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# PFAS Analytical Methods, and Impacts for Fluoropolymers

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- 2. Overview of PFAS Family Tree
- 3. Promulgated Methods
- 4. Screening Methods
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- 6. Fluoropolymers
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#### Not All PFAS Are the Same





# Fluoropolymers





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### What constitutes a PFAS?





OECD, 2021 = "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."

USEPA Office of Pollution Prevention and Toxics: Instructions for Reporting PFAS Under TSCA Section 8(a)(7), 2023

1.  $R-(CF_2)-CF(R')R''$ , where both the  $CF_2$  and CF moieties are saturated carbons 2.  $R-CF_2 OCF_2 - R'$ , where R and R' can either be F, O, or saturated carbons 3.  $CF_3 C(CF_3)R'R''$ , where R' and R'' can either be F or saturated carbons

Delaware = "non-polymeric perfluoroalkyl and polyfluoroalkyl substances that are a group of man-made chemicals that contain at least 2 fully fluorinated carbon atoms, excluding gases and volatile liquids"

# What is a PFAS?



| PFAS List                                       | #        |
|---|----------|
| EPA SDWA: Contaminant Candidate<br>List (CCL 5) | 10,239   |
| Industry/commercial products<br>today           | ~600     |
| Target analyte list: academic labs              | ~500     |
| Target analyte list: commercial labs            | ~40 - 70 |
| Standardized methods for soil/wate              | r 40     |
| Toxicity value (human health)                   | ~8       |



PFOS

6:2-FTOH





PTFE





Fluoxetine

# **Analytical Chemistry Methods**



| Screening<br>Methods | EPA Promulgated<br>Methods | Other Test<br>Methods |
|----------------------|----------------------------|-----------------------|
| • TF                 | • 1621 AOF                 | • OTM-45 (SVOC        |
| • TOF                | • 1633                     | • OTM-50 (VFC)        |
| • TOP                | • 537.1                    |                       |
| • PIGE               | • 8327                     |                       |
| • INAA               | • 533                      |                       |
|                      |                            |                       |

# **Screening Methods**



#### > Total fluorine methods:

- > Total Fluorine analysis (TF)
  - Performed by Combustion Ion Chromatography (CIC)
- > Total Organic Fluorine (TOF):
  - > Falls into two areas:
  - Extractable Organic Fluorine (EOF) used for solids
  - Absorbable Organic Fluorine (AOF) used for aqueous samples, mostly drinking water
  - > Measure fluorine/fluoride by CIC

- > Both methods are or can be destructive
- TF measures all fluorine, whether organic or inorganic – from any source(s)
- > TF is not a promulgated method
- > TOF can bifurcate fluorine and fluoride
- > TOF-EOF not a promulgated method
- > TOF-AOF Method 1621
  - > AOF promulgated for DW ONLY
- Potential to measure fluorine from other sources pharma and Ag. chemicals

#### Screening methods – TOF



| Case 1:22-cv-02696-AT Documer  | 1 Filed 04/01/22 Page 1 of 37 |  |
|--|-------------------------------|--|
| UNITED STATES DISTRICT COURT<br>SOUTHERN DISTRICT OF NEW YORK                  |                               |  |
| DEBORAH BROWN, individually and on<br>behalf of all others similarly situated, | Civil Action No.:             |  |
| Plaintiffs,<br>v.  | COMPLAINT FOR DAMAGES         |  |
| COVER GIRL COSMETICS and COTY, INC,  |                               |  |
| Defendants.  | DEMAND FOR JURY TRIAL         |  |
|  | 1                             |  |

Plaintiff Deborah Brown, on behalf of herself and all others similarly situated, files this class action complaint against Defendants Cover Girl Cosmetics and Coty, Inc. On personal knowledge of her own circumstances and upon investigation and information and belief of her counsel, Plaintiff alleges the following:

#### JURISDICTION AND VENUE

This Court has subject matter jurisdiction over this action pursuant to 28 U.S.C. 1. § 1332(d)(2) because this civil action is a class action in which the matter in controversy exceeds \$5,000,000 exclusive of interest and costs, and Plaintiff and members of the putative class are citizens of a state that is different than the states in which Defendants are citizens.

2. Venue is proper in this Court pursuant to 28 U.S.C. § 1391(b) because a substantial part of the events or omissions giving rise to Plaintiff's and the Class Members' claims occurred in this District, and Defendant is subject to the Court's personal jurisdiction.

3. Defendant Coty, Inc. ("Coty") maintains its corporate headquarters in New York, where it directed the activities of designing, developing, advertising, selling, and distributing the cosmetic products described herein to consumers throughout New York, either directly or indirectly through third parties or related entities. Coty obtained the benefits of New York law and profited from New York commerce. Similarly, Defendant Cover Girl Cosmetics ("Cover Girl") advertised, sold, and distributed the cosmetic products described herein to consumers throughout New York, either directly or indirectly through third parties or related entities.

