



**SLOVENSKI STANDARD**  
**SIST EN 16377:2014**

**01-april-2014**

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**Karakterizacija odpadkov - Določevanje bromiranih zaviralcev gorenja (BFR) v trdnih odpadkih**

Characterization of waste - Determination of brominated flame retardants (BFR) in solid waste

Charakterisierung von Abfällen - Bestimmung bromierter Flammschutzmittel (BFR) in Feststoffabfall

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Caractérisation des déchets - Détermination des retardateurs de flamme bromés (BFR) dans les déchets solides

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**ICS:**

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EUROPEAN STANDARD

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## Characterization of waste - Determination of brominated flame retardants (BFR) in solid waste

Caractérisation des déchets - Détermination des retardateurs de flamme bromés (BFR) dans les déchets solides

Charakterisierung von Abfällen - Bestimmung bromierter Flammenschutzmittel (BFR) in Feststoffabfall

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## Foreword

This document (EN 16377:2013) has been prepared by Technical Committee CEN/TC 292 "Characterization of waste", the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by March 2014, and conflicting national standards shall be withdrawn at the latest by March 2014.

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EN 16377:2013 (E)

## Introduction

**WARNING** — Persons using this European Standard should be familiar with common 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.

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## 1 Scope

This European Standard specifies a method for the determination of selected polybrominated flame retardants (BFR), chemically known as polybrominated diphenylethers (BDE), in waste materials using gas chromatography/mass spectrometry (GC-MS) in the electron impact (EI) ionisation mode (GC-EI-MS).

When applying GC-EI-MS, the method is applicable to samples containing 100 µg/kg to 5 000 µg/kg of tetra- to octabromodiphenylether congeners and 100 µg/kg to 10 000 µg/kg of decabromo diphenylether (see Table 1). It is also possible to analyse other brominated flame retardants applying the method described in this European Standard, provided the method's applicability has been proven.

**Table 1 — Brominated flame retardants determined by this method**

No.	Congener	Formula	Abbreviation <sup>a</sup>	Molar mass g/mol
1	2,2',4,4'-Tetrabromodiphenylether	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	BDE-47	485,795 0
2	2,2',4,4',5-Pentabromodiphenylether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	BDE-99	564,691 1
3	2,2',4,4',6-Pentabromodiphenylether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	BDE-100	564,691 1
4	2,2',4,4',5,6'-Hexabromodiphenylether	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	BDE-154	643,587 2
5	2,2',4,4',5,5'-Hexabromodiphenylether	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	BDE-153	643,587 2
6	2,2',3,4,4',5',6-Heptabromodiphenylether	C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	BDE-183	722,483 2
7	Decabromodiphenylether	C <sub>12</sub> Br <sub>10</sub> O	BDE-209	959,171 4

<sup>a</sup> Numbering for the BDE according to IUPAC nomenclature for PCB.

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## 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 14346, *Characterization of waste — Calculation of dry matter by determination of dry residue or water content*

EN 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

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

Brominated diphenylethers (BDE) are extracted from the dried sample using an organic solvent. In case of high levels of plastic waste matrices, cryo-grinding is required in order to provide particle sizes that allow the complete extraction of the analytes. Appropriate extraction techniques are soxhlet, sonication or pressurised fluid extraction. The obtained extracts are concentrated and cleaned up by column chromatography and Gel Permeation Chromatography (GPC).

Following the concentration and clean-up process, the brominated diphenylethers are separated by capillary gas chromatography and detected by mass spectrometry in the selected ion monitoring mode using electron impact ionisation (EI). Quantification is carried out by the internal standard method.

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## 4 Interference

Naturally produced brominated compounds, such as halogenated bipyrrols or brominated phenoxyanisols can be considered as potential sources of interference.

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

## 5 Reagents and standards

Only use reagents with negligibly low concentrations of brominated diphenylethers (BDE), 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 (4 °C in the case of BDE). Temperatures < 4 °C may lead to precipitation.

### 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 solutions. Toluene (C<sub>7</sub>H<sub>8</sub>), or acetone (C<sub>3</sub>H<sub>6</sub>O), or a mixture of acetone (C<sub>3</sub>H<sub>6</sub>O) and hexane (C<sub>6</sub>H<sub>14</sub>), or heptane (C<sub>7</sub>H<sub>16</sub>), or iso-octane (2,2,4-trimethylpentane C<sub>8</sub>H<sub>18</sub>), or nonane (C<sub>9</sub>H<sub>20</sub>), cyclohexane (C<sub>6</sub>H<sub>12</sub>) or dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) for residual analysis.

Toluene is highly recommended, especially when the volume of the solvent is reduced to a minimum.

