# PFAS in Consumer and Related Products – Current Technical and Regulatory Update for ASTM F15.81

ASTM INTERNATIONAL

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# Agenda

- Introductions/ Problem Statement
- ASTM F15.81 Standard Guide
- WHY to Test (and why NOT to Test)?
- WHAT to Test?
- HOW to Test?
- Mission Critical Take Aways

# Introductions

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*Pace® Analytical*
*PFAS Product Manager*

**Rock J. Vitale, CEAC**

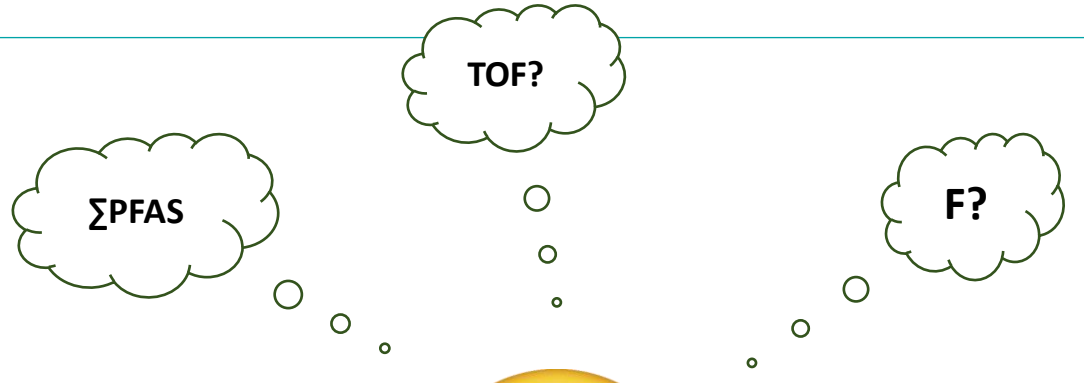
*National PFAS Leader/*
*Senior Principal Chemist*

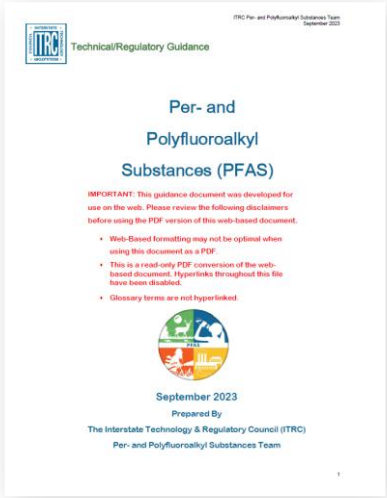
**Jeffrey Stull**

*International Personnel Protection*
*President*

# Problem Statement

- There is a clear understanding of the availability of several domestic and international published/consensus methods to test drinking water, non-potable water, soil/sediment, tissue, and other environmental matrices. However, there is a lack of a consensus understanding (in general) and lack of published test methods that quantify “PFAS” in ***Consumer and Related Articles***.





Technical/Regulatory Guidance

Per- and Polyfluoroalkyl Substances (PFAS)

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- Web-Based formatting may not be optimal when using this document as a PDF.
- This is a read-only PDF conversion of the web-based document. Hyperlinks throughout this file have been disabled.
- Glossary terms are not hyperlinked.

September 2023

Prepared By

The Interstate Technology & Regulatory Council (ITRC)

Per- and Polyfluoroalkyl Substances Team


Designation: E3302 - 21

Standard Guide for PFAS Analytical Methods Selection[1]

# ASTM F15.81

## Members and Steering Committee

- **Members**: 168 members; 370+ participants
- **Represented**: Manufacturing, distribution/retail, associations, laboratory, consulting, academia, regulatory
- **Steering Committee**: Jeff Stull and Rock Vitale (Co-Chairs) and Nick Nigro (Secretary); Molly Lynyak (ASTM Staff Manager)
- **Charter:**
  - As of July 2022, the majority of the analytical approaches that have been developed for measuring PFAS have focused on low molecular weight PFAS in environmental samples.
  - Consensus that there is a lack of consistent and validated extraction/leaching/preparatory methods for application to these highly variable Consumer and related material matrices.

