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OMNIPHOBIA AND ANALYTICAL CHALLENGES OF PFAS IN POLYMERS

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ABSTRACT

The unique fluid – repellent properties of modern synthetic polymers owe their existence to the physical phenomenon of omniphobicity-the simultaneous rejection of both aqueous and organic fluid phases. Per-and polyfluoroalkyl substances (PFAS) represents the chemical zenith of this attribute. Due to the extreme electronegativity and compact atomic radius of fluorine, fluorinated polymer matrices exhibit ultra-low surface free energy, exceptional thermal endurance, and profound chemical inertness. These characteristics make fluoropolymers irreplaceable across industrial processing equipment, specialized analytical tubing, and implantable biomedical devices. The very physical manifestation that makes per-and polyfluoroalkyl substances (PFAS) indispensable in polymer engineering-their profound omniphobicity-creates a severe analytical paradox during liquid chromatography-tandem mass spectrometry (LC-MS/MS) determination. The ultra-low surface free energy, amphiphilic partition coefficients, pervasive environmental presence, and chemical resistance of PFAS introduce severe hurdles throughout sample solubilisation, solid-phase extraction, fluidic transport, ionization, and mass filtering. This treatise explores the critical analytical vulnerabilities encountered when extracting and quantifying trace fluorochemicals from complex polymeric architectures under the thematic lens of omniphobic surface interactions. This paper explores the underlying molecular architecture of PFAS-driven omniphobicity, details its critical role in bio-interface engineering and leachable management, and evaluates the material science hurdles currently facing non-fluorinated alternatives.

KEYWORDS: Ominiphobicity; Fluoropolymers; PFAS Extraction; LC-MS/MS; Matrix Interference.

A. Introduction and Molecular Foundations:[1]

In surface chemistry and soft-matter physics, the term omniphobicity denotes a surface state capable of resisting wetting by liquids across the entire spectrum of surface tensions- high-tensions polar liquids like pure water (72.8mN/m) to low-tension nonpolar hydrocarbons and lipids (20-30mN/m). Achieving this dual repellency requires a material surface with an exceptionally low solid surface energy (γ_{sv}) typically below 18mN/m.

$$= = C\text{-}CF_2 - CF_2 - CF_2 - CF_2 = = \text{ [Highly stable C-F Backbone]}$$

Per-and polyfluoroalkyl substances (PFAS) deliver this capability through the unique structural dynamics of the carbon-fluorine (C-F) bond:

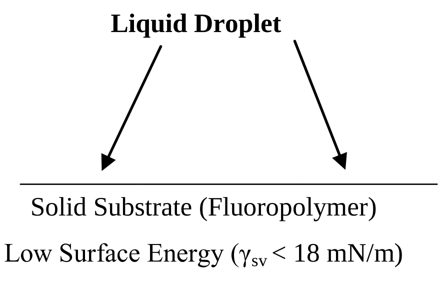
1. **Bond Dissociation Energy:** The C-F bond is among the strongest single bonds in covalent chemistry (~ 485 kJ/ mol). The severe electronegativity of the fluorine atom draws electron density away from the carbon center, yielding pronounced ionic character that resists thermal and chemical cleavage.
2. **Steric Shielding:** The unshared electron pairs of fluorine form a rigid, highly dense electron sheath surrounding the carbon backbone. In fully fluorinated polymers such as Polytetrafluoroethylene (PTFE), this steric constraint forces the carbon chain into a helical conformation, shielding the core from nucleophilic or electrophilic attack.
3. **Low Polarizability:** Fluorine's tightly bound electrons exhibit minimal polarizability. As a consequence, dispersion forces (London forces) between fluoropolymer chains and contacting liquids are drastically reduced, preventing interfacial adhesion and capillary wetting.

B. Omniphoric Behaviour at the Material-Fluid Interface:[2]

The macro –scale expression of omniphobicity is governed by the Young-Dupre balance and modified by surface morphology as described by the Wenzel and Cassie-Baxter models. For a liquid droplet resting on an ideal, smooth planar substrate, the intrinsic contact angle (θ_γ) is defined by interfacial free energies:

$$\text{Cos } \theta_\gamma = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv}$$

Where γ_{sv}, γ_{sl} and γ_{lv} represent the solid-vapor, soild-liquid and liquid-vapor surface tensions respectively.



