SLOVENSKI STANDARD
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Tekstil in tekstilni izdelki - Organski fluor - 2. del: Določevanje hlapnih spojin z ekstrakcijsko metodo s plinsko kromatografijo

Textiles and textile products - Organic fluorine - Part 2: Determination of volatile compounds by extraction method using gas chromatography

Textilien und textile Erzeugnisse - Organisches Fluor - Teil 2: Bestimmung des Gehaltes an flüchtigen Verbindungen durch Extraktionsverfahren mittels Gaschromatographie

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Textiles and textile products - Organic fluorine - Part 2: Determination of volatile compounds by extraction method using gas chromatography

Textilien und textile Erzeugnisse - Organisches Fluor - Teil 2: Bestimmung des Gehaltes an flüchtigen Verbindungen durch Extraktionsverfahren mittels Gaschromatographie

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 248.

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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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European foreword

This document (prEN 17681-2:2021) has been prepared by Technical Committee CEN/TC 248 “Textiles and textile products”, the secretariat of which is held by BSI.

This document is currently submitted to the CEN Enquiry.

Introduction

In the European Union, according to Regulation (EU) 2019/1021 persistent organic pollutants (POP), Article 3, Clause 1, in connection with Annex I amended by COMMISSION DELEGATED REGULATION (EU) 2020/784, the manufacturing, placing on the market and use of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds, whether on their own, in mixtures or in articles, shall be prohibited. This is in addition to the existing prohibition of perfluorooctane sulfonic acid and its derivatives (PFOS).

According to Article 4 Clause 1. (b) this shall not apply in the case of a substance present as an unintentional trace contaminant, as specified in the relevant entries of Annex I in substances, mixtures or articles.

Annex I Part A, describing perfluorooctane sulfonic acid and its derivatives (PFOS), contains the specific exemption (Point 2) to concentrations of PFOS in semi-finished products or articles, or parts thereof, if the concentration of PFOS is lower than 0,1 % by weight calculated with reference to the mass of structurally or micro-structurally distinct parts that contain PFOS or, for textiles or other coated materials, if the amount of PFOS is lower than 1 µg/m² of the coated material. PFOS compounds have the formula $C_8F_{17}SO_2X$ where X = OH, Metal salt (O-M^+), halide, amide and other derivatives, including polymers.

Annex I also states (point 5) that once standards are adopted by the European Committee for Standardisation (CEN) they shall be used as the analytical test methods for demonstrating the conformity of articles to point 2.

In Annex I Part A, describing perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds, contains the specific exemption (Point 1) to concentrations of PFOA or any of its salts equal to or below 0,025 mg/kg (0,000 002 5 % by weight) where they are present in substances, mixtures or articles. In addition, (Point 2) Article 4(1) shall apply to concentrations of any individual PFOA-related compound or a combination of PFOA-related compounds equal to or below 1 mg/kg (0,000 1 % by weight) where they are present in substances, mixtures or articles.

PFOA, its salts and PFOA-related compounds means the following:

(i) perfluorooctanoic acid, including any of its branched isomers;

(ii) its salts;

(iii) PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety $(C_7F_{15})C$ as one of the structural elements.

The following compounds are not included as PFOA-related compounds:

(i) C_8F_{17}-X, where X= F, Cl, Br;

(ii) fluoropolymers that are covered by $CF_3[CF_2]n$-R', where R'=any group, n>16;

(iii) perfluoroalkyl carboxylic acids (including their salts, esters, halides and anhydrides) with ≥8 perfluorinated carbons;

(iv) perfluoroalkane sulfonic acids and perfluoro phosphonic acids (including their salts, esters, halides and anhydrides) with ≥9 perfluorinated carbons;

(v) perfluorooctane sulfonic acid and its derivatives (PFOS), as listed in Annex I.

As a further exemption in Annex I Part A (Point 5 c) the manufacturing, placing on the market and use of PFOA, its salts and PFOA-related compounds shall be allowed in textiles for oil and water repellency for the protection of workers from dangerous liquids that comprise risks to their health and safety, until 4 July 2023.

Several per- and poly-fluorinated alkylated substances (PFAS), which are not restricted under the POP regulation have been added as Substances of Very High Concern (SVHC) to the Candidate List according to Regulation (EC) No 1907/2006 (REACH), Article 59.

Per- and poly-fluorinated compounds from C4 – C14 (PFAS) occur, for example, in soil and water repellent finishes within textiles or can be introduced as contaminants (e.g. from water sources). Categories of PFAS are shown in Table 1. Table 2 lists classes of regulated compounds (i.e. listed in regulation) including acids, telomers, sulfonates and sulfonamidalcohols. Compounds of concern (i.e. not listed yet in regulation) are shown in the informative Annex C.