# ASTM F15.81

## Work Item in Balloting Process Now

WK83978 Standard Guide for Selecting and Applying Analytical Methods to Evaluate PFAS in Consumer and Related Products

## Two Additional ASTM F15.81 Work Items in Process

WK88581 Standard Test Method for Determination of Extractable Per- and Polyfluoroalkyl Substances (PFAS) in Solid Matrices by Solvent Extraction, Filtering and followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

WK90492 New Test Method for Total Organic Fluorine (TOF) in Solid Matrices by Solvent Extraction followed by Combustion Ion Chromatography (CIC)

# ASTM F15.81 WK83978 Standard Guide for Selecting and Applying Analytical Methods to Evaluate PFAS in Consumer and Related Products

- **Section 1:** Scope
- **Section 2:** Referenced Documents
- **Section 3:** Terminology
- **Section 4:** Significance and Use
- **Section 5:** Project Planning Considerations
- **Section 6:** Sample Preparation Considerations
- **Section 7:** Analytical Method Considerations
- **Section 8:** Data Review and Interpretation Considerations

# WHY Test for PFAS? – Key Concepts

**“Intentionally Added”-** PFAS that a manufacturer has **intentionally added** to a product and has 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 has a functional or technical effect in the product.

## Why Intentionally Add PFAS to Products?

- Water-repellent and anti-condensation
- Oil and stain-repellent
- Chemically inert and biocompatible
- Non-stick and slippery • High temperature stability
- Electrically insulating and flame retardant
- Resistant to ultraviolet (UV) light • Oxidation resistant

