METHOD OF ANALYSIS OF PFAS IN LEATHER AND LEATHER PRODUCTS. THE NEW STANDARDS, THE NEW REGULATIONS

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Abstract
Since its publication, the REACH regulation has changed many things in Europe and even in the world. From now on, tanners, manufacturers of leathergoods, control bodies are used to the publication of lists of chemical substances that will be regulated or soon banned. One family of substances is particularly concerned, the PFAS (Perfluoroalkyl and Polyfluoroalkyl Substances). They were generally used as surfactants and are identified as persistent organic pollutants hazardous for humans and the environment. Leather is concerned by these regulations.
In 2006, the first substances of this family, PFOS, were banned. Since then, new families of PFASs have been added on a regular basis, with some stakeholders even calling for a total ban on all PFAS. For 3 years, the CEN standardization groups (leather, footwear and textile) have been working together to establish a coherent list of PFAS, i.e., both concerned by the legislation and potentially used in our fields of activities.
The various works carried out by these standardization groups have identified several inaccuracies that can generate important troubles on the market. This article will describe the present situation,
- The list of PFAS, more than 40 substances are concerned, which carbon chain lengths?
- Which materials, in particular which polymers concerned? which additives
- Which extractions, the ECHA (European Chemical Agency) has confirmed that energetic extractions are necessary
- Which analytical techniques, chromatography of substances or global research of a fluorine index?
- The inventory of the different standard projects in progress.

Keywords: PFAS, standardization, leather, Reach

1. Introduction

Per- and polyfluoroalkyl substances are chemicals that have partially or fully fluorinated carbon chains of various lengths see figure 1. There are several thousands of PFASs and they are widely used in the industries (automotive, aerospace, textile/leather, defence, construction products, electronics, firefighting…). They are stable under a wide range of conditions such as intense heat. Many of them also have surfactant properties and function, e.g., as water and grease repellents.

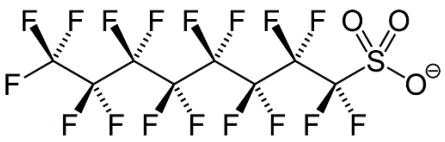


Figure 1 Example of PFAS (PFOS here)

This "fluorine-carbon" chemical bond is one of the most stable chemical bonds in organic chemistry. This means that PFAS do not degrade during use or when released into the environment. these persistent substances will gradually contaminate the soil, water, living organisms and humans.

Without complex and costly decontamination, it is not envisaged that their level will decrease in the environment. Even if all releases of PFASs would cease tomorrow, they would continue to be present in the environment, and humans, for generations to come.

Humans can be exposed to them every day at home, in their workplace and through the environment. PFASs are released into the environment from direct and indirect sources:

- From professional and industrial facilities,
- during use of consumer products (e.g., cosmetics, ski waxes or clothing)
- from food, drinking water

Certain PFASs are known to accumulate in living species and cause toxic effects. Certain PFASs are toxic for reproduction and immuno-toxic. Several PFASs may cause cancer in humans. Some PFASs are also suspected of interfering with the human endocrine (hormonal) system.

This situation has led authorities around the world to put in place restrictions or even bans on PFAS. PFAS are therefore mentioned in different geographical areas (EU, USA, China...), with different legislation, detection limits and analytical methods. The purpose of this article is to clarify the current situation.

2. Which PFASs are concerned?

First of all, it is necessary to define more clearly the terms and abbreviations that are sometimes used imprecisely.

- PFAS: Per- and polyfluoroalkyl substances
- PFSA: Perfluoro sulfonic acids
- PFOA: Perfluorooctanoic acid, most the time include also the salts of PFOA and the related compounds
- PFOS: Perfluorooctane sulfonic acid, most the time include also the salts of PFOS and the parent intermediate Perfluorooctane sulfonyl fluoride (PFOSF)
- PFHxS: Perfluorohexane-1 sulfonic acid
- PFCA: Perfluorocarboxylic acids

PFOA, PFOS, PFHxS and PFCAs are all PFAS.

One important remark, most of the time the substances classified as PFAS are not only molecules composed of Carbon and fluorine. In fact, these chemical products will include a more or less long and more or less fluorinated carbon chain on which chemical functions will be synthesised, for example, carboxylates, amides, amines also called hydrophilic arrowheads. Legislators will therefore be confronted with an extremely complex and varied chemistry.

