

Appendix 10:

Procedure for the Analysis of PFAS in Pellets

Global Monitoring Plan on Persistent Organic Pollutants

**PROCEDURE FOR THE ANALYSIS
OF PFAS IN PELLETS**

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Operation Procedure and Methodology

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List of acronyms and abbreviations

μL	Microliters
°C	Celsius degree
ADONA	4,8-dioxa-3H-perfluorononanoic acid
CSIC	Spanish National Research Council
EPA	United States Environmental Protection Agency
ESI(-)	Negative electrospray ionization
g	Gram
GEF	Global Environment Facility
GMP	Global Monitoring Plan
H	Hour
HPLC	High-performance liquid chromatography
IDAEA	Institute of Environmental Assessment and Water Research
IS	Internal standard
L	Litre
LC	Liquid chromatography
LC-MS/MS	Liquid chromatography couple to tandem mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
mL	Millilitres
MLOD	Method limit of detection
MLOQ	Method limit of quantification
ng	Nanograms
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid

PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPeA	Perfluoropentanoic acid
PFTA	Perfluorotetradecanoic acid
PFTTrDA	Perfluorotridecanoic acid
PFUnA	Perfluoroundecanoic acid
PP	Polypropylene
POPs	Persistent Organic Pollutants
SSFA	Small scale funding agreement
SRM	Selected reaction monitoring mode
SUR	Surrogate standard
TFA	Trifluoroacetic acid
TFSA	Trifluoromethanesulfonic acid
UNEP	United Nations Environment Programme

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1. Introduction

This procedure has been elaborated by IDAEA-CSIC to provide support for the implementation of the Global Monitoring Plan (GMP) on Persistent Organic Pollutants (POPs) under the Stockholm Convention. The programme includes the participating countries in Africa, Asia, the Pacific, and Latin America and the Caribbean in the projects financed by the Global Environment Facility (GEF). This procedure is part of the activity 1.1 of the SSFA signed in 2023 between UNEP and CSIC.

The objective of this procedure is to describe the main steps for analysis of PFAS in pellets's surfaces samples. Figure 1 show the main structures of the per- and polyfluoroalkyl substances.

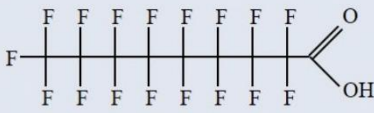


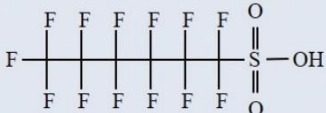


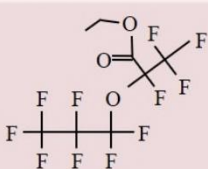
Long Chain	Perfluorononanoic acid (PFNA)	$C_9HF_{17}O_2$	
	Perfluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	
	Perfluorooctane sulfonic acid (PFOS)	$C_8F_{17}SO_3H$	
	Perfluorohexane sulfonic acid (PFHxS)	$C_6HF_{13}O_3S$	
Short Chain	Perfluorobutanoic acid (PFBA)	$C_4HF_7O_2$	
	Perfluorobutane sulfonic acid (PFBS)	$C_4HF_9O_3S$	
	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (GenX)	$C_6HF_{11}O_3$	

Figure 1. Molecular formula of PFAS.

The PFAS that are considered in this document are given in the next table. However, this procedure can be eventually used for other similar compounds:

Table 1. List of PFAS considered in this document

Compound	Acronym	CAS number
Trifluoroacetic acid	TFA	76-05-1
Trifluoromethanesulfonic acid	TFSA	1493-13-6
Perfluorobutanoic acid	PFBA	406-93-9
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluoroundecanoic acid	PFUnA	2058-94-8
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4e

2. Reagents and Materials

- MPFAC-MXG, Wellington Laboratories (Guelph, ON, Canada)
- MFTA-MXA, Wellington Laboratories (Guelph, ON, Canada)
- MPFOSA, Wellington Laboratories (Guelph, ON, Canada)
- Methanol, HPLC grade
- Water, HPLC grade
- Polypropylene tube
- 10 mL graduated cylinder
- Ultrasonic bath
- Laboratory furnace
- Polypropylene flask
- Polypropylene pipette
- Polypropylene Erlenmeyer
- Polypropylene beaker
- Automatic micropipettes
- LC vials with a 250 μ L insert
- HPLC C18 analytical column Hypersil GOLD PFP LC (50 \times 3 μ m) (Thermo Fisher Scientific, San Jose, CA, USA)
- HPLC C8 analytical column BDS Hypersil C8 (50 \times 3) (Thermo Fisher Scientific, San Jose, CA, USA)
- Triple quadrupole mass spectrometer, Thermo Scientific Quantiva triple quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA)

3. Extraction of PFAS from plastic pellets

This chapter describes the main steps for the analysis of PFAS in pellets's surfaces:

1. About 2 g of plastic pellets were exactly weighted in a polypropylene tube.



Figure 2. Plastic samples.