# PFAS Definition – Overview

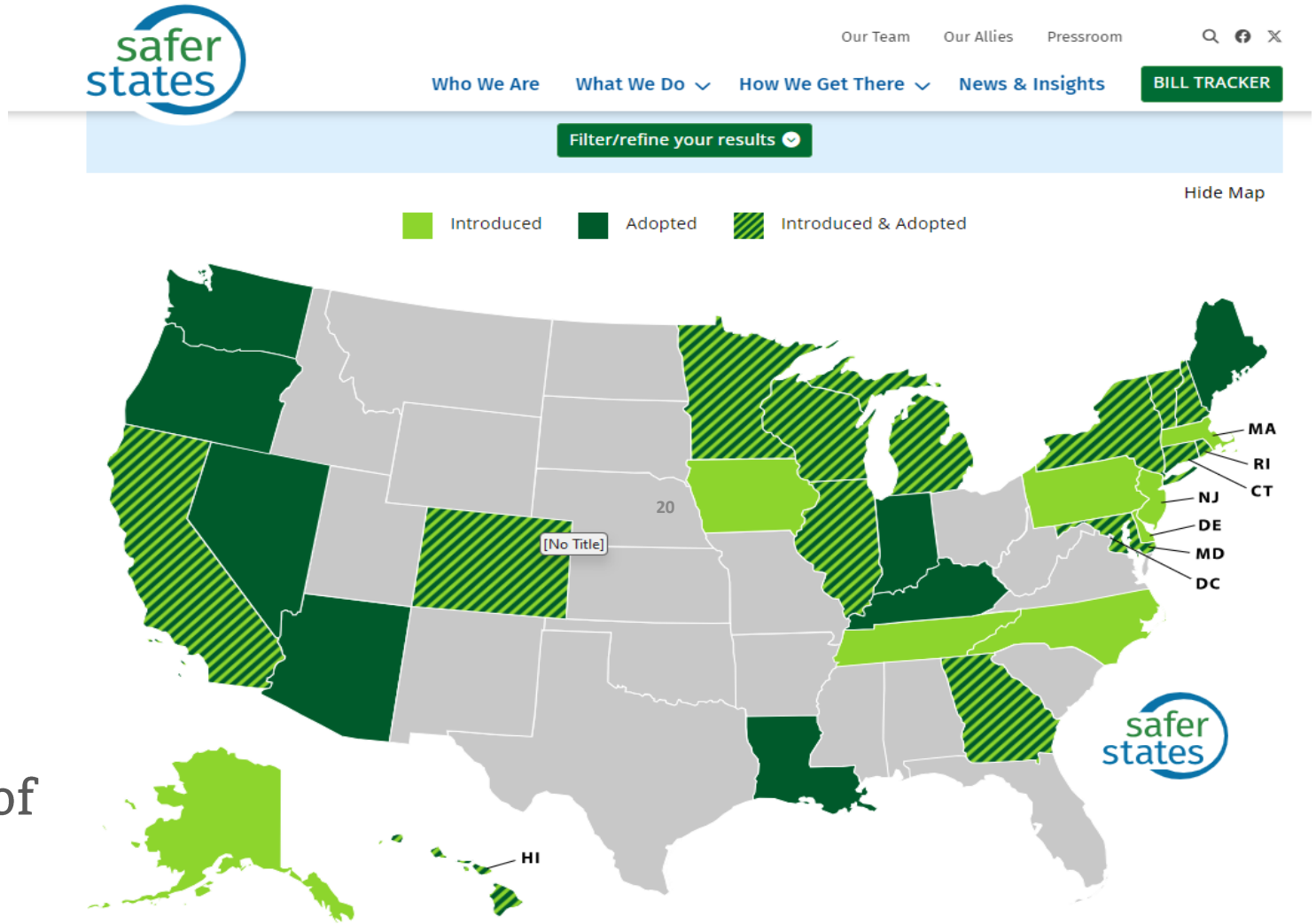
| SOURCE | Key Definition | HOW MANY? |
|---|---|---|
| **Buck et al. (2011)** | **One** or more carbon atom that are bound to three F atoms ($-CF_3$). Must be saturated with no double or triple bonds. **Must be "commercially relevant."** | 268 (excludes fluoropolymers) |
| **OECD 2018** | **Three** carbon atoms on which all H replaced by F. Inter alia. | 4,729 |
| **OECD 2021 and ECHA 2023 (proposed)** | **One** or more carbon atom that are bound to two ($-CF_2$) or three F atoms ($-CF_3$). Inter alia. | >7 million (PubChem, based on OECD definition) |
| **California AB 1200 (and many NGOs)** | "a class of fluorinated organic chemicals containing at least **one fully fluorinated** carbon atom."<br><br>NOTE: this is their PFAS definition, but PFAS are only ***regulated*** if (a) intentionally added, or (b) >100 ppm TOF. | MANY |
| **US EPA** | Original EPA OPPT "Working Definition": at least **two adjacent carbon atoms**, where one is fully fluorinated and the other is at least partially fluorinated.<br><br>**Most recently (2023), EPA eliminated its definition, citing that it will look at the definition on a case-by-case basis, depending on the context and regulatory program that is being considered.** | Program-dependent (2023) |

# Why does the Definition for PFAS Matter?

- Can the definition be specific to a jurisdiction or regulation?
- Will differing definitions result in widely disparate or confused interpretation?
- Without clear definition, will it be difficult to design toxicological studies for PFAS as a Class?
- Without a clear definition, will it be difficult to develop or determine appropriate analytical methods?

# Why Test for PFAS ? What are Data Being Used For?

- Compliance with Regulations
- Diligence/Prudence - Evaluating supply chain and manufacturing applicability
- Legal Proceedings - For example: NGO class actions
- Treatment/Removal- Assessing the feasibility of replacement chemistries



# Other Reasons WHY to Test?

1. Fill data gaps, questions, or uncertainties associated with a product at its intermediate or finished stages.
2. Evaluate the presence of PFAS in a product relative to viable exposure (use) scenarios.
3. Determine how to optimize a manufacturing process.

## EXAMPLES: Why NOT to Test?

- TRI Reporting? (Only 15 of 196 compounds can be analyzed for.)
- TSCA Reporting? (Only 15 of >12,000 compounds can be analyzed for.)

# WHY to Test?

## Comply with a current or pending future regulation.

- Example of phase-out guide:

**PHASEOUT GUIDANCE**

Version 01 | 2023

https://afirm-group.com/

# PER- & POLYFLUOROALKYL SUBSTANCES (PFAS)

### Purpose

This document serves as a guideline for brands, manufacturers, and suppliers of raw materials and chemicals to align on a common approach and definition for the phaseout of PFAS from materials used in the production of apparel, footwear, accessories, and related products.

