The Flemish Government

Ministerial Decree approving the compendium for the sampling, measurement and analysis of water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 containing general and sectoral provisions on environmental hygiene, the Decree of the Flemish Government of 19 November 2010 establishing the Flemish regulation on environmental accreditations and the Ministerial Decree of 16 June 2023 approving the compendium for the sampling, measurement and analysis of water (WAC) and amending annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 containing general and sectoral provisions on environmental hygiene

Legal bases

This Decree is based on:
- the Decree of 5 April 1995 laying down general provisions concerning environmental policy, Article 5.4.1, inserted by the Decree of 25 April 2014, and Article 5.6.5, included by the Decree of 25 April 2014 and amended by the Decree of 8 December 2017;
- the Flemish Government Decree of 1 June 1995 laying down general and sectoral provisions concerning environmental hygiene, Article 1.1.2, last amended by the Flemish Government Decree of 07 July 2023, and Article 1.2.1.1;
- the VLAREL of 19 November 2010, Article 3 and Article 45(1)(2), inserted by the Decree of the Flemish Government of 3 May 2019.

Procedural requirements

The following procedural requirements have been met:
- The Section for Area Development, Environmental Planning and Projects of the Environment Department has made a proposal to amend the Compendium for the sampling, measurement and analysis of water (WAC) on 26 June 2023.
- The Flemish Supervisory Commission for the Processing of Personal Data issued Opinion 2023/084 on 18 July 2023.
- The Data Protection Authority issued standard opinion No 65/2023 of 24 March 2023 on the drafting of normative texts on 18 July 2023.
- This draft was notified to the European Commission on 14 July 2023, pursuant to Article 5 of Directive (EU) 2015/1535 of the European Parliament and of the Council of 9 September 2015 laying down a procedure for the provision of information in the field of technical regulations and of rules on Information Society services with the exception of the method “Determination of short-chain per- and polyfluoroalkyl compounds (PFAS) in water with LC-MS/MS,

(WAC/IV/A/026, version date October 2023)" notified to the European Commission under the urgency procedure referred to in Article 6(7) of the Directive.
- The Council of State gave opinion … on (date), pursuant to Article 84(1)(1), 2° of the Laws on the Council of State, coordinated on 12 January 1973;

Statement of grounds

This Decree is based on the following grounds:
- As a result of international and Flemish developments and recent research, adaptations to a number of existing methods and the inclusion of new methods in the compendium for the sampling, measurement and analysis of water (WAC) are necessary.
- Article 45 of the Flemish Environmental Recognitions Regulation [VLAREL] states that recognised laboratories shall apply the methods of the compendia for water [WAC], air [LUC], soil protection [BOC], the Manure Decree [BAM] and the Materials and Soil Decree [CMA] for the sampling, testing, measurements and analyses for which they are recognised. There exist cross-references between the compendia.
- For practical, organisational and legal reasons for the benefit of the laboratories, as well as the government and clients, the same date of entry into force is stated for all compendia. The date of entry into force is 15 January 2024. The laboratories have been informed about the new water sampling, measurement and analysis compendium (WAC), which can be consulted online.
- In order to harmonise the Title II of VLAREM with the proposed changes to the compendium for the sampling, measurement and analysis of water (WAC), a series of identical changes are implemented to the organic parameters in Article 4, §1 of Annex 4.2.5.2 to Title II of VLAREM.
- The PFAS compounds 6:2/8:2 fluorotelomer phosphate diester (6:2/8:2 diPAP), perfluoro-n-octadecanoic acid (PFODA) and 6:2 fluorotelomer phosphate diester (6:2 diPAP) shall be removed from the table of organic parameters listed in Article 4,
§1 of Annex 4.2.5.2 to title II of the VLAREM is deleted because of a standard that is difficult to enforce, given the measurement uncertainty of 100 %.
- A new method for the determination of short-chain per- and polyfluoroalkyl compounds (PFAS) in water with LC-MS/MS (WAC/IV/A/026) is introduced in the compendium, in addition to a corresponding new recognition package in Annex 3 of the VLAREL. The current PFAS package W.7.9 (organofluor connections) is split into 2 sub-packages: W.7.9.1 (standard series of per- and polyfluoroalkyl compounds (WAC/IV/A/025)) and W.7.9.2 (short chain per- and polyfluoroalkyl compounds (WAC/IV/A/026)). Laboratories in the field of water are given the necessary time to obtain recognition for the new W.7.9.2 package, i.e. until 1 October 2024.
- The processing of the sampler's personal data is lawful on the basis of Article 6(1)(c) and (e) of the General Data Protection Regulation, in particular the legal obligation to lay down conditions to protect humans and the environment from certain nuisances and risks emanating from (un)classified establishments or activities and the adoption of usage requirements, as well as the detailed rules for the suspension or expiry of approvals. The processing is also necessary for the performance of a task carried out in the public interest or in the exercise of official authority conferred on the controller. The retention periods are governed by, inter alia, Articles 49 and 50 of the VLAREL and the Administrative Decree of 7 December 2018.
- A correction of a textual omission in Article 3 of the Ministerial Decree of 16

