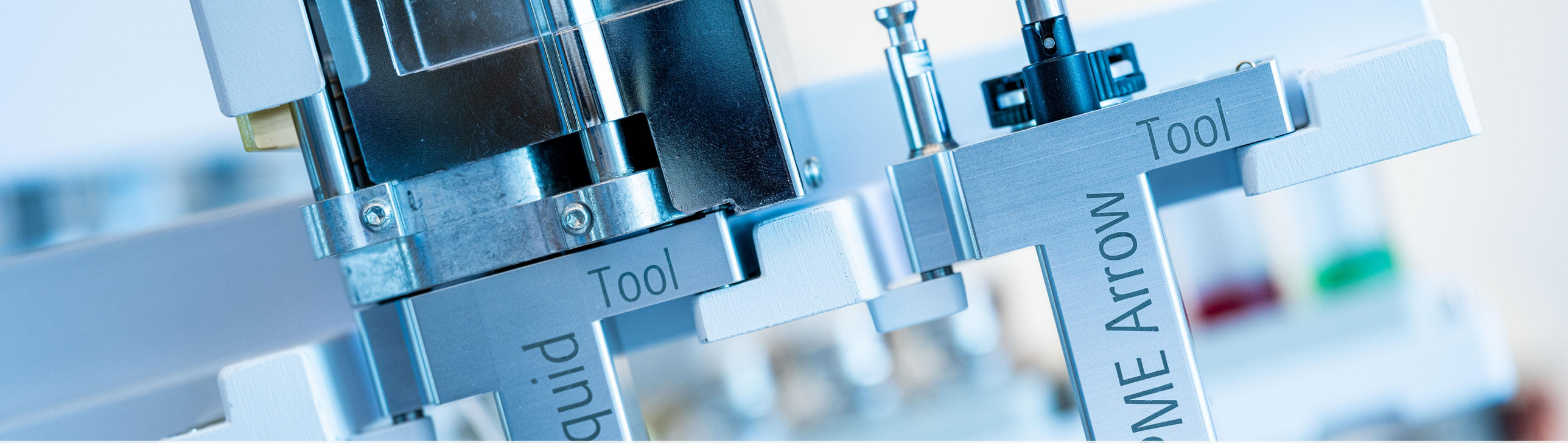

PFAS in Cosmetics

A Focus on Solid Phase Microextraction (SPME)

Part 2 of the Webinar Series

PAL SYSTEM
Ingenious sample handling

Webinar Maintenance

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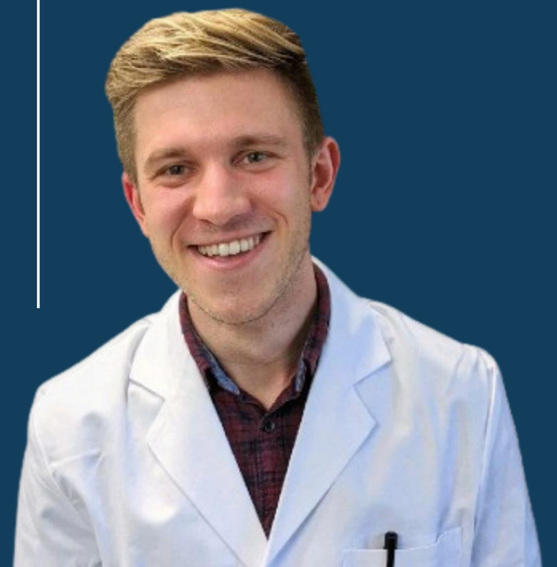
Webinar Maintenance

A webinar series around PFAS – Part 2

Hagen M. Gegner, PhD

Scientific Communications and Projects, CTC Analytics AG

- Background in clinical metabolomics
- Method development in LC-MS and study design
- Focused on sample preparation and quality control



PFAS in Cosmetics

Agenda

Why Cosmetics?

A Direct Exposure Route & An Analytical Challenge

What is SPME?

Principles of a Solvent-Free Microextraction

How is it automated?

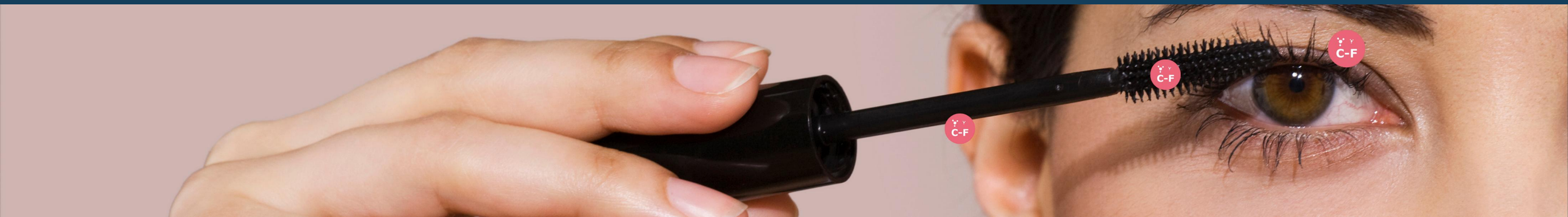
A "Walk-Away" Workflow for PFAS in Water

How does it perform?

SPME and PFAS

A Mascara Case Study: SPME vs. µSPE

Conclusion & Q&A

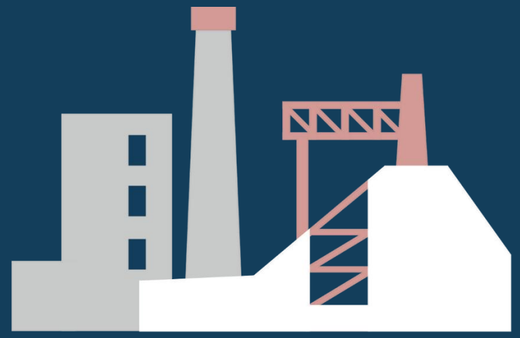


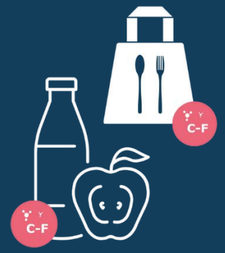
Why Cosmetics?

Ubiquitous PFAS Contamination: From Industry to Your Plate

Di Giorgi, A., et al. (2023). Analysis of perfluoroalkyl substances (PFAS) in conventional and unconventional matrices: Clinical outcomes. Journal of Pharmaceutical and Biomedical Analysis Open, 1, 100002.

