
Kakovost vode - Določevanje polifluoriranih alkilnih spojin (PFAS) v vodi - Metoda z ekstrakcijo na trdni fazi in s tekočinsko kromatografijo-tandemsko masno spektrometrijo (LC-MS/MS)

Water quality - Determination of polyfluorinated alkyl substances (PFAS) in water - Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)

Qualité de l'eau - Détermination des substances d'alkyle perfluorés et polyfluorés (SPFA) dans l'eau - Méthode par extraction en phase solide et chromatographie liquide et spectrométrie de masse en tandem (CL-SM/SM)

Ta slovenski standard je istoveten z: ISO/FDIS 21675:2019

ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

oSIST ISO/FDIS 21675:2019

en,fr,de

FINAL
DRAFT

INTERNATIONAL
STANDARD

ISO/FDIS
21675

ISO/TC 147/SC 2

Secretariat: DIN

Voting begins on:
2019-07-10

Voting terminates on:
2019-09-04

**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)**

*Qualité de l'eau — Détermination des substances d'alkyle perfluorés
et polyfluorés (SPFA) dans l'eau — Méthode par extraction en phase
solide et chromatographie liquide et spectrométrie de masse en
tandem (CL-SM/SM)*

SIST ISO 21675:2019

<https://standards.iteh.ai/catalog/standards/sist/e17f4a4c-4b65-4067-b922-97cd8b896ca6/sist-iso-21675-2019>

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.



Reference number
ISO/FDIS 21675:2019(E)

© ISO 2019

iTeh STANDARD PREVIEW (standards.iteh.ai)

SIST ISO 21675:2019
<https://standards.iteh.ai/catalog/standards/sist/e17f4a4c-4b65-4067-b922-97cd8b896ca6/sist-iso-21675-2019>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2019

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	2
4 Principle	2
5 Interferences	4
5.1 Interferences with sampling and extraction	4
5.2 Interferences with LC-MS/MS	4
6 Reagents	4
7 Apparatus	7
8 Sampling	8
9 Procedure	8
9.1 Solid-phase extraction	8
9.1.1 General	8
9.1.2 Sample preparation	8
9.1.3 Conditioning of the solid-phase extraction material	9
9.1.4 Sample extraction	9
9.1.5 Elution	9
9.2 LC-MS/MS operating conditions	10
9.3 Blank determination	12
9.4 Identification	12
10 Calibration	13
10.1 General requirements	13
10.2 Calibration using an external standard	13
10.3 Calibration using an internal standard	14
11 Calculation	15
11.1 Use of a calibration curve to determine concentration	15
11.2 Calculation of concentration using calibration with external standards	15
11.3 Calculation of concentration using calibration with internal standards	16
11.4 Treatment of results outside the calibration range	16
12 Determination of analyte recovery	16
12.1 Recovery	16
12.2 Recovery of internal standards	17
13 Expression of results	18
14 Test report	18
Annex A (informative) Examples of suitable sorbents	19
Annex B (informative) Examples of suitable LC columns	20
Annex C (informative) Examples of suitable LC-MS/MS conditions	21
Annex D (normative) Filtration and extraction of suspended matter in the sample	25
Annex E (informative) Examples of chromatographic separation of individual linear and branched PFAS isomers	27
Annex F (informative) Rapid method by direct injection	31
Annex G (informative) Rapid method by online solid phase extraction LC-MS/MS	32
Annex H (informative) Performance data by DIN 38407-42 for selected PFAS	35

ISO/FDIS 21675:2019(E)

Annex I (informative) Performance data	37
Bibliography	42

iTeh STANDARD PREVIEW
(standards.iteh.ai)

SIST ISO 21675:2019
<https://standards.iteh.ai/catalog/standards/sist/e17f4a4c-4b65-4067-b922-97cd8b896ca6/sist-iso-21675-2019>

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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)

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.

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

1 Scope

This document specifies a method for the determination of selected perfluoroalkyl and polyfluoroalkyl substances (PFAS) in non-filtrated waters, for example drinking water, natural water (fresh water and sea water) and waste water containing less than 2 g/l solid particulate material (SPM) using liquid chromatography-tandem mass spectrometry (LC-MS/MS). The compounds monitored by this method are typically the linear isomers. The group of compounds determined by this method are representative of a wide variety of PFAS. The analytes specified in [Table 1](#) can be determined by this method. The list can be modified depending on the purpose for which the method is intended. The lower application range of this method can vary depending on the sensitivity of the equipment used and the matrix of the sample. For most compounds to which this document applies $\geq 0,2$ ng/l as limit of quantification can be achieved. Actual levels can depend on the blank levels realized by individual laboratory.

