

SLOVENSKI STANDARD

SIST EN 16190:2019

01-marec-2019

Nadomešča:

SIST-TS CEN/TS 16190:2012

Tla, obdelani biološki odpadki in blato - Določevanje dioksinov in furanov ter dioksinom podobnih polikloriranih bifenilov s plinsko kromatografijo z masno selektivnim detektorjem visoke ločljivosti (HR GC/MS)

Soil, treated biowaste and sludge - Determination of dioxins and furans and dioxin-like polychlorinated biphenyls by gas chromatography with high resolution mass selective detection (HR GC-MS)

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Boden, behandelter Bioabfall und Schlamm - Bestimmung von Dioxinen und Furanen sowie Dioxin-vergleichbaren polychlorierten Biphenylen mittels Gaschromatographie und hochauflösender massenspektrometrischer Detektion (HR GC-MS)

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Sols, bio-déchets traités et boues - Dosage des dioxines et furanes et polychlorobiphényles de type dioxine par chromatographie en phase gazeuse avec spectrométrie de masse à haute résolution (HR CG-SM)

Ta slovenski standard je istoveten z: EN 16190:2018

ICS:

13.030.20	Tekoči odpadki. Blato	Liquid wastes. Sludge
13.080.10	Kemijske značilnosti tal	Chemical characteristics of soils
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

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EUROPEAN STANDARD

EN 16190

NORME EUROPÉENNE

EUROPÄISCHE NORM

December 2018

ICS 13.030.01; 13.080.10

Supersedes CEN/TS 16190:2012

English Version

Soil, treated biowaste and sludge - Determination of dioxins and furans and dioxin-like polychlorinated biphenyls by gas chromatography with high resolution mass selective detection (HR GC-MS)

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This European Standard was approved by CEN on 23 October 2018.

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.

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This document was corrected and reissued by the CEN-CENELEC Management Centre on 22 January 2019.



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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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EN 16190:2018 (E)**European foreword**

This document (EN 16190:2018) has been prepared by Technical Committee CEN/TC 444 “Test methods for environmental characterization of solid matrices”, the secretariat of which is held by NEN.

This document shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2019, and conflicting national standards shall be withdrawn at the latest by June 2019.

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

This document supersedes CEN/TS 16190:2012.

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Introduction

Two groups of related chlorinated aromatic ethers are known as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); they consist of a total of 210 individual substances (congeners): 75 PCDD and 135 PCDF.

A group of chlorinated aromatic compounds similar to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is known as polychlorinated biphenyls (PCBs) which consist of 209 individual substances.

PCDD and PCDF can form in the combustion of organic materials; they also occur as undesirable by-products in the manufacture or further processing of chlorinated organic chemicals. PCDD/PCDF enter the environment via these emission paths and through the use of contaminated materials. In fact, they are universally present at very small concentrations. The 2,3,7,8-substituted congeners are toxicologically significant. Toxicologically much less significant than the tetrachlorinated to octachlorinated dibenzo-p-dioxins/dibenzofurans are the 74 monochlorinated to trichlorinated dibenzo-p-dioxins/dibenzofurans.

PCB have been produced over a period of approximately 50 years until the end of the 1990s for the purpose of different use in open and closed systems, e.g. as electrical insulators or dielectric fluids in capacitors and transformers, as specialized hydraulic fluids, as a plasticizer in sealing material. Worldwide more than one million tons of PCB were produced.

PCDD/PCDF as well as PCB are emitted during thermal processes as e.g. waste incineration. In 1997 a group of experts of the World Health Organization (WHO) fixed toxicity equivalent factors (TEF) for PCDD and twelve PCB, known as dioxin-like PCB (see Annex A). These twelve dioxin-like PCB consist of four non-ortho PCB and eight mono-ortho PCB (no or only one chlorine atoms in 2-, 2'-, 6- and 6'-position), having a planar or mostly planar structure. Dioxin-like PCB can contribute considerably to the total WHO-TEQ.

Only skilled operators who are trained in handling highly toxic compounds should apply the method described in this document.

