

Introduction

PFAS (per- and polyfluoroalkyl substances) are a class of man-made chemical compounds that contain high amounts of fluorine bonded to carbon atoms. A very strong bond that ensures that these substances are not only non-biodegradable, but indestructible in the environment, unfortunately with harmful effects on human health and ecosystems, given their bioaccumulation. For this reason they are called *forever chemicals*.

PFAS were created in the 1930s, with the first compound discovered in 1938 by DuPont chemist Roy J. Plunkett. During an experiment on refrigerants, Plunkett accidentally discovered polytetrafluoroethylene (PTFE), better known as Teflon. Since that time, the chemical industry has developed thousands of PFAS variants, using them in numerous applications. Due to their resistance, they have found use in the production of non-stick pans, electroplating, firefighting foams, medical devices, detergents and even in pizza boxes and baking papers. One of the most widespread uses today are the so-called "Teflon" anti-dirtiness treatments that are applied in various car washes and which unfortunately end up dispersed in the effluents.

The tanning use has never been very significant, except for some sporadic uses as water-repellent or anti-drip, stain-resistant, and non-stick for finishing. There are still available in the market in shoe care products.

Fluorine

Fluorine is a very abundant element on Earth, although it is not present in free elemental form due to its high reactivity. In the earth's crust it is the thirteenth most widespread element, **with an average concentration of about 625 ppm**.

Fluoride is an essential trace element for the human body, although it is required in very low quantities. We find it in toothpastes because it helps prevent cavities, forming fluorapatite, a compound more resistant to acid erosion than the natural hydroxyapatite of the teeth. It also contributes to bone mineralization and can affect bone density, although an excess can be harmful.

There are countless persistent substances that contain organic fluorine and for this reason it is virtually impossible for any analytical laboratory to find such a number of standard references and to define methods capable of identifying them precisely.

Inorganic fluorine

Inorganic fluorine is found in several minerals that contain it, among which the most widespread is fluorite (CaF_2), which has various industrial applications, and Fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$).

Mineral fluorine is widespread and can be present in varying proportions in products of mineral origin such as bentonite, kaolin, dolomite and consequently in some of their derivatives, which we regularly use in the tanning sector such as hydrated lime and magnesium oxide.

Organic fluorine, per- and polyfluorinated substances (PFAS)

Organofluorinated compounds are those that contain at least one carbon-fluorine (C-F) bond and can be either aliphatic or aromatic. This bond is rare in nature and is developed by some plants in the form of fluoroacetate as a defence mechanism against herbivores and by a Gram-positive bacterium *Streptomyces cattleya*, which generates a *fluorinase enzyme*¹ in addition to the antibacterial *4-fluoro-L-threonin*.² Except for a few rare cases similar to this, the organic fluorinated products that we find in the environment have been synthesized and are much more complex.

¹ O'Hagan, David, Christoph Schaffrath, Steven L. Cobb, John T. G. Hamilton and Cormac D. Murphy. "Biochemistry: Biosynthesis of an organofluorine molecule." *Nature* 416 (2002): 279-279.

² Reid KA, Bowden RD, Dasaradhi L, Amin MR, Harper DB. Biosynthesis of fluorinated secondary metabolites by *Streptomyces cattleya*. *Microbiology (Reading)*. 1995 Jun; 141 (Pt 6):1385-1393.

For per- and polyfluorinated substances or PFAS, there are several definitions in the literature, one of the most cited is that of Buck et al. in 2011:³ “... highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1} –”. Perfluorinated substances are those where all hydrogen atoms bonded to aliphatic carbon atoms have been replaced by fluorine, while the definition of polyfluorinated compounds admits the presence of some hydrogen atoms. In the example (Figure 1), pentafluorophenol falls under the definition of perfluorinated, but not under the definition of PFAS. A classic example of a perfluorinated substance is perfluorooctanesulfonic acid (PFOS), while as an example of polyfluorinated we can cite 6:2 fluorotelomersulfonic acid or 4H-PFOS. Both molecules are represented in Figure 2 (fluorine atoms are represented in olive green and hydrogen atoms in white). A few years ago, perfluorooctane compounds like these were called C8.