Table 1 — Categories of PFAS<Tbl_-></Tbl_->

Type of PFAS	Sub-group	Applications		Category
		Use	Sources of contamination [a]	
PFAS salts	K^+, Li^+, diethanolamine (DEA) salt Analysed as acids	Surfactant for alkaline cleaners	Surfactant in fire-fighting foam, emulsifier in floor polish mist, suppressant for metal plating baths, surfactant for etching acids for circuit boards, pesticide active ingredient for ant bait traps	A
	Amines		Mist suppressant for metal plating baths	B
	Ammonium salts Analysed as acids		Emulsifier for fluoropolymer production	C
	Amphoterics	Water/solvent repellence for leather/paper		D
PFAS substances	Carboxylates		Antistatic agent in photographic paper	E
	Amides		Pesticide active ingredient	F
	Oxazolidinones		Waterproofing casts (electronics)	G
PFAS polymers/oligomers	Alcohols, silanes, alkoxylates, fatty acid esters, adipates, urethanes, polyesters, acrylates	Soil/water repellence for carpets, fabric/upholstery, apparel, leather, metal/glass		H
	Copolymers, phosphate esters	Water repellence for carpet, fabric/upholstery, apparel, leather, metal/glass	Soil/oil/water repellence for plates, food containers, bags, wraps, folding cartons, containers, carbonless forms, masking papers	I

[a] These substances are not relevant in the manufacturing process of textiles but it is possible to find them as contaminants.

Table 2 — Regulated PFAS<Tbl_--></Tbl_-->

No	Chemicals		CAS No.	LC	GC	law (§) [a]	PFAS category (Table 1)
Perfluorinated carboxylic acids							
1	PFHxA	Perfluoro-n-hexanoic acid	307-24-4	x		under evaluation (REACh)	A and C
2 [b]	PFOA	Perfluoro-n-octanoic acid	335-67-1	x		POP	A and C
2.2 [b]	APFO Na-PFO K-PFO Ag-PFO F-PFO	Perfluoro-n-octanoic salts - Ammonium pentadecafluorooctanoate - Sodium perfluorooctanoate - Potassium perfluorooctanoate - Silver perfluorooctanoate - Perfluorooctanoyl fluoride	3825-26-1 335-95-5 2395-00-8 335-93-3 335-60-0	x		POP	C A A A A
3 [b]	8:2 FTS	1H,1H,2H,2H-Perfluorodecanesulfonic acid	39108-34-4	x		POP	A
4 [b]	Me-PFOA	Methyl perfluorooctanoate	376-27-2		x	POP	H
5 [b]	Et-PFOA	Ethyl perfluorooctanoate	3108-24-5		x	POP	H
6	PFNA	Perfluoro-n-nonanoic acid	375-95-1	x		Reach (SVHC)	
7	PFDA	Perfluoro-n-decanoic acid	335-76-2	x		Reach (SVHC)	
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	x		Reach (SVHC)	
9	PFDoA	Perfluorododecanoic acid	307-55-1	x		Reach (SVHC)	
10	PFTrA	Perfluorotridecanoic acid	72629-94-8	x		Reach (SVHC)	
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	x		Reach (SVHC)	
12	PF-3,7-DMOA	Perfluoro(3,7-dimethyloctanoic acid)	172155-07-6	x		POP	
13 [b]	4HPFUnA	2H,2H,3H,3H-Heptadecafluoroundecanoic Acid	34598-33-9	x		POP	
Perfluorinated sulfonic acids							
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	x		Reach (SVHC)	A
15	PFHxS	Perfluorohexanesulfonic acid	355-46-4	x		Reach (SVHC)	H
16 [c]	PFOS	Perfluoro octanesulfonic acid	1763-23-1	x		POP	H

