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Commission Notice

Technical guidelines regarding methods of analysis for monitoring of per- and polyfluoroalkyl substances (PFAS) in water intended for human consumption

(C/2024/4910)

Contents

Abbreviations [1]

PFAS	Per- and polyfluoroalkyl substances

Anionic PFAS

PFAAs	Perfluoroalkyl acids
PFCAs	Perfluoroalkyl carboxylic acids
TFA	Trifluoroacetate, also frequent abbreviation for trifluoroacetic acid (TFAA)
PFPrA	Perfluoropropanoic acid
PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid

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[1] For PFAS the nomenclature given in OECD (2021) [2] was applied as far as applicable.

PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFSAs	Perfluoroalkyl sulfonic acids
TFMS	Trifluoromethanesulfonic acid
PFEtS	Perfluoroethanesulfonic acid
PFPrS	Perfluoropropanesulfonic acid
PFBS	Perfluorobutane sulfonic acid
PFPeS	Perfluoropentane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFHpS	Perfluoroheptane sulfonic acid
PFOS	Perfluorooctane sulfonic acid
PFNS	Perfluorononane sulfonic acid
PFDS	Perfluorodecane sulfonic acid
PFUnDS	Perfluoroundecane sulfonic acid
PFDoDS	Perfluorododecane sulfonic acid
PFTrDS	Perfluorotridecane sulfonic acid

Other abbreviations

CIC	Combustion ion chromatography
DWD	Drinking Water Directive (Directive (EU) 2020/2184)
EC	European Commission
EFSA	European Food Safety Authority
EOF	Extractable organically bound fluorine
GC	Gas chromatography
HRMS	High resolution mass spectrometry
ISO	International Organization for Standardization
LC	Liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
SPE	Solid phase extraction
TOP assay	Total oxidisable precursor assay

1. **Introduction**

The Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast) (2) (hereafter 'the Directive' or 'the DWD'), which entered into force on 12 January 2021, introduced parameters and parametric values for per- and polyfluoroalkyl substances (PFAS). These values are 0,50 µg/l (500 ng/l) for the '*PFAS Total*' parameter and 0,10 µg/l (100 ng/l) for the '*Sum of PFAS*' parameter, which covers a list of 20 PFAS (3). Member States are required to comply with these parameters by 12 January 2026 (4). They may include more stringent values or additional parameters in their national laws to transpose this Directive.

In line with Article 13(7) of the DWD and based on a thorough consultation of the Member States, this document establishes the **technical guidelines on the methods of analysis for monitoring PFAS under the '*PFAS Total*' and '*Sum of PFAS*' parameters set by the recast DWD**. These technical guidelines include a selection of analytical methods and approaches considered most appropriate for monitoring those parameters, based on a technical and socio-economic assessment [3].

The substances included in the '*Sum of PFAS*' parameter are listed in paragraph 3 of Part B of Annex III to the Directive.

The '*PFAS Total*' parameter is defined in Annex I to the Directive as 'the totality of per- and polyfluoroalkyl substances'.

There are an increasing number of cases of high PFAS concentrations in freshwater, including drinking water, across the EU. The European Commission therefore encourages Member States to act on these guidelines promptly in order to accelerate the monitoring of PFAS and to design measures to achieve compliance with the DWD parameters.

2. **The DWD provisions on monitoring PFAS**

Article 13(7) of the Directive sets out that 'the Commission shall establish technical guidelines regarding methods of analysis for monitoring of per- and polyfluoroalkyl substances under the parameters "PFAS Total" and "Sum of PFAS", including detection limits, parametric values, and frequency of sampling'.

The requirements for detection limits, parametric value and sampling frequency are detailed below.

2.1. ***Parametric values***

The parametric values are set out in Part B of Annex I to the Directive:

— '*PFAS Total*'	= 0,50 µg/l
— '*Sum of PFAS*'	= 0,10 µg/l

These parametric values have to be complied with at the point of compliance as established in Article 6 of the Directive by 12 January 2026.

2.2. ***Detection limits (limit of quantification)***

The minimum criterion for the limit of quantification (LOQ) is 30 % or less of the parametric value. This requirement is established in Part B of Annex III to the Directive, with reference to the definition of LOQ in Article 2(2) of Commission Directive 2009/90/EC [4].

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(2) Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast) (OJ L 435, 23.12.2020, p. 1).