It includes a harmonized implementation and verification approach based on supply chain communication, documentation, and laboratory analytical testing.

We encourage value chain actors to use this document to demonstrate the elimination of PFAS and conformity with the current AFIRM RSL.[1] Individual AFIRM member brands may have their own policies and expectations related to PFAS elimination since many have already begun transitioning away from or have successfully completed their phaseouts of certain or all PFAS uses.

### What Are PFAS?

**Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are synthetic chemicals defined as "fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS."**

This definition is provided by the Organisation for Economic Co-operation and Development (OECD) which, along with the United States Environmental Protection Agency (U.S. EPA), defines several thousand substances as belonging to the group of PFAS.[2, 3]

New legislation in, e.g., California and New York, defines PFAS more broadly as "fluorinated organic chemicals containing at least one fully fluorinated carbon atom."[4, 5] Since the current OECD, U.S. EPA, and U.S. state definitions are not harmonized, this guidance and the AFIRM RSL employ the broadest possible interpretation of PFAS (i.e., the U.S. state definition) for purposes of testing and compliance.[6]

### Recommended Testing Approach

This guidance recommends a methodology for testing that combines two general analytical approaches, each with two comparable standardized methods included in the AFIRM RSL (Table 3). These methods for performing PFAS analysis[9] are the most widely available among international commercial testing laboratories and come with advantages and disadvantages.

**Table 3. Test Methods Available at Scale**

| Method 1 : Total Fluorine | Method 2 : Organic Solvent Extraction |
|---|---|
| EN 14582:2016 or ASTM D7359:2018 | EN ISO 23702-1 or EN 17681-1:2022 & 17681-2:2022 |
| • Screening method that provides indication of the presence of any Fluorine.<br>• Does not differentiate between inorganic and organic Fluorine.<br>• Does not provide information on the specific Fluorine compounds present. (Total Fluorine content is not the same as PFAS content.)<br>• Best detection limit among global commercial labs is generally 20 ppm;* however, AFIRM specifies a reporting limit of 50 ppm since this is consistently testable across the international commercial lab networks.<br>• Not sufficient to demonstrate compliance with legally regulated PFAS included in the AFIRM RSL; trace amounts of specific PFAS may be present above AFIRM RSL limits without exceeding the 50 ppm reporting limit for Total Fluorine or the 100 ppm regulated limit beginning in 2025. | • Quantitative analysis for specific PFAS substances.<br>• Very selective; reference standards not available for most PFAS.<br>• Harmonized methods to demonstrate compliance with legally regulated PFAS included in the AFIRM RSL.<br>• Low detection limit (10 – 100 ppb) for targeted analytes.<br>• List of target analytes may differ between labs due to availability of reference standards and other factors.<br>• Not a guarantee that PFAS have not been used in production or that PFAS are not present in the sample as contamination: PFAS which are not specifically analyzed may still be present.** |

* Some commercial labs with specialized equipment may be able to reliably measure lower concentrations, but the majority of international commercial labs do not yet have this ability.

** Appendix B of the AFIRM RSL covers the main analytes to expect to find if PFAS chemistry has been intentionally used or if there is significant contamination. AFIRM recommends this harmonized list of PFAS analytes for which to test, quantify, and generate results in test reports.

# What to Test – Textiles Treated with PFAS

Once PFAS is added, it can be released during manufacture, use, and disposal:

- Treatment steps add PFAS to protect against water, stain, and oil. PFAS found in wastewater and dust include PFOA, PFDA and fluorotelomer alcohols as the dominant species.
- The effective repellency of treated cloths during use reduces over time and PFAS can be released from clothing through a number of mechanisms including:
  - Evaporation of volatile and wash-out of water-soluble compounds
  - Abrasion creates the loss of particles and fiber fragments
  - Fluoropolymer (and fragment) loss biotransformation in cleaning wastewater
- Most textiles are disposed of in landfills once no longer useful.
  - Landfill leachate contaminated with PFAS infiltrates through the waste mass in landfills.
  - Scores of PFAS compounds have been measured in anaerobic landfill leachate in moderate per-per-billion levels.

