SLOVENSKI STANDARD
SIST-TS CEN/TS 15968:2010

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Določevanje izločljivega perfluorooktansulfonata (PFOS) v prevlečenih in impregniranih trdnih predmetih, tekočinah in protipožarnih penah - Metode vzorčenja, ekstrakcije in analize s pomočjo LC-MS ali LC-MS/MS

Determination of extractable perfluorooctanesulphonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LC-qMS or LC-tandem/MS

Bestimmung von extrahierbarem Perfluoroctansulfonat (PFOS) in beschichteten und imprägnierten Feststoffartikeln, Flüssigkeiten und Feuerlöschschäumen - Verfahren zur Probenahme, Extraktion und Analyse mittels LC-MS oder LC-MS/MS

Détermination du sulfonate de perfluorooctane (SPFO) extractible dans des articles solides couchés et imprégnés, des liquides et des mousses anti-incendie - Méthode d'échantillonnage, d'extraction et d'analyse par LC-MS ou LC-MS/MS

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English Version

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Foreword

This document (CEN/TS 15968:2010) has been prepared by Technical Committee CEN/TC 382 “Project Committee - PFOS”, the secretariat of which is held by NEN.

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

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of REACH (1907/2006), annex XVII, designation 53 [1].

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

For implementation of REACH (1907/2006), annex XVII, designation 53 [1] the European Commission asked CEN to develop an European Technical Specification with test methods for measuring levels of PFOS containing compounds in preparations, semi-finished products and articles including textile and coated materials.

REACH (1907/2006), annex XVII, designation 53 [1] states that the substances that are under the Directive are perfluorooctanesulfonates (PFOS), that means substances with the formula $C_8F_{17}SO_2X$ (where X=OH, Metal salt (O-M+), halide, amide and other derivatives including polymers).

1 Scope

This Technical Specification describes the determination of perfluorooctanesulfonate (PFOS) in concentrated extracts from coated and impregnated solid articles, liquids and fire extinguishing foams using high performance liquid chromatography-tandem mass spectrometry (LC-tandemMS) or quadrupole mass spectrometry (LC-qMS).

The method is applicable for a concentration range for PFOS in the extract solution of 0,5 µg/l to 50 µg/l.

WARNING — Persons using this Technical Specification should be familiar with normal laboratory practice. This Technical Specification 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 in accordance with this Technical Specification be carried out by suitably qualified staff.

2 Normative references

The following referenced documents are indispensable for the application 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 20187, *Paper, board and pulps — Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples (ISO 187:1990)*

EN ISO 2419, *Leather — Physical and mechanical tests — Sample preparation and conditioning (ISO 2419:2006)*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

EN ISO 8130-9, *Coating powders — Part 9: Sampling (ISO 8130-9:1992*)

EN ISO 15194, *In vitro diagnostic medical devices — Measurement of quantities in samples of biological origin — Requirements for certified reference materials and the content of supporting documentation (ISO 15194:2009)*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Terms and definitions

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

3.1
analyte
substance or chemical constituent that is subjected to measurement

3.2
blank matrix
matrix which is largely identical with the analytical one, but does not contain the analyte or contains it in low and known content

NOTE Blanks are used to check the analytical process.

3.3
constituents
all pure chemical materials and substances of which a material is composed

3.4
extract
concentrated preparation of the analytes isolated from the treated material

3.5
foams
fire extinguishing foams

3.6
overall treated materials
materials with a seamless finish

3.7
internal standard
compound different from the analyte, present in the sample with known content or added to the sample, simultaneously detected with the analyte, with physical and chemical properties as similar as possible to the analyte

3.8
reference material
RM
material, sufficiently homogeneous and stable regarding one or more properties, used in calibration, assignment of a value to another material, or quality assurance (conform EN ISO 15194)

3.9
coated materials
materials that are treated with chemicals to provide them with water and soil repellent properties; or treated for aesthetic or decorative reasons

4 Symbols and abbreviations

LC-qMS	liquid chromatography (LC) coupled with quadrupole mass spectrometry (qMS)
LC-tandemMS	liquid chromatography (LC) coupled with tandem mass spectrometry (tandemMS)
LC-TOFMS	liquid chromatography (LC) coupled with time of flight mass spectrometer (TOFMS)

5 Principle

The analytes listed in Table 1, after extraction with methanol, are determined by liquid chromatography with tandem mass spectrometric detection (LC-tandemMS) or liquid chromatography mass spectrometric detection (LC-qMS). The list of analytes is not comprehensive for all possible PFOS derivates.

Table 1 — Analytes determinable by this method

Compound name	Chemical formula	Acronym	CAS No.
Perfluorooctane sulphonic acid	C8F17SO3H	PFOS	1763-23-1
Perfluorooctane sulphonamide	C8F17SO2NH2	PFOSA	754-91-6
N-Methyl-heptadecafluorooctane sulphonamide	C8F17SO2NH(CH3)	N-Me-FOSA	N.A.[a]
N-Ethyl-heptadecafluorooctane sulphonamide	C8F17SO2NH(C2H5)	N-Et-FOSA	N.A.[a]
N-Methyl-heptadecafluorooctane sulphonamidoethanol	C8F17SO2N(CH3)CH2CH2OH	N-Me-FOSE alcohol	24448-09-7
N-Ethyl-heptadecafluorooctane sulphonamidoethanol	C8F17SO2N(C2H5)CH2CH2OH	N-Et-FOSE alcohol	1691-99-2

NOTE PFOS may be present in its salt form e.g. potassium salt (CAS 2795-39-3), lithium salt (CAS 29457-72-5), ammonium salt (CAS 29081-56-9) and diethanolamine salt (CAS 70225-39-5). Others may exist. The method described in this protocol is valid for all these different chemical forms.