The applicability of the method to further substances, not listed in [Table 1](#), or to further types of water is not excluded, but is intended to be validated separately for each individual case.

NOTE 1 PFAS is used in this document to describe the analytes monitored. Many of the compounds in [Table 1](#) are perfluoroalkyl and are also considered polyfluoroalkyl substances

NOTE 2 The linear PFAS isomers are specified in this document. The branched isomers can be present in environmental samples, especially for PFOS. [Annex E](#) provides an example of an analytical approach to the chromatographic and spectroscopic separation of individual isomers.

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 3696, *Water for analytical laboratory use — Specification and test methods*

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 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*¹⁾

1) Under preparation. Stage at time of publication: ISO 21253-1.

ISO/FDIS 21675:2019(E)

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 <http://www.electropedia.org/>

3.1
perfluoroalkyl and polyfluoroalkyl substances
PFAS
 commonly used international abbreviation for organic compounds with replacement of most or all hydrogen atoms by fluorine in the aliphatic chain structure

Note 1 to entry: The term is used in the broader sense for per- and polyfluoroalkyl substances (PFAS) and per- and polyfluorinated compounds (PFC) as well.

4 Principle

The analytes listed in [Table 1](#) are extracted from the water sample by solid-phase extraction using a weak anion exchange sorbent followed by solvent elution and determination by liquid chromatography-tandem mass-spectrometry.

The user should be aware that each analyte has its own specific optimum conditions and therefore modification of the analyte list could require the specification of additional conditions for each additional parameter.

Table 1 — Analytes determinable by this method

Analyte	IUPAC ^a name	Formula	Abbreviation	CAS-RN ^b
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> -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
Perfluoro- <i>n</i> -octanesulfonic acid	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluorooctane-1-sulfonic acid	C ₈ HF ₁₇ O ₃ S	PFOS	1763-23-1
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-Hen-icosafafluorodecane-1-sulfonic acid	C ₁₀ HF ₂₁ O ₃ S	PFDS	335-77-3
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> -methyl perfluorooctanesulfonamide	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro- <i>N</i> -methyl-1-octanesulfonamide	C ₉ H ₄ F ₁₇ NO ₂ S	<i>N</i> -MeFOSA	31506-32-8
<i>N</i> -ethyl perfluorooctanesulfonamide	<i>N</i> -Ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide	C ₁₀ H ₆ F ₁₇ NO ₂ S	<i>N</i> -EtFOSA	4151-50-2
<i>N</i> -methyl perfluorooctanesulfonamidoacetic acid	2-[1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluorooctylsulfonyl(methyl)amino]acetic acid	C ₁₁ H ₆ F ₁₇ NO ₄ S	<i>N</i> -MeFOSAA	2355-31-9
<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

^a IUPAC: International Union of Pure and Applied Chemistry.
^b CAS-RN: Chemical Abstract Services Registry Number.

Table 1 (continued)

Analyte	IUPAC ^a name	Formula	Abbreviation	CAS-RN ^b
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
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
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-Henicosafuoroundecanoic 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-Tricosafuorododecanoic 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-Pentacosafuorotridecanoic acid	C ₁₃ HF ₂₅ O ₂	PFTrDA	72629-94-8
Perfluoro- <i>n</i> -tetradecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptacosafuorotetradecanoic acid	C ₁₄ HF ₂₇ O ₂	PFTeDA	376-06-7
Perfluoro- <i>n</i> -hexadecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Hentriacontafuorohexadecanoic acid	C ₁₆ HF ₃₁ O ₂	PFHxDA	67905-19-5
Perfluoro- <i>n</i> -octadecanoic acid	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Pentatriacontafuorooctadecanoic acid	C ₁₈ HF ₃₅ O ₂	PFOcDA	16517-11-6
8:2 Fluorotelomer unsaturated carboxylic acid	3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Hexadecafluorodec-2-enoic acid	C ₁₀ H ₂ F ₁₆ O ₂	8:2 FTUCA	70887-84-2
8:2 Polyfluoroalkyl phosphate diester	Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) hydrogen phosphate	C ₂₀ H ₉ F ₃₄ O ₄ P	8:2 diPAP	678-41-1
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
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
^a IUPAC: International Union of Pure and Applied Chemistry.				
^b CAS-RN: Chemical Abstract Services Registry Number.				