For the European Union, the story of the ban on PFAS began in 2006. The European Directive 2006/122/EC, establishes restrictions on the marketing and use of substances and preparations, for the PFOS. Very quickly this text is included in the Annex XVII of the REACH regulation as the entry 53. The requirements were given as:

- less than 01% for semi-finished products and articles
- 1µg/m² for textile and coated material (for example coated leather or textiles).

In 2011, REACH entry 53 is deleted (regulation 2011/207) and transferred to another worldwide regulation "POP" (persistent organic pollutant, UN Stockholm Convention). Then POP became a European regulation (2019/1021) and a new family of PFAS in included in this text, the PFOA (2020/784 revised 2021/115). The associated requirement is no more than 1mg/kg in articles.

But PFAS are not only persistent chemicals, the European Union has included in Annex XVII of REACH several families of

- PFAS, PFOA (2017/1000), associated requirements: less than 25ppb of PFOA or 1000ppb of substances related to PFOA

- Perfluorocarboxylic acids C 9 to 14 (2021/1297), associated requirements less than 25 ppb for PFCA in C9-C14 or 260 ppb of related substances to C 9 to 14

Very clearly, POP and REACH Annex XVII include in their scope textile and leather materials and therefore clothing, footwear and leather goods. Faced with this complex situation, the marketers have had a major challenge in defining their specifications. The control laboratories quickly had to set up analysis techniques where almost every customer had a personal list of PFAS. To conclude this critical situation, it should be noted that the authorities in charge of market control had also developed their own lists country by country...

In May 2019 in this critical situation, three standardisation groups of the European Committee for Standardisation (CEN) have decided to work together to clarify the situation:

- CEN TC248 WG26 textiles - Test methods for analysis of EC restricted substance
- CENTC289 WG1 Leather - chemical analysis
- CEN TC309 WG2 Footwear – Environmental aspects

After several meetings, they have defined a list of PFAS likely to be present in the products of the leather and textile industries, see table 1. The column 'Law" identifies the legislation (s) concerning the substances.

3. How to analyse the PFOS ?

The publication of the European PFOS Directive in 2006 came as a surprise to the laboratories. The first test methods were coming from the firefighting sector (fire-extinguishing foam). the first test method for PFOS was published in August 2010, CEN TS 15968 "Determination of extractable perfluorooctanesulfonate (PFOS) in coated and impregnated solid articles; liquids and firefighting foams – Method for sampling, extraction and analysis by LC qMS or LC-tandem/MS" (see table 2).

In 2017 with the inclusion of PFAS in Annex XVII of REACH and in the EU POP regulation, more and more manufacturers and distributors requested analyses and CEN TC 289 WG1 (working group in charge of chemical analysis of leather) developed a method that takes into account the specificities of the leather matrix (EN ISO 23702-1:2018), see table 2

Since 2019, the three standardisation groups have tried to standardise the analysis methods. With the number of substances increasing significantly (47 substances and/or families of substances), the chemists have set up two procedures, one for non-volatile substances by liquid chromatography and the other for volatile substances by gas chromatography.

Three standards will be published soon by CEN (see table 2). 2 for textile Fpr EN 17681:2022 parts 1 and 2 and 1 for Leather prEN ISO 27702-1:2022 (known also as IULTCS / IUC 39-1). In a near future 3 other new standards will arrive, 1 for leather prEN ISO 27702-2 (known also as IULTCS / IUC 39- 2) and 2 for footwear (non-volatile and volatile PFAS).

4. Important issues to be addressed

The situation is still complex and despite all the work and efforts made there are still critical grey areas.

Firstly, there are polymers that contain chemically grafted perfluoroalkyl groups also called side chain fluorinated polymers (PFS). Several laboratories have registered "strange tests results" and especially

when there is a problem of pH during the extraction. If the pH is higher than 11, the amount of PFAS can increase dramatically.

After research, it has been shown that 8:2 FTOH ester bonded was present, releasing perfluorohepthyl group after a basic treatment. With a neutral extraction, the PFAS are close to the limit of quantification. The result for the same sample is several thousand ppm with a basic treatment.