### 5.2 Standards

#### 5.2.1 Calibration standards

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

#### 5.2.2 Internal standards

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

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

No.	Name	Formula	Abbreviation	Molar mass g/mol
1	2,2',4,4'-Tetrabromo[ <sup>13</sup> C <sub>12</sub> ]diphenylether	<sup>13</sup> C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	<sup>13</sup> C-BDE-47	497,703 5
2	2,2',4,4',5-Pentabromo[ <sup>13</sup> C <sub>12</sub> ]diphenylether	<sup>13</sup> C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	<sup>13</sup> C-BDE-99	576,599 5
3	2,2',4,4',5,5'-Hexabromo[ <sup>13</sup> C <sub>12</sub> ]diphenylether	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	<sup>13</sup> C-BDE-153	655,495 5
4	2,2',3,4,4',5',6-Heptabromo[ <sup>13</sup> C <sub>12</sub> ]diphenylether	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	<sup>13</sup> C-BDE-183	734,391 6
5	Decabromo[ <sup>13</sup> C <sub>12</sub> ]diphenylether	<sup>13</sup> C <sub>12</sub> Br <sub>10</sub> O	<sup>13</sup> C-BDE-209	971,079 7

#### 5.2.3 Injection standard

To determine recovery rates for the internal standard in each sample e.g. dibromooctafluorobiphenyl (C<sub>12</sub>Br<sub>2</sub>F<sub>8</sub>) is used as an injection standard.



#### 5.2.4 Solutions of the single standards / internal standards

Use commercially available solutions or prepare stock solutions by dissolving 10 mg of each of the reference substances in toluene (5.2.1 and 5.2.2) in an amber 10 ml volumetric flask and bring to volume, resulting in a final concentration of 1 mg/ml. Store all solutions at approximately 4 °C in the dark to avoid potential photodegradation.

#### 5.2.5 Multicomponent stock solution of standards

Accurately transfer between 100 µl to 500 µl of each single standard solution (5.2.4) into an amber 10 ml volumetric flask and bring to volume, resulting in final concentrations between 10 µg/ml and 50 µg/ml per substance.

#### 5.2.6 Multicomponent stock solution of internal standards

Prepare a stock solution of the internal standards at an appropriate concentration in toluene (e.g. 2 µg/ml).

#### 5.2.7 Calibration solutions

Prepare, e.g. seven, calibration solutions with concentrations according to the detection capacity of the mass spectrometer. Combine the multi-component stock solutions of standards (5.2.5), internal standards (5.2.6) and, if necessary, injection standard (5.2.3) to produce the solutions e.g. shown in Table 4 by appropriate dilution with toluene.

**5.3 Sodium sulphate**, anhydrous, Na<sub>2</sub>SO<sub>4</sub>, powdered.

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

**5.5 Liquid nitrogen**, to cool waste matrices for cryo-grinding.

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

**5.7 Clean-up material**, according to Annex A.

**5.8 Baked sand and fine gravel**

Bake sand and fine gravel (0,7 mm to 12 mm) for at least 8 h at 400 °C.

## 6 Equipment

### 6.1 Customary laboratory glassware

Clean all glassware by rinsing with acetone (5.1). Heating the glassware to 400 °C will reduce blanks. Heated volumetric apparatuses will require recalibration prior to use.

### 6.2 Freeze drying apparatus

### 6.3 Deep freezer

### 6.4 Mortar and pestle, or a grinding mill

**6.5 Drying oven**, capable of maintaining temperatures in the range of 100 °C to 550 °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.

**EN 16377:2013 (E)****6.7 Desiccator****6.8 Extraction apparatuses****6.8.1 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, heating apparatus.

**6.8.2 Sonication apparatus**

Sonication should be applied for at least 3 h in a temperature controlled sonicator.

**6.8.3 Pressurised fluid extraction apparatus**

Consisting of extraction cells which can be heated to 150 °C at static pressures up to 10 MPa. The device should be programmable regarding the temperature, duration and number of extraction cycles. The cells need to be flushed with extraction solvent.

**6.9 Evaporation device**, such as rotary evaporator, turboevaporator 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, programmable temperature vaporiser (PTV) or an on-column injection port coupled to a mass spectrometer with electron impact ionisation (GC-EI-MS).**6.17 Analytical column**

Fused silica column with non-polar low bleed separating phase, 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. See Annex B for examples.

**7 Sample pretreatment**

Prepare the laboratory sample as specified in EN 15002. Store and transport in the dark at approximately 4 °C. Pretreat the samples in the laboratory by homogenising and freeze-drying. Grind the samples (6.4) and sieve (6.6) according to the requirements of the analytical task.

Waste matrixes may have to be ground carefully before being extracted. In order to avoid analyte losses and decomposition of matrix components, cryo-grinding with liquid nitrogen is recommended. Hereby, the sample is cooled in liquid nitrogen before grinding. Use a mill that allows cooling with liquid nitrogen during grinding (especially in case of plastic matrixes).

## 8 Procedure

### 8.1 Blank determination

Regardless of the selected extraction procedure, perform a blank determination using the same amount of reagents that are used for the pretreatment, extraction, clean-up and analysis of a sample. Analyse the blank immediately prior to the analysis of the samples to prove that samples are free of contaminants.

