Beyond the Basics – Total Oxidizable Precursors

BUREAU VERITAS
A GLOBAL LEADER IN TESTING, INSPECTION & CERTIFICATION SERVICES

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A BUSINESS TO BUSINESS TO SOCIETY COMPANY

Bureau Veritas has supported **PFAS** specific projects in Canada and the US for over a decade, providing technical expertise, method development and analytical support to practitioners and stakeholders.

Our North American laboratory network is organized into four operating groups: Environmental, Oil & Petrochemicals, Safety & Specialty Services

OUR MISSION

Shaping a World of Trust by ensuring a responsible progress.

4700	Common estimate across various sources
12000	US EPA Estimates
15000	US EPA CompTox Database
7 Million	PubChem collection of PFAS compounds
21 Million	PubChem collection of Fluorinated compounds
40+	Targeted compounds & limited reference standards

SITE INVESTIGATION

NevaLeek – Liquid and Stain resistant underwear manufacturing company. Suspected site contamination.

Clue # 1

Eyewitness: Observed dumping ooze near building.

Clue # 2

Limited data available - elevated Fluorine.

Clue # 3

Historical fire event – stopped with “*Phyre Phome*”.

Clue # 4

Anonymous tip – follow the *Precursors…?*

SITE INVESTIGATION

NevaLeek – Liquid and Stain resistant underwear manufacturing company. Suspected site contamination.

Liquid and stain resistance of *NevaLeek* underwear

Site history of fire event and suppression

High onsite Fluoride concentrations

Anonymous tip regarding “precursors”…

When you have eliminated the impossible, whatever remains, however improbable, must be the truth – Sherlock Holmes.

PFAS!

EMERGING METHODOLOGY

PRECURSORS

WHAT IS A PRECURSOR?

A PFAS PRECURSOR:

- Chemical compound that can transform into a more **stable**, **persistent** perfluoroalkyl acid (PFAA).
- Less persistent on their own but contribute to **the total amount** of PFAS exposure.
- Can degrade into the more well-know regulated PFAAs, such as **PFOA and PFOS**, through **biological** or **chemical** processes.
- Common examples include fluorotelomer alcohols and sulfonamides.

EMERGING METHODOLOGY

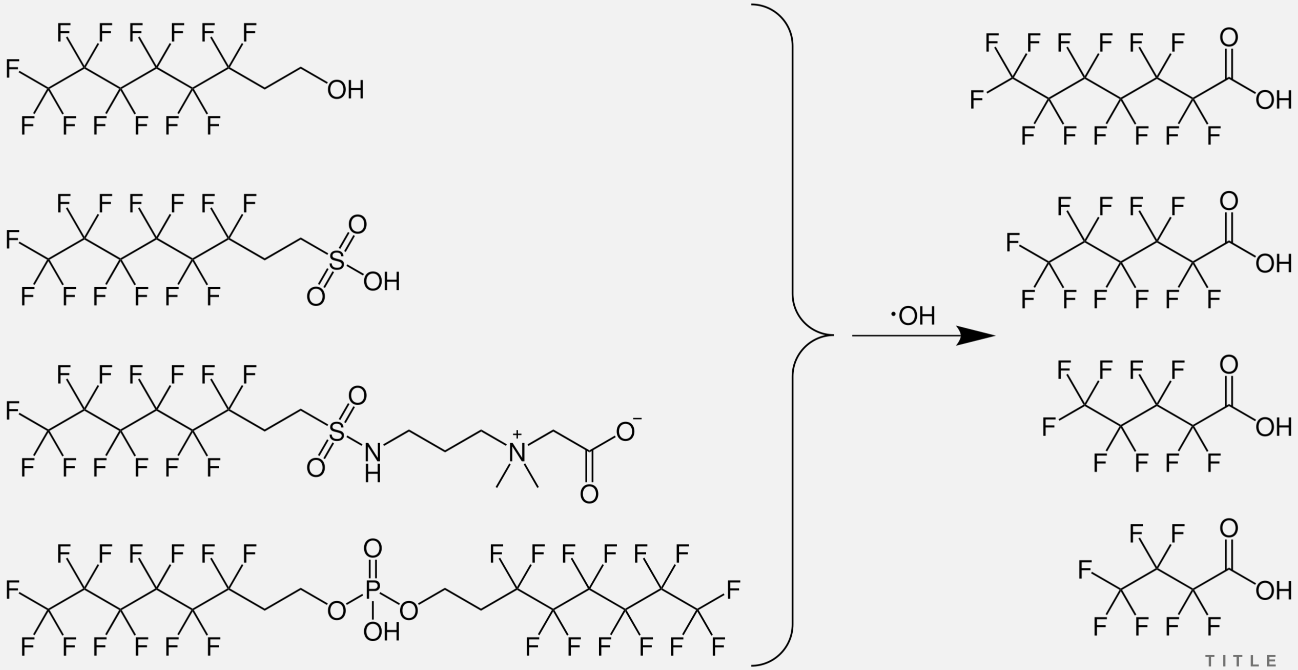
PRECURSORS

WHAT IS A PRECURSOR?