June 2023 approving the Compendium for the Sampling, Measurement and Analysis of Water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 laying down general and sectoral provisions on environmental hygiene is required to lift the entire Ministerial Decree of 23 January 2023, including the amendments to Annex 4.2.5.2 of VLAREM II. The intention was to discontinue only the version of the compendium approved by Article 1 of the Ministerial Decree of 23 January 2023, following the adoption of a new version of the compendium.

Legal context

This Decree is consistent with the following regulation:
- the Ministerial Decree of 16 June 2023 approving the compendium for the sampling, measurement and analysis of water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 laying down general and sectoral provisions on environmental hygiene.

THE FLEMISH MINISTER FOR JUSTICE AND ENFORCEMENT, ENVIRONMENT, ENERGY AND TOURISM HEREBY DECREES:

Article 1. The compendium for the sampling, measurement and analysis of water, abbreviated WAC, and the corresponding table of contents, as set out in the Annex to this Decree, are hereby approved.

Article 2. The processing of personal data by the Environment Department, the Flemish Environment Agency and the reference laboratory of the Flemish Region in the context of the application of the compendium referred to in Article 1 is limited to the name of the sampler and the date, time and place of the sampling. The location data is only used for the legally determined purposes.

Article 3. In Article 4(1) of Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 laying down general and sectoral provisions on environmental hygiene, last amended by the Decree of the Flemish Government of 16 June 2023, the following amendments are made to the table under the organic parameters:

1° after the row

“

8:2 fluorotelomer phosphate diester (8:2 diPAP)	20 ng/l	50 %	WAC/IV/A/025

”

the following row shall be removed:

‘

6:2/8:2 fluortelomer phosphate diester 6:2/8:2 diPAP	50 ng/l	100 %	WAC/IV/A/025

”;

2° after the row

“

10:2 fluorotelomer sulfonic acid (10:2 FTS)	50 ng/l	50 %	WAC/IV/A/025

”

the following row shall be removed:

“ ”;

perfluoro-n-octadecanoic acid (PFODA)	50 ng/l	100 %	WAC/IV/A/025

3° after the row

“

perfluorotridecane sulfonic acid (PFTrDS)	50 ng/l	50 %	WAC/IV/A/025

”

the following row shall be removed:

“

6:2 fluorotelomer phosphate diester (6:2 diPAP)	50 ng/l	100 %	WAC/IV/A/025

”;

4° the rows

“

perfluorooctanoic acid (sum of linear and branched forms) (PFOA total)	50 ng/l	50 %	WAC/IV/A/025
perfluorooctane sulfonic acid	50 ng/l	50 %	WAC/IV/A/025

(sum of linear and branched forms) (PFOS total)			
perfluorooctane sulphonamide (sum of linear and branched forms) (PFOSA total)	50 ng/l	50 %	WAC/IV/A/025
N-methylperfluorooctane sulphonamide (sum of linear and branched forms (MePFOSA total)	50 ng/l	50 %	WAC/IV/A/025
N-ethylperfluorooctane sulfonamide (sum of linear and branched forms) (EtPFOSA total)	50 ng/l	50 %	WAC/IV/A/025
perfluororhexane sulfonic acid (sum of linear and branched forms) (PFHxStotal)	50 ng/l	50 %	WAC/IV/A/025

”

are replaced by the rows

‘

perfluorooctanoic acid (total of linear and branched forms) (PFOA total)	50 ng/l	50 %	WAC/IV/A/025
perfluorooctane sulfonic acid (total of linear and branched forms) (PFOS total)	50 ng/l	50 %	WAC/IV/A/025
perfluorooctane sulphonamide (total linear and branched forms) (PFOSA total)	50 ng/l	50 %	WAC/IV/A/025
N-methylperfluorooctane sulphonamide (total of linear and branched forms) (MePFOSA total)	50 ng/l	50 %	WAC/IV/A/025
N-ethylperfluorooctane sulphonamide (total linear and branched forms) (EtPFOSA total)	50 ng/l	50 %	WAC/IV/A/025
perfluorohexane sulphonic acid (total linear and branched forms) (PFHxStotal)	50 ng/l	50 %	WAC/IV/A/025

”;

2° after the row

“

8:2 fluorotelomer phosphate diester (8:2 diPAP)	20 ng/l	50 %	WAC/IV/A/025

”

the following row shall be removed:

“

6:2/8:2 fluortelomer phosphate diester 6:2/8:2 diPAP	50 ng/l	100 %	WAC/IV/A/025

”.