The concentrations of the blank should be negligible, compared with the concentrations of BDEs to be determined.

### 8.2 Extraction

#### 8.2.1 General

<sup>13</sup>C-labelled compounds as internal standards are expensive and would need to be added in extremely high amounts in order to match the concentrations of the analytes to be expected in plastic containing waste matrices (much higher than in case of sludge and sediments, for example). Furthermore, the analytes are bound within the matrix particles and have to diffuse into the extraction solvents while <sup>13</sup>C-labelled standard compounds added prior to extraction are dissolved directly. Thus, the idea of compensating for incomplete extraction by addition of <sup>13</sup>C-labelled standard compounds is obsolete. These two reasons suggest <sup>13</sup>C-labelled standard compounds should be added after extraction and before clean-up (8.3). If <sup>13</sup>C-labelled compounds are added to the sample before extraction an internal standard solution containing for example 2 µg/ml of each labelled compound is recommended (ISTD I). If <sup>13</sup>C-labelled compounds are added after extraction and before clean-up to an aliquot of the whole extract, an internal standard solution containing for example 0,2 µg/ml of each labelled compound is recommended (ISTD II).

Protect samples and extracts carefully from sunlight to avoid photodegradation of the higher brominated analytes.

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

#### 8.2.2 Soxhlet extraction

Transfer a suitable mass, e.g. 1 g to 3 g, of the pretreated, dry sample into a Soxhlet thimble. Depending on the expected concentration in the sample, optionally add between 200 µl and 800 µl of the internal standard solution (ISTD I, 5.2.4), to the Soxhlet thimble. Place the thimble in the Soxhlet extractor.

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 recommended. 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, reduce the extract volume to below 50 ml using a suitable evaporation device (6.9) and make up to 100 ml in a volumetric flask.

Other extraction techniques, e.g. accelerated solvent extraction, and shorter extraction times may be used after performing a comparability exercise with a 16 h Soxhlet extraction. In case of waste matrices, especially those containing portions of plastic with technically incorporated BDEs and/or decabromodiphenylethane (DBDPE), sonication and pressurised fluid extraction are likely to be successful and lead to shorter extraction times. Solvents other than toluene, especially solvents of higher polarity, are likely to extract more matrix components which might complicate subsequent clean-up. The use of highly polar solvents should be carefully tested for comparability especially regarding the effectiveness of the clean-up procedure.

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### 8.2.3 Sonication

Alternatively transfer a suitable mass, e.g. 1 g to 3 g of the pretreated, dry sample into a sealable glass container (50 ml), optionally add between 200 µl and 800 µl of the internal standard solution (5.2.4) and then 20 ml of toluene and sonicate the closed vial for 3 h. Collect the solvent and repeat this procedure with another portion of toluene (20 ml). Pool the toluene extracts and fill up to 50 ml in a volumetric flask.

### 8.2.4 Pressurised fluid extraction

Alternatively transfer a suitable mass, e.g. 1 g to 3 g, of the pretreated, dry sample into an extraction cell. Optionally add between 200 µl and 800 µl of the internal standard solution (5.2.3). Fill the void volume with baked sand or fine gravel (see 5.8). To avoid clogging of the frit it may be useful to mix the sample with sand or fine gravel before filling into the cell. The following conditions for one extraction cycle were seen to be successful: heating period of the cell 5 min at 100 °C and 140 bar; static extraction period 5 min (solvent: toluene; flush: 60 %; purge: 60 s). It is recommended that two additional cycles be performed. The total extract volume of about 40 ml is to be made up to a volume of 50 ml in a volumetric flask.

### 8.3 Clean-up

For clean-up, a suitable aliquot of the extract (8.2), e.g. 1/10, is taken and if the internal standard was not added before extraction (ISTD I, see 8.2) add now the isotope standards (e.g. 250 µl of ISTD II, see 8.2). The extract is evaporated under reduced pressure to a volume of 0,5 ml. Evaporation is not done to complete dryness because polymers from the matrix once precipitated as dry film might not re-dissolve and lead to analyte loss.

Depending on the different sample matrices encountered, a variety of extract clean-up procedures may be suitable. Examples of clean-up procedures are given in Annex A. The suitability of the chosen clean-up procedure can be checked for each sample on the basis of the recovery of the internal standards.

NOTE In most cases, using a clean-up given in A.1 followed by the procedure in A.3 and A.2 is successful.

### 8.4 Measurement

Optimise 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 (5.2.3), 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 time during the injection and separation stages, because of the thermal degradation of BDE-209 at temperatures higher than 300 °C. Optimise the injection step, paying special attention to the peak height of BDE-209.

In case of GC-MS with electron impact ionisation BDE-209 can exhibit an exponential increase of detector response factor with increasing concentrations of the calibration standards. Therefore, it is necessary to use <sup>13</sup>C-labelled BDE-209 as an internal standard to obtain a linear range of the ratio native/labelled compound over a reasonable concentration range.