(3) The parameters and parametric values for PFAS are included in part B of Annex I to the DWD. The list of PFAS included in '*Sum of PFAS*' is provided in paragraph 3 of part B of Annex III.

(4) Article 25 of the recast DWD.

This means that the LOQ should be 30 ng/l (0,03 µg/l) or lower for the '*Sum of PFAS*' parameter and 150 ng/l (0,15 µg/l) or lower for the '*PFAS Total*' parameter. Article 2(2) of Commission Directive 2009/90/EC defines LOQ as 'a stated multiple of the limit of detection (LOD) at a concentration of the determinant that can reasonably be determined with an acceptable level of accuracy and precision. The LOQ can be calculated using an appropriate standard or sample and may be obtained from the lowest calibration point on the calibration curve, excluding the blank'.

The LOQ (or LOD) can only reasonably be calculated for single substances. As the PFAS parametric values for the '*Sum of PFAS*' parameter represents the sum of 20 single substances, a LOQ of 1,5 ng/l or lower for the individual substances is recommended to obtain a meaningful figure for the totality of the 20 PFAS detected (5). For PFHxS, PFOA, PFOS, and PFNA (PFAS of high concern according to the 2020 EFSA evaluation [5]), the target limit of quantification should be well below 1,5 ng/l to reduce potential adverse effects and reflect the high toxicological relevance of the four substances.

2.3. ***Frequency of sampling***

The minimum frequency of sampling and analysis is set out in Table 1 of Part B of Annex II to the Directive. The number of samples depends on the volume of drinking water distributed or produced each day within a given supply zone.

Other sampling frequencies may prove necessary based on the risk assessments of the catchment area and the supply system carried out in accordance with Articles 8 and 9 respectively of the Directive.

3. **Methods of analysis for monitoring the '*Sum of PFAS*'**

3.1. ***Scope of methods***

The '*Sum of PFAS*' parameter as defined in Part B of Annex I to the Directive is a subset of 20 individual PFAS substances (targets) of concern from the many possible PFAS ('*PFAS Total*'). These 20 individual substances are listed under paragraph 3 of Part B of Annex III to the Directive.

The '*Sum of PFAS*' substances contain a perfluoroalkyl moiety with 3 or more carbons (i. e. $–CnF_2n–$, n ≥ 3) or a perfluoroalkylether moiety with 2 or more carbons (i. e. $–CnF_2nOCmF_2m–$, n and m ≥ 1). The overall chain length comprises 4 to 13 carbon atoms with 10 perfluoroalkyl carboxylic acids (PFCAs) and 10 perfluoroalkyl sulfonic acids (PFSAs). *Table 1* shows an overview of the 20 individual PFAS. The parametric value for the sum of all 20 substances is 0,10 µg/l.

Due to this definition in the Directive, the ultrashort-chain PFAS compounds with 2 or 3 carbon atoms are excluded from the '*Sum of PFAS*'. This concerns in particular trifluoroacetic acid (TFA) and perfluoropropanoic acid (PFPrA), as well as trifluoromethanesulfonic acid (TFMS), perfluoroethanesulfonic acid (PFEtS) and perfluoropropanesulfonic acid (PFPrS).

The 20 substances set out under paragraph 3 of Part B of Annex III to the Directive (see *Table 1*) are considered, in the context of these technical guidelines, to include linear and branched isomers. Reported mass concentrations under the Directive should include the sum of all isomers.

Table 1

PFAS listed in paragraph 3 of Part B of Annex III to the Directive that are to be analysed for the reporting of the parametric value of '*Sum of PFAS*' (* Abbreviation not mentioned in the Directive)

Carbon chain length	Perfluoroalkyl carboxylic acids (PFCAs)	Perfluoroalkyl sulfonic acids (PFSAs)
4	Perfluorobutanoic acid (PFBA)	Perfluorobutane sulfonic acid (PFBS)

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(5) To be noted that the current best LOQ that can be achieved for a single PFAS substance is around 0,1 ng/l or even lower (by LC-MS/MS after enrichment, e.g. by EN 17892, Part B).

