



SLOVENSKI STANDARD

oSIST prEN 17892:2022

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Kakovost vode - Določevanje vsote perfluoriranih snovi (vsota PFAS) v pitni vodi - Metoda s tekočinsko kromatografijo in masno spektrometrijo (LC-MS)

Water quality - Determination of the sum of perfluorinated substances (Sum of PFAS) in drinking water - Method using liquid chromatography/mass spectrometry (LC/MS)

Wasserqualität - Bestimmung der Summe der perfluorierten Substanzen (Summe der PFAS) im Trinkwasser - Methode mittels Flüssigkeitschromatographie / Massenspektrometrie (LC/MS)

Qualité de l'eau - Détermination de la somme des substances perfluorées (somme des PFAS) dans l'eau potable - Méthode utilisant la chromatographie liquide / spectrométrie de masse (LC / MS)

Ta slovenski standard je istoveten z: prEN 17892

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Water quality - Determination of the sum of perfluorinated substances (Sum of PFAS) in drinking water - Method using liquid chromatography/mass spectrometry (LC/MS)

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This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 230.

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prEN 17892:2022 (E)

European foreword

This document (prEN 17892:2022) has been prepared by the Technical Committee CEN/TC 230 “Water analysis”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

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Introduction

Per- and polyfluoralkyl substances (PFAS) (Reference [1]) are industrially manufactured chemicals, where some or all hydrogen atoms at the carbon skeleton have been replaced by fluorine atoms. PFAS is a chemical family consisting of almost 5 000 individual substances. They are a group of widely used, man-made chemicals. The perfluoralkyl substances are persistent and depending on their carbon chain length accumulate over time in humans and in the environment. Because of their special properties and stability, some of these compounds were widely used in industry, as components in firefighting foam or for consumer products.

Due to the widespread usage and the resistance to biodegradation PFAS can now be found ubiquitous as background contamination in the environment. Release during production processes or the application of firefighting foams containing PFAS led to high local concentrations in some areas (Reference [2]).

In 2001 the largest producer of PFOS voluntarily phased the substance out and since 2011 respectively 2020 apart from a few exceptions, PFOS and PFOA as well as any compounds derived from these are no longer permitted to be used or marketed in the European Union (Reference [4]). Despite these measures PFAS represent a major legacy issue to be managed.

PFAS - especially the shorter-chain - can enter the water cycle as a result of manufacture, application and disposal. In the EU Drinking Water Directive EU 2020/2184 (Reference [5]) PFAS are included as parameter to be under surveillance with a maximum parametric limit value of 0,10 µg/l for the sum of 20 selected PFAS, i.e. the perfluorinated carbonic acids as well as the perfluorinated sulfonic acids with chain length of four to thirteen carbon atoms.

Longer-chain compounds such as PFOA, PFNA, PFHxS and PFOS accumulate in the blood and the liver, and their half-lives in the human body amount to several years. In 2020 the European Food Safety Authority (EFSA) has derived on the basis of epidemiological studies and the most sensitive effect on the human immune system a tolerably weekly intake (TWI) for the sum of the four substances PFOA, PFNA, PFHxS and PFOS of 4,4 ng/kg body weight (Reference [3]).

Due to the low TWI the EFSA recommends for the four substances PFOA, PFNA, PFHxS and PFOS, the analysis of at least these four EFSA-PFAS should be possible with a limit of detection far below the maximum parametric limit value of 0,10 µg/l.

WARNING — Persons using this document should be familiar with usual 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.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

prEN 17892:2022 (E)**1 Scope**

This document specifies a method for the determination of the dissolved fraction of selected perfluoroalkyl and polyfluoroalkyl substances (PFAS) in non-filtrated drinking water containing less than 0,5 g/l solid particulate material (SPM) using liquid chromatography-tandem mass spectrometry (LC-MS/MS). The applicability of the method to further types of water like fresh waters (e.g. ground water, surface water) or e.g. treated waste water is to be validated separately for each individual case.

For each target compound both, eventually occurring branched isomers and the respective non-branched isomer, are quantified together. The selected set of substances determined by this method is representative for a wide variety of PFAS. The analytes specified in Table 1 have been validated and can be determined by this method. The list given in this table can be modified depending on the purpose and focus of the method. The lower application range of this method can vary depending on the sensitivity of the equipment used and the matrix of the samples. For many substances to which this document applies a limit of quantification (LOQ) of 1 ng/l can be achieved. Using high volume direct injection as described in part A or SPE as described in part B of the method allows lower LOQs. Analytical limitations can occur with short-chain PFAS or PFAS with more than ten carbon atoms in the carbon chain. Actual LOQs can depend on the blank values realized by individual laboratories as well.

NOTE This document enables the analysis of those 20 PFAS which are listed in point 3 of Part B of Annex III of the EU Drinking Water Directive, EU 2020/2184, for the surveillance of the parametric limit value of 0,10 µg/l for the sum of PFAS.

Furthermore, alternatives and substitutes for these PFAS substances can be analysed using this document as well.