A PFAS PRECURSOR:

- PFAS compounds will transform under **oxidative** conditions to form **measurable** known substances.

Perhaps this can be exploited for investigation?



EMERGING METHODOLOGY

TOTAL OXIDIZABLE PRECURSOR ASSAY

FUNDAMENTALS OF THE TOP ASSAY

ANALYTICAL APPROACH TO QUANTIFY PFAS PRECURSORS

- Measures the difference between PFAS concentrations BEFORE and AFTER oxidation.
- Utilizes a hydroxyl radical-driven oxidative conversion of polyfluorinated precursors to stable perfluorinated acids.
- Can capture PFAS compounds not part of routine parameter lists.
- Provides a potential picture of total PFAS contamination.
- Offers critical information for future risk and remediation planning.
- Known that precursors can often dominate to PFAS burden.

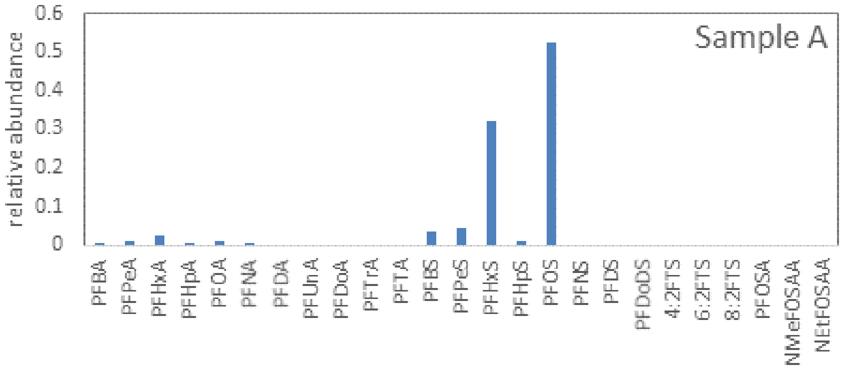
Principle: Oxidize precursors → convert to terminal perfluoroalkyl acids (PFAAs) → measure increase in target PFAAs by LC/MS

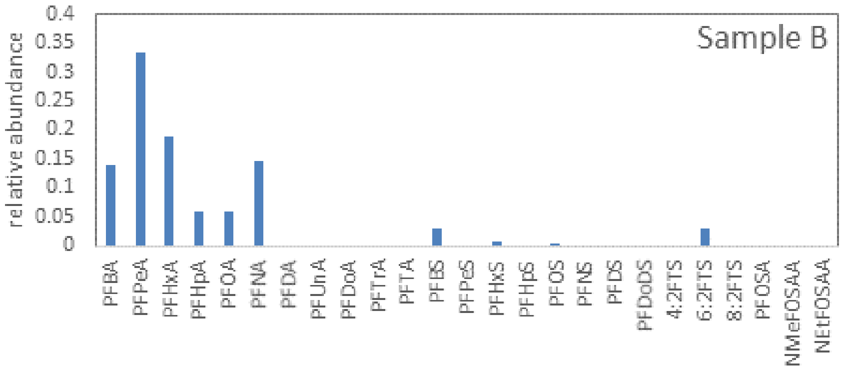
SITE INVESTIGATION

NevaLeek Underwear

Investigative Action

Analyse samples from different areas – let the data tell the story.





