

# PFAS

## THE PROBLEM

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## Analytical Approach to Manage PFAS-Related Regulatory Requirements

Perfluoroalkyl substances (PFAS) are a group of several thousand synthetic organic substances characterized by a fully fluorinated hydrophobic alkyl chain of variable length (4-16 carbon atoms) and a hydrophilic end. It is a family containing a very large number of substances.

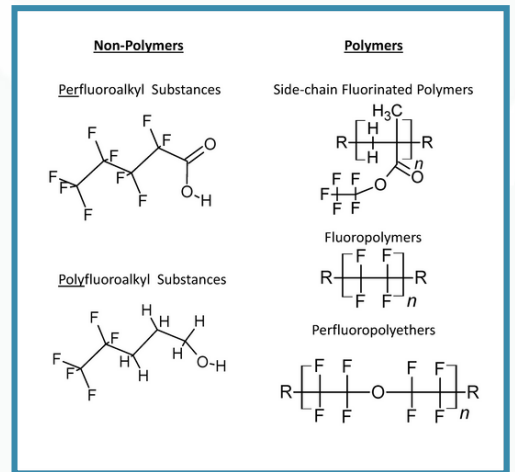
**PPWR Definition:** 'PFAS' means any substance that contains at least one fully fluorinated methyl ( $\text{CF}_3$ -) or methylene ( $-\text{CF}_2-$ ) carbon atom (without any H/Cl/Br/I attached to it), except substances that only contain the following structural elements:  $\text{CF}_3-\text{X}$  or  $\text{X}-\text{CF}_2-\text{X}$ , where X = -OR or -NRR' and X' = methyl (-CH<sub>3</sub>), methylene (-CH<sub>2</sub>-), an aromatic group, a carbonyl group (-C(O)-), -OR'', -SR'' or -NR''R'''; and where R/R'/R''/R''' is a hydrogen (-H), methyl (-CH<sub>3</sub>), methylene (-CH<sub>2</sub>-), an aromatic group or a carbonyl group (-C(O)-).

### Official classifications:

~4700 PFAS with at least 3 perfluorinated Cs [OECD]

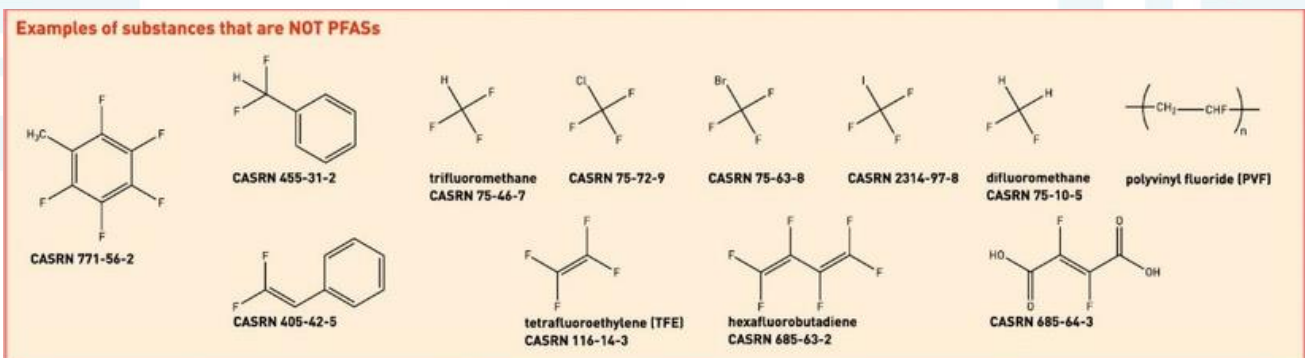
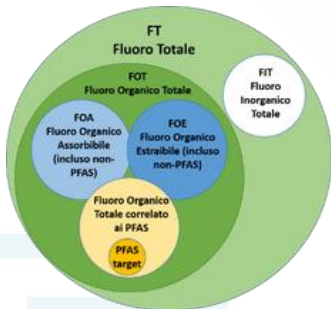
~10700 PFAS Listate for EPA [DSSTox DB]

PFAS are under global scrutiny and content limits in food, water, and consumer goods have currently been published. The entry into force of the new **Packaging and Packaging Waste Regulation (PPWR) 2025/40** provides for even stricter restrictions. To date, many companies on the FCM market have to counter analytical results related to **TOF (Total Organic Fluorine)** values, which is the reference limit in some legislations such as the Danish and Californian ones.