# How to Test

## Targeted Analysis

- Identification of individual target PFAS compounds:
  - FDA has a list of 16 compounds.
  - EPA has a list of 40 compounds.
  - Commercial labs have lists of up to 80 compounds.
- Dependent on available standards for each target – *Note* - some laboratories are obtaining reference standards from non-certified sources.
- Various speciated LC/MS/MS methods
- Total oxidizable precursor assay (TOPs) – This is theoretical, but it is targeted.

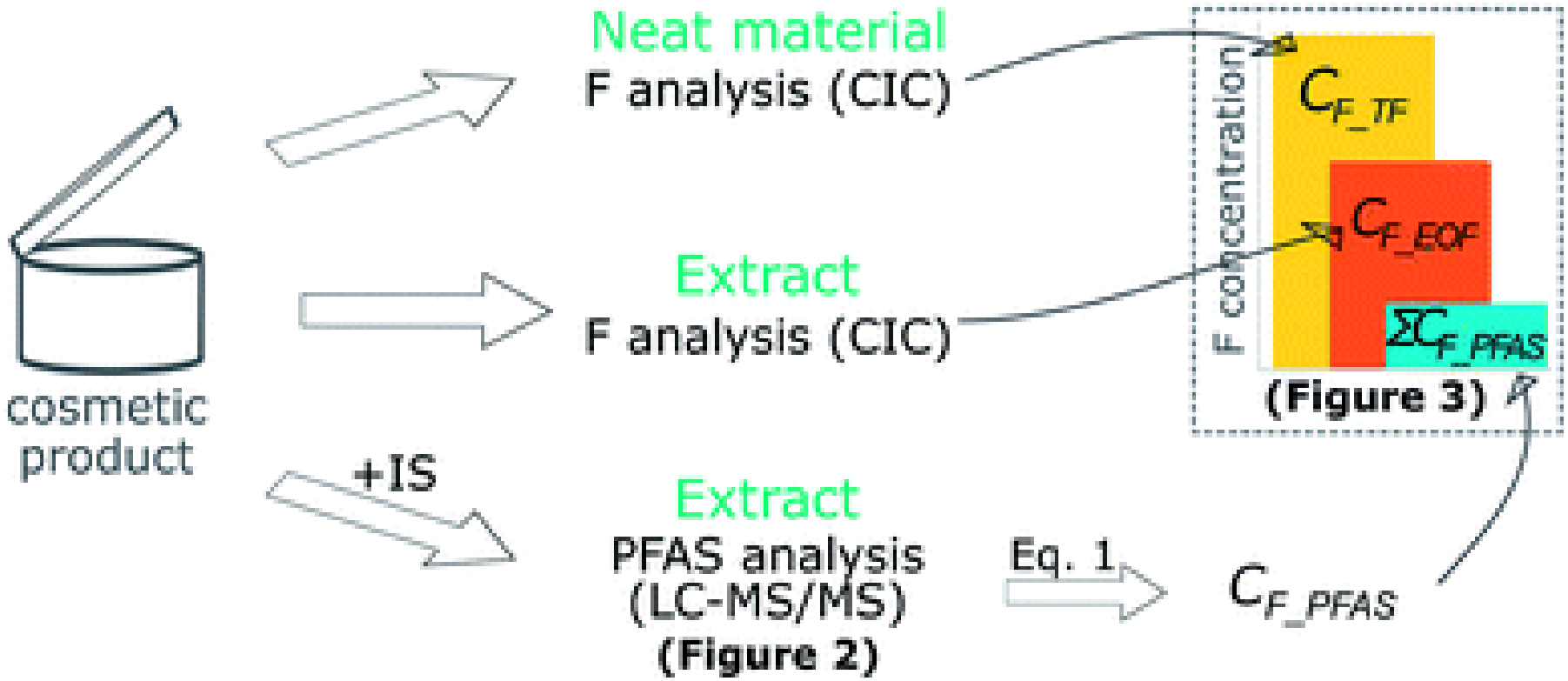
## Non-Targeted Analysis

- Cumulative measurement of both known and unknown PFAS compounds
- Can be used as screening methods in conjunction with LC/MS/MS analysis.
- Total fluorine (TF)
  - Combustion ion chromatography (CIC)
  - Particle-induced *gamma*-ray emission (PIGE)
  - Neutron activation analysis (NAA)
  - $^{19}F$ nuclear magnetic resonance (NMR) spectroscopy
- Total organic fluorine (TOF) – nothing reliable that includes **all** organic fluorine.