This document is applicable for several types of matrices and validated for municipal sludge (see also Annex A for the results of the validation).

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 document be carried out by suitably trained staff.

1 Scope

This document specifies a method for quantitative determination of 17 2,3,7,8-chlorine substituted dibenzo-p-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls in sludge, treated biowaste and soil using liquid column chromatographic clean-up methods and GC/HRMS.

The analytes to be determined with this document are listed in Table 1.

Table 1 — Analytes and their abbreviations

Substance	Abbreviation
Tetrachlorodibenzo-p-dioxin	TCDD
Pentachlorodibenzo-p-dioxin	PeCDD
Hexachlorodibenzo-p-dioxin	HxCDD
Heptachlorodibenzo-p-dioxin	HpCDD
Octachlorodibenzo-p-dioxin	OCDD
Tetrachlorodibenzofuran	TCDF
Pentachlorodibenzofuran	PeCDF
Hexachlorodibenzofuran	HxCDF
Heptachlorodibenzofuran	HpCDF
Octachlorodibenzofuran	OCDF
Polychlorinated biphenyl	PCB
Trichlorobiphenyl	TCB
Tetrachlorobiphenyl	TeCB
Pentachlorobiphenyl	PeCB
Hexachlorobiphenyl	HxCB
Heptachlorobiphenyl	HpCB
Decachlorobiphenyl	DecaCB

The limit of detection depends on the kind of sample, the congener, the equipment used and the quality of chemicals used for extraction and clean-up. Under the conditions specified in this document, limits of detection better than 1 ng/kg (expressed as dry matter) can be achieved.

This method is “performance based”. It is allowed to modify the method if all performance criteria given in this method are met.

NOTE In principle this method can also be applied for sediments, mineral wastes and for vegetation. It is the responsibility of the user of this document to validate the application for these matrices. For measurement in complex matrices like fly ashes adsorbed on vegetation it can be necessary to further improve the clean-up. This can also apply to sediments and mineral wastes.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

EN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

3.1

internal standard

¹³C₁₂-labelled 2,3,7,8-PCDD/PCDF analogue added to samples prior to extraction against which the concentrations of native PCDD and PCDF are calculated

[SOURCE: ISO 18073:2004, 3.1.5]

3.2

recovery standard

¹³C₁₂-labelled 2,3,7,8-chloro-substituted PCDD/PCDF, added before injection into the GC

[SOURCE: ISO 18073:2004, 3.1.12]

4 Abbreviations

I-TEF NATO/CCMS	International toxic equivalent factor proposed by NATO-CCMS in 1988 (for detailed description, see Annex A)
I-TEQ	International toxic equivalent obtained by multiplying the mass determined with the corresponding I-TEF including PCDD and PCDF (for detailed description, see Annex A). Should only be used for comparison with older data
PCDD/PCDF or PCDD/F	Polychlorinated dibenzo-p-dioxins/dibenzofurans
WHO-TEF	Toxic equivalent factor proposed by WHO in 2005 (for detailed description, see Annex A)
WHO-TEQ	Toxic equivalent obtained by multiplying the mass determined with the corresponding WHO-TEF including PCDD, PCDF and PCB (for detailed description, see Annex D). WHO-TEQ _{PCB} , WHO-TEQ _{PCDD/PCDF} should be used to distinguish different compound classes

EN 16190:2018 (E)**5 Principle**

This document is based on the use of gas chromatography/mass spectrometry combined with the isotope dilution technique to enable the separation, detection and quantification of PCDD/PCDF and dioxin-like PCB in sludge, biowaste and soil. For the isotope dilution method 17 labelled PCDD/PCDF and 12 labelled PCB internal standards are used. The extracts for the GC-MS measurements contain one or two recovery standards. The gas chromatographic parameters offer information which enables the identification of congeners (position of chlorine substitutes) whereas the mass spectrometric parameters enable the differentiation between isomers with different numbers of chlorine substitutes and between dibenzo-p-dioxins, furans and PCB.