To maintain an omniphobic state ($\theta_\gamma > 90^0$) against low-surface-tension organic solvents, γ_{sv} must be substantially lower than γ_{lv}. Fluorocarbon moieties (-CF_2- and –CF_3) lower surface energy down to 6-18mN/m.

1. Re-entrant Topography and Oleophobicity

When dealing with extremely low-tension organic liquids where intrinsic contact angles on smooth surfaces fall below 90^0, physical surface structuring becomes necessary. The creation of micro-scale or nano-scale re-entrant (overhanging or mushroom like) topographies traps an air layer beneath the liquid phase. This metastable Cassie-Baxter state prevents liquid penetration into the surface texture, yielding apparent contact angles exceeding 150^0 and roll –off angles below 10^0.

Material/Coating Class	Surface Energy (mN/m)	Water Contact Angle (θ_{H2o})	Hexadecane Contact Angle (θ_{C16})	Primary Failure Mechanism
Polytetrafluoroethylene (PTFE)	18.5	~115^0	~46^0	Physical mechanical wear
Fluorinated Ethylene Propylene (FEP)	16.5	~118^0	~ 53^0	Creep under sustained load
Perfluoroalkoxy (PFA)	16.0	~120^0	~58^0	High-temperature stress cracking
Omniphobic Nano-textured Surfaces	<10.0	>150^0	>120^0	Mechanical shearing of micro-structures
Nano-Fluorinated Silanes(PDMS)	22.0-25.0	~108^0	<20^0 (wetting)	Swelling in nonpolar Solvents

C. Critical Utility in Polymer Processing & Analytical Systems:[3]

The industrial utility of fluoropolymers extends far beyond simple non-stick coatings. In high-purity fluid transport, polymer extrusion, and analytical sample handling, omniphobicity prevents cross-contamination, biofilm accretion, and mechanical fouling.

[Fluid Stream]

=========================

Fluoropolymer Liner (PFA/PTFE) ⟵ Smooth, Low-Energy Inner Wall (Prevents boundary –layer retention and sorptive carryover)

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1. Fluid Dynamics and Boundary Layer Shear

In fluid delivery channels-such as liquid chromatography feed lines, microfluidic chips and specialized medical tubing-boundary layer friction dictates flow dynamics. Omniphobic channel linings minimize viscous drag and eliminate localized dead-volume zones where fluid stagnation typically occurs.

a. Sorptive Inertness

Fluorinated polymers resist the absorption and adsorption (sorption) of volatile organic compounds (VOCs), lipids and hydrophobic pharmaceutical active ingredients (APIs).

b. Extractable and Leachable (E&L) Integrity

Because fluoropolymers do not require plastifying additives, processing aids, or heavy-metal stabilizers, their baseline extractable profile is exceptionally clean. This eliminates background noise in sensitive mass spectrometry (LC-MS/MS, GC-MS) workflows and protects high-purity medical formulations.

D. Biomedical Imperatives: Bio-Interface Dynamics[4]

PFAS (per-and polyfluoroalkyl substances) are critical to polymer products and biomedical devices primarily due to their extreme chemical inertness, exceptional thermal stability, and uniquely low surface energy. These properties stem from the carbon-fluorine (C-F) bond-one of the strongest single bonds in organic chemistry-making fluoropolymers like PTFE, PVDF, and FEP indispensable in demanding applications.

When a synthetic polymer is introduced into a biological milieu, the initial event occurring within nanoseconds is the adsorption of water molecules and plasma proteins onto the material surface. The composition and structural conformation of this adsorbed protein layer dictate subsequent biological response, including platelet activation, cellular adhesion, and foreign body giant cell reaction.

[Plasma stream: Albumin, Fibrinogen, Platelets]

[Non-Fouling Omniphobic Fluoropolymer Surface]

Result: Supressed Denaturation & Reduced Thrombus Formation

1. Blood-contacting Devices and Hemocompatibility

In vascular grafts, central venous catheters, and structural heart valves, thrombus formation triggered by surface-induces coagulation present a severe clinical challenges. Non-fluorinated hydrophobic polymers tend to adsorb plasma proteins such as fibrinogen in denatured, unfolded conformations, exposing cryptic binding sites that trigger platelet aggregation.

Fluoropolymer surfaces, through their extreme omniphobicity and minimal surface polarizability, reduce the thermodynamic driving force for protein denaturation at the interface. Proteins retain their native, globular conformation, significantly dampening the coagulation cascade and reducing the incidence of deice-induced thrombosis.