Dhiman, S., & Ansari, N. G. (2024). A review on extraction, analytical and rapid detection techniques of Per/Poly fluoro alkyl substances in different matrices. Microchemical Journal, 196, 109667.





PFAS

(Per- and polyfluoroalkyl substances) are a class of over 4,700 synthetic chemicals used since the 1940s.

Teflon

Textiles

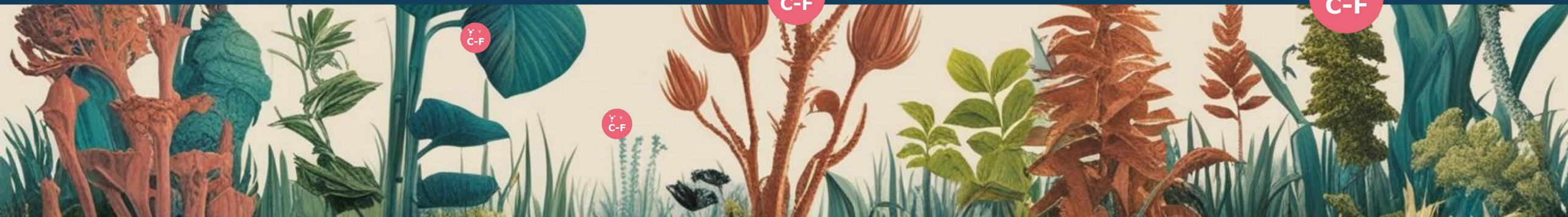
Packaging

Paint

The strength of the Carbon-Fluorine (C-F) bond makes them extremely resistant to heat, chemical, and biological degradation.

C-F

C-F



Why Cosmetics?

A Direct Exposure Route

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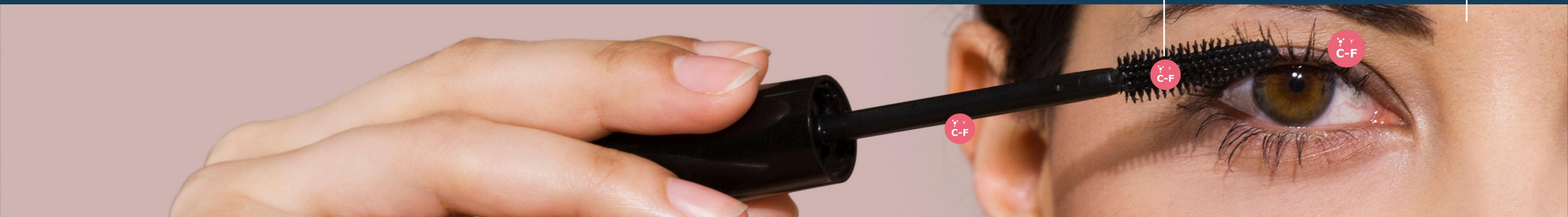
Oddný Ragnarsdóttir, Mohamed Abou-Elwafa Abdallah, Stuart Harrad, Dermal bioavailability of perfluoroalkyl substances using in vitro 3D human skin equivalent models,Environment International,Volume 188, 2024,108772, ISSN 0160-4120, https://doi.org/10.1016/j.envint.2024.108772.

A Direct Exposure Pathway

The application of these products represents a direct route for human exposure.

Intentionally Added Ingredients

Unlike many environmental samples where PFAS are unintended contaminants, they are often added to cosmetics on purpose



Why Cosmetics?

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Cosmetics are a proven exposure route, as a 2024 study confirmed PFAS are absorbed through the skin.

- Shorter-chain PFAS were readily absorbed, with up to 59% of the applied dose permeating the skin barrier.
- Longer-chain PFAS were retained at high concentrations within the skin tissue, even if not directly absorbed.

A Direct Exposure Pathway

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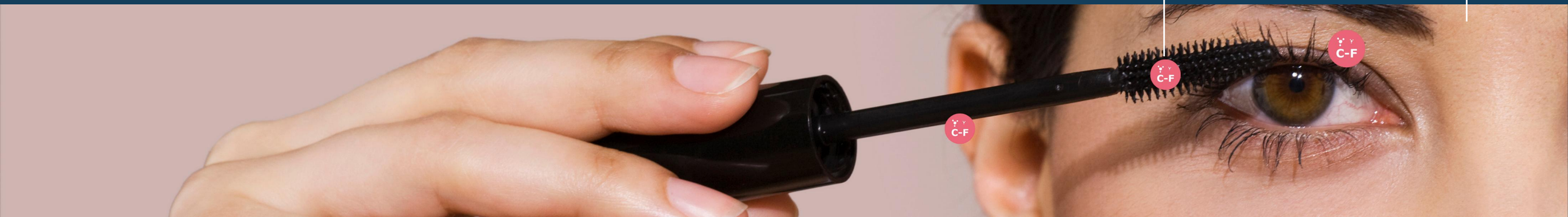

The Analytical Challenge of Mascara

Why is Analysis So Difficult?

Di Giorgi, A., et al. (2023). Analysis of perfluoroalkyl substances (PFAS) in conventional and unconventional matrices: Clinical outcomes. Journal of Pharmaceutical and Biomedical Analysis Open, 1, 100002.

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Trace Concentrations

PFAS are often present at very low levels (ng/g or parts-per-billion), demanding highly sensitive analytical instruments.

Matrix Effects

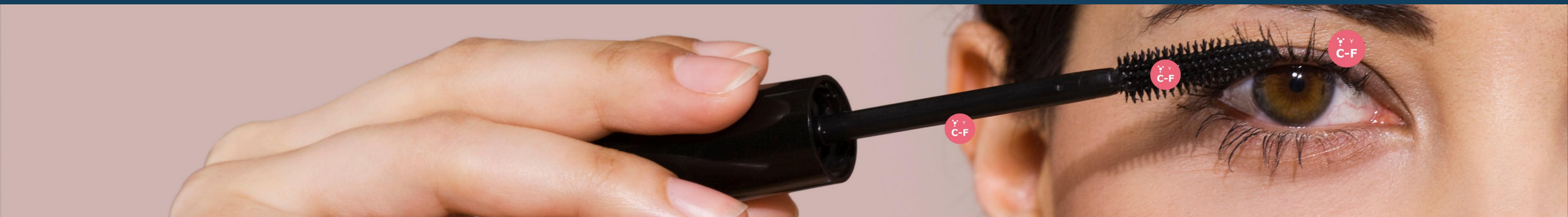
During analysis, co-extracted ingredients can artificially suppress or enhance the PFAS signal in the mass spectrometer, a common challenge requiring careful method design.