Article 4. In Annex 3, 1°, to the VLAREL of 19 November 2010, replaced by the Flemish Government Decree of 1 March 2013 and last amended by the Flemish Government Decree of 24 June 2022, point W.7.9 is replaced by the following:

“W.7.9 organofluor compounds:
W.7.9.1 standard series of per- and polyfluoroalkyl compounds (WAC/IV/A/025)
W.7.9.2 short-chain per- and polyfluoroalkyl compounds (WAC/IV/A/026)”.

Article 5. A laboratory in the field of water referred to in Article 6, 5° (a) of the VLAREL of 19 November 2010, recognised for the W.7.9 package on the day before the date of entry into force of this Article, is recognised for packages W.7.9.1 and W.9.2.2.2 listed in Annex 3, 1°, of the aforementioned Decree, as in force after the date of entry into force of this Article.

The approval referred to in paragraph 1 shall cover only those sub-domains for which the laboratory is approved on the day preceding the date of entry into force of this Article.

Article 6. A laboratory in the field of water referred to in Article 6(5)(a) of the VLAREL of 19 November 2010 shall be exempted from the condition for approval of the W.7.9.2. package until 1 October 2024 at the latest.

Article 7. Article 1 of the Ministerial Decree of 16 June 2023 approving the Compendium for the sampling, measurement and analysis of water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 laying down general and sectoral provisions on environmental hygiene is repealed.

Article 8. In Article 3 of the Ministerial Decree of 16 June 2023 approving the compendium for the sampling, measurement and analysis of water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 containing general and sectoral provisions on environmental hygiene, the words “The Ministerial Decree” shall be replaced by the phrase “Article 1 of the Ministerial Decree” with effect from 16 July 2023, except with regard to compliance with obligations under the VLAREL of 19 November 2010 for which the effective date shall be 15 January 2023.

Article 9. This Decree shall enter into force on 15 January 2024 as regards compliance with obligations under VLAREL of 19 November 2010.

Brussels, (date).

The Flemish Minister of Justice and Enforcement, Environment, Energy and Tourism,

Zuhal DEMIR

Annex. Compendium for the sampling, measurement and analysis of water (WAC) referred to in Article 1

Table of contents of the Compendium for the sampling, measurement and analysis of water (WAC)

PART I. GENERALITIES

A. Sampling and pre-treatment

(On tap) instant sampling of water for human consumption	WAC/I/A/001	October 2023
(On tap) instant sampling of water	WAC/I/A/002	May 2023
Immediate sampling (schepmonster) of water	WAC/I/A/003	May 2023
Procedure for taking a sample	WAC/I/A/004	March 2022
Sampling of water via an observation well, including preservation and transport	WAC/I/A/005	October 2023
Sampling of macro-invertebrates and processing of samples	WAC/I/A/006	November 2017
Sampling of drainage water	WAC/I/A/007	October 2023
Preservation and handling of water samples	WAC/I/A/010	June 2023
On-site measurement of temperature, pH, electrical conductivity, dissolved oxygen, free chlorine and bound chlorine	WAC/I/A/011	January 2020
Determination of flow rate in control devices for waste water	WAC/I/A/012	October 2023

PART II. ORGANOLEPTIC METHODS OF ANALYSIS

A. Organoleptic parameters

Methods for the determination of organoleptic parameters	WAC/II/A	March 2013
CIE 1976 total colour difference – ΔE*ab	WAC/II/A/001	January 2005
Research and determination of colour	WAC/II/A/002	March 2013
Qualitative and quantitative determination of smell and taste	WAC/II/A/003	June 2017

PART III. INORGANIC METHODS OF ANALYSIS

A. General testing

Methods for determining general inorganic parameters	WAC/III/A	October 2021
Determination of dry residue	WAC/III/A/001	June 2020
Determination of temperature	WAC/III/A/003	November 2016

Determination of electrical conductivity	WAC/III/A/004	November 2020
Determination of pH	WAC/III/A/005	November 2016
Determination of alkalinity and buffer capacity	WAC/III/A/006	November 2016
Determination of dissolved oxygen	WAC/III/A/008	October 2020
Determination of total hardness	WAC/III/A/009	October 2015
Determination of the turbidity	WAC/III/A/010	October 2018
Calculation of the saturation index	WAC/III/A/011	November 2018

B. Determination of elements

Methods for determining elements	WAC/III/B	May 2022
Disclosure for the determination of selected elements in water — nitric acid digestion	WAC/III/B/001	October 2018
Disclosure for the determination of selected elements in water — aqua regia decomposition	WAC/III/B/002	April 2021
Determination of selected elements with inductively coupled plasma — atomic emission spectrometry	WAC/III/B/010	June 2023
Determination of elements with inductively coupled plasma — mass spectrometry (ICP-MS)	WAC/III/B/011	June 2023
Determination of antimony, arsenic and selenium with hydride — atomic absorption spectrometry	WAC/III/B/012	June 2019
Determination of mercury	WAC/III/B/014	June 2023