UNITED STATES DISTRICT COURT 5 NORTHERN DISTRICT OF CALIFORNIA 6 BRITTANY BOUNTHON, et al., Case No. 23-cv-00765-AMO Plaintiffs, **ORDER GRANTING IN PART AND** 8 **DENYING IN PART MOTION TO** V. DISMISS SECOND AMENDED 9 **COMPLAINT WITH LEAVE TO** THE PROCTER & GAMBLE COMPANY. **AMEND: GRANTING REOUEST FOR** 10 JUDICIAL NOTICE Defendant. 11 Re: Dkt. Nos. 71, 72 12 13 14 This is one of three proposed class actions raising mislabeling claims based on the presence of per- and polyfluoroalkyl substances ("PFAS") in tampons.<sup>1</sup> Defendant Procter & 15 Gamble Company ("P&G") moves to dismiss the second amended complaint filed by Plaintiffs 16 Britanny Bounthon, Viviana Rivera, and Gina Allen. The Court held a hearing on the matter on 17 18 October 10, 2024. Having considered the papers filed by the parties, the arguments advanced during the hearing, and the relevant legal authority, the motion is GRANTED IN PART AND 19 20 **DENIED IN PART WITH LEAVE TO AMEND** for the reasons set forth below. 21 111 22 111

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# **Screening Methods**



# > Total Oxidizable Precursors (TOP):

- Blasting the matrix with very strong oxidative condition
- Likely marginally applicable to fluorotelomers
- > Theory is to oxidize all "PFAS" to "terminal products"
  - > Terminal products would be fully-fluorinated "PFAS"

- > Not a promulgated method
- TOP conditions not relevant to any environmental or biological process
- Not useful for sites heavily contaminated with fluorotelomers
- Likely limited impact on fullyfluorinated compounds

# **Screening Methods**



### > Surface Methods:

- PIGE = Particle induced gamma emission
- INAA = Instrument Neutron Activation Analysis
- Aiming a beam (gamma or neutron) at the matrix and measuring emission – supposedly emission is proportional to fluorine

- Measures all fluorine, whether fluoride or fluorine
- Measures fluorine from other sources – pharma and Ag.
- Measures fluorine/fluoride only on the surface
- > Not promulgated methods
- > Not readily reproducible



### > EPA Method 1621:

- > Measures TOF via AOF
- > Absorb PFAS onto a matrix, back flush with MeOH
- Method calls for measurement of total fluorine via CIC
- > Applicable to ONLY DW

- > Method is pretty robust
- Modifications" can be made to utilize analytes on 1633 analyte list



## > EPA Method 1633:

- > Measures 40 individual analytes
- > Isotope dilution method
- Promulgated for aqueous, solids, sediments, and complex matrices (with some help)

- > Still some issues with fish tissue
- Eurofins have 70 individual analytes that can be measured with 1633
- Internal standards are not available for all 40 analytes









### > EPA Method 537.1:

- First promulgated method for "PFAS"
- Isotope dilution method
- > 18 individual analytes
- Promulgated for only DW



- Can also be "modified" for complex matrices
- Can be "modified" to 40 analytes under 1633



# > EPA Method 533:

- > Measures 25 individual analytes
- Promulgated for only DW
- > Isotope dilution method
- Can be "modified" in a number of ways:
  - > 1633 list of individual analytes
  - > 537.1 combo adds 4 analytes to make 29
  - > For complex matrices

# > Additional thoughts:

Method does not have a full list of internal standards



# **Other Test Methods - OTMs**



#### **)** OTM-45 – SVOC:

- Measurement of selected PFAS from stationary sources
- > Measures >50 individual analytes
- Samples withdrawn iso-kinetically from stream and collected in sample probe
- Maybe used for federally or local enforcement programs..."

- Method does not have a full list of internal standards
- > Not a promulgated method
- > Third-party validation
- > Reproducibility questions
- Variability in SOP for sample collection

# **Other Test Methods - OTMs**



#### > OTM-50 – VFCs:

- Volatile Fluorinated Chemicals (VFCs) from stationary sources
- > Uses a passive stainless-steel cannister with absorbent
- Measures 30 individual analytes
- Maybe used for federally or local enforcement programs..."