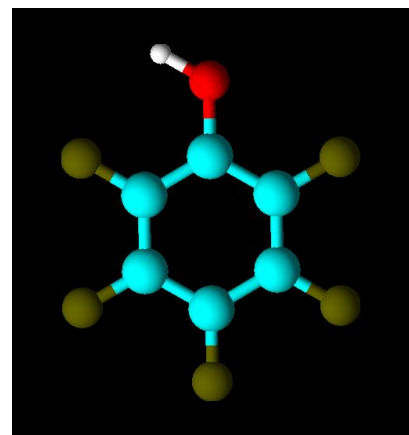


Figure 1 - Pentafluorophenol

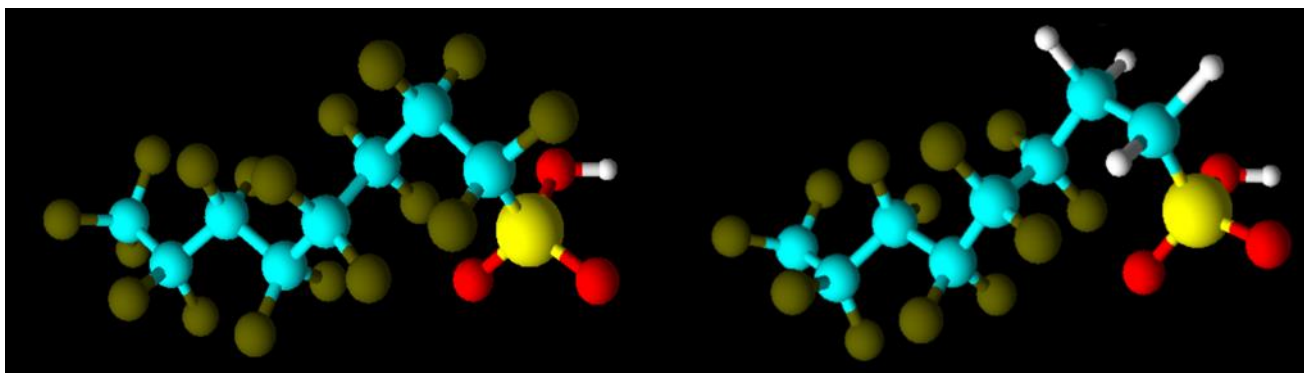


Figure 2 - on the left PFOS (an example of aliphatic perfluorinated), on the right the 6:2 fluorotelomersulfonic acid (an example of aliphatic polyfluorinated). Both molecules fall under the definition of PFAS.

In the report "Poly and perfluoroalkyl substances (PFAS)⁴ of the European Commission, accompanying the document "Chemical strategies for sustainability through a free environment of toxic substances", we read that "... functional groups in PFAS substances can be variable, and this variability explains both the large number of PFAS and their different applications. A 2015 study reported that more than 3,000 PFAS were on the global market for commercial use. In 2018, the OECD found over 4,700 different CAS numbers for PFAS. The number of PFAS commercially produced and used could be even higher, as in some cases their identities are considered confidential business information and impurities and by-products are not declared."

In recent years, the number of substances belonging to the PFAS family that have been limited in official regulations and private specifications has grown in arithmetic progression, imposing new challenges on regulatory commissions, which must provide robust methods to testing laboratories covering a large number of analytes.

³ Buck, Robert C., James Franklin, Urs Berger, Jason M. Conder, Ian T. Cousins, Pim de Voogt, Allan Astrup Jensen, Kurunthachalam Kannan, Scott A. Mabury, and Stefan P. J. van Leeuwen. 2011. "Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins." *Integrated Environmental Assessment and Management* 7 (4):513-541.

⁴ European Commission, Commission staff working document "Poly- and perfluoroalkyl substances (PFAS)" accompanying the document "Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions"- "Chemicals Strategy for Sustainability Towards a Toxic-Free Environment- Brussels, 14.10.2020 SWD(2020) 249 final

International legislation

The legal limitations of organofluorinated compounds are not new: the first date back to 1987 with the Montreal Protocol which imposed the progressive ban of CFCs (chlorofluorocarbons) and the reduction of HCFCs (hydrochlorofluorocarbons), given their harmful action in the ozone layer (which absorbs about 99% of the harmful UV radiation from the Sun, blocking UV-C rays and most UV-B).

As for PFAS, they have been considered highly concerned by the Stockholm Convention (2009, 2019, 2023) which included PFOS and PFOA among persistent organic pollutants (POPs), banning them progressively, and by the EU REACH regulation (Reg. 1907/2006) and subsequent updates that refer to them.

EU Regulation 757-2010 introduced limitations for PFOS by establishing a limit of 0.1% in articles in general and less than 1µg/m² in coated materials and subsequently PFOA was included in EU Regulation 2017/1000, limiting this substance to 25 µg/kg. Recently, EU Regulation 2023/1608 also extended the limits to perfluorohexanesulfonic acid (PFHxS), its salts and derived compounds.

The "Assembly Bill No. 1817" of the state of California⁵, regulates the use of PFAS in clothing (including accessories) by referring to voluntary use and defining it as "... PFAS that a manufacturer has intentionally added to a product and that have a functional or technical effect in the product, including the PFAS components of intentionally added chemicals and PFAS that are intentional breakdown products of an added chemical that also have a functional or technical effect in the product."

The limitations proposed in Assembly Bill No. 1817(g)(2) are as follows:

The presence of PFAS in a product or product component at or above the following thresholds, as measured in total organic fluorine:

(A) Commencing January 1, 2025, 100 parts per million.

(B) Commencing January 1, 2027, 50 parts per million."