C. Determination of anions

Methods for the determination of anions	WAC/III/C	February 2023
Determination of dissolved anions by liquid-chromatography. Determination of bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulphate	WAC/III/C/001	May 2022
Determination of ions with a discreet analytical system and spectrophotometric detection — ammonium, chloride, nitrate, nitrite, orthophosphate and sulfate	WAC/III/C/002	November 2016
Determination of orthophosphate content and total phosphorus using flow analysis	WAC/III/C/010	October 2019
Determination of fluoride with ion selective electrode	WAC/III/C/020	February 2023
Determination of fluoride with flow analysis	WAC/III/C/022	May 2022
Determination of the free cyanide content with use of continuous flow analysis	WAC/III/C/030	October 2016
Potentiometric determination of dissolved sulphides and sulphides soluble in acidic environments	WAC/III/C/040	October 2016
Spectrometric determination of dissolved sulphides and sulphides soluble in acidic environments	WAC/III/C/041	October 2016
Determination of dissolved chromium VI in water by ion chromatography	WAC/III/C/050	February 2023

D. Determination of group parameters

Methods for determining group parameters	WAC/III/D	May 2022
Determination of the settleable solids	WAC/III/D/001	December 2012
Determination of solids in suspension. Method by filtration on fiberglass filter	WAC/III/D/002	May 2022
Determination of the size of suspended substances	WAC/III/D/003	January 2013
Determination of biochemical oxygen demand (BOD) after 5 days	WAC/III/D/010	July 2021
Determination of Chemical Oxygen Demand (COD)	WAC/III/D/020	June 2023
Determination of oxidising in heat	WAC/III/D/022	June 2019
Determination of Kjeldahl nitrogen. Method after mineralisation with selenium	WAC/III/D/030	October 2013
Determination of nitrite nitrogen and nitrate nitrogen content and the sum of both by means of flow analysis	WAC/III/D/031	October 2016
Determination of the total nitrogen content after oxidative digestion with peroxodisulphate	WAC/III/D/032	November 2016
Determination of total bonded nitrogen (TNb) and dissolved bonded nitrogen (DNb) after catalytic oxidative combustion at high temperature	WAC/III/D/033	May 2022
Determination of the total cyanide content with use of continuous flow analysis	WAC/III/D/036	October 2016
Determination of the methylene blue active substances (MBAS) index using flow analysis	WAC/III/D/040	May 2017
Determination of total organic carbon (TOC) and/or dissolved organic carbon (DOC)	WAC/III/D/050	May 2022

E. Determination of cations

Methods for determining cations	WAC/III/E	June 2023
Determination of ammonium nitrogen by manual spectrophotometry	WAC/III/E/020	October 2016
Determination of ammonium nitrogen content by means of flow analysis	WAC/III/E/021	October 2012
Determination of ammonium nitrogen content using ion chromatography	WAC/III/E/023	October 2012

PART IV. ORGANIC METHODS OF ANALYSIS

A. Determination of specific parameters

Determination of phenolic compounds in water	WAC/IV/A/001	October 2021
Determination of polycyclic aromatic hydrocarbons in water	WAC/IV/A/002	September 2021
Determination of urea	WAC/IV/A/003	October 2017
Determination of di-2-ethylhexyl phthalate and other phthalates in surface water	WAC/IV/A/004	October 2021
Determination of octylphenol, nonylphenol and bisphenol A in wastewater using LC-MS/MS	WAC/IV/A/005	August 2015

Device settings of GC-MS/MS when determining organic parameters	WAC/IV/A/006	November 2018
Determination of formaldehyde in water	WAC/IV/A/007	October 2019
Determination of phthalates in water with GC-MS/MS	WAC/IV/A/008	October 2020
Determination of organophosphorus pesticides in water	WAC/IV/A/010	October 2021
Determination of moderately volatile chlorine hydrocarbons in water	WAC/IV/A/015	June 2022
Determination of volatile organic compounds in water	WAC/IV/A/016	May 2022
Specific determination of non-ionic surfactants in water with LC-am-MS	WAC/IV/A/021	June 2022
Specific determination of cationic surfactants in water with LC-MS	WAC/IV/A/022	May 2022
Determination of dioxins and dioxin-like compounds in water	WAC/IV/A/023	May 2022
Determination of aromatic amines in water	WAC/IV/A/024	October 2021
Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water with LC-MS/MS	WAC/IV/A/025	June 2023
Determination of short-chain per- and polyfluoroalkyl compounds (PFAS) in water with LC-MS/MS	WAC/IV/A/026	October 2023
Determination of pesticides in water with LC-MS	WAC/IV/A/027	October 2021
Determination of pesticides in water with GC-MS	WAC/IV/A/028	October 2021
Determination of glyphosate and AMPA in water with LC-MS	WAC/IV/A/029	November 2020
Determination of brominated fire retardants in water	WAC/IV/A/030	November 2018
Determination of organotin compounds in water	WAC/IV/A/031	November 2018

