store and transport in the dark at approximately 4 °C. Pre-treat the samples immediately in the laboratory by homogenizing and freeze-drying. Grind the samples using apparatus (6.4) and sieve them using a sieve shaker (6.6) according to the analytical task.

8 Procedure

8.1 Extraction

Transfer a suitable mass, e.g. 5 g to 10 g, of the pre-treated, dry sample into a Soxhlet thimble. Depending on the expected concentration in the sample, add 100 µl to 1 000 µl of the internal standard solution (5.10), to the Soxhlet thimble. Place the thimble in the Soxhlet extractor. The various solvents given in 5.1 produce similar extraction efficiencies after a 16 h Soxhlet extraction. Certain sample matrices may require a more polar solvent to efficiently extract the PDBE congeners, e.g. a mixture of acetone (propanone) and hexane, or dichloromethane.

Other extraction techniques, e.g. accelerated solvent extraction, and shorter extraction times may be used after performing comparability exercise with a 16 h Soxhlet extraction.

Fill the round-bottomed flask with, e.g. 100 ml of the solvent (5.1) and connect it to the Soxhlet extractor. The addition of boiling chips is useful. Lower the flask into the heating apparatus. Adjust the temperature of the heating device until the refluxing solvent reaches the lower part of the vertical condenser. Extract the sample for 16 h.

After the extraction is complete, concentrate the extract nearly to dryness using a suitable evaporation device (6.9).

Protect samples and extracts carefully from sunlight to avoid photodegradation of the decabromo diphenyl ether ($C_{12}Br_{10}O$).

Extraction of BDE-209 requires specific attention and, sometimes, longer extraction times than other PBDE congeners. Use toluene as an extraction solvent for extraction of BDE-209. During concentration, use toluene as a keeper.

8.2 Clean-up

Depending on the different sample matrices encountered, a variety of sample extract clean-up procedures may be suitable. Examples of clean-up procedures are given in Annex A. The recovery efficiency of all internal standards (see also 9.3 and 9.5) shall be 60 % or better. In most cases, use of a clean-up column given in A.1 followed by the procedure in A.2 is successful.

8.3 Measurement

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

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.

Add the injection standard (5.12), if necessary, and analyse the sample with GC-MS.

Especially for the analysis of BDE-209, minimise the exposure of the samples to high temperatures for long periods of times during the injection and separation stages, because of the thermal degradation of BDE-209 at temperatures higher than 300 °C. Optimize the injection step, paying special attention to the peak height of BDE-209.

8.4 Blank determination

Analyse as a blank, a clean Soxhlet thimble in exactly the same way as the sample, but replacing the sample by the appropriate amount of baked sand (5.13). The concentration of PBDE in the blank should be negligible, compared with the concentrations of PBDEs to be determined.

8.5 Identification

Consider an analyte to be identified,

- if the retention time of the analyte in the mass chromatogram of the sample is the same as the retention time of the reference substance in the mass chromatogram of the calibration standard solution measured under identical experimental conditions (the deviation shall be below 1 %, and not exceeding 12 s), and
- if the ratio of the quantification and qualifier mass is within ± 10 % of the theoretical bromine isotope ratio.

See Table 3 for typical ions when negative ion chemical ionization detection used.