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Textiles and textile products - Organic fluorine - Part 1: Determination of non-volatile compounds by extraction method using liquid chromatography

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EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 17681-1

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English Version

Textiles and textile products - Organic fluorine - Part 1: Determination of non-volatile compounds by extraction method using liquid chromatography

Textiles et produits textiles - Fluor organique - Partie 1 : Détermination de composés non volatils par une méthode d'extraction utilisant la chromatographie en phase liquide

Textilien und textile Erzeugnisse - Organisches Fluor - Teil 1: Bestimmung des Gehaltes an nichtflüchtigen Verbindungen durch Extraktionsverfahren mittels Flüssigkeitschromatographie

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European foreword

This document (EN 17681-1:2022) has been prepared by Technical Committee CEN/TC 248 “Textiles and textile products”, the secretariat of which is held by BSI.

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of an identical text or by endorsement, at the latest by March 2023, and conflicting national standards shall be withdrawn at the latest by March 2023.

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Introduction

In the European Union, according to Regulation (EU) 2019/1021 on 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, is 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 does 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 % mass fraction 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/m^2 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.

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 % mass fraction), where they are present in substances, mixtures or articles. In addition, (Point 2) Article 4(1) applies 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 % mass fraction) 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:

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

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

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

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

viii) 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 is 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.

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Commission Regulation (EU) 2021/1297 amending Regulation (EC) No 1907/2006 (REACH), Annex XVII [7] restricts perfluorocarboxylic acids containing 9 to 14 carbon atoms in the chain (C9-C14 PFCAs), their salts and C9-C14 PFCA-related substances from 25 February 2023.

This restriction concerns the following substances:

Linear and branched perfluorocarboxylic acids of the formula C_nF_{2n+1}-C(= O)OH where *n* = 8, 9, 10, 11, 12, or 13 (C9-C14 PFCAs), including their salts, and any combinations thereof;

Any C9-C14 PFCA-related substance having a perfluoro group with the formula C_nF_{2n+1}- directly attached to another carbon atom, where *n* = 8, 9, 10, 11, 12, or 13, including their salts and any combinations thereof;

Any C9-C14 PFCA-related substance having a perfluoro group with the formula C_nF_{2n+1}- that it is not directly attached to another carbon atom, where *n* = 9, 10, 11, 12, 13 or 14 as one of the structural elements, including their salts and any combinations thereof.

The following substances are excluded from this designation:

C_nF_{2n+1}-X, where X = F, Cl, or Br

where *n* = 9, 10, 11, 12, 13 or 14, including any combinations thereof,

C_nF_{2n+1}-C(= O)OX' where *n* > 13 and X' = any group, including salts.

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 (for example from water sources). Categories of PFAS are shown in Table 1. Table 2 lists classes of regulated compounds (i.e. listed in a Regulation) including acids, telomers, sulfonates and sulfonamidalcohols. Compounds of concern (i.e. not listed yet in a Regulation) are shown in the informative Annex C.

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Table 1 — Categories of PFAS

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 and water repellence for carpets, fabrics, upholstery, apparel, leather, metal, glass	-	H
	Copolymers, phosphate esters	Water repellence for carpets, fabrics, 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.

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Table 2 — Regulated PFAS

No.	Substance		CAS Registry Number® (CAS RN®)[1]	Applicable test method		EU regulation [a]	PFAS category (Table 1)
				EN 17681-1	EN 17681-2		
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 and REACH (SVHC)	A and C
2.2 [b]	APFO Na-PFO K-PFO Ag-PFO F-PFO	Perfluoro-n-octanoic acid salts - Ammonium pentadecafluorooctanoate - Sodium perfluorooctanoate - Potassium perfluorooctanoate - Silver perfluorooctanoate - Perfluorooctanoyl fluoride	3825–26–1 335–95–5 2395–00–8 335–93–3 335–66–0	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 Annex XVII and SVHC	
6.2	NH_4-PFN Na-PFN	Perfluoro-n-nonanoic acid salts - Ammonium perfluorononanoate - Sodium perfluorononanoate	4149–60–4 21049–39–8	x		REACH Annex XVII and SVHC	