ISO/FDIS 21675:2019(E)

5 Interferences

5.1 Interferences with sampling and extraction

Sample bottles (7.1) shall consist of materials that do not contaminate or change the composition of the sample during sample storage. All types of fluoropolymer plastics, including polytetrafluoroethylene (PTFE) and fluoroelastomer materials, shall be avoided during sampling, sample storage and extraction. Sample bottles (7.1) shall be checked for possible background contamination before use. If background contamination is suspected or detected in sample bottles (7.1), then wash sample bottles (7.1) with water (6.1) and methanol (6.6) prior to use. To avoid cross contamination, the sample bottles (7.1) should only be used once. The use of intermediate sample tubes (7.6) and vials (7.10) should be limited in the overall process to avoid contamination of loss by sorption. To avoid losses resulting from adsorption of target analytes to the wall of sample bottle (7.1) and reservoir column (7.4), extract all of the sample from the sample bottle (7.1) and rinse the wall of sample bottle (7.1) and reservoir column (7.4) with methanol (6.6).

Commercially available adsorbent materials often vary in quality or activity. Considerable batch-to-batch differences in quality and selectivity of these materials are possible. The recovery of a single substance may also vary with respect to its concentration. Therefore, check analyte recovery periodically at different concentrations and whenever new batches/lots of reagents or labware are used (12.1).

5.2 Interferences with LC-MS/MS

Substances with similar retention times that can produce ions with similar mass to charge ratios (m/z) to those produced by the analytes of interest may interfere with the determination.

These interferences may lead to incompletely resolved signals and/or additional signals in the mass chromatograms of target substances. Depending on their levels in the sample, such substances may affect the accuracy and precision of the results. The chromatographic separation is different with the LC column (see Annex C for examples). As long as the peak of interest can be separately integrated from interferences, it may be used.

Matrix interferences may be caused by contaminants that are co-extracted from the samples. The extent of matrix interferences varies considerably, depending on the nature of the samples. In drinking water and ground water, matrix interferences are usually negligible, whereas waste water and sea water matrices can be affected by matrix interferences that lead to ionization suppression or enhancement resulting in bias or reduced sensitivity of the method. As long as the required limits of quantification can be achieved in samples, samples can be diluted to minimize matrix effects.

Interferences arising directly from analytical instruments can be significant for unmodified commercial LC systems because many parts are made of PTFE and other fluoropolymers. It is necessary to check for possible blank contamination from the individual parts, such as tubing, solvent inlet filters, valve seals and the degassing equipment, and replace these with materials such as stainless steel and polyetheretherketone (PEEK), where possible.

NOTE Background contamination can arise from within the instrument. A delay column can be attached between the solvent mixer and injection valve to chromatographically resolve these background contaminants from the instrument and/or mobile phases from the target analytes.

The LC-vial caps shall be free of fluoropolymer material. Efforts should be taken to minimize background levels in procedural blank materials such that the procedural blank, including the instrumental blank, is at least 10-fold below the reporting limit.

6 Reagents

Whenever possible, use certified or analytical-grade reagents or residue free-analytical grade reagents stored in glass or polypropylene containers with metal or polypropylene lined caps. Avoid using reagents with fluoropolymer lined caps and check contamination levels of target substances

using repeated blank determinations. Carry out additional cleaning or conditioning steps to ensure background levels are minimized, if necessary.

6.1 Water, blank-value free, e.g. complying with grade 1 as specified in ISO 3696.

Purified laboratory water can be used, but should be confirmed to be free of PFAS. The quality of water is checked by the same procedure given in [9.3](#).

6.2 Acetic acid, $w(\text{CH}_3\text{COOH}) = 99,9 \%$ mass fraction (999 g/kg).

6.3 Acetonitrile, CH_3CN .

6.4 Ammonia solution, $w(\text{NH}_3) = 25 \%$ mass fraction (250 g/kg).

6.5 Ammonium acetate, $w(\text{CH}_3\text{COONH}_4) = 97 \%$ mass fraction (970 g/kg).

6.6 Methanol, CH_3OH , blank-value free.

NOTE The quality of methanol is checked by evaporating 10 ml of methanol with a gentle stream of nitrogen gas ([6.13](#)) to 0,5 ml and determining levels according to this document.