¹³C¹²-labelled PCDD/PCDF and PCB congeners are added to the sample prior to extraction and HRGC/HRMS measurement. Losses during extraction and clean-up are detected and compensated by using these added congeners as internal standards for quantification together with recovery standards which are added just before the HRGC/HRMS analysis. For the determination of these substances it is necessary to separate PCB from PCDD/PCDF and vice versa.

The main purpose of the clean-up procedure of the raw sample extract is the removal of sample matrix components, which may overload the separation method, disturb the quantification or otherwise severely impact the performance of the identification and quantification method and the separation of PCDD/PCDF from dioxin-like PCB. Furthermore, the enrichment of the analytes in the final sample extract is achieved. Extraction procedures are usually based on Soxhlet or equivalent extraction methods of dried, preferably freeze-dried, samples. Sample clean-up is usually carried out by multi-column liquid chromatographic techniques using different adsorbents. The determination of PCDD/PCDF and PCB is based on quantification by the isotope-dilution technique using HRGC/HRMS.

6 Reagents

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6.1 Chemicals:

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Solvents used for extraction and clean-up shall be of pesticide grade or equivalent quality and checked for blanks. Adsorbents like aluminium oxide, silica gel, diatomaceous earth and others used for clean-up shall be of analytical grade quality or better and pre-cleaned and activated if necessary.

NOTE See Annex B for a specific list of solvents and chemicals.

6.2 Standards:

- ¹³C-spiking solution for PCDD/PCDF (internal Standard);
- ¹³C-spiking solution for PCB (internal Standard);
- calibration solutions PCDD/PCDF;
- calibration solutions PCB;
- recovery standard PCDD/PCDF;
- recovery standard PCB.

NOTE See Annex B for examples of concentration of the standard solutions.

7 Apparatus and materials

The apparatus and materials listed below are meant as minimum requirements for “conventional” sample treatment with Soxhlet extraction and column chromatographic clean-up. Additional apparatus and materials may be necessary due to different methods of sample extraction and clean-up methods.

7.1 Equipment for sample preparation:

7.1.1 Laboratory fume hood, of sufficient size to contain the sample preparation equipment listed below.

7.1.2 Desiccator.

7.1.3 Balances, consisting of an analytical type capable of weighing 0,1 mg and a top-loading type capable of weighing 10 mg.

7.2 Soxhlet extractor:

7.2.1 Soxhlet, 50 mm internal diameter, 150 ml or 250 ml capacity with 500 ml round bottom flask.

7.2.2 Thimble, 43 mm × 123 mm, to fit Soxhlet.

7.2.3 Hemispherical heating mantle, to fit 500 ml round-bottom flask.

7.3 Clean-up apparatus:

7.3.1 Disposable pipettes, either disposable Pasteur pipettes, or disposable serological pipettes.

7.3.2 Glass chromatographic columns of the following sizes:

- 150 mm length × 8 mm internal diameter, with coarse-glass frit or glass-wool plug, 250 ml reservoir and glass or polytetrafluoroethylene (PTFE) stopcock;
- 200 mm length × 15 mm internal diameter, with coarse-glass frit or glass-wool plug, 250 ml reservoir and glass or PTFE stopcock;
- 300 mm length × 25 mm internal diameter, with coarse-glass frit or glass-wool plug, 300 ml reservoir and glass or PTFE stopcock.

7.3.3 Oven, capable of maintaining a constant temperature (± 5 °C) in the range of 105 °C to 450 °C for baking and storage of adsorbents.

7.4 Concentration apparatus:

7.4.1 Rotary evaporator, equipped with a variable temperature water bath and:

- vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge;
- recirculating water pump and chiller, providing cooling water of (9 ± 4) °C (use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary);
- round-bottom flask, 100 ml and 500 ml or larger, with ground-glass fitting compatible with the rotary evaporator.

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7.4.2 Nitrogen blowdown apparatus, equipped with either a water bath controlled in the range of 30 °C to 60 °C or a heated stream of nitrogen or of another suitable inert gas, installed in a fume hood.

7.4.3 Kuderna-Danish¹⁾ concentrator.

7.4.4 Sample vials, of the following types:

- amber glass, nominated volume 2 ml to 5 ml, with PTFE-lined screw cap;
- glass, 0,3 ml, conical, with PTFE-lined screw or crimp cap.