B. Determination of group parameters

Determination of the phenol index using continuous flow analysis	WAC/IV/B/001	April 2021
Determination of petroleum ether extractable substances in water	WAC/IV/B/005	January 2012
Extractable organic halogen compounds (EOX) in water	WAC/IV/B/010	January 2012
Adsorbable organic halogen compounds (AOX) in water	WAC/IV/B/011	May 2022
Purgable organic halogen compounds (POX) in water	WAC/IV/B/012	October 2020
Determination of the adsorbable organic fluorine (AOF) content with combustion ion chromatography	WAC/IV/B/013	June 2023
Organic screening	WAC/IV/B/020	January 2013
Organic screening: Guideline on the identification of organic compounds in water using UHPLC-HRMS	WAC/IV/B/021	February 2018
Qualitative GC Screening	WAC/IV/B/022	November 2018

Determination of mineral oil in water with gas chromatography	WAC/IV/B/025	June 2023
Determination of tetrachloroethylene-extractable substances in water with IR spectrophotometry	WAC/IV/B/026	November 2016
Gel Permeation Chromatography (GPC) for the purification of sample extracts in the determination of organic parameters	WAC/IV/B/040	September 2010

PART V. BIOLOGICAL METHODS OF ANALYSIS

A. Determination of bacteriological parameters

Determination of total plate count	WAC/V/A/001	May 2022
Determination of total coliforms and *E.coli*	WAC/V/A/002	May 2022
Determination of enterococci	WAC/V/A/003	August 2021
Determination of S*almonella* spp.	WAC/V/A/004	August 2021
Determination of *Legionella* in drinking water and in cooling tower water	WAC/V/A/005	May 2023
Determination of *Pseudomonas aeruginosa*	WAC/V/A/006	October 2023
Determination of *Clostridium perfringens*	WAC/V/A/007	August 2021
Determination of coagulase positive staphylococci	WAC/V/A/008	August 2021
Determination of the measurement uncertainty when carrying out microbiological analyses	WAC/V/A/009	November 2020

B. Determination of ecotoxicity

Ecotoxicity test with invertebrates: acute toxicity for the water flea (*Daphnia magna*) or the brine lobster (*Artemia franciscana*)	WAC/V/B/001	May 2022
Fish ecotoxicity test: acute toxicity in zebrafish embryo (*Danio rerio*)	WAC/V/B/002	June 2023
Ecotoxicity test with algae: growth inhibition test with the freshwater algae (*Pseudokirchneriella subcapitata*) or marine algae (*Phaeodactylum tricornutum*)	WAC/V/B/003	June 2023
Bacterium ecotoxicity test: acute toxicity in the luminescent bacterium (*Aliivibrio fischeri*)	WAC/V/B/004	June 2023
Zahn-Wellens test for wastewaters: bioeliminability of DOC and toxicity after 7 to 28 days of treatment	WAC/V/B/005	November 2020
Fish ecotoxicity test: acute toxicity in trout (*Oncorhynchus mykiss*)	WAC/V/B/007	June 2023

C. Determination of biodiversity

BBI calculation based on macro-invertebrates collected in the field	WAC/V/C/001	September 2015
MMIF calculation based on macro-invertebrates collected in the field	WAC/V/C/002	September 2015

PART VI. VALIDATION

A. General

Performance characteristics	WAC/VI/A/001	June 2023
Measurement uncertainty	WAC/VI/A/002	April 2020
Quality requirements for analytical methods	WAC/VI/A/003	June 2023
Conditions for reporting of sampling data and analytical results by an approved laboratory	WAC/VI/A/004	June 2023

The compendium for sampling, measurement and analysis of water (WAC)

The compendium mentioned in article 1 is available in extenso via the website https://emis.vito.be/nl/erkende-laboratoria/water-gop/compendium-wac with reference MB 2024.

For inclusion in the Ministerial Decree approving the compendium for the sampling, measurement and analysis of water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 containing general and sectoral provisions on environmental hygiene, the Decree of the Flemish Government of 19 November 2010 establishing the Flemish regulation on environmental accreditations and the Ministerial Decree of 16 June 2023 approving the compendium for the sampling, measurement and analysis of water (WAC) and amending Annex 4.2.5.2 to the Decree of the Flemish Government of 1 June 1995 containing general and sectoral provisions on environmental hygiene.