The state of New York in SECTION 37-0121 *Prohibition against the use of perfluoroalkyl and polyfluoroalkyl substances in apparel and outdoor apparel for severe wet conditions*, Environmental Conservation (ENV) CHAPTER 43-B, ARTICLE 37, TITLE 1 has established with effect from January 1, 2025 the prohibition of the marketing of clothing ⁶*containing perfluoroalkyl and polyfluoroalkyl substances as intentionally added chemicals" defining intentional use (a) "Intentionally added chemical" means a chemical in a product that serves an intended function or technical effect in the product or product component, including the PFAS within intentionally added chemicals and PFAS that are intentional breakdown products of an added chemical that also have a functional or technical effect in the product or product component.*

Analytical methods for the quantification of PFAS

Several analytical methods have been adopted to comply with the requirements of legislation and the number of prohibited analytes. The first official European method for the determination of PFOS was drawn up by the transversal technical commission CEN/TC 382 created ad hoc to develop the procedure for the determination of PFOS in critical matrices. Given the critical issues encountered in the various sectors, the leather and textile standardization commissions subsequently produced specific analytical methods.

⁵ Assembly Bill No. 1817, Chapter 762 "Product safety: textile articles: perfluoroalkyl and polyfluoroalkyl substances (PFAS). (2021-2022)" (g) (1)

⁶ The Laws of New York, Environmental Conservation (ENV) CHAPTER 43-B, ARTICLE 37, TITLE 1 SECTION 37-0121 "Prohibition against the use of perfluoroalkyl and polyfluoroalkyl substances in apparel and outdoor apparel for severe wet conditions", "1. After January first, two thousand twenty-five, no person shall sell or offer for sale in this state any new, not previously used, apparel containing perfluoroalkyl and polyfluoroalkyl substances as intentionally added chemicals."

CEN/TS 15968:2010 - Determination of extractable perfluorooctanesulphonate (PFOS) in coated and impregnated solid articles, liquids and firefighting foams - Method for sampling, extraction and analysis by LC-qMS or LC-tandem/MS

This method was not suitable for the quantification of PFAS in leather considering its specificity as a material and its misdefinition as a coated material. The CEN/TC 382 committee admitted that it was not applicable⁷, suggesting that CEN/TC 289 (Committee on Skin Normalization) should develop a specific one.

ISO 23702-1:2023 - Leather - Per- and polyfluoroalkyl substances - Part 1: Determination of non-volatile compounds by extraction method using liquid chromatography

This method is indicated for the quantification of ionic PFAS on the skin and admits the possibility of extending the number of analytes beyond PFOS and PFOA.

Analytical methods for the quantification of fluorine

Considering that the OECD report described above, reports that approx. **4700 CAS numbers are identifiable as PFAS** and that Assembly Bill No. 1817 regulates limits based on the content of **Total Organic Fluorine**, it becomes imperative to count with reliable test methods the Fluorine quantification as Total Organic Fluorine.

The official methods currently available, which can be applied to solid or liquid samples, have been developed for environmental matrices and hydrocarbons and allow only the determination of total fluorine. They may serve as a screening for the leather matrix, aware that they are not specific methods. There are no reliable methods developed for the determination of Total Organic Fluorine that consider the criticalities of the skin and the possible impurities that we can find.

The available methods are based on two types of samples' burning:

1. through combustion in the presence of oxygen in closed systems (calorimetric or Mahler bomb) and then analysed in Ion Chromatography,
2. through Combustion Ion Chromatography (CIC) where the sample is burned at 1000°C in the presence of oxygen, absorbed in an aqueous medium and analysed continuously.

EN 14582:2016 - Characterization of waste - Halogen and sulfur content - Oxygen combustion in closed systems and determination methods

This method was developed for environmental matrices and determines the presence of fluorine as well as other halogens and sulfur with combustion in a calorimetric bomb and subsequent quantification in ion chromatography as fluoride.

ASTM D7359-18 Standard Test Method for Total Fluorine, Chlorine and Sulphur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)

This method was developed for hydrocarbons and determines the presence of fluorine as well as other halogens and sulfur with combustion at 1000°C in the presence of oxygen, absorbed in aqueous medium and analyzed in combustion ion chromatography-CIC.

EN 17813:2023 - Environmental solid matrices - Determination of halogens and sulfur by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography

⁷ Revised letter of CEN/TC 382 'PFOS' with respect to CEN/TS 15968 'Determination of extractable perfluorooctane sulfonate (PFOS) in coated and impregnated solid articles, firefighting liquids and foams – Method for sampling, extraction and analysis by LCqMS or LC-tandem/MS' and possible problems with the measurement of PFOS in leather.

This method (analogous to ASTM D7359-18) was developed for environmental matrices and determines the presence of fluorine as well as other halogens and sulphur with combustion at 1000°C in the presence of oxygen, absorbed in aqueous medium and analysed in combustion ion chromatography-CIC.

Preventing fluoride in the tanning industry

Contrary to what happens in other sectors such as textiles where the presence of inorganic fluorine is quite unusual, in the leather process it may come from inorganic or organic contamination and rarely because of voluntary use.

Possible sources of contamination can be the following:

1. Products of mineral origin such as magnesium oxide, dolomite, lime, kaolin, bentonite and other mineral fillers may contain inorganic fluorides in varying proportions.
2. A possible contamination of PFAS surfactants (such as 4H-PFOS, PFOS, PFBS) can be found in chromium salts, obtained from the recycling of electroplating chromium baths.
1. Fluoropolymers and fluorotelomeres can be present in small proportions in finishing compounds or as non-stick agents.
3. Anti-stain or water repellent agents.