7.5 Other equipment:

7.5.1 Gas chromatograph, equipped with a splitless or on-column or temperature programmed injection port for the use with capillary columns, and an oven temperature programme which enables isothermal hold.

7.5.2 GC column for PCDD/PCDF and for isomer specificity for 2,3,7,8-TCDD (e.g. 60 m length × 0,32 mm internal diameter; 0,25 µm; 5 % phenyl, 94 % methyl, 1 % vinyl silicone bonded-phase fused-silica capillary column).

7.5.3 Mass spectrometer, 28 eV to 80 eV electron impact ionization, capable of repetitively selectively monitoring of twelve exact masses minimum at high resolution (>10 000) during a period of approximately 1 s.

7.5.4 Data system, capable of collecting, recording, and storing mass spectrometric data.

8 Sample storage and sample pretreatment

8.1 Sample storage

Samples should be stored in suitable containers with an appropriate closure material such as polytetrafluoroethylene (PTFE). Samples to be frozen may be stored in aluminium containers pre-cleaned by heating to 450 °C for minimum 4 h or by rinsing with a non-chlorinated solvent.

Samples should be kept cold (<8 °C) and in the dark. The sample pretreatment should take place within three days of sampling. If not achievable, samples may be frozen (-18 °C) directly after sampling and kept frozen before sample pretreatment.

8.2 Sample pretreatment

Drying and homogenization should be carried out according to EN 16179, if not otherwise specified. Store the ground material in a desiccator or a tightly closed glass container.

Determination of water content shall be carried out according to EN 15934.

1) Kuderna Danish is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product.

9 Extraction and clean-up

9.1 General

In this document the minimum requirements for extraction and clean-up to be met are described as well as examples of operation. The analyst may use any of the procedures given below and in Annex C or any suitable alternative procedures.

The determination of PCDD/PCDF is based on quantification by the isotope-dilution technique using HRGC/HRMS. $^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDD/PCDF congeners are added at different stages of the whole method. Losses during extraction and clean-up can be detected and compensated by using these added congeners as internal standards for quantification together with recovery standards which are added just before the HRGC/HRMS analysis. However, due to possible differences in the binding and adsorption characteristics between the native PCDD/PCDF and the $^{13}\text{C}_{12}$ -labelled congeners, which are added during analysis, complete substantiation of the extraction efficiency and compensation of losses during clean-up is not ensured. Therefore, in addition the applied methods shall be validated thoroughly. Examples of well-proven extraction and clean-up methods are given in Annex C.

The main purpose of the clean-up procedure of the raw sample extract is the removal of sample matrix components, which may overload the separation method, disturb the quantification or otherwise severely impact the performance of the identification and quantification method and to separate dioxin-like PCB from PCDD/PCDF. Furthermore, an enrichment of the analytes in the final sample extract is achieved. Extraction procedures are normally based on soxhlet extraction of the < 2 mm fraction of the dry and ground or sieved solid sample. Sample clean-up is usually carried out by multi-column liquid chromatographic techniques using different adsorbents.

In principle any clean-up method can be used which recovers the analytes in sufficient quantities. Furthermore, the final sample extract shall not affect adversely the performance of the analytical system or the quantification step. However, all applied methods shall be tested thoroughly and shall pass a set of method validation requirements before they can be employed (see Annex D). In addition, the verification of the method performance for each single sample shall be part of the applied quality assurance protocol.

9.2 Extraction

The sample amount used for extraction can vary from 5 g to 50 g depending on the expected level of contamination.

The internal standard consisting of $^{13}\text{C}_{12}$ -labelled congeners listed in Table 2 shall be added directly onto the sample before extraction.

The extraction procedure is carried out using soxhlet extraction with toluene. Duration of extraction should be adjusted according to kind and amount of sample used. The minimum requirement is 50 extraction cycles or approximately 12 h.

Other solvents or other methods like pressurized liquid extraction can also be used but shall be of proven equal performance.