Brussels, (date).

The Flemish Minister for Justice and Enforcement, Environment, Energy and Tourism,

Zuhal Demir

Determination of short-chain per- and polyfluoroalkyl compounds (PFAS) in water with LC-MS/MS

CONTENTS

1 OBJECTIVE AND SCOPE

The analytical method described below is used to determine short-chain per- and polyfluoroalkyl compounds (PFAS):

in drinking, ground and surface water
in waste water

and aims to quantify the following components:

PFAS	*Abbreviation*	*CAS no.*
trifluoroacetic acid	TFA	76-05-1
perfluoro-n-propanoic acid	PFPrA	422-64-0
perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-propanesulphonic acid	PFPrS	423-41-6
perfluoro-n-butanesulphonic acid	PFBS	375-73-5
Trifluoro-n-methanesulphonic acid	TFMS	1493-13-6
Pentafluoro-n-ethane sulphonic acid	PFEtS	354-88-1
2,3,3,3-tetrafluoro-n-propanoic acid	2,3,3,3-TFPA	756-09-2
2,2,3,3-tetrafluoro-n-propanoic acid	2,2,3,3-TFPA	359-49-9

The determination limits are summarised in the table below:

BG (ng/l)	Direct injection	Solid phase extraction (SPE)
TFA	4000	*
PFPrA	120	100
PFBA	600	100
PFPrS	575	100
PFBS	150	150
PFEtS	200	100
TFMS	500	150
2,3,3,3-TFPA	2000	*
2,2,3,3-TFPA	175	*

*Component cannot be determined with SPE extraction

2 PRINCIPLE

Known amounts of isotope-marked fluorine compounds are added to water samples. The water samples are then extracted by solid phase extraction. The solid phase is eluded with methanol and the methanol extract evaporates. The residue is absorbed in a known mobile phase volume and analysed with liquid chromatography by mass spectrometric detection. The content of the different PFAS is calculated using the internal standard method.

Notes:

- Depending on the nature of the samples, the device sensitivity and the desired reporting limits, the measurement can be done directly by direct injection. In addition, the steel is diluted 1 to 1 with acetonitrile.
- For some PFAS, no isotope dilution can be applied because the identical isotope-marked compound is not available. These PFAS are quantified by means of an isotopic compound as closely as possible (see also table under 6.2.2). Alternatively, the external standard method may be used for these components (checking for the presence of matrix effects), or quantification by standard addition, provided that the validation demonstrates that the results are improved. In case the measurement series includes the same type of sample, the calibration series can be created in the sample or sample extract (‘matrix matched calibration’).

3 MATERIAL

3.1 Common laboratory glassware
3.2 Syringes from 25 to 100 µl for doping isotope-marked fluorine compounds or matrix additives
3.3 Analytical balance with a read-out accuracy of 0.1 mg
3.4 Single-pan balance with a read-out accuracy of 0.01 g
3.5 Set-up for elution of the SPE cartridges
3.6 SPE cartridges with a weak anion exchange phase: e.g. OASIS WAX 6cc cart, 150 mg. Other cartridges can also be used if validated
3.7 Unit for evaporation under nitrogen flow with adjustable flow rate
3.8 LC-MS system consisting of:

- A HPLC or UPLC liquid chromatograph with injection machine, liquid pump, thermostated column and degassing unit.
  Remark: In order to reduce the system blank, an insulator or delay column, placed between LC pump and injector, is highly recommended
- a tandem quadruple mass spectrometer with electrospray ionisation chamber *Remark*: Alternatively, an ion staircase or a high resolution accurate mass (time-of-flight (TOF) or Fourier Transform) mass spectrometer can be used
- a data station for the setting of the instrumental settings, the data acquisition and the data analysis

3.9 LC column:

- e.g. for UPLC: Grace Davison PREVAIL 3µM C18-SELECT COLUMN 150X2.1MM or PREVAIL 5µM C18-SELECT COLUMN 150X2.1MM

4 REAGENTS AND STANDARDS

4.1 Methanol, p.a.
4.2 Acetonitrile p.a.
4.3 Water, ultrapure
4.4 Ammonium acetate p.a.
4.5 NH_3 solution, p.a.: e.g. 25 %
4.6 Ammonia/methanol solution: 0.4 ml of a 25 % NH_3 solution in 99.6 ml methanol

4.7 Stock calibration solutions from native PFAS in methanol: monocomponent stock solutions, purchased or self-produced from the pure substances
4.8 Stock control standard of Native PFAS: this is an independent mixing standard in methanol
4.9 Standard solution of isotope-enriched PFAS (internal standards): it is purchased or produced as a mixing standard solution with individual standards at a concentration of e.g. 400 µg/l. The following isotopic PFAS will be used as a minimum:

Pefluoro-n-[1,2,3-13C1]-propanoic acid	$^{13}C_3$—PFPrA
Perfluoro-n-[1,2,3,4-13C1]-butanoic acid	$^{13}C_4$—PFBA
Perfluoro-n-[1,2,3,4-13C1]-butanesulfonic acid	$^{13}C_3$—PFBS

4.10 Calibration standards: build from native stock calibration solutions PFAS and the standard solution of isotope-enriched PFAS a series of dilutions in acetonitrile/water (1/1) with varying concentrations of Native PFAS, ranging from e.g. 0.1 to 150 µg/l, and constant concentrations of isotope-enriched PFAS of e.g. 4 µg/l; these solutions are re-created for each measurement series
4.11 QC Standards: based on the stock control standard, QC standards are created in acetonitrile/water (1/1) at one or more concentration levels

5 SAMPLE STORAGE

For sample preservation, reference is made to WAC/I/A/010 for sample retention at 4°C in the dark and up to 1 week. Groundwater samples (usually sampled as part of soil research) are shaken upon arrival in the lab and the samples are left to rest for at least 4 hours so that the particles can sink. The samples are then carefully decanted. Not more than half of the top water layer is decanted to minimise the number of particles in operation. Water samples analysed in the context of human consumption shall not be decanted.

6 ANALYSIS PROCEDURE

6.1 EXTRACTION

- Weigh the sample flask with stopper and contents.
- Add an appropriate amount of the standard isotope-labelled PFAS solution so that the theoretical concentration of the IS in the measurement extract is equal to that in the calibration standards.
- Shake it up vigorously.
- An SPE pattern (3.6) is used for extraction. The procedure includes the following steps:
    - condition the SPE cartridge with 4 ml ammonia/MeOH solution
    - condition the SPE cartridge with 4 ml MeOH
    - spool the SPE cartridge with 4 ml ultrapure water be careful not to let the sample dry;
    - transfer the entire sample over the SPE pattern;

- rinse the sample flask with 4 ml of methanol and elude the SPE cartridge with it; catch this fraction;
- rinse the sample flask with 4 ml of methanol/ammonia solution (4.6) and elucidate the SPE cartridge with it; combine this fraction with the previous one;
- If necessary, vaporise the extract under an N_2 current at 40 °C up to 500 µl; do not allow the extract to dry vapour;
- if desired, dilute the extract with ultrapure water and/or acetonitrile; the calibration standards shall be produced in the same solvent mixture as the measuring extracts;
- transfer to a measuring vial;
- determine the volume of the applied sample by reweighing the sample flask with stopper.

Of the extract, 2 µl is typically injected into the LC-MS/MS.

The shelf life of preparations will be 1 month when stored in the refrigerator. Preparations that have been in the refrigerator are best vortexed before placing them in the injection machine.

6.2 MEASUREMENT

6.2.1 LC CONDITIONS

The following are typical settings for a Grace Davison PREVAIL 3µM C18- SELECT 150X2.1MM column.

Typical UPLC settings are:
- mobile phase:
  A= 10mM ammonium acetate (pH 5)
  B= acetonitrile
- flow rate: 0.3 ml/min
- column temperature: 45 °C
- injection volume: 2 µl
- gradient:

Time	A %	B %
min	**%**	**%**
0	98	2
3	98	2
9	60	40
10	5	95
10.5	5	95
11	98	2
15	98	2

Notes:

- The LC analysis can also be done with an HPLC configuration, using a Grace Davison PREVAIL 5µM C18-SELECT COLUMN 150X2.1MM column and gradient elution.

6.2.2 MS CONDITIONS

All recordings are performed with Multiple Reaction Monitoring (MRM), with ionisation via electrospray in negative mode (ES-).

For a Waters Xevo TQ-S, typical settings for the MS acquisition are given below as an example:

Ion Mode:	ES-
Capillary Voltage:	0.5 kV
Cone Voltage:	component dependent
Source Offset:	30 V
Desolvation Temperature:	450 °C
Source Temperature:	150 °C
Desolvation:	1000 L/Hr
Cone:	150 L/Hr
Nebuliser:	7 Bar
Ion Energy1:	1.0
Ion Energy2:	2.0
Collision gas flow:	0.20 ml/min
Collision energy:	component dependent

The following ion transitions are recorded. At the same time, typical UPLC retention times are indicated. The table also shows which isotope marked internal standard can be used for the quantification of the native compound. In order to avoid as many problems as possible of low recovery or dispersion of results (e.g. absorption to container wall or injector and/or matrix submerging/strengthening), efforts should be invested to use as many of the corresponding internal standards as possible.