# But FIRST – Solid Sample Cryomilling Preparation for Targeted and Non-Targeted PFAS


Liquid (and semi-liquid) matrices require a much more detailed discussion with Planning Team.

# Non-Targeted Fluorine Methods: Combustion – Ion Chromatography

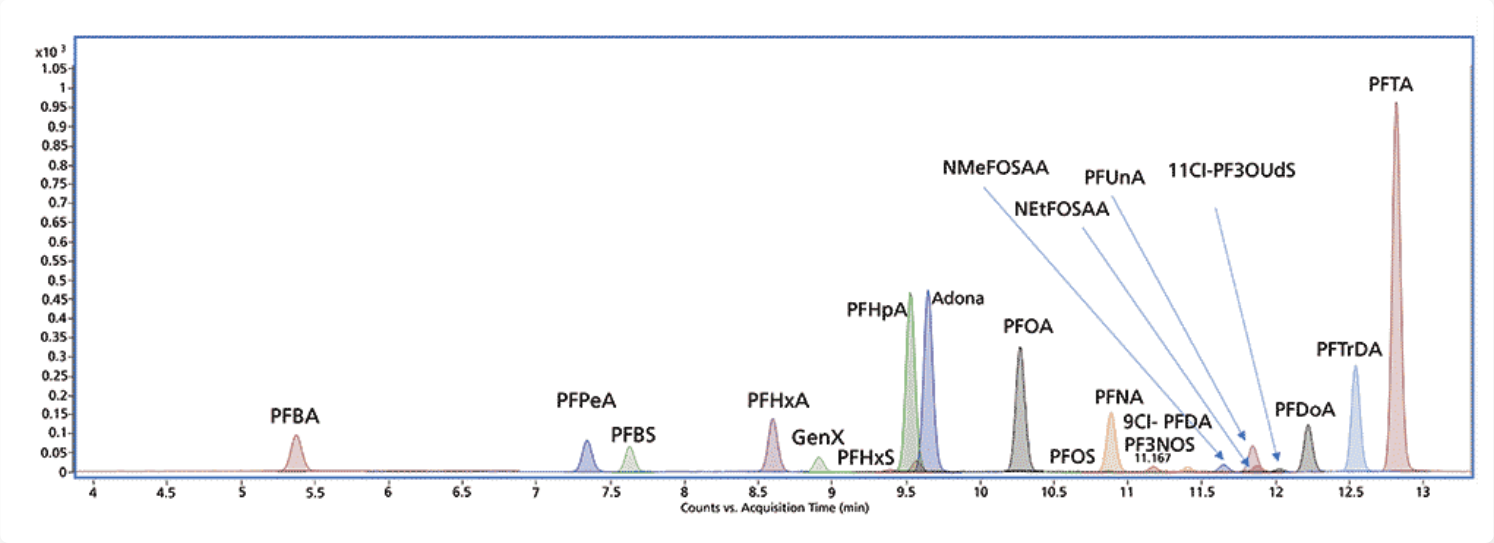



*Per- and polyfluoroalkyl substances and fluorine mass balance in cosmetic products from the Swedish market: implications for environmental emissions and human exposure; Environmental Science, 2018*

# Targeted PFAS Test Methods

- Uses LC/MS/MS
- Requires extraction of “target” compounds into solvent (typically methanol)



# Critical Mission Take-Away Items

- Planning Team needs to establish PFAS project objectives with special attention on sampling and analytical design.
- Include subject-matter experts (SMEs) to plan and execute your project.
- Select the correct published methods, with pros and cons in mind.
    - If you do not use published methods, understand the pros and cons.
- Be skeptical of any and all PFAS or proxy PFAS data until those data are critically validated by qualified professionals, especially when dealing with complex matrices.

# Thank you
# Questions?

ENVIRONMENTAL® STANDARDS
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ASTM INTERNATIONAL
Helping our world work better

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