The legislation was not fully clear on this subject therefore the 3 standardisation groups have sent an official question to ECHA (European Chemicals Agency). The answer was clear "Articles containing individual PFOA-

related compound or a combination of PFOA-related compounds at concentration above 1 mg/kg (0,0001 % by weight) are not compliant with the POPs Regulation, unless covered by any of the exemptions defined in the Annex I of the POPs Regulation"

Extractable PFAS and grafted PFAS are forbidden. The laboratories have worked to develop a new test method capable of releasing of PFAS chemically bonded to the matrix (see table 2). An interlaboratory trial has been launched in April 2022 to validate this new method. the first results seem encouraging.

It is therefore very likely that the standards currently undergoing final validation (leather: prEN ISO 23702-1 and textiles: prEN 17681) will be revised rapidly to include the hydrolysis method for the quantification of grafted PFAS. This uncertain context has led CEN TC309 WG2 (footwear- environmental aspects) to suspend its work on PFASs until the situation has stabilised.

All the standards mentioned in this article allow for the determination of PFAS on a substance-by- substance basis. Currently, another analytical strategy is being developed, the determination of total fluorine. These methods have been developed mainly for the analysis of PFAS in wastewater.

After mineralisation of the samples, the total fluorine content is determined by various techniques (ICP inductively coupled plasma, ion chromatography, specific detectors, etc.). These screenings allow to demonstrate the absence of fluorine derivatives by the absence of total fluorine. This technique is economically interesting because it allows to define the presence of a large number of substances with a single analysis. However, the limits of quantification must be further improved to meet the low restriction limits of legislation.

Last but not least, the number of banned PFAS will continue to increase. In the future it seems that legislators want to ban PFAS in general. This observation is worldwide, currently legislation is evolving rapidly in the European Union, in the United States & Canada and in Asia.

5. Conclusion

To date, the results recorded in our laboratories [1] suggest that the presence of PFAS in leather has a rare occurrence Often it is technical leather with particular physical-mechanical properties (water repellency, heat stability...) However, the limits of acceptability are extremely low (mg or even µg per kg of leather). Contamination from outside the tannery or polluted raw materials can be a significant source of non-compliance.

Acknowledgements

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Reference

[1] C Bourgeois, Thèse de doctorat de l'université de Lyon, Mise au point de méthodes pour l'analyse de substances mentionnées dans le règlement Européen REACH et potentiellement présentes dans les process et produits de la filère cuir. Formaldéhyde -fluorocarbonés.

Table 1: list of PFAS likely to be present in textile/leather matrices, their regulatory types and applicable test methods