[1] CAS Registry Number® (CAS RN®) is a trademark of CAS corporation. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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No.	Substance		CAS Registry Number® (CAS RN®)[1]	Applicable test method		EU regulation [a]	PFAS category (Table 1)
				EN 17681-1	EN 17681-2		
7	PFDA	Perfluoro-n-decanoic acid	335–76–2	x		REACH Annex XVII and SVHC	
7.2	NH_4-PFD Na-PFD	Perfluoro-n-decanoic acid salts - Ammonium perfluorodecanoate - Sodium perfluorodecanoate	 3830–45–3 3108–42–7	x		REACH Annex XVII and SVHC	
8	PFUnA	Perfluoroundecanoic acid	2058–94–8	x		REACH Annex XVII and SVHC	
9	PFDoA	Perfluorododecanoic acid	307–55–1	x		REACH Annex XVII and SVHC	
10	PFTrDA	Perfluorotridecanoic acid	72629–94–8	x		REACH Annex XVII and SVHC	
11	PFTeDA	Perfluorotetradecanoic acid	376–06–7	x		REACH Annex XVII and SVHC	
12	PF-3,7-DMOA	Perfluoro(3,7-dimethyloctanoic acid)	172155–07–6	x		REACH Annex XVII	
13 [b]	4HPFUnA	2H,2H,3H,3H-Heptadecafluoroundecanoic acid	34598–33–9	x		POP	

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No.	Substance		CAS Registry Number® (CAS RN®)[1]	Applicable test method		EU regulation [a]	PFAS category (Table 1)
				EN 17681-1	EN 17681-2		
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	Perfluorooctanesulfonic 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 [c]	PFOSA	Perfluorooctane sulfonamide	754–91–6	x		POP	F
18 [c]	N-MeFOSA	N-Methylperfluoro-1-octanesulfonamide	31506–32–8	x		POP	F
19 [c]	N-EtFOSA	N-Ethylperfluoro-1-octanesulfonamide	4151–50–2	x		POP	F
Perfluoro-octanesulfonamido ethanol (FOSE)							
20 [c]	N-MeFOSE	2-(N-methylperfluoro-1-octanesulfonamideo)-ethanol	24448–09–7	x	x	POP	H
21 [c]	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
23	10:2 FTOH	2-Perfluorodecylethanol	865–86–1	x		REACH Annex XVII [a]	H

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No.	Substance		CAS Registry Number® (CAS RN®)[1]	Applicable test method		EU regulation [a]	PFAS category (Table 1)
				EN 17681-1	EN 17681-2		
Fluorinated telomer acrylates							
24 [b]	8:2 FTA	1H,1H,2H,2H-Perfluorodecyl acrylate	27905–45–9		x	POP	H
25	10:2 FTA	1H,1H,2H,2H-Perfluorododecyl acrylate	17741–60–5		x	REACH Annex XVII [a]	H
Other							
26 [c]	PFOSF	Heptadecafluorooctanesulfonyl fluoride	307–35–7	x		POP	
27 [b]	8:2 FTMA	1H,1H,2H,2H-heptadecafluorodecylmethacrylate	1996–88–9		x	POP	
28		1-decanaminium, N-decyl-N, N dimethyl-0,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonate	251099–16–8	x		POP	A
29	HPFO-DA	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	13252–13–6	x		REACH (SVHC)	A and C
29.2 [d]	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 2022–06–23 and might not be exhaustive. Readers should pay attention for updated information. Regulation (EU) 2021/1297 on C_9-C_{14} carboxylic acid substances will be enforced in 02/2023.

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

[c] The results of PFOS and related substances to be summed up – calculated as PFOS.

[d] For the halides a hydrolysation with water from the methanol extract is necessary.

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1 Scope

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

NOTE 1 CEN/TR 16741 defines which materials are applicable to this determination.

A test method (using gas chromatography, GC) for detection and quantification of selected extractable perfluorinated and polyfluorinated substances is specified in EN 17681-2.

NOTE 2 Both this document and EN 17681-2 are needed for the determination and totalization of the PFOA related substances.

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.

NOTE 3 Commission Delegated Regulation (EU) 2020/784 amending Annex I to the POP Regulation (EU) 2019/1021 as regards the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds defines among other that "'...PFOA-related compounds' means the following: ... 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." To determine whether these are intentionally present it could be necessary to introduce an alkaline hydrolysis method to remove the side-chain from the polymer. According to Commission Regulation (EU) 2021/1297 [7], this applies similarly to C9-C14 PFCAs-related compounds. A future revision of this document will address this aspect.

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 17681-2, *Textiles and textile products - Organic fluorine - Part 2: Determination of volatile compounds by extraction method using gas chromatography*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

EN ISO 4787, *Laboratory glass and plastic ware - Volumetric instruments - Methods for testing of capacity and for use (ISO 4787)*

EN ISO 5089, *Textiles - Preparation of laboratory test samples and test specimens for chemical testing (ISO 5089)*

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:

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

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

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