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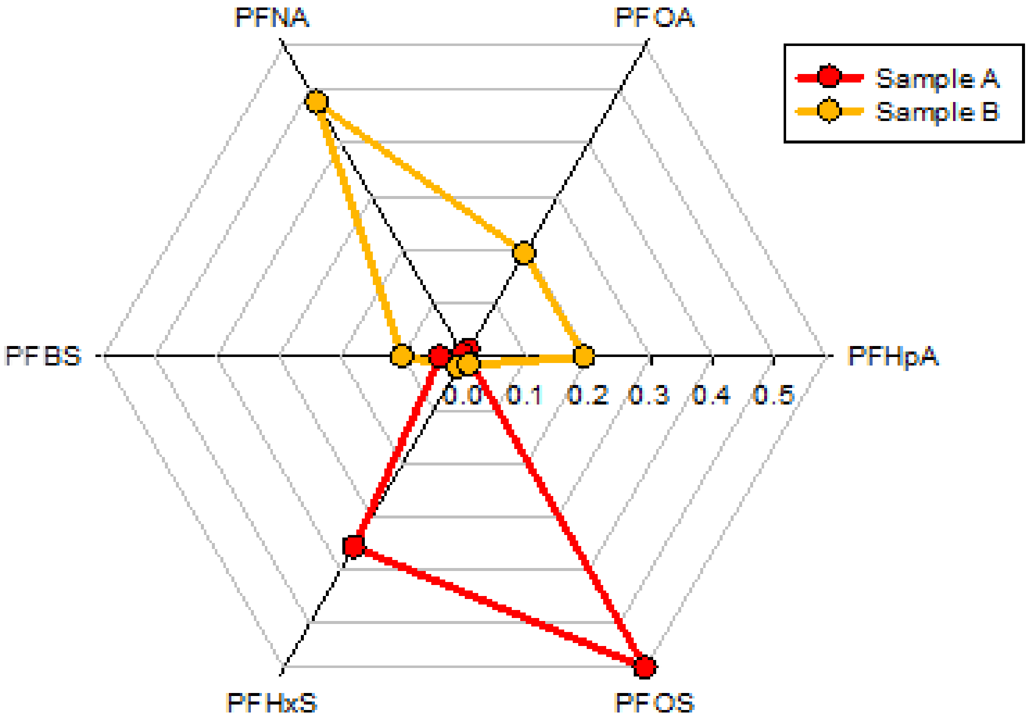

SITE INVESTIGATION

NevaLeek Underwear

Solving the case!

2 distinct sets/patterns of measurable PFAS compounds.

Can compare TOP assay of site samples to those of the product mixes to confirm a match.

Use this evidence to confirm impacts due to contaminant dumping vs fire fighting.

Bad guys – caught with their NevaLeak pants down.

SOUNDS EASY!!!

SAMPLING AND PREPARATION

Sample Collection and Preservation:

Environmental samples require appropriate collection and storage protocols to maintain sample integrity

Oxidation Process:

Controlled thermal activation of persulfate generates hydroxyl radicals for precursor conversion

Matrix Preparation:

Different sample types (water, soil, sediment, biota) require specific preparation approaches

Analytical Detection:

Post-oxidation analysis using LC-MS/MS for quantification of formed perfluoroalkyl acids

THE TOP ASSAY PROTOCOL INVOLVES SEVERAL CRITICAL STEPS

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TARGETS MULTIPLE PFAS CLASSES

Short-Chain PFCAs: C4-C7 (perfluorocaboxylic acids)
Long-Chaing PFCAs: 8+

PFSAs: Perfluorosulfonic acids of various lengths

Precursor Compounds: Fluorotelomer alcohols, sulfonamides, and other transformation products

EMERGING METHODOLOGY

TOTAL OXIDIZABLE PRECURSOR ASSAY

CRITICAL CHALLENGES WITH SOILS/SOLIDS

MATRIX EFFECTS

- **Organic Matter interference**
  - Competes for oxidant consumption
  - Reduces oxidation efficiency
  - High TOC soils particularly problematic
- **Mineral interactions**
  - Clay minerals can bind PFAS
  - Iron/Manganese oxides affect oxidation
  - Carbonate buffering affects pH

EXTRACTION EFFICIENCY ISSUES

- Incomplete extraction of precursors from soil particles
- Strong sorption to organic matter
- Heterogeneous distribution in samples

OXIDATION CHALLENGES

- Incomplete oxidation of complex precursors
- Scavenging effects – Matrix components consume oxidant
- Variable recovery – depending on precursor structure

ANALYTICAL INTERFERENCES

- High Background, Ion suppression on LCMS, Co-extracted matrix components

EMERGING METHODOLOGY

TOTAL OXIDIZABLE PRECURSOR ASSAY

DIVING DEEPER INTO SOIL CHALLENGES

HIGH ORGANIC SOILS
- **Problem**: Oxidant scavenging reduces efficiency to <30%
- **Solution**: Increase persulfate 2-5x, consider pre-treatment

CLAY-RICH SOILS
- **Problem**: Strong PFAS sorption; difficult extraction
- **Solution**: Aggressive extraction (elevated temp, longer time), consider ion-pairing agents

CALCEROUS SOILS
- **Problem**: pH buffering interferes with alkaline oxidation
- **Solution**: Increase base concentration, monitor pH during oxidation

HETEROGENEOUS SAMPLES
- **Problem**: Variable results from subsampling
- **Solution**: Larger sample mass; homogenization; multiple replicates

NOT SIMPLY A "*ONE SIZE FITS ALL*" METHOD APPROACH

EMERGING METHODOLOGY

STRATEGIES TO MAXIMIZE OXIDATION & REDUCE MATRIX EFFECTS

Increased Oxidant Concentration

- Use 100-200 mM persulfate (vs standard 50 mM)
- Consider oxidant : sample ratio optimization

Trade-Off: Cost vs Efficiency

Extend Oxidation Time

- Standard: 6 hours → Consider 12-24 hours for soils
- Monitor oxidation kinetics for specific matrices