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.

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-5, *Water quality — Sampling — Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods — Part 1: Linear calibration function*

ISO 21253-1, *Water quality — Multi-compound class methods — Part 1: Criteria for the identification of target compounds by gas and liquid chromatography and mass spectrometry*

ISO 21675, *Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)*

CEN/TS 16800, *Guideline for the validation of physico-chemical analytical methods*

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:

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

3.1

per- and polyfluoroalkyl substances

PFAS

fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom

Note 1 to entry: The term is used in the broader sense for substances that contain chlorine and oxygen in a polyfluoroalkyl structure as well (Reference [1]).

Note 2 to entry There are a few noted exceptions, so that any chemical with at least a perfluorinated methyl group (-CF₃-) or a perfluorinated methylene group (-CF₂-)

Note 3 to entry: Within legal regulations (e.g. European Drinking water Directive (Reference [5]) the definition of PFAS might be different and for example be restricted to substances with a defined chain length.

4 Principle

Part A of this document comprises a method using direct injection LC-MS/MS: An aliquot of the unfiltered water sample is diluted with methanol and amended with a solution of isotopically labelled internal standards. The diluted water sample is injected directly into the analysis system. The identification and quantitative determination of the substances listed in Table 1 is performed using liquid chromatography coupled with tandem mass-spectrometry detection (LC-MS/MS).

Part B of this document comprises a method using a solid-phase extraction protocol similar to ISO 21675 before LC-MS/MS measurement: The analytes listed in Table 1 are extracted from the water sample by solid-phase extraction using a weak anion exchange sorbent. The identification and quantitative determination of the substances in the extract is performed using liquid chromatography coupled with tandem mass-spectrometry detection (LC-MS/MS).

The method can be used to determine additional PFAS substances provided that accuracy has been tested and verified for each case as well as storage conditions of both samples and reference solutions have been validated.

Table 1 — Analytes for which a determination was validated in accordance with this method

Analyte	IUPAC name ^a	Formula	Abbreviation	CAS-RN ^b
Perfluoro- <i>n</i> -butanoic acid	2,2,3,3,4,4,4-Heptafluorobutanoic acid	C ₄ HF ₇ O ₂	PFBA	375-22-4
Perfluoro- <i>n</i> -pentanoic acid	2,2,3,3,4,4,5,5,5-Nonafluoropentanoic acid	C ₅ HF ₉ O ₂	PFPeA	2706-90-3
Perfluoro- <i>n</i> -hexanoic acid	2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexanoic acid	C ₆ HF ₁₁ O ₂	PFHxA	307-24-4
Perfluoro- <i>n</i> -heptanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptanoic acid	C ₇ HF ₁₃ O ₂	PFHpA	375-85-9
Perfluoro- <i>n</i> -octanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctanoic acid	C ₈ HF ₁₅ O ₂	PFOA	335-67-1
Perfluoro- <i>n</i> -nonanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononanoic acid	C ₉ HF ₁₇ O ₂	PFNA	375-95-1
Perfluoro- <i>n</i> -decanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluorodecanoic acid	C ₁₀ HF ₁₉ O ₂	PFDA	335-76-2
Perfluoro- <i>n</i> -undecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heneicosafleuroundecanoic acid	C ₁₁ HF ₂₁ O ₂	PFUnDA	2058-94-8
Perfluoro- <i>n</i> -dodecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Tricosafleurododecanoic acid	C ₁₂ HF ₂₃ O ₂	PFDoDA	307-55-1
Perfluoro- <i>n</i> -tridecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Pentacosafleurotrudecanoic acid	C ₁₃ HF ₂₅ O ₂	PFTTrDA	72629-94-8
Perfluoro- <i>n</i> -butanesulfonic acid	1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonic acid	C ₄ HF ₉ O ₃ S	PFBS	375-73-5
Perfluoro- <i>n</i> -pentanesulfonic acid	1,1,2,2,3,3,4,4,5,5,5-Undecafluoropentane-1-sulfonic acid	C ₅ HF ₁₁ O ₃ S	PFPeS	2706-91-4
Perfluoro- <i>n</i> -hexanesulfonic acid	1,1,2,2,3,3,4,4,5,5,6,6,6-Tridecafluorohexane-1-sulfonic acid	C ₆ HF ₁₃ O ₃ S	PFHxS	355-46-4
Perfluoro- <i>n</i> -heptanesulfonic acid	1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-Pentadecafluoroheptane-1-sulfonic acid	C ₇ HF ₁₅ O ₃ S	PFHpS	375-92-8