2. Resistance to Biofilm and Nosocomial Pathogens

Bacterial adhesion relies on a combination of hydrophobic interactions, electrostatic forces, and outer-membrane appendages (pili and fimbriae). Omniphobic polymers disrupt the initial conditioning film required for bacterial attachment. Lacking a stable anchor, bacteria are easily dislodged by physiological shear stress, preventing the transition from planktonic cells to mature, antibiotic-resistant biofilms on indwelling catheters and surgical implants. In medical tubing, catheters and peristaltic pumps, fluoropolymer linings prevent chemical degradation from aggressive reagents and minimize friction, allowing smooth passage through vessels and tissues without binding.

3. Hydrophobicity & Oleophobicity

PFAS coatings repel both water and lipids. In medical diagnostics, microfluidics, and surgical instruments, this prevents protein fouling, surface contamination, and unwanted fluid retention.

4. Thermal & Sterilization Stability

Medical equipment made with fluoropolymers can withstand harsh, repeated sterilization protocols-including steam autoclaving, gamma radiation, and ethylene dioxide exposure-without polymer chain scission or mechanical failure.

5. Permeability Barriers

In specialized polymer barrier films and pharmaceutical packaging, PFAS –derived materials prevent oxygen and moisture transport, ensuring drug and device shelf-life.

E. Omniphobia in Mass Spectrometry: Analytical Challenges of PFAS Quantification in Polymer Matrices via LC-MS/MS:[5]

1. The Omniphobic Extraction Paradox: Solubilisation and Matrix Disruption

Extracting fluorochemicals locked within synthetic polymers (such as polyethylene, fluoropolymers or thermoplastic elastomers) presents an immediate thermodynamic challenge. The non-stick, oil- and water repellent nature of PFAS drives strong physical entrapment and interfacial sorption within host polymer networks.

- **Solvent Incompatibility and Phase Isolation**

Conventional polar or non-polar extraction solvents struggle to wet highly omniphobic matrices. Dissolving or swelling the polymer, using tetrahydrofuran, dimethylformamide or toluene, often co-extracts low-molecular-weight oligomers, plasticizers and processing additives. When these crude extracts are diluted or exchanged into LC-compatible polar mixtures like methanol with water, the dissolved polymer host undergoes rapid micro precipitation, occluding and co-precipitating the target PFAS analytes.

- **Sorption Hysteresis on Extraction Vessel Walls**

Fluorochemicals liberated during extraction exhibit a high affinity for hydrophobic and omniphobic surfaces. In glass or conventional polymer vessels, carboxylic and sulfonic PFAS analogs adsorb onto vessel walls or aggregate at liquid-gas interfaces, causing significant recovery losses prior to chromatographic introduction.

Analytical Paradox of Omniphobia

[Polymeric Matrix]
PFAS embedded due to chemical inertness
↓
Requires harsh extraction (solubilisation/swelling)

[LC-MS/MS Instrumentation]
PFAS adsorbs to PTFE/PFE lines
Causes background contamination
↓
System blank elevation & severe interfacial sorption hysteresis

2. Systemic Fluorochemical Ubiquity: Instrument Blank Contamination

Unlike typical organic pollutants, PFAS are ubiquitous components of the LC-MS/MS hardware itself, owing to the widespread use of fluoropolymers for chemical resistance and smooth fluidic transport.

- **Fluoropolymer Leaching:** PTFE, FEP and PFA components within LC degasser membranes, pump seals, rotor valves, and internal fluidic tubing continuously leach trace perfluorinated alkyl acids such as PFOA and PFOS into the mobile phase.
- **Chromatographic Co-elution:** System-derived background contaminants co-elute with target analytes from the sample extract, drastically inflating detection limits and distorting isotopic accuracy.
- **Migration (Delay Columns):** To decouple instrument-derived PFAS from sample-derived PFAS, analysts must install an auxiliary delay column (a high-retention C18 column) between the gradient pump and the auto sampler. This delays background PFAS signals, separating them temporally from sample analyte peaks.

[Mobile Phase Reservoir] → [PTFE Instrument Tubing] → [Degasser Membrane]

↓

[Continuous PFAS Leaching]

↓

[Baseline Interferences]

3. Interfacial Phenomena and Chromatographic Separation Challenges

One sample extracts are injected, the omniphobic character of long-chain PFAS continues to complicate liquid chromatography.