Trade-Off: Increased TATs

Enhanced Extraction

- Multi-step extraction: Sequential extractions with fresh solvent
- Solvent selection: Methanol, acetonitrile, or mixtures
- Assisted extraction: Sonication, elevated temperature

Trade-Off: Increased costs

Sample Cleanup

- SPE (Solid phase extraction): Remove interfering organics
- Activated carbon treatment: Remove bulk organic matter
- Dilution: Reduce matrix effects

Trade-Off: May remove PFAS & reduces sensitivity

Matrix-Matched Calibration

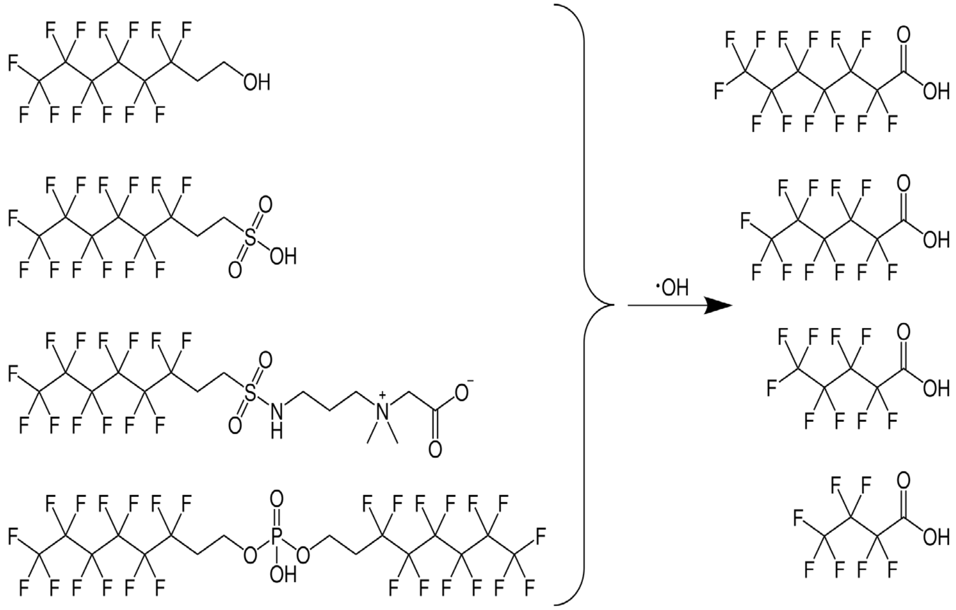
- Use soil extracts for calibration standards
- Accounts for matrix-specific suppression/enhancement

EMERGING METHODOLOGY

APPLICATION OF THE PFAS TOOL KIT

ANALYTICAL NEED	PFAS BY LC/MS/MS	TOPS ASSAY	TOF BY CIC
Regulatory compliance	✓		
Site characterization	✓	(✓)	
Contaminant delineation	✓	✓	(✓)
Completeness of remedial actions	(✓)	✓	✓
Site risk (Future liability)		✓	✓
PFAS-Free AFFF			✓

EMERGING METHODOLOGY **PRECURSORS**



PRECURSOR TRANSFORMATION PATHWAYS

The **TOP Assay** can provide insights into the broader environmental behaviour of **PFAS** by simulating oxidative transformation processes that may occur naturally or under specific conditions (e.g. remediation efforts) in environmental systems.

Source Identification – Distinguishing between direct PFAS releases and in-situ precursor transformation

Fate Modelling – Predicting long-term environmental behavior of PFAS contamination

Remediation Planning – Designing effective treatment strategies that address both target PFAS and their precursors

REGULATORY CONSIDERATIONS

CURRENT STATUS - EVOLVING

- No standardized method yet (as of today)
- EPA interest – Mentioned in PFAS Action plans
- State-level – Some US States (MI, MA) discussing inclusion in guidance
- International – European agencies exploring for risk assessment

EMERGING TRENDS

- Likely future requirement for comprehensive site investigations
- Data gaps – Regulators recognize direct measurement misses significant contamination
- As regulation expands – growing reliance on summed parameters and total measurements
- Precautionary approach – TOP assay supports conservative risk assessment

IMPLICATIONS FOR CONSULTANTS

- Proactive inclusion in Phase II ESAs recommended
- Data interpretation challenges – need to communicate uncertainties
- Cost considerations

TOP Assay is essential for comprehensive PFAS assessment – but has its limitations

Matrix effects are a challenge – require method optimization for soils

Maximizing Oxidation requires increased oxidant, extended time and careful sample preparation

Need to consider major precursor classes (FTOH, FOSA, diPAPs etc in interpretation

Regulatory landscape is evolving – expect increased use

Communication remains key – identify the uncertainties to stakeholders

Questions?

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