[a] N.A.: Not available.

This Technical Specification describes the method for determining the PFOS concentration in the following steps:

a) sampling (see Clause 7);

b) extraction with methanol (see Clause 9);

c) clean up of the methanol solution (see 9.2);

d) analysis by LC-qMS or LC-tandemMS (see Clause 11);

e) calculation of the results (see Clause 13).

6 Apparatus and Reagents

6.1 General

Sample containers shall be rinsed thoroughly with water (0) and methanol (0) prior to use. Sample containers shall be checked for possible background contamination before use.

Equipment or any accessible part of which that may come into contact with the sample or the extract should be free from interfering compounds.

Clean all lab-ware and accessible parts of apparatus for extraction by rinsing with methanol (0).

6.2 Equipment

Use equipment free from glass (e.g. PP, PE):

— cutting die or template and cutting tool to measure and cut area materials (textiles, leather, paper, etc.). Mill to grind granular bulk solids;

— 125 µm sieve;

— volumetric flasks, with inert stopper;

— vials, polypropylene or polyethylene;

— ultrasonic bath, equipped with adjustable and stable bath temperature (20 °C to 70 °C);

— concentration equipment (e.g. hydrophilic lipophilic base, SPE, weak anion exchange resin or rotavapor);

— high performance liquid chromatograph, temperature-controlled and with all required accessories including gases, LC columns, injector and a mass spectrometric detector either tandemMS or qMS. Alternative methods e.g. LC-/TOFMS are discussed in Annex A.

6.3 Reagents for extraction

6.3.1 Methanol, CH_3OH (ultra pure).

6.4 Reagents for LC and MS

6.4.1 Water, complying with at least grade 3 as specified in EN ISO 3696:1995, also applicable for blank determinations.

6.4.2 Acetic Acid, $w(CH_3COOH) \geq 99{,}9$ %.

6.4.3 Ammonium acetate, $w(CH_3COONH_4) \geq 97$ %.

6.4.4 Formic Acid, $w(HCOOH) \geq 99$ %.

6.4.5 Methanol, CH_3OH (HPLC grade).

6.4.6 Gases for MS.

— Nitrogen, GC grade 5.0 or better;

— Collision gas (e.g. Argon);

— Helium, GC grade 5.0 or better.

6.4.7 Reference solutions.

— $^{13}C_x$-PFOS (e.g. $[F(CF_2)_8SO_3^- H^+]$-, 1,2,3,4-$^{13}C_4$); or

— $^{18}O_x$-PFOS (e.g. $[F(CF_2)_8SO_3^- H^+]$-, $^{18}O_2$).

In addition, when other types of labelled internal standards become available, they may be used.

Solutions of the reference compounds are available commercially. They should be diluted to required concentrations.

If reference compounds are obtained as neat, weigh 100 mg of each standard separately into a 100 ml volumetric flask and make up to the mark with methanol. Dilute this solution with methanol at a ratio 1:1 000.

The impurity levels of the internal standards should be determined prior to the use of new of every new lot.

6.4.8 Range of calibration solutions, in concentration range 0,5 µg/l to 50 µg/l.

7 Sampling

7.1 General

The chosen sample should be representative for the lot it is taken from. This document describes two different ways of reporting results which require two different ways of sample collection. One way is based on the content per area (mass/area). The other way is based on content per mass (mass/percentage).

7.2 Conditioning samples

Materials and samples shall be stored preferably at 4 °C and in clean containers, see 6.2, before testing.

Conditioning of leather shall be done according to EN ISO 2419.

Conditioning of paper shall be done according to EN 20187.

7.3 Sampling solids

7.3.1 Coated materials like paper, textile, leather, carpets, clothes and footwear

If applicable take a sample of at least 200 cm^2 using a cutting die or any other suitable tool and template; weigh the sample to make sure results can be reported as well in percentage/weight as in micrograms per square metre.

NOTE Make sure that the sample is not stretched (be aware that crinkled materials can easily have a much higher surface area).

If the material is not suitable to provide area-based samples, take a sample by weight, using at least 2 g of material.

7.3.2 Non-coated materials

Powders, granulates and other bulk materials shall be sampled according to EN ISO 8130-9.

For any other material an appropriate representative amount of the product shall be cut off, see 7.3.1.

7.4 Sampling products that have separate distinct parts

Products consisting of separate distinctive parts shall be dismounted and each part shall be treated according to 7.3.1.

7.5 Sampling liquids

The samples for testing shall be taken and delivered by the supplier using a method which will provide a representative sample of the liquid to be tested.