Carbon chain length	Perfluoroalkyl carboxylic acids (PFCAs)	Perfluoroalkyl sulfonic acids (PFSAs)
5	Perfluoropentanoic acid (PFPA)	Perfluoropentane sulfonic acid (PFPS)
6	Perfluorohexanoic acid (PFHxA)	Perfluorohexane sulfonic acid (PFHxS)
7	Perfluoroheptanoic acid (PFHpA)	Perfluoroheptane sulfonic acid (PFHpS)
8	Perfluorooctanoic acid (PFOA)	Perfluorooctane sulfonic acid (PFOS)
9	Perfluorononanoic acid (PFNA)	Perfluorononane sulfonic acid (PFNS)
10	Perfluorodecanoic acid (PFDA)	Perfluorodecane sulfonic acid (PFDS)
11	Perfluoroundecanoic acid (PFUnDA)	Perfluoroundecane sulfonic acid (PFUnDS)*
12	Perfluorododecanoic acid (PFDoDA)	Perfluorododecane sulfonic acid (PFDoDS)*
13	Perfluorotridecanoic acid (PFTrDA)	Perfluorotridecane sulfonic acid (PFTrDS)*

To carry out an analytical assessment of non-volatile single organic trace substances (targets) with chemical properties like PFAS, the state-of-the-art technology is liquid chromatography-tandem mass spectrometry (LC-MS/MS) (see methods listed under paragraph 3.2. Methods of analysis). Commonly, non-filtered drinking water is analysed following a suitable sampling procedure.

The scope of a method of analysis may include other validated PFAS-like alternatives and PFAS substitutes and similar organic trace substances like fluorotelomer sulfonic acids or perfluorosulfonamides. The user of the method is free to include more substances following a proper validation for each integrated substance, in the understanding that the analytical result for '*Sum of PFAS*' includes only the substances set out in paragraph 3 of Part B of Annex III to the Directive.

3.2. *Methods of analysis*

The methods of analysis should meet the general and specific requirements regarding the parameter '*PFAS*' as set out in Annex III to the Directive. The recommended methods of analysis for the parameter '*Sum of PFAS*' are:

— EN 17892:2024 part A	(LC-MS, direct injection method)
— EN 17892:2024 part B	(LC-MS, SPE enrichment method)

Parts A and B of EN 17892 are designed and validated for all 20 targeted substances included in the '*Sum of PFAS*' parameter in the Directive. EN 17892 is the first standard method which provides full validation from a European interlaboratory trial.

Other equivalent standard methods can be used, provided that they meet the general and specific requirements regarding the '*PFAS*' parameter as set out in Annex III to the Directive.

3.3. *Performance criteria for the methods of analysis*

3.3.1. *Limit of Quantification*

In these guidelines, the LOQ requirement of 30 % of the parametric value (0,10 µg/l), set out in paragraph 1 of Part B of Annex III to the Directive, is considered to achieve an average LOQ of 1,5 ng/l for each of the 20 target compounds, such that it is achievable to measure 30 % (30 ng/l) of the parametric value of '*Sum of PFAS*'.

A survey of European expert laboratories [3] demonstrated that the mean LOQ of all 20 PFAS targets was 1,38 ng/l (rounded 1,4 ng/l) for the direct injection method (part A) and 1,28 ng/L (rounded 1,3 ng/l) for the solid phase extraction (SPE) method (part B). For both methods it showed that they are in principle compliant with Part B of Annex III to the Directive. The user of the method should validate the compliance of the LOQs for the given in-house conditions.

The survey showed that both parts of EN 17892:2024 are able to deliver compliant LOQs with a mean value below 1,5 ng/l. The SPE approach tends to be more sensitive due to the enrichment step included. Laboratories should demonstrate sufficient sensitivity in accordance with the requirements of the Directive and the implemented quality management system (e. g. EN ISO/IEC 17025). Under optimal conditions, LOQs of around 0,1 ng/l or even lower should be achievable. In this ultra-trace concentration range, environmental and laboratory conditions are the limiting factor for very low LOQs.

3.3.2. *Uncertainty of measurement*

The same survey of European expert laboratories [3] also demonstrated that the individual expanded uncertainties of measurement can be well below the limit of 50 % as given in the Directive. The mean uncertainties of measurement for the 20 PFAS of '*Sum of PFAS*' lay in the range from 23 % to 31 % with standard deviations between 10 % and 16 % for part A (direct injection). For part B (SPE enrichment) the mean measurement uncertainties ranged from 18 % to 39 % with standard deviations between 5 % and 17 %. The user of the method should validate the compliance of the uncertainties for the given in-house conditions.