Analyte	IUPAC name ^a	Formula	Abbreviation	CAS-RN ^b
Perfluoro- <i>n</i> -octanesulfonic acid	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluorooctane-1-sulfonic acid	C ₈ HF ₁₇ O ₃ S	PFOS	1763-23-1
Perfluoro- <i>n</i> -nonanesulfonic acid	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Nonaadecafluorononane-1-sulfonic acid	C ₉ HF ₁₉ O ₃ S	PFNS	68259-12-1
Perfluoro- <i>n</i> -decanesulfonic acid	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heneicosafluorodecane-1-sulfonic acid	C ₁₀ HF ₂₁ O ₃ S	PFDS	335-77-3
Perfluoro- <i>n</i> -undecanesulfonic acid	1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Tricosafleuroundecane-1-sulfonic acid	C ₁₁ HF ₂₃ O ₃ S	PFUnDS	749786-16-1
Perfluoro- <i>n</i> -dodecanesulfonic acid	<u>1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Pentacosafleurododecane-1-sulfonic acid</u>	C ₁₂ HF ₂₅ O ₃ S	PFDoDS	79780-39-5
Perfluoro- <i>n</i> -tridecanesulfonic acid	1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Pentacosafleurododecane-1-sulfonic acid	C ₁₃ HF ₂₇ O ₃ S	PFTrDS	791563-89-8
4:2 Fluorotelomer sulfonic acid	3,3,4,4,5,5,6,6,6-Nonafluorohexane-1-sulfonic acid	C ₆ H ₅ F ₉ O ₃ S	4:2 FTSA	27619-93-8
6:2 Fluorotelomer sulfonic acid	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulfonic acid	C ₈ H ₅ F ₁₃ O ₃ S	6:2 FTSA	27619-97-2
8:2 Fluorotelomer sulfonic acid	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecane-1-sulfonic acid	C ₁₀ H ₅ F ₁₇ O ₃ S	8:2 FTSA	39108-34-4
Perfluorooctanesulfonamide	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro-1-octanesulfonamide	C ₈ H ₂ F ₁₇ NO ₂ S	FOSA	754-91-6
<i>N</i> -ethyl perfluorooctanesulfonamidoacetic acid	2-[Ethyl(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctylsulfonyl)amino]acetic acid	C ₁₂ H ₈ F ₁₇ NO ₄ S	<i>N</i> -EtFOSAA	2991-50-6
Hexafluoropropylene oxide dimer acid	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	C ₆ HF ₁₁ O ₃	HFPO-DA	13252-13-6

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Analyte	IUPAC name ^a	Formula	Abbreviation	CAS-RN ^b
4,8-Dioxa-3H-perfluorononanoic acid	2,2,3-Trifluoro-3-[1,1, 2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy] propanoic acid	C ₇ H ₂ F ₁₂ O ₄	DONA	919005-14-4
Perfluoro-3-methoxypropanoic acid	2,2,3,3-Tetrafluoro-3-(trifluoromethoxy)propanoic acid	C ₄ HF ₇ O ₃	PFMPA (PF4OPeA)	377-73-1
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	2-(6-Chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexoxy)-1,1,2,2-tetrafluoroethanesulfonic acid	C ₈ HClF ₁₆ O ₄ S	9Cl-PF3ONS	73606-19-6
^a IUPAC: International Union of Pure and Applied Chemistry ^b CAS-RN: Chemical Abstract Services Registry Number				

5 Interferences

5.1 Sampling

Long chain PFAS (e.g. perfluoralkyl carboxylic acids with $x \geq 7$ and perfluoralkane sulfonic acids with $x \geq 6$, x being the number of perfluorinated C-atoms in the chain) may distribute to the water/vessel and water/air interfaces. These interference depend on the geometry and material of the sample vessels and can be minimized by minimizing the sample surface, e.g. by using narrow vessels with a small surface area.

5.2 Background contamination

<https://standards.iteh.ai/catalog/standards/sist/c5a55c5a-e7f3-43e0-bd9d->

Efforts should be taken to minimize background levels in procedural blank materials such that the procedural blank, including the instrumental blank, is at least one third below the limit of quantification (9.4).

Low molecular residuals in fluoropolymer-containing materials such as polyvinylidene fluoride or polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE) etc., which are often used in LC-equipment, may cause blank values, e.g. in the case of PFOA. In order to avoid blank values, objects made of glass, steel, polyether ether ketone (PEEK), polystyrene (PS), polypropylene (PP) or polyethylene (PE) shall preferably be used for sampling, extraction and analysis. Sampling vessels (7.2) and sample vials (7.12) shall be checked for possible background contamination before use.

Typical contamination sources in the LC-system include vacuum degassers, frits and hoses as well as pump head seals. In the case of such interferences, degassing of the eluents, for example, can be carried out using helium instead of vacuum degassers. Fluoropolymer frits and hoses shall be replaced by frits and hoses made of stainless steel or PEEK. If available, pump head seals made of PE shall be used.

Background contamination, originating from the instrument and/or mobile phases can be controlled by using a delay column (7.14.3).

5.3 Interferences encountered during liquid chromatography and mass spectrometry

Peak tailing, peak fronting and/or broadened peaks are indicative of interferences in chromatography.

Particles in the measurement solution, e.g. fine fractions of the SPE material in case of analytical protocol B of this document or solid phase matter in the sample in case of analytical protocol A of this document, can block the inlet sieves or frits, respectively, of the LC column and result in interferences