6.7 Reference substances, see [Table 1](#).

Reference substances are analytical standards used for quantitative determination of the method analytes. Use only reference substances or solutions, where the content of linear isomers is at least 95 %. Make sure that the individual reference substances do not contain detectable concentrations of other target analytes to be determined by analysing alternate lots or second sources.

NOTE Solutions of reference substances are commercially available.

<https://standards.iteh.ai/catalog/standards/sist/e17f4a4c-4b65-4067-b922-iso-21675-2019>

6.8 Internal standard substances, see [Table 3](#).

Internal standard substances are labelled forms of the reference substances to be used in the analytical procedure to correct for recovery due to losses of analyte or changes in analytical conditions that could result in bias. Make sure that the internal standard substances do not contain detectable concentrations of the analytes to be determined by analysing new lots using this document.

NOTE Solutions of internal standard substances are commercially available.

6.9 Preparation of the solutions

Calculate the concentration of all reference substances and internal standard solutions with regard to the anion content.

Store the solutions at $(5 \pm 3) ^\circ\text{C}$ in the dark, protected against evaporation. Bring them to room temperature prior to use (i.e. before dilution or spiking or injection).

6.9.1 Individual stock solutions of the reference substances

Stock solutions of the individual reference substances ([6.7](#)) in methanol ([6.6](#)) or acetonitrile ([6.3](#)) should be of mass concentration to enable dilution to the desired range, e.g. 50 µg/ml each.

6.9.2 Individual stock solutions of internal standard substances

Stock solutions of the individual internal standard substances ([6.8](#)) in methanol ([6.6](#)) or acetonitrile ([6.3](#)) should be of mass concentration to enable dilution to the desired range, e.g. 50 µg/ml each.

6.13 Nitrogen, N₂, purity >99,9 %.

7 Apparatus

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

The blank determination shall be conducted before the sampling. Clean labware and apparatus for solid-phase extraction by washing with water (6.1) and methanol (6.6) if background contamination is detected in labware and apparatus.

Equipment in contact with sample or reference solutions should be made of polypropylene or polyethylene. It was not tested except for compounds listed in [Annex H](#) for sampling whether the use of glassware may lead to adsorption of some of the analytes within the scope of the method.

7.1 Sample bottles

Narrow-neck flat-bottomed polypropylene or polyethylene bottles, normal volume 50 ml, 100 ml, 250 ml, 500 ml and 1 000 ml, with conical shoulders and screw caps.

NOTE Glass bottles can be used for compounds listed in [Annex H](#). Glass bottles can be used for sampling provided that storage conditions of samples have been validated in each case. See [Annex H](#) for examples.

The entire sample shall be extracted and the appropriate-sized sample bottle should be used to collect the sample.

Sample bottles shall be checked for possible background contamination before use. The bottles and screw caps are washed with methanol (6.6) and dried before use in order to minimize contamination, if background contamination is detected in sample bottles.

7.2 Pipettes, with polypropylene tips.

7.3 Solid-phase extraction medias (cartridges or disks), made of inert non-leaching plastic, e.g. polypropylene or polyethylene frits.

The cartridges shall be packed with 50 mg to 1 000 mg of solid-phase extraction material (6.12) as sorbent. In general, 150 mg to 250 mg of sorbent (see [Annex A](#)) in a single cartridge is sufficient for up to 500 ml of water.

NOTE 1 The 500 mg of sorbent (see [Annex A](#)) in a single cartridge is sufficient for 1 000 ml of sea water.

NOTE 2 The stationary phase can be modified if analytes are not recovered quantitatively (for example neutral substances such as FOSA, *N*-MeFOSA and *N*-EtFOSA) using solid-phase extraction material (6.12) for example strongly hydrophilic reversed -phase copolymer or silica-based.

7.4 Reservoir column, normal volume 60 ml, with adaptor for cartridges (7.3), made of polypropylene or polyethylene.

7.5 Vacuum or pressure assembly, for the extraction step.

7.6 Sample tubes, made of, for example, polypropylene or polyethylene, for collecting and concentrating the eluate, e.g. test tube, nominal volume of 15 ml.

7.7 Volumetric flasks, with inert stoppers, made of polypropylene or polyethylene not containing fluoropolymer materials, normal volume 10 ml, 50 ml, 100 ml and 500 ml.

7.8 Graduated cylinder, normal volume 50 ml, 100 ml and 500 ml.