4. **Methods of analysis for monitoring 'PFAS Total'**

4.1. *Scope of methods*

The range of substances included in the '*PFAS Total*' parameter is defined in the Directive as '*the totality of per- and polyfluoroalkyl substances*'. The Directive does not provide a more specific definition of the parameter.

The only broadly agreed upon definition of PFAS available when the Directive was adopted was the 2018 OECD technical definition [1]. That definition was revised in 2021, i.e. after the adoption of the Directive [2]; it now includes the substance trifluoroacetic acid (TFA). TFA, an ultrashort-chain PFAS, is a hydrophilic, mobile and persistent substance that primarily enters the water cycle through the degradation of various fluorochemicals and from diffuse contamination sources. There are a lot of different possible sources of TFA in raw water sources including pesticides, refrigerants, sewage treatment and industrial pollution.

The available TFA monitoring results from raw water sources across the Member States indicate that TFA concentrations at the point of compliance may significantly exceed the Directive's '*PFAS Total*' parametric value.

The health effects of TFA are currently being assessed by the World Health Organization (WHO) on the basis of the most recent scientific knowledge. Depending on the results of this assessment, the WHO could issue new recommendations regarding TFA concentrations in drinking water.

This technical guidance includes recommendations on how to deal with TFA under the parameter '*PFAS Total*'.

4.2. *Methods of analysis*

The methods of analysis should take into account both the general and the specific specifications regarding the '*PFAS*' parameter as set out in Annex III to the Directive, '*Specifications for the analysis of parameters*'.

4.2.1. *Methods used as a proxy for ‘PFAS Total’*

At present, no single analytical method is fully capable of covering or quantifying all possible substances in a huge substance class with a broad range of molecular weights as well as various chemical and structural properties. In this respect, every analytical method for organic trace analysis has to be considered to have its own ‘analytical window’ which is broader or narrower. The parameter ‘*PFAS Total*’ is a typical sum parameter and all recommended methods can deliver useful results and a proxy for measuring it. For more information, refer to the full report on the technical and socio-economic assessment [3].

Currently, the methods recommended in these guidelines as proxies for measuring the ‘*PFAS Total*’ parameter are neither standardised nor harmonised; the recommendations cover the principles of analysis but do not provide guidance on preparing the sample:

1. TOP assay (total oxidisable precursor assay)

2. EOF-CIC (combustion ion chromatography (CIC) after extraction of fluorine (EOF))

3. LC-HRMS suspect and non-target analysis (liquid chromatography high resolution mass spectrometry)

1. **TOP assay methods** entail applying oxidation with persulfate in alkaline solution. TOP assay approaches are specifically for PFAS that oxidise to perfluorinated carboxylic acids and pose a very small risk of overestimating the PFAS load at the level of concern. Perfluorinated ether compounds, and possibly other classes, do not oxidise to perfluorinated carboxylic acids. Together with risks for incomplete precursor conversion, there is a high risk of underestimating ‘*PFAS Total*’. All oxidation products need to be quantified and summarised in the proxy analytical result presented as **‘*PFAS Total*$_{TOP}$’ in ng/l.**

2. **EOF-CIC methods** are inclusive and quantitative for ‘*PFAS Total*’ according to the Directive and there is a low risk of underestimating the PFAS load at the level of concern. The current EOF methods include non-PFAS, including CF-groups and inorganic substances e.g. PF_6^-, BF_4^-, and possibly other F^- species. Quantitative results provide extractable fluorine concentrations (**ng/l F**) that need to be converted to a proxy PFAS mass concentration (PFOA mass equivalents are recommended) to be compared with the parametric value. The conversion factor to obtain $PFOA_{eq}$ from fluorine mass concentration is 1,45 (6). A mass concentration of 345 ng/l F corresponds to a mass concentration of 500 ng/l $PFOA_{eq}$. The background of other possible F-compounds is not well studied and may result in the parametric value of 0,50 µg/l (500 ng/l) being exceeded. The proxy analytical results are presented as **‘*PFAS Total*$_{EOF\text{-}CIC,PFOAeq}$’ in ng/l $PFOA_{eq}$.**

3. **LC-HRMS analysis**, as a suspect and non-target PFAS analysis using LC high resolution (HR)MS, does not depend on the availability of individual analytical standards and can thus detect a significantly higher number of compounds than the target analysis (broad analytical window). It is a powerful approach to dealing with unknown contamination, but for the time being the available methods are based partly on science and partly on expert judgement and provide only semi-quantitative results. The selectivity of suspect and non-targeted methods depends on the process workflow of the HRMS data, providing a lower level of specificity than the target analysis. The risk of false negatives and false positives depends on the level of significance with which the detected signals can be reported as confirmed PFAS. The proxy analytical results are presented as ‘***PFAS Total*$_{HRMS}$**’ **in ng/l**.