	Type of PFAS	Chemicals			Law	P (%)	L_I (□)	L_{II} ($)	T1 (▲)	T2 (▲)
		symbol	name	CAS No						
1	I. Perfluorinated carboxylic acids	PFHxA	Perfluoro-n-hexanoic acid	307-24-4				Part 1	Part 1	
2		PFOA	Perfluoro-n-octanoic acid	335-67-1	[2] [3]		Part 1	Part 1	Part 1	
3		APFO Na-PFO K-PFO Ag-PFO F-PFO	Perfluoro-n-octanoic salts* - Ammonium pentadecafluorooctanoate - Sodium perfluorooctanoate - Potassium perfluorooctanoate - Silver perfluorooctanoate - Perfluorooctanoyl fluoride	 3825-26-1 335-95-5 2395-00-8 335-93-3 335-60-0	[3]			Part 1	Part 1	
4		8:2 FTS	1H,1H,2H,2H-Perfluorodecanesulfonic acid	39108-34-4	[3]			Part 1	Part 1	
5		Me-PFOA	Methylperfluorooctanoate	376-27-2	[3]					Part 2
6		Et-PFOA	Ethylperfluorooctanoate	3108-24-5	[3]					Part 2
7		PFNA	Perfluoro-n-nonanoic acid	375-95-1	[1] [2]		Part 1	Part 1	Part 1	
8		NH_4-PFN Na-PFN	Perfluoro-n-nonanoic acid salts - Ammonium perfluorononanoate - Sodium perfluorononanoate	 4149-60-4 21049-39-8	[1] [2]				Part 1	
9		PFDA	Perfluoro-n-decanoic acid	335-76-2	[1] [2]			Part 1	Part 1	
10		NH_4-PFD Na-PFD	Perfluoro-n-decanoic acid salts - Ammonium perfluorodecanoate - Sodium perfluorodecanoate	 3830-45-3 3108-42-7	[1] [2]				Part 1	
11		PFUnA	Perfluoroundecanoic acid	2058-94-8	[1] [2]		Part 1	Part 1	Part 1	
12		PFDoA	Perfluorododecanoic acid	307-55-1	[1] [2]		Part 1	Part 1	Part 1	
13		PFTrA	Perfluorotridecanoic acid	72629-94-8	[1] [2]		Part 1	Part 1	Part 1	
14		PFTeA	Perfluorotetradecanoic acid	376-06-7	[1] [2]		Part 1	Part 1	Part 1	
15		PF-3,7-DMOA	Perfluoro (3,7-dimethyloctanoic acid)	172155-07-6	[1]			Part 1	Part 1	
16		4HPFUnA	2H,2H,3H,3H-Heptadecafluoroundecanoic Acid	34598-33-9	[3]			Part 1	Part 1	
17		PFBA	Perfluorobutanoic acid	375-22-4				Part 1	Part 1	
18		PFPeA	Perfluoropentanoic acid	2706-90-3				Part 1	Part 1	
19		PFHpA	Perfluoro-n-heptanoic acid	375-85-9				Part 1	Part 1	
20	II. Perfluorinated sulfonic acids	PFBS	Perfluorobutanesulfonic acid	375-73-5	[2]			Part 1	Part 1	
21		PFHxS	Perfluorohexanesulfonic acid	355-46-4	[2]		Part 1	Part 1	Part 1	
22		PFOS	Perfluorooctanesulfonic acid	1763-23-1	[3]		Part 1	Part 1	Part 1	
23		PFOS-X	Perfluorooctanesulfonicacid salts* $C_8F_{17}SO_2X$ - potassium Perfluorooctane sulfonate - lithium Perfluorooctane sulfonate - ammonium Perfluorooctane sulfonate - bis-2-(hydroxyethyl)ammonium perfluorooctane sulfonate - tetraethyl ammonium heptadecafluorooctane sulfonate	 2795-39-3 29457-72-5 29081-56-9 70225-14-8 56773-42-3	[3]	yes		Part 1	Part 1	
24		PFDS	Perfluorodecanesulfonic acid	335-77-3				Part 1	Part 1	
25		PFHpS	Perfluoroheptane sulfonic acid	375-92-8				Part 1	Part 1	
26	III.Perfluorooctane sulfonamides (FOSA)	PFOSA	Perfluorooctane sulfonamide	754-91-6	[3]	yes		Part 1	Part 1	
27		N-MeFOSA	N-Methylperfluoro-1-octanesulfonamide	31506-32-8	[3]	yes		Part 1	Part 1	
28		N-EtFOSA	N-Ethylperfluoro-1-octanesulfonamide	4151-50-2	[3]	yes		Part 1	Part 1	
29	IV. Perfluoro-octanesulfon amidoethanol (FOSE)	N-MeFOSE	2-(N-methylperlfuoro-1-octanesulfonamideo)-ethanol	24448-09-7	[3]	yes		Part 1	Part 1	Part 2
30		N-EtFOSE	2-(N-Ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	[3]	yes		Part 1	Part 1	Part 2

Table 1: list of PFAS likely to be present in textile/leather matrices, their regulatory types and applicable test methods

	Type of PFAS	Chemicals			Law	P (%)	L_I (□)	L_{II} ($)	T1 (▲)	T2 (▲)
		symbol	name	CAS No						
31	**V. Fluorinated telomer alcohols (FTOH)**	8:2 FTOH	2-Perfluorooctylethanol	678-39-7	[3]			Part 1	Part 1	
32		10:2 FTOH	2-Perfluorodecylethanol	865-86-1	[1]			Part 1	Part 1	
33		4:2 FTOH	2-Perfluorobutylethanol	2043-47-2				Part 1	Part 1	
34		6:2 FTOH	2-Perfluorohexylethanol	647-42-7				Part 1	Part 1	
35	**VI. Fluorinated telomer acrylate (FTA)**	8:2 FTA	1H,1H,2H,2H-Perfluorodecyl acrylate	27905-45-9	[3]					Part 2
36		10:2 FTA	1H,1H,2H,2H-Perfluorododectyl acrylate	17741-60-5	[1]					Part 2
37		6:2 FTA	1H,1H,2H,2H-Perfluorooctyl acrylate	17527-29-6						Part 2
38	**V. Others**	PFOSF	Heptadecafluorooctanesulfonyl fluoride	307-35-7	[3]			Part 1	Part 1	
39		8:2 FTMA	1H,1H,2H,2H-heptadecafluorodecyl methacrylate	1996-88-9	[3]					Part 2
40			1-decanaminium, N-decyl-N, N dimethyl-,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octane sulfonate	251099-16-8	[3]			Part 1	Part 1	
41		HPFO-DA	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	13252-13-6	[2]			Part 1	Part 1	
42		HPFO-DA-X	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid salts and acyl halides - X=F - X=NH4 - X=K	 21062-98-8 62037-80-3 67118-55-2	[2]			Part 1	Part 1	
43		4:2 FTS	1H,1H,2H,2H-Perfluorohexanesulfonic acid	75124-72-4	Part 1			Part 1	Part 1	
44		6:2 FTS	1H,1H,2H,2H-Perfluorooctane sulfonic acid	27619-97-2	Part 1			Part 1	Part 1	
45		10:2 FTS	1H,1H,2H,2H-Perfluorododecanesulfonic acid	120226-60-0	Part 1			Part 1	Part 1	
46		6:2 FTMA	1H,1H,2H,2H-Perfluorooctylmethacrylate	2144-53-8	Part 2					Part 2
47		7HPFHpA	7H-Dodecafluoroheptanoic acid	1546-95-8	Part 1			Part 1	Part 1	