## Why Total Fluorine Is Not Enough?

- Also includes inorganic fluorine that may be present in the sample.
- It is misleading because high total fluorine values do not always correspond to elevated PFAS concentrations in the sample, there are numerous fluorine-containing organic compounds that do not fall within the definition of PFAS, as illustrated for example in the work *Environ. Sci. Technol.* 2021, 55, 23, 15575-15578, which reports the presence of several fluorine-containing organic substances that do not belong to the PFAS class (see image)



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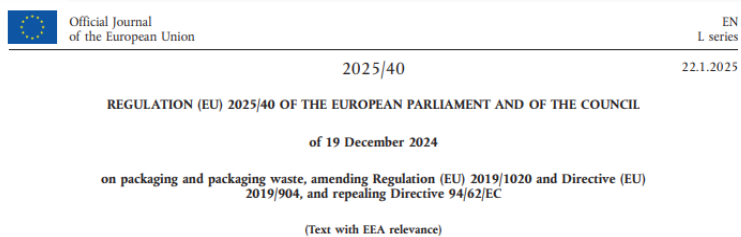
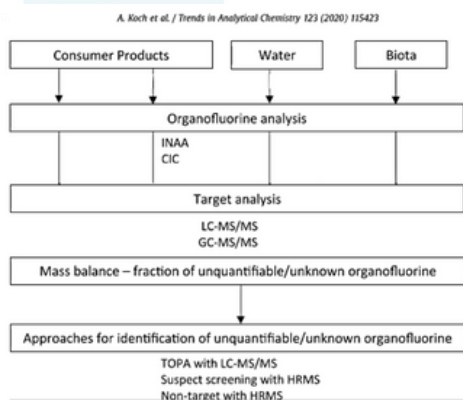


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## Thesis of the supporters of the total Fluorine test

Some theories, now outdated, argued that it was impossible to quantify all PFAS with techniques other than total Fluorine analysis; in Italy, the results of analyses carried out by the European body BEUC and Italian universities were published by the magazines Altroconsumo and Il Salvagente in spring-summer 2021. The analytical approaches stated that "target analyses were only able to determine the substances for which analytical standards are available, yet thousands of PFAS exist." (\*)

## Correct analytical approach dictated by ECHA and introduced in Regulation (EC) 2025/40 – Packaging and Packaging Waste Regulation (PPWR)



- 25 ppb for PFAS measured by targeted PFAS analysis (polymeric PFAS excluded from quantification);
- 250 ppb for the sum of PFAS measured as the sum of targeted PFAS analyses, where applicable, with prior degradation of precursors (polymeric PFAS excluded from quantification); and
- 50 ppm for all PFAS (including polymeric PFAS).

**THE ANALYSIS OF TOTAL FLUORINE ALONE IS NO LONGER SUFFICIENT AS IT IS NON-SPECIFIC AND HAS POOR SENSITIVITY WITH RESPECT TO THE LIMITS IMPOSED BY THE PPWR AND BY FOOD SAFETY RELATED REGULATIONS.**

**The correct approach is to combine targeted and untargeted screening analyses to monitor all compounds classifiable as PFAS.**

Even assuming a TOF value lower than the LOQ of the technique (e.g. 5 mg/kg), and performing stoichiometric calculations to convert this value to a theoretical migration of perfluoroalkyl compounds, **the analysis of total fluorine alone cannot guarantee compliance with the legal limits** imposed by the PPWR and also by Regulation 2022/2388, which sets out the legal limits for the content of PFOS, PFOA, PFNA and PFHxS expressed as µg/kg of fresh weight for certain foods.

## OUR SOLUTION TO THE PROBLEM

Since 2010, Food Contact Center has invested in the study and research of useful solutions to perform the recognition of unknown molecules in screening analysis. Several instrumental libraries have been built, also thanks to the partnership with [SCIEX](#), and university/CNR centers. The analyses, with a screening approach, accredited by the laboratory, are a unique solution on the market and able to solve the criticality highlighted above in the studies published in 2021. (\*)

- **Targeted-untargeted approach**, which combines the target search for the most well-known compounds with untargeted screening by searching for the characteristic marker fragments of PFAS.
- Use of **three different analytical techniques** to detect the presence of perfluorinated compounds with different chemical-physical characteristics: HS-GC-MS, GC-MS and LC-HRMS.
- Use of an **in-house developed spectra database and library** to perform screening analysis in LC-MS/MS with a high-resolution mass spectrometer (AB SCIEX QTOF 4600).
- Determination of the presence of **polymeric PFAS by TOP Assay**: it consists of subjecting the sample to a pre-treatment with an oxidizing agent capable of breaking the polymers into smaller PFAS, which are subsequently identified by chromatographic techniques.

**Currently Food Contact Center is the only Laboratory at a global level to have the accreditation on a**

**Please see: [package of target and untarget screenings of more of > 10.000 PFAS!](#)**

[Accreditation scope](#)

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