Compound	**Parent**	**Daughter**		**Cone**	**Collision**	**IS**	**RT**
	m/z	**m/z**	**(Q/q)**	**r**	**r**		**(min)**
TFA	113	69	Q	20	20	13C-PFBA	3.12
PFPrA	163	119	Q	20	10	13C-PFPrA	6.04
PFBA	213	169	Q	30	8	13C-PFBA	8.12
PFPrS	249	80	Q	20	30	13C-PFBS	9.56
PFBS	299	80	Q	50	41	13C-PFBS	10.0
PFBS	299	99	q	50	41	13C-PFBS	10.0
PFEtS	199	80	Q	10	20	13C-PFBS	8.00
TFMS	149	80	Q	20	10	13C-PFBS	5.40
2,3,3,3-TFPA	145	101	Q	10	15	13C-PFBA	3.23
2,2,3,3-TFPA	145	81	q	10	10	13C-PFBA	3.86
2,2,3,3-TFPA	145	81	Q	10	15	13C-PFBA	3.86
13C-PFPrA	166	121	IS	20	10		6.08
13C-PFBA	217	172	IS	30	8		8.15
13C-PFBS	302	80	IS	50	30		10.0

Q: transition for quantification of the component q: transition confirming (qualification) the quantification transition

6.2.3 IDENTIFICATION AND INTEGRATION

Per- and polyfluoroalkyl compounds and internal standards shall be identified on the basis of the criteria for retention times and ion ratios as specified in WAC/VI/A/003.

The identified peaks are integrated using the equipment software and manually verified.

6.3 CALIBRATION

Calibration can be done in a number of different ways (for the quality requirements the calibration must comply with, please refer to WAC/VI/A/003):

- using calibration straight lines. In this case, at the beginning of the analysis series, at least 4 calibration solutions will be analysed with concentrations greater than 0 and spread over the linear area. The lowest concentration will not exceed 2 times the lower limit of the measuring range. The ratios of the concentrations and peak areas of the native PFAS and the corresponding internal standard are deployed on the X-axis and the Y-axis. Then, linear regression will be used to calculate the equation of the calibration straight line. The deviation from each point to the straight line shall not exceed 20 %.

- using quadratic curves. If the linearity test has shown that there is no linear but a square relationship between concentration and response, quadratic curves may be used for calibration. To this end, a minimum of 5 calibration solutions will be analysed at the start of the analysis series with concentrations spread over the measurement area. The lowest concentration will not exceed twice the lower limit of the measuring range. On the X axis and the Y axis, the ratios of respectively the concentrations and peak areas of the native PFAS and the corresponding internal standard will be deployed. The equation of the curve is then calculated by quadratic curve fitting. The deviation from each point to the curve shall not exceed 15 %.

6.4 QUANTIFICATION

For the sample extracts, the transitions are recorded in the same way as described above for the standard solutions. Based on the sample integration values and the calibration straight line/curve determined for the calibration standard, the contents of the different compounds in the sample will be calculated.

Notes:

- The final extract is 1 ml as a rule, the sample volume 50 ml for drinking and surface water and 25 ml for waste water for SPE concentration and 0.5 mL for direct injection.
- If the upper limit of the operating range is exceeded, the extract should be diluted for the determination of the fluorine compound concerned with mobile phase and remeasured. It may be diluted a maximum of 10 times so that the internal standard is still measurable. If the concentrations are so high that it needs to be diluted more than 10 times, fresh internal standard should be added.
- If a sum of PFAS is made then the “lower bound” principle must be applied.
  applied.

7 QUALITY CONTROLS

For the quality requirements relating to calibration, procedure blank, control of sensitivity, control sample, drift control and independent control standard, reference is made to WAC/VI/A/003.

7.1 DISCOVERY OF THE ISOTOPE-MARKED FLUORINE COMPOUNDS

For each sample, the recovery of isotope-marked internal standards is determined, i.e. the experimentally recovered quantity of each of the standards added at the beginning of the analysis. This is achieved by comparing the area of the isotope-enriched compound obtained for the sample (A_{is}(sample)) compared to the surface area obtained for a calibration standard (A_{is}(calibration standard)), where there is approximately the same concentration of native compound as measured in the sample preparation (this to take into account the suppression of the isotope-marked compound signal by the cohesive native compound). The recovery is given by:

$$R\% = A_{is}(sample) * 100 / A_{is}(calibration\ standard)$$

The recovery efficiency depends on sorption phenomena, signal suppression/reinforcement by matrix components and extraction efficiency. For responsible quantification, the recovery efficiency of the ^{13}C-marked fluorine compounds will be between 30 % minimum and 200 % maximal.

Remark:
If a particular internal standard is systematically over-recovery or too low in practice, this need not be mentioned as a deviation from the analytical report, provided that validation data demonstrates that this does not adversely affect the result.

8 REPORTING

Indicate in the analysis report the content of each component in µg/l or ng/l. Also indicate possible determined deviations in the report.