2. Next, 10 mL of methanol was added.
3. PFAS from pellets' surfaces were extracted by ultrasonic-assisted extraction for 10 min.
4. Afterwards, methanol is recovered.
5. This process was repeated twice.
6. All methanol extracts (30 mL) were combined and evaporated until approximately 1 mL of methanol.
7. Then 20 μ L of water was added and the methanol was evaporated.
8. The 20 μ L of water was transferred to an LC vial with a 250 μ L insert, 100 μ L of methanol was used to clean the PP tube and was transferred to the LC vial.
9. Finally, the PP tube was cleaned with 80 μ L of water and transferred to the LC-vial.

10.

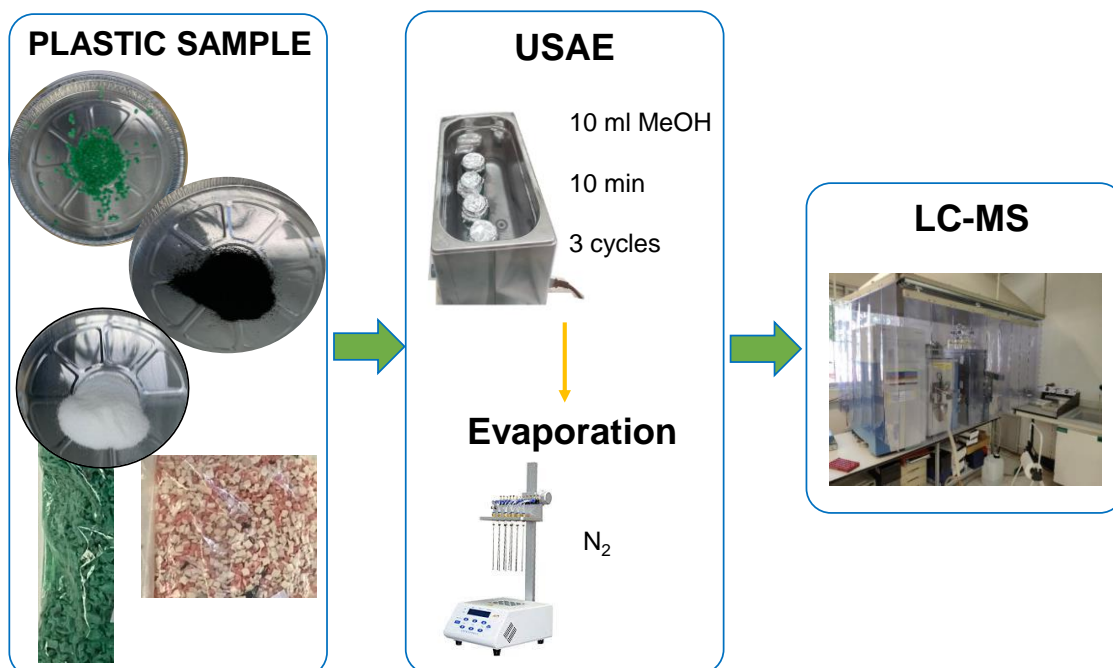


Figure 3. Scheme of the analytical procedure.

4. Analysis by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS)

The chromatographic separation is achieved using a Thermo Scientific Aria TLX-1 system (Thermo Fisher Scientific, Franklin, MA, USA) equipped with a C18 analytical column Hypersil GOLD PFP LC (50 × 3 μm) (Thermo Fisher Scientific, San Jose, CA, USA).

An extra column, BDS Hypersil C8 (50 × 3) (Thermo Fisher Scientific, San Jose, CA, USA), is used after the LC pumps and before the injection system to delay the contamination from the system pumps.

The total run time for each injection (20 μL) is 9 min with a flow rate of 0.4 mL/min. The LC system is coupled to a Thermo Scientific Quantiva triple quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a Heated Ion Spray source.