Law

[1] EU regulation 2006/1907 (REACH) annex XVII
[2] REACH Regulation Substances of Very High Concern
[3] Stockholm convention on persistent organic pollutants (POP) annex B

Standard

- P (%) CEN TS 15968:2010 Determination of extractable perfluorooctanesulfonate (PFOS) in coated and impregnated solid articles; liquids and firefighting foams – Method for sampling, extraction and analysis by LCq-MS or LC-tandem/MS
- L_I (□) EN ISO 23702-1:2018 Leather - Organic fluorine – part1 determination of non-volatile compounds content by extraction method using LC-MS/MS
- L_{II} ($) prEN ISO 23702-1:2021 Leather – Per and polyfluoroalkyl substances – part1 determination of non-volatile compounds content by extraction method using LC
- T1 (▲) FprEN 17681-1:2022 Textile and textile products - Organic fluorine – part1 determination of non-volatile compounds by extraction method using LC
- T2 (▲) FprEN 17681-2:2022 Textile and textile products - Organic fluorine – part2 determination of volatile compounds by extraction method using GC

Table 2 : Major technical methods for PFAS analysis

	CEN TS 15968 2010	EN ISO 23702-1: 2018	prEN ISO 23702-1: 2022	Fpr EN 17681-1: 2022	Fpr EN 17681-2: 2022	New method for PFAS and grafted PFAS (2022)
Number of covered PFAS	6 (PFOS and similar substances)	8 (PFOS and PFOA and similar substances)	38 (all types of PFAS)	40 (all types of PFAS)	9 (all types of PFAS)	40 (all types of PFAS)
Sampling:	Leather 2g, cut in pieces of max 25mm² - Textile 2 g, cut in pieces of max 1cm²	Leather 1g	Leather 1g	At least 1g of textile or area 100cm²	At least 1g of textile	At least 1g
Extraction solvent	: 25 ml methanol	10 ml methanol	10 ml methanol	10 ml methanol	10 ml methanol	14ml methanol + 1.4 ml NaOH (pH>11)
Extraction conditions	Ultrasonic bath 2H at 60°C	Ultrasonic bath 1H at 60°C	Ultrasonic bath 2H at 60°C	Ultrasonic bath 2H at 60°C	Ultrasonic bath 2H at 60°C	Ultrasonic bath 1H at 60°C
Clean up,	possible	Not specified	Not specified		Concentration step possible	PH to 6-7 with acetic acid
Calibration	internal standard	internal standard	internal standard	internal standard	internal standard	internal standard
Analysis:	LC-tandem MS or LC-qMS	LC-MS/MS	LC-MS/MS	LC-MS/MS	GC-MS/MS	LC-MS/MS
Performance given in the test method	0.5µg/l of PFOS in the extracted solution	LQ = 0.2 mg/kg	LQ = 2.5 µg/kg	LQ = 2.0 µg/kg	LQ = 10 to 25 ng/ml in the extracted solution	To be defined

LC-qMS or LC-tandem MS or LC-MS/MS liquid chromatography with mass spectroscopy tandem
GC-MS/MS gas chromatography with mass spectroscopy tandem
LQ limit of quantification

Note