Matrix Complexity

Cosmetics are a dense mixture of waxes, oils, pigments, and polymers that can interfere with extraction and lead to inaccurate results.

Background Contamination

The ubiquity of PFAS in laboratory environments (e.g., from PTFE tubing) requires strict contamination controls and specialized equipment to ensure reliable results.



The Solution: A Deeper Look at SPME

What is Solid Phase Microextraction (SPME)?

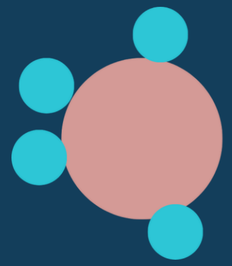
Jiang, G., Huang, M., Cai, Y., Lv, J., & Zhao, Z. (2006). Progress of Solid-Phase Microextraction Coatings and Coating Techniques. Journal of Chromatographic Science, 44(6), 324–333.
Dugheri, S., Mucci, N., Cappelli, G., Trevisani, L., Bonari, A., Bucaletti, E., Squillaci, D., & Arcangeli, G. (2022). Advanced Solid-Phase Microextraction Techniques and Related Automation: A Review of Commercially Available Technologies. Journal of Analytical Methods in Chemistry, 2022, 8690569.

The Principle

SPME is a solvent-free sample preparation technique developed by Prof. Janusz Pawliszyn (1989). It works on the principle of equilibrium partitioning.

Extraction

The way analytes are extracted depends on the fiber's coating material, which can be either a liquid-like polymer or a solid porous layer.



Adsorption

This is the primary mechanism for solid, porous coatings like Divinylbenzene (DVB) or Carboxen (CAR).

Analytes accumulate on the outer surface of the sorbent material

Absorption

Analytes partition from the sample and diffuse into the entire volume of the coating. This occurs with liquid-like coatings such as polydimethylsiloxane (PDMS) or polyacrylate (PA).

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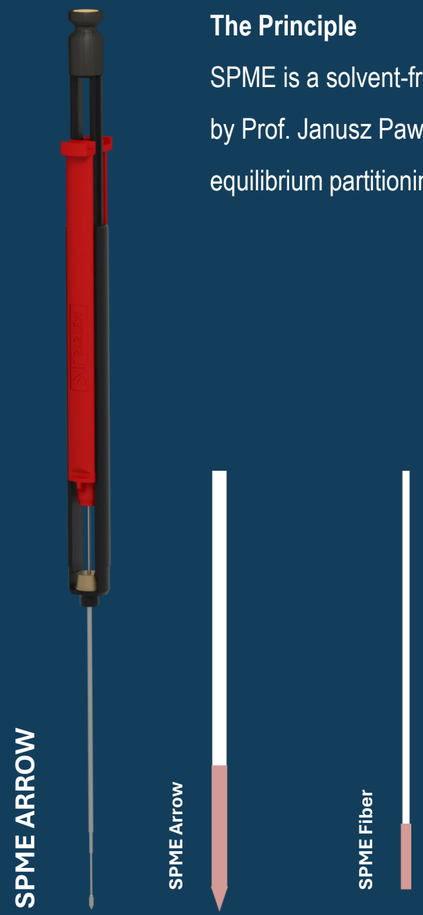

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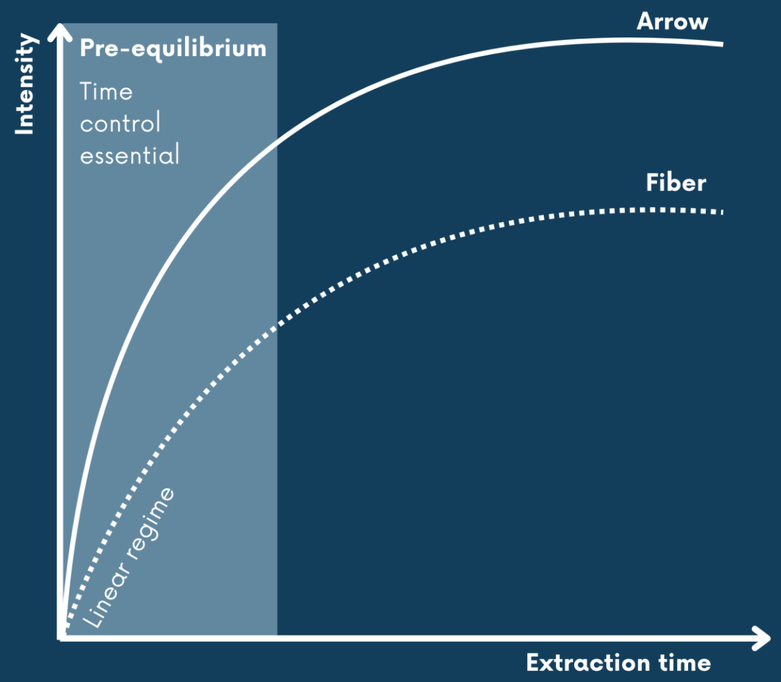
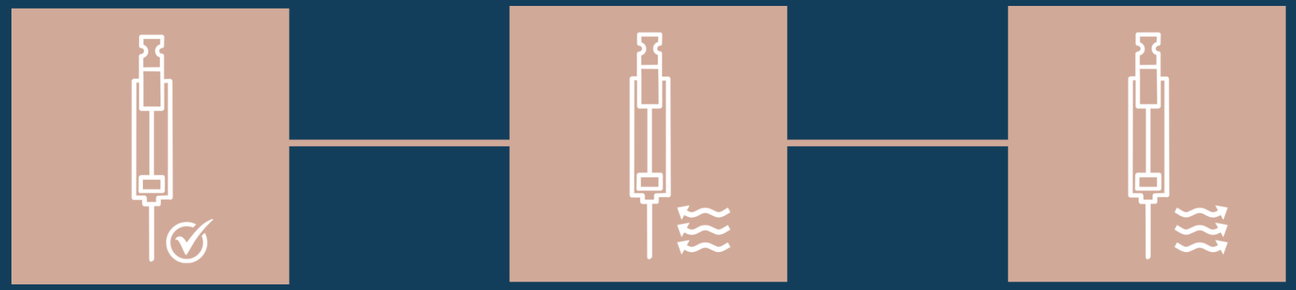
Key Differences