Analytical Metric	Mechanism / Vulnerability	Impact on LC-MS/MS Workflow
Carryover & Peak Tailing	Adsorption onto LC auto-injector needles, stainless steel, and PEEK tubing	Severe ghost peaks, memory effects and compromised calibration linearity
Isomer Resolution	Branched vs. linear PFAS isomers possess varying hydrophobic moments.	Chromatographic peak broadening and inaccurate integration of total PFAS content
Solvent Deprotonation State	Surface tension and pH shifts alter ionization state ($-CF_2CF_2COO^-$ vs neutral)	Variable retention times on reversed-phase (C18, C8) and ion-exchange columns.

Because perfluoroalkyl chains repel both polar aqueous eluent and non-polar stationary phase ligands, long-chain homologs tend to partition toward phase boundaries or accumulate at micro-voids in column packing materials, leading to severe peak tailing and persistent retention drift.

4. Ionization Suppression and Matrix Effects in ESI

Target PFAS species are typically monitored in Negative Electrospray Ionization (ESI^-) mode using Multiple Reaction Monitoring (MRM). However, polymer extracts carry high concentrations of non-volatile oligomeric matrix constituents that compete directly for surface charge on evaporating electrospray droplets.

1. Surface Tension Alteration

Co-extracted oligomers alter the surface tension of the atomized Taylor cone droplets. Because ESI depends on the field-assisted ejection of analyte ions from the droplet surface (Ion Evaporation Model), changes in interfacial surface tension drastically reduce PFAS ionization efficiency.

2. Mass Transition Inefficiency

Short-chain perfluoroalkyl acids (PFBA, PFPEA) undergo extensive in-source fragmentation and yield non-specific precursors-to –product ion transitions (loss of CO2, $[M-H]^- \rightarrow [F]^-$ at m/z 19) compromising signal selectivity against polymer background noise.

F. PFAS Challenges in Polymeric Media

Stage of Workflow	Analytical Challenges	Underlying Physical Phenomenon	Technical Mitigation
Sample Preparation	Entrapment in Polymer core	High surface tension mismatch & swelling limits	Cryogenic milling followed by pressurized solvent extraction (PSE)
Sample Clean-up	Co-extracted oligomer interference	Non-selective solubility in extraction media	Weak anion exchange (WAX) solid phase extraction
Instrument Setup	Continuous background	Degradation of PTFE/PFA	Replacement with

	leaching	seals and degasser lines	PEEK/polyolefin lines & installation of a PFAS delay column
Liquid Chromatography	Severe ghosting and peak tailing	Sorption on hydrophobic/omniphobic interfaces	Optimization of organic wash cycles (Isopropanol /Methanol blends)
Mass Spectrometry	Severe matrix suppression	Charge competition within ESI aerosol droplets	Matrix-matched calibration & isotopically labelled Internal standards

G. Conflict of Interest

The authors declare that they have no known competing financial interests, personal relationships, intellectual property claims or commercial affiliations that could have appeared to influence the work reported in this manuscript.

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I. REFERENCES

1. Ameen, R., et al., Challenges in PFAS Postdegradation Analysis: Insights from the PFAS-CTAB Model System. ACS Measurement Science Au, 2025; 5(1): 45–56. (Highlights ion-pairing phenomena, calibration non-linearity, and mobile-phase pH adjustments to prevent signal suppression.)
2. Gaines, L. G., Historical and current usage of per- and polyfluoroalkyl substances (PFAS): A review. American Journal of Industrial Medicine, 2022; 66(5): 353–378. (Details the material incorporation of fluorochemicals into commercial polymeric matrices and the thermodynamic challenges of extraction.)
3. Shoemaker, J. A., & Tettenhorst, D. R., Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. U.S. EPA Office of Research and Development, 2019. (Focuses on short-chain PFAS behavior, interfacial sorptive losses, and extraction recovery parameters.)
4. Körfali, B., & Reemtsma, T., Matrix effects and ionization suppression in negative electrospray ionization LC-MS/MS analysis of perfluoroalkyl acids in complex organic extracts. Journal of Chromatography A, 2023; 1689: 463750. (Addresses charge competition, droplet surface tension shifts during ESI-, and matrix-matched calibration strategies.)
5. U.S. Environmental Protection Agency (EPA). (2024). Method 1633: Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Wastewater, Wastewater Sludge, and Tissue Samples by LC-MS/MS. U.S. EPA Office of Water. (The definitive multi-laboratory validated standard detailing weak anion exchange [WAX] SPE, isotope dilution quantification, and system contamination mitigation.)