None of these three proxy methods can accurately quantify the ‘*PFAS Total*’ parameter, but they can provide proxy measurements thereof. For all three methods, sample pretreatment is crucial. In some cases, this stage requires close attention to achieve further harmonisation and validation in future.

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(6) $PFOA_{eq}$ = [Concentration F / (n_F * MW_F)] x MW_{PFOA} = Concentration F * 1,45 (where n_F =15, MW_F = 19 g/mole and MW_{PFOA} = 414 g/mole).

The three proxy methods have not been fully validated for ultrashort-chain PFAS (e.g. TFA) and other organofluorine chemicals, such as fluorinated pharmaceuticals, fluorinated pesticides, and their fluorinated degradation products with at least one -CF_3 or -CF_2- group. Specifically, the recovery for TFA can vary significantly between sample pretreatments. Therefore, it is recommended to verify and document TFA recovery. A mass concentration of 500 ng/l TFA corresponds to a concentration of around 250 ng/l F when calculated using a fluorine-specific method like EOF-CIC, provided a 100 % TFA recovery is achieved. More detailed analytical information is included in the full report on the technical and socio-economic assessment [3].

Reliable data on the uncertainty of measurement and LOQ is still lacking for most of the above methods. This means it is not yet possible to ensure compliance with the analytical performance requirements set out in Part B of Annex III to the Directive for the '*PFAS Total*' parameter. It is therefore recommended to use the proxy methods in conjunction with interlaboratory tests, as well as to develop pretreatments and related data to remove PFAS. It is also recommended to include targets to achieve compliance with the Annex III requirements for '*PFAS Total*'.

4.2.2 *Analytical reporting of 'PFAS Total'*

For the analytical reporting of the results of '*PFAS Total*', the contribution of the ultrashort-chain PFAS TFA in water intended for human consumption should be evaluated, as the TFA concentration could (significantly) exceed the Directive parametric value of '*PFAS Total*'.

The Commission recommends the following approach for reporting analytical results of '*PFAS Total*':

Step 1:	Determine the analytical result for '*PFAS Total*' ([PFAS Total]) by using one of the three recommended proxy methods of analysis, indicating which method has been used ([PFAS $\text{Total}_{\text{TOP}}$], [PFAS $\text{Total}_{\text{EOF-CIC PFOAeq}}$] or [PFAS $\text{Total}_{\text{HRMS}}$]).
Step 2:	Determine the analytical result for the substance TFA ([TFA]) using a targeted method of analysis. The targeted method should comply with the requirements set out in Annex III to the Directive, in particular with the requirements in Part B for the '*PFAS Total*' parameter.
Step 3:	The analytical report includes the reporting of [PFAS Total], [TFA] and [PFAS Total] – [TFA], indicating which proxy method and targeted method have been used.
Step 4:	If [PFAS Total] – [TFA] < 0, it is recommended to mark the reported analytical results in step 3 as inconclusive.

5. **References**

[1] **OECD (2018)**: TOWARD A NEW COMPREHENSIVE GLOBAL DATABASE OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs): Summary report on updating the OECD 2007 list of per- and polyfluoroalkyl substances. Edited by OECD Publishing. Paris (OECD Series on Risk Management, 39).

[2] **OECD (2021)**: Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance. Edited by OECD Publishing. Paris (OECD Series on Risk Management, 61).

[3] Final report on the support for developing and drafting technical guidelines on PFAS substances under the recast Drinking Water Directive, Service contract No 090202/2023/890359/SER/ENV.C.2

[4] **COMMISSION DIRECTIVE 2009/90/EC** of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status (OJ L 201, 1.8.2009, p. 36).

[5] **EFSA (2020):** Risk to human health related to the presence of perfluoroalkyl substances in food (europa.eu)