- Method does not mention internal standards
- > Not a promulgated method
- > Third-party validation
- Reproducibility questions

# **Non-Targeted Analysis (NTA)**



- > Fluorinated chemicals that are outside any typical analyte list
- > EPA ORD and others have performed this analysis
- Not entirely a random screening
- Analyze for exact Mw; extrapolate to elemental analysis; propose structure(s)

- > Not a promulgated method
- > Some judgment required
- > Internal standards

# Fluoropolymers



# Gel Permeation Chromatography (GPC)

- > GPC Mw, MWD, oligomeric content
- > Method can be modified
- > GC-MS residual monomers
- Extraction followed by LC-MS leaching test
- > <sup>1</sup>H NMR & <sup>19</sup>F NMR
  - > For individual FPs only

- > Not a promulgated methods
- > SOP variable
- May not be environmentally relevant
- > Life-cycle analysis
- > PLC criteria

### Fluoropolymers



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#### **Critical Review**

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#### A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

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#### Abstract

Fluoropolymers are a distinct class of per- and polyfluoroalkyl substances (PFAS), high molecular weight (MW) polymers with fluorine attached to their carbon-only backbone. Fluoropolymers possess a unique combination of properties and unmatched functional performance critical to the products and manufacturing processes they enable and are irreplaceable in many uses. Fluoropolymers have documented safety profiles; are thermally, biologically, and chemically stable, negligibly soluble in water, nonmobile, nonbioavailable, nonbioaccumulative, and nontoxic. Although fluoropolymers fit the PFAS structural definition, they have very different physical, chemical, environmental, and toxicological properties when compared with other PFAS. This study describes the composition, uses, performance properties, and functionalities of 14 fluoropolymers, including fluoroplastics and fluoroelastomers, and presents data to demonstrate that they satisfy the widely accepted polymer hazard assessment criteria to be considered polymers of low concern (PLC). The PLC criteria include physicochemical properties, such as molecular weight, which determine bioavailability and warn of potential hazard. Fluoropolymers are insoluble (e.g., water, octanol) solids too large to migrate into the cell membrane making them nonbioavailable, and therefore, of low concern from a human and environmental health standpoint. Further, the study results demonstrate that fluoropolymers are a distinct and different group of PFAS and should not be grouped with other PFAS for hazard assessment or regulatory purposes. When combined with an earlier publication by Henry et al., this study demonstrates that commercial fluoropolymers are available from the seven participating companies that meet the criteria to be considered PLC, which represent approximately 96% of the global commercial fluoropolymer market. Integr Environ Assess Manag 2023;19:326-354. © 2022 The Authors. Integrated Environmental Assessment and Management published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Applications, Fluoropolymers, Low concern, PFAS, Property Combinations

#### 316

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#### **Critical Review**

#### A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

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#### ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated substances that are in the focus of researchers and regulators due to widespread presence in the environment and biota, including humans, of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Fluoropolymers, high molecular weight polymers, have unique properties that constitute a distinct class within the PFAS group. Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability. They have negligible residual monomer and oligomer content and low to no leachables. Fluoropolymers are practically insoluble in water and not subject to long-range transport. With a molecular weight well over 100 000 Da, fluoropolymers cannot cross the cell membrane. Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by toxicology studies on polytetrafluoroethylene (PTFE): acute and subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, cytotoxicity, in vitro and in vivo genotoxicity, hemolysis, complement activation, and thrombogenicity. Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity. This paper brings together fluoropolymer toxicity data, human clinical data, and physical, chemical, thermal, and biological data for review and assessment to show that fluoropolymers satisfy widely accepted assessment criteria to be considered as "polymers of low concern" (PLC). This review concludes that fluoropolymers are distinctly different from other polymeric and nonpolymeric PFAS and should be separated from them for hazard assessment or regulatory purposes. Grouping fluoropolymers with all classes of PFAS for "read across" or structure-activity relationship assessment is not scientifically appropriate. Integr Environ Assess Manag 2018;14:316–334. © 2018 The Authors. Integrated Environmental Assessment and Management published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

Keywords: Fluoropolymer International regulation Polytetrafluoroethylene Polymer of low concern PFAS

# **Conclusions and Precautions**



#### > Choose the lab with caution

- > Accreditation(s)
- > ISO and ASTM
- Communication with lab is key matrix interferences
- > Choose the promulgated method with caution
  - > Screen or individual analytes?
  - > How many analytes?
- > Before analysis establish clear objectives from the analysis
- > "PFAS" Analysis = Disclosure
  - > If the analysis is being done for internal knowledge ensure confidentiality
  - > Part of a lawsuit confirmatory analysis replication

# **Conclusions and Precautions (cont.)**



- > MDLs caution when being promised the earth
  - > For complex matrices maybe 0.5 ppb at best
- > Internal standards are limited adds some uncertainty
- > Screening is fine with lots of caveats
  - > These screening methods are NOT a surrogate for individual analyte analysis

# QUESTIONS?

# **IGSI** ENVIRONMENTAL