All analyses were performed operating in the negative electrospray ionization (ESI(-)) mode, and the acquisition relied on selected reaction monitoring mode (SRM) to obtain enough identification points (two transitions for each compound) according to current legislations (Commission Decision, 2002/657/EC).

The linearity, limit of detection (LOD), limit of quantification (LOQ), precision and estimation of measurement uncertainty are assessed in accordance with the

SANTE/12682/2019 Guidelines. Linearity is evaluated by injecting four calibration points in triplicate into a range from 0.004 to 10 ng/L for native standards.

In accordance with EPA, the MLOD is determined using two approaches that were chosen according to the presence or absence of the analytes of interest in the procedural blank. For the first approach, MLODs are estimated as three times the standard deviation of the background concentrations of the procedural blank (n = 10).

In the second case, the MLODs are determined using the lowest spiking level (n = 6). The MLOQ is estimated as the lowest concentration of the sample fortified with acceptable precision, by applying the complete analytical method and identification criteria.

Precision is obtained by using spiking experiments at three concentration levels. Each level was analysed three times on two different days.

The inter-day precision is evaluated as the relative standard deviation for each level and the trueness was obtained from the average recovery for each level.

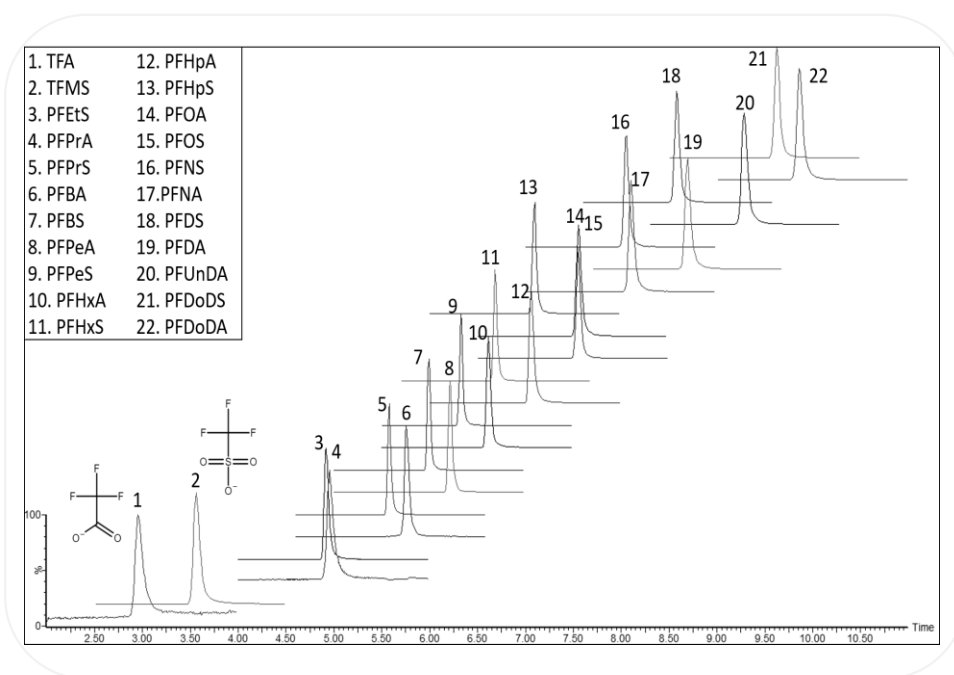


Figure 4. PFAS LC-MS chromatogram

5. Quality control and quality assurance

In order to avoid important cross-contamination and interferences some important analytical measures must be applied:

- ✓ All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by a reagent water rinse. Non-volumetric glassware can be heated in a muffle furnace at 400 °C for 2 h or solvent rinsed. Volumetric glassware should be solvent rinsed and not be heated in an oven above 120 °C. Store clean glassware inverted or capped. Do not cover with aluminium foil because PFAS can be potentially transferred from the aluminium foil to the glassware.
- ✓ PFAS analyte, IS and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers.
- ✓ Method interferences may be caused by contaminants in solvents, reagents, sample bottles and caps, and other sample processing hardware that led to discrete artefacts. PFASs can also be found in many common laboratories supplies and equipment. Therefore, all items such as these must be routinely demonstrated to be free from interferences under the conditions of the analysis by analysing laboratory reagent blanks.

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