

## Pôda, upravené bioodpady a kaly Stanovenie dioxínov a furánov a dioxínom podobných polychlórovaných bifenylov plynovou chromatografiou s detekciou vysokorozlišovacou hmotnostnou spektrometriou (HR GC-MS)

STN EN 16190

83 8465

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)

Táto norma obsahuje anglickú verziu európskej normy. This standard includes the English version of the European Standard.

Táto norma bola oznámená vo Vestníku ÚNMS SR č. 05/19

Obsahuje: EN 16190:2018

Oznámením tejto normy sa ruší STN P CEN/TS 16190 (83 8465) z januára 2013

# EUROPEAN STANDARD NORME EUROPÉENNE EUROPÄISCHE NORM

EN 16190

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)

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

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.

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, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

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

Contents		Page			
Europe	uropean foreword4				
Introd	uction	5			
1	Scope	6			
2	Normative references				
3	Terms and definitions				
4	Abbreviations				
5	Principle				
6	Reagents				
	_				
7	Apparatus and materials				
8 8.1	Sample storage and sample pretreatment				
8.1 8.2	Sample storage Sample pretreatment				
_	• •				
9	Extraction and clean-up				
9.1 9.2	General				
9.2 9.3	Extraction				
9.3 9.3.1	Clean-upGeneral				
9.3.1 9.3.2	Gel permeation chromatography				
9.3.2 9.3.3	Multilayer column				
9.3.3 9.3.4	Sulphuric acid treatment				
9.3. <del>4</del> 9.3.5	Activated carbon column				
9.3.5 9.3.6	Aluminium oxide column				
9.3.7	Removal of sulphur				
9.3. <i>7</i> 9.4	Final concentration of cleaned sample extract				
9.4 9.5	1				
	Addition of recovery standard				
10	HRGC/HRMS analysis				
10.1	General				
10.2	Gas chromatographic analysis				
10.3	Mass spectrometric detection				
10.4	Minimum requirements for identification of PCDF/PCDD and PCB				
10.5	Minimum requirements for quantification of PCDF/PCDD and PCB				
10.6	Calibration of the HRGC/HRMS system				
	General				
	Calibration for 2,3,7,8-congeners				
	Calibration for sum of homologue groups  Quantification of HRGC/HRMS results				
10.7	· · · · · · · · · · · · · · · · · · ·				
	Quantification of concentrations of 2,3,7,8-congeners				
	Quantification of recovery rates of <sup>13</sup> C-labelled standards				
	Calculation of the toxic equivalent				
	Calculation of the limit of detection and the limit of quantification				
11	Fynression of results	22			

12	Precision	22
13	Test report	<b>2</b> 3
Anne	x A (informative) Toxic equivalency factor (TEF)	24
Anne	x B (informative) Examples of extraction and clean-up methods	26
<b>B.1</b>	Example A	
B.1.1	General	26
<b>B.1.2</b>	Chemicals	26
B.1.3	Procedure	
<b>B.2</b>	Example B: Approved clean-up methods	
Anne	x C (informative) Examples of operation of GC/HRMS determination — Example	34
<b>C.1</b>	Gèneral	
<b>C.2</b>	Gas chromatographic analysis	34
<b>C.3</b>	Mass spectrometric detection	35
Anne	x D (informative) Repeatability and reproducibility data	38
D.1	Materials used in the interlaboratory comparison study	
<b>D.2</b>	Interlaboratory comparison results	
D.3	Calculation of toxicity factors on the basis of interlaboratory datadata	
Biblic	ography	45

### **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.

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, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom

#### 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	ТеСВ	
Pentachlorobiphenyl	РеСВ	
Hexachlorobiphenyl	НхСВ	
Heptachlorobiphenyl	НрСВ	
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

koniec náhľadu – text ďalej pokračuje v platenej verzii STN