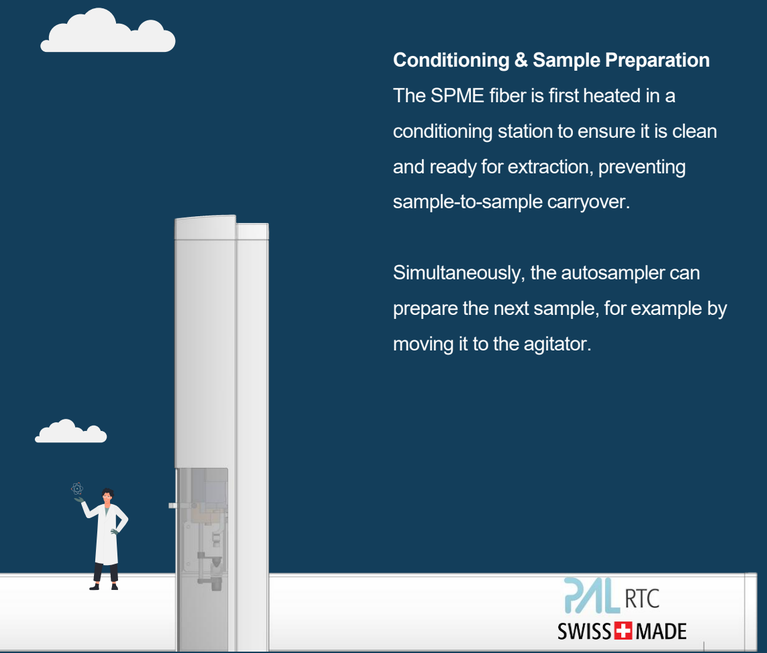
- The Arrow is fabricated with a robust stainless-steel core and a protective outer sheath. This design confers superior mechanical stability and durability, reducing the risk of fracture common to the more fragile fused-silica core of standard fibers.
- The Arrow possesses a significantly greater sorptive phase volume than traditional fibers. This increased volume provides a higher analyte loading capacity, which can lead to a greater preconcentration factor from the sample matrix.



The Automated SPME Workflow Principle

The Automated Workflow in 3 Key Steps



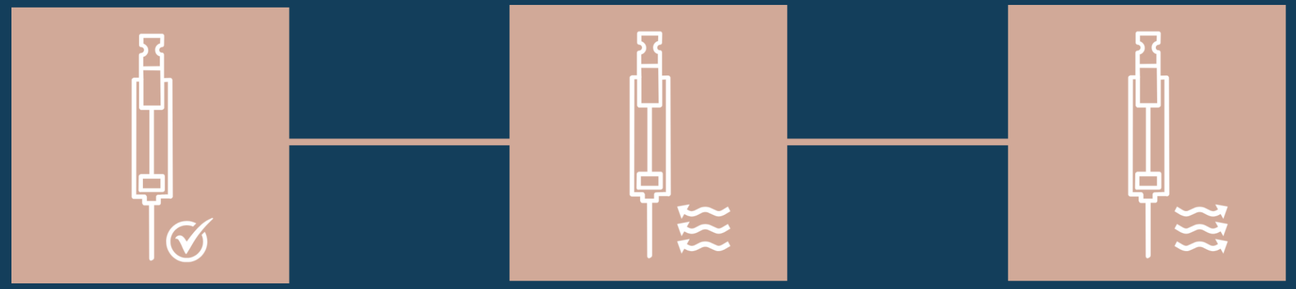


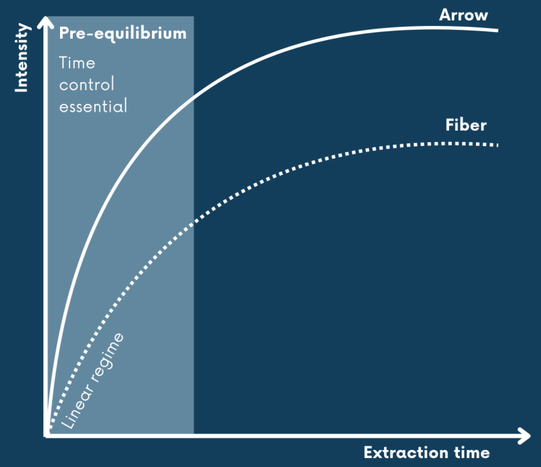
Conditioning & Sample Preparation
The SPME fiber is first heated in a conditioning station to ensure it is clean and ready for extraction, preventing sample-to-sample carryover.

Simultaneously, the autosampler can prepare the next sample, for example by moving it to the agitator.

The Automated SPME Workflow Principle

The Automated Workflow in 3 Key Steps





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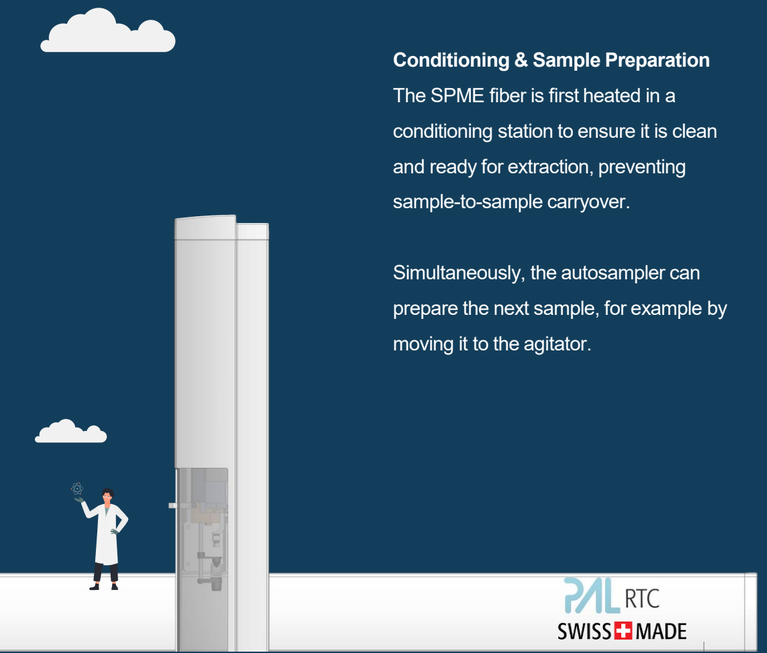
Incubation & Extraction
The sample vial is heated and agitated for a set time to help the PFAS partition out of the complex matrix.

The conditioned SPME is then automatically exposed to the sample (either via direct immersion or headspace) for a precisely controlled extraction time.



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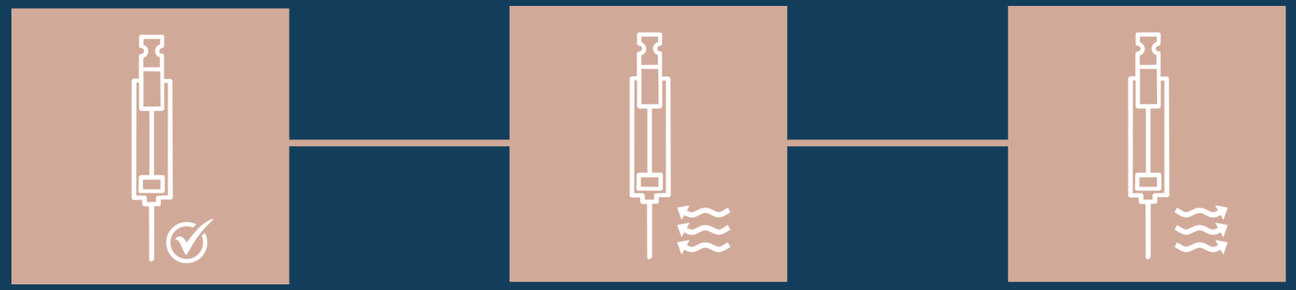

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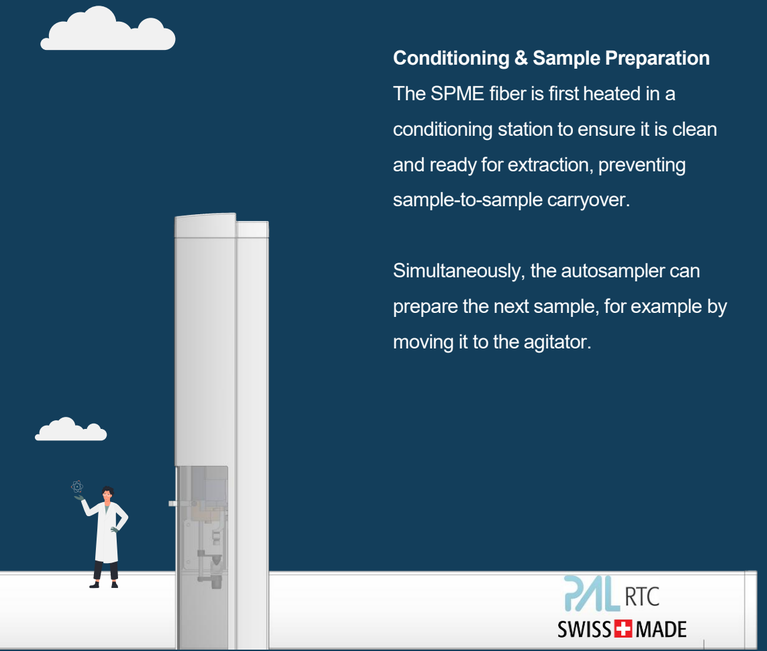
Desorption & Injection
The SPME, now loaded with the concentrated PFAS, is withdrawn from the sample and ready for analysis.

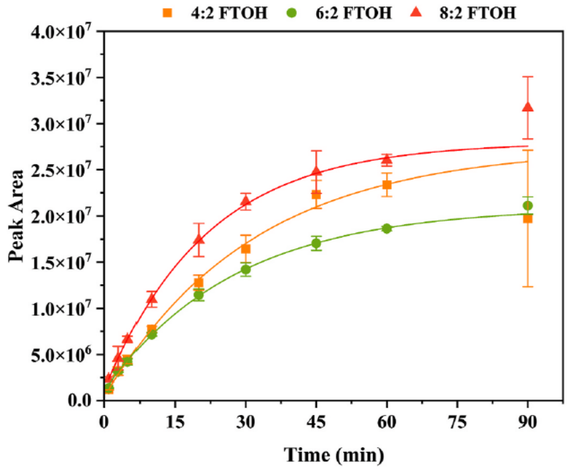
For GC-MS: Desorption is a single, rapid thermal step directly inside the hot GC injector.

For LC-MS: Desorption is a two-step process: first, the analytes are desorbed using a solvent in a separate vial, and then that solvent is injected into the instrument



The Automated SPME Workflow Application

Optimizing the Extraction: Time is Key

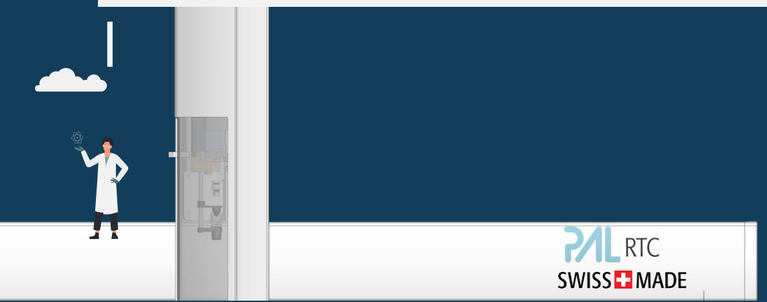


Extraction Time Profile for Volatile PFAS using Direct Immersion SPME (DI-SPME).

This graph shows the amount of different volatile PFAS extracted over 90 minutes, measured as GC-MS peak area. For this experiment, a DVB/Car/PDMS SPME fiber was immersed directly into ultrapure water spiked with the target analytes. The extraction was performed at 60 °C with an agitation of 250 rpm. This type of profile is critical for method development, as it helps determine the optimal time needed to extract enough analyte for sensitive detection. Under these conditions, most of the tested PFAS approach equilibrium after approximately 60 minutes.

Automation is key

Its precise control of all parameters allows for highly reproducible results and efficient overlapping of sample prep and injection.



Extraction is a dynamic process

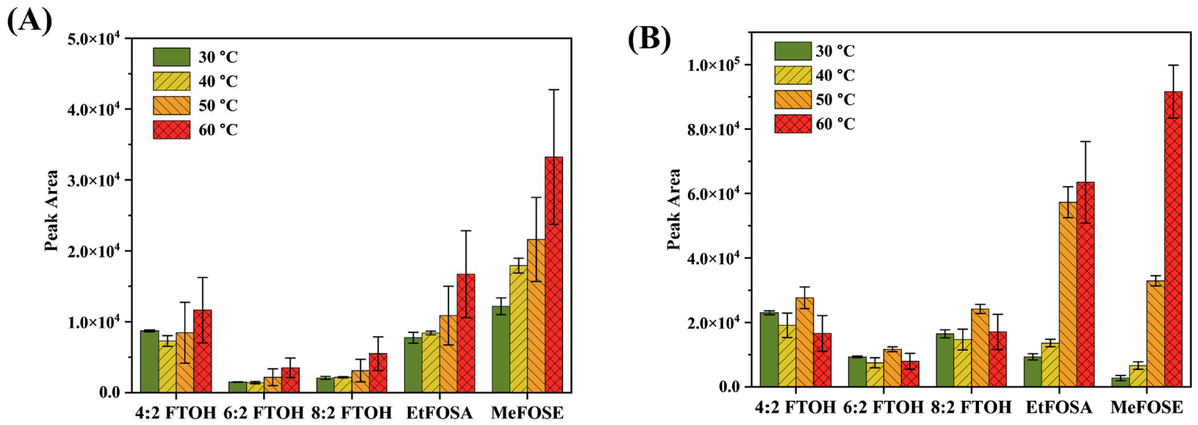
The amount of analyte captured by the SPME increases over time until it reaches equilibrium with the sample.

- For Direct Immersion (DI-SPME), equilibrium for many volatile PFAS is reached in approximately 60 minutes.
- For Headspace (HS-SPME), the process is significantly faster, with most analytes reaching equilibrium in about 25 minutes.

Martínez-Pérez-Cejuela, H., Williams, M. L., McLeod, C., & Gionfriddo, E. (2025). Effective preconcentration of volatile per- and polyfluoroalkyl substances from gas and aqueous phase via solid phase microextraction. Analytica Chimica Acta, 1345, 343746. https://doi.org/10.1016/j.aca.2025.343746

The Automated SPME Workflow Application

Optimizing the Extraction: The Effect of Temperature



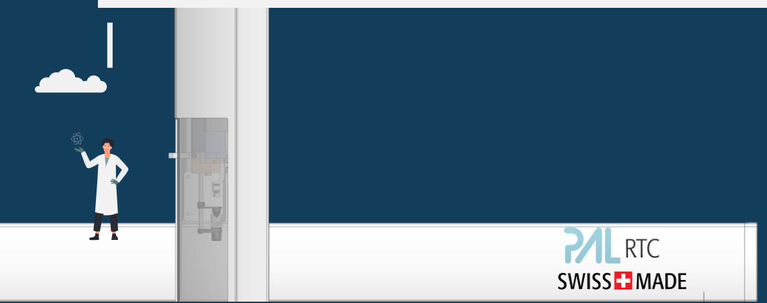
The Effect of Extraction Temperature on SPME Efficiency for Volatile PFAS.
These charts compare the extraction efficiency (measured as GC-MS peak area) for volatile PFAS at temperatures from 30 °C to 60 °C using two different modes: (**A) Direct Immersion (DI-SPME)** and (**B) Headspace (HS-SPME).**

In Direct Immersion (A), extraction efficiency increases with temperature for all compounds, which is particularly evident for the less volatile EtFOSA and MeFOSE.

In Headspace (B), the trend is different; while extraction of EtFOSA and MeFOSE still increases with temperature, the extraction of the more volatile FTOHs peaks at 50 °C and then declines. This illustrates the need to carefully optimize temperature based on the specific analytes and the chosen extraction mode

Account for contamination sources
There are upgrade kits available for PFAS Analysis.
They focus on the tubing, LC/MS Tool, vials and syringes.

Always run blanks for your QC/QA strategies.



Temperature directly influences the efficiency of the SPME process and must be carefully optimized for target analytes.

- In Direct Immersion (DI-SPME), higher temperatures generally increase the amount of analyte extracted by speeding up diffusion, especially for less volatile compounds.An optimal temperature (e.g., 60 °C) is often chosen to maximize recovery while maintaining good reproducibility.
- In Headspace (HS-SPME), the effect is more complex, creating a trade-off:Higher temperatures help less volatile compounds move into the headspace, increasing their extraction.However, because sorption onto the fiber is an exothermic process, temperatures that are too high can reduce the extraction of the most volatile compounds.

Martínez-Pérez-Cejuela, H., Williams, M. L., McLeod, C., & Gionfriddo, E. (2025). Effective preconcentration of volatile per- and polyfluoroalkyl substances from gas and aqueous phase via solid phase microextraction. Analytica Chimica Acta, 1345, 343746. https://doi.org/10.1016/j.aca.2025.343746

The Automated SPME Workflow Application

Automated Analysis of Volatiles in Water

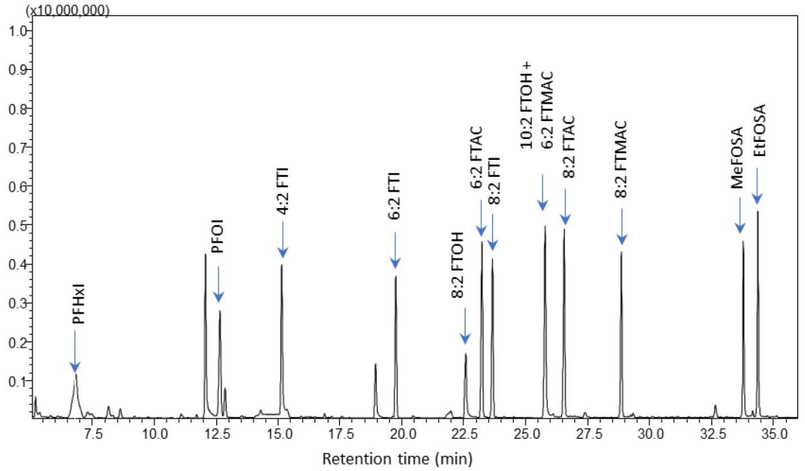
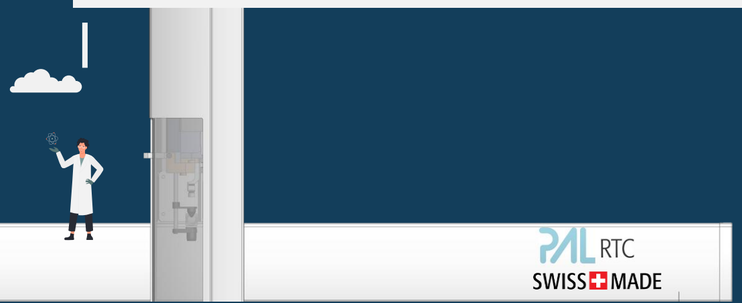


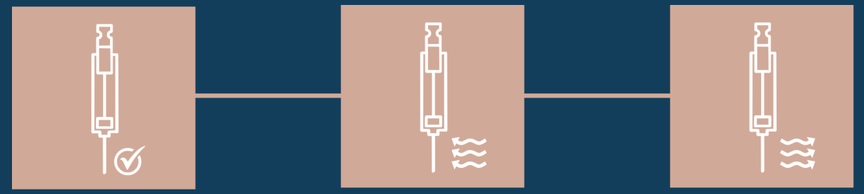
Table 4: Summary of PFAS calibration range and linearity results

Compound	Calibration Range (ng/L)	R^2	RF (Response Factor) %RSD
PFHxI	2.5-2000	0.993	10.89
PFOI	2.5-2000	0.997	10.26
4:2 FTI	2.5-800	0.993	8.28
6:2 FTI	25-800	0.994	13.53
8:2 FTOH	25-2000	0.997	5.37
6:2 FTAC	25-2000	0.998	19.87
8:2 FTI	2.5-800	0.996	13.59
10:2 FTOH	2.5-2000	0.999	10.38
6:2 FTMAC	2.5-800	0.995	12.43
8:2 FTAC	5-250	0.995	14.81
8:2 FTMAC	2.5-250	0.998	19.51
MeFOSA	5-2000	>0.999	17.79
EtFOSA	10-2000	0.999	11.40

A fully automated and cost-effective method

The selected extraction temperature (50 °C) and time (30 min) represent an effective compromise, providing good sensitivity across a diverse group of PFAS with varying volatilities in a single, unattended run.





Sample Preparation
Water samples were "salted out" with 2% NaCl to enhance the extraction efficiency of the target compounds.

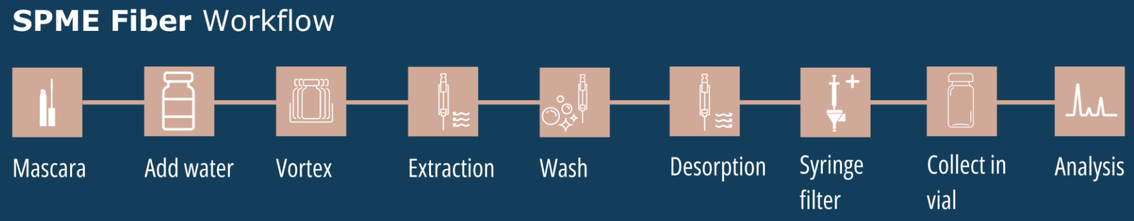
Automated Incubation & Extraction
The autosampler incubated the sample for 5 minutes at 50 °C and then exposed the SPME fiber to the vial's headspace for 30 minutes.

Desorption & Analysis
The fiber was transferred directly to the hot GC inlet (240 °C) for a rapid 7-minute thermal desorption.

Analysis of Volatile PFAS in Water Using Head-Space Solid Phase Microextraction-Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS)Source: Shimadzu Scientific Instruments

Tackling the Complex Mascara Matrix

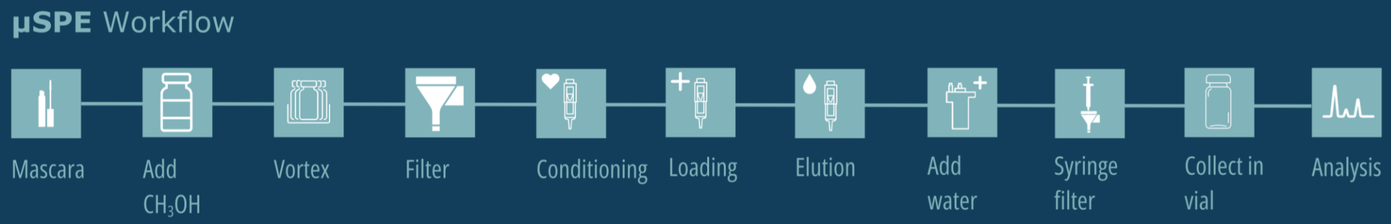
Choosing the Right Tool for the Job



SPME Fiber Workflow

This workflow was performed manually in the study to establish a proof-of-concept for this challenging matrix.

- 0.5 g of mascara was dispersed in 5 mL of 100% water.
- The SPME fiber was immersed directly into the mascara-water mixture for 60 minutes to extract the PFAS.
- Analytes were desorbed from the fiber using a small amount of solvent, which was then collected for analysis.



Olomukoro, A. A., Lüthy, L., Flug, T., & Gionfriddo, E. (2025). Evaluation of extraction methodologies for PFAS analysis in mascara: a comparative study of SPME and automated µSPE. Analytical and Bioanalytical Chemistry. https://doi.org/10.1007/s00216-025-05908-x

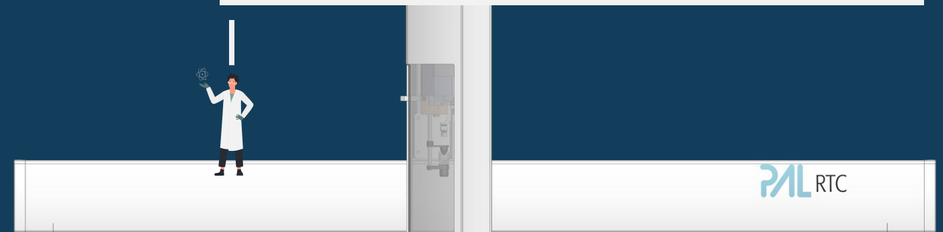
µSPE Workflow

The core extraction and elution steps of this workflow were automated on a PAL System

- 0.5 g of mascara was dispersed in 5 mL of 100% methanol to dissolve the sample matrix.
- The mascara-methanol mixture required manual filtration before being placed on the autosampler to prevent the µSPE cartridges from clogging.
- The PAL System then handled the conditioning of the µSPE cartridge, loading of the filtered sample, and elution of the final extract.

Both workflows benefit significantly from automation.

SPME Fibers/Arrows can be fully automated for unattended batch processing. The core steps of µSPE are automated, and the initial filtration step can also be integrated into the workflow for a complete walk-away solution.



Head-to-Head: SPME vs. Automated µSPE

Choosing the Right Tool for the Job

SPME (Fiber)	Micro-SPE Cartridges
Extraction Equilibrium Partitioning	**Extraction** Exhaustive Extraction (SPE)
Sample Pre-treatment No filtration required	**Sample Pre-treatment** Filtration of sample is required
Optimal Dispersion Solvent 100% Water	**Optimal Dispersion Solvent** 100% Methanol
Sensitivity (LOQ) Better for hydrophilic PFAS (e.g., PFBS)	**Sensitivity (LOQ)** Better for hydrophobic PFAS (e.g., PFOS)
Device Reusability Reusable Fiber	**Device Reusability** Single-use Cartridges

Both methods are effective for real-world product safety testing, successfully detecting and quantifying regulated PFAS in commercial mascara products.

- SPME offers a simpler, filtration-free workflow, while the automated µSPE method required a manual filtration step to handle the complex mascara matrix. The techniques are complementary, not competing.
- SPME showed superior sensitivity for hydrophilic PFAS , whereas automated µSPE was more effective for key hydrophobic PFAS.

"Analytical Toolbox" concept, where the best strategy is to choose the right combination of tools for the job. For this matrix, SPME had a simpler workflow for hydrophilic targets, while automated µSPE offered higher sensitivity for hydrophobic ones. For instrumentation, LC-MS is the standard for ionizable PFAS, while GC-MS excels for the neutral and volatile species.

Olomukoro, A. A., Lüthy, L., Flug, T., & Gionfriddo, E. (2025). Evaluation of extraction methodologies for PFAS analysis in mascara: a comparative study of SPME and automated µSPE. Analytical and Bioanalytical Chemistry. https://doi.org/10.1007/s00216-025-05908-x

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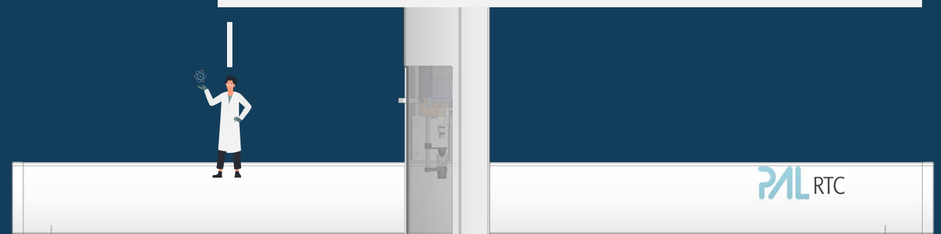


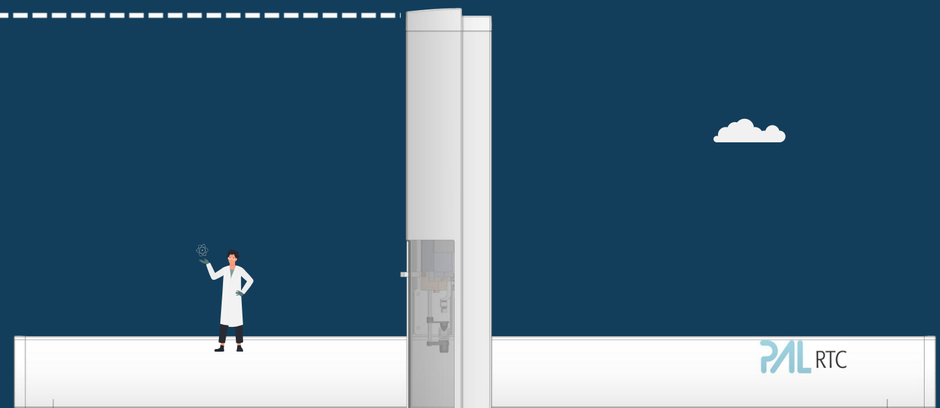
Summary & Key Takeaways

SPME is a Powerful and Versatile Tool

Cosmetics are a Direct Exposure Route
PFAS are absorbed through the skin. Studies show shorter-chain PFAS can be readily absorbed, while longer-chain compounds are retained within the skin tissue itself.

SPME is a Powerful and Versatile Tool
Solid Phase Microextraction is a sensitive, solvent-free technique that effectively extracts PFAS from complex matrices , making it an excellent choice for modern, environmentally conscious labs.

SPME performance depends on the **precise optimization** of factors such as extraction time and temperature. Automation secures these ideal conditions for each sample, guaranteeing exceptional reproducibility and facilitating dependable, high-throughput "walk-away" operation.



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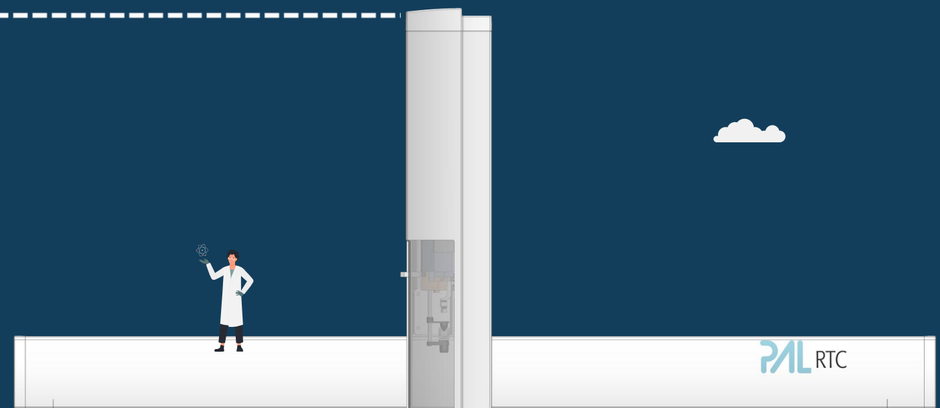