16.2 [c]	PFOS-X	Perfluorooctane sulfonic acid salts $C_8F_{17}SO_2X$ - potassium Perfluorooctane sulfonate - lithium Perfluorooctane sulfonate - ammonium Perfluorooctane sulfonate - bis2(hydroxyethyl)ammonium Perfluorooctane sulfonate - tetraethyl ammonium heptadecafluorooctane sulfonate	2795-39-3 29457-72-5 29081-56-9 70225-14-8 56773-42-3	x		POP	A A A A A
Perfluoro-octanesulfonamides (FOSA)							
17	PFOSA	Perfluorooctane sulfonamide	754-91-6	x		POP	F
18	N-MeFOSA	N-Methylperfluoro-1-octanesulfonamide	31506-32-8	x		POP	F
19	N-EtFOSA	N-Ethylperfluoro-1-octanesulfonamide	4151-50-2	x		POP	F
Perfluoro-octanesulfonamido ethanol (FOSE)							
20	N-MeFOSE	2-(N-methylperlfuoro-1-octanesulfonamideo)-ethanol	24448-09-7	x	x	POP	H
21	N-EtFOSE	2-(N-Ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	x	x	POP	H
Fluorinated telomer alcohols (FTOH)							
22 [b]	8:2 FTOH	2-Perfluorooctylethanol	678-39-7	x		POP	H
Fluorinated telomer acrylate (FTA)							
23 [b]	8:2 FTA	1H,1H,2H,2H-Perfluorodecyl acrylate	27905-45-9		x	POP	H
Other							
24 [c]	PFOSF	Heptadecafluorooctanesulfonyl fluoride	307-35-7	x		POP	
25 [b]	8:2 FTMA	1H,1H,2H,2H-heptadecafluorodecylmethacrylate	1996-88-9		x	POP	
26		1-decanaminium, N-decyl-N, N dimethyl-,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonate	251099-16-8	x		POP	A
27	HPFO-DA	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	13252-13-6	x		Reach (SVHC)	A and C
27.2 [c]	HPFO-DA -X	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid salts and acyl halides X=F X=NH_4 X=K	21062-98-8 62037-80-3 67118-55-2	x x x		Reach (SVHC)	A and C

[a] Table 2 states the situation of the regulated PFAS on 2021-03-1. Readers should pay attention to update the information.

[b] The results of PFOA related substances to be summed up.

[c] For the halides a hydrolysation, with water, of the methanol extract is necessary.

1 Scope

This document specifies a test method (using gas chromatography, GC) for detection and quantification of selected extractable perfluorinated and polyfluorinated substances in textile materials (fibres, yarns, fabrics) and coated fabrics.

NOTE CEN/TR 16741 defines which materials are applicable to this determination.

A test method (using liquid chromatography, LC) for detection and quantification of selected extractable perfluorinated and polyfluorinated substances is specified in prEN 17681-1.

Classes of regulated compounds are listed in Table 2. Classes of other non-regulated compounds that can be determined by this document are defined in Annex C, Table C.1. This document is also applicable for further PFAS substances provided that the method is validated with the additional compounds.

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.

<std>prEN 17681-1:2021, *Textiles and textile products — Organic fluorine — Part 2: Determination of volatile compounds by extraction method using gas chromatography*</std>

<std>EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*</std>

<std>EN ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use (ISO 4787)*</std>

<std>EN ISO 5089, *Textiles — Preparation of laboratory test samples and test specimens for chemical testing (ISO 5089)*</std>

3 Terms and definitions

No terms and definitions are listed in this document.

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

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle of method

The selected compounds listed in Table 2 and in Table C.1 are extracted in an ultrasonic bath with methanol and the extract is analysed by gas chromatography with a mass spectrometric detector (GC-MS/MS, GC-MS/PCI or GC-MS/EI).

5 Reagents

Unless otherwise specified, all reagents shall be of a recognised analytical grade.

5.1 Methanol, LC-MS grade, CAS number 67-56-1.

5.2 Internal standards

5.2.1 Dimethylicosafluorododecane-1,10-dioate (PFDodiAOMe), Internal standard (fluorotelomer), CAS number 84750-88-9.

5.2.2 1H,1H,2H,2H-Perfluoro(9-methyldecan)-1-ol, CAS number 31200-98-2.

5.3 Selected PFAS listed in Table 2 and Table C.1

Target compounds are available commercially as certified solutions, or a solution of target compounds may be made.

6 Equipment

The usual laboratory apparatus and laboratory glassware, according to EN ISO 4787, shall be used, in addition to the following:

6.1 Test specimen containers, shall be rinsed thoroughly with water (5.3) and methanol (5.1) prior to use. Containers shall be checked for possible background contamination before use.

6.2 Cutting die or template and cutting tool, to measure and cut area materials.

6.3 Extraction vials (glass, polypropylene) e.g. 40 ml, free from interfering compounds.

NOTE Further information about interferences can be found in Annex B.

6.4 GC Vials of glass, polypropylene or polyethylene free from interfering compounds.

NOTE Further information about interferences can be found in Annex B.

6.5 Ultrasonic bath, equipped with heater (bath temperature to be set at (60 ± 5) °C).

6.6 Concentration equipment (e.g. hydrophilic lipophilic base, weak anion exchange resin or rotavapor).

6.7 Gas chromatograph, with a mass spectrometric detector with MS/MS, MS/PCI or MS/EI.

6.8 Balance, with a resolution of 1 mg or better.

6.9 Analytical balance, with a resolution of at least 0,1 mg.

6.10 Filter, cellulosic filter, 0,45 µm pore size.

7 Sampling

7.1 General

The chosen sample shall be representative of the lot it is taken from. If possible, sampling is carried out according to EN ISO 5089. When the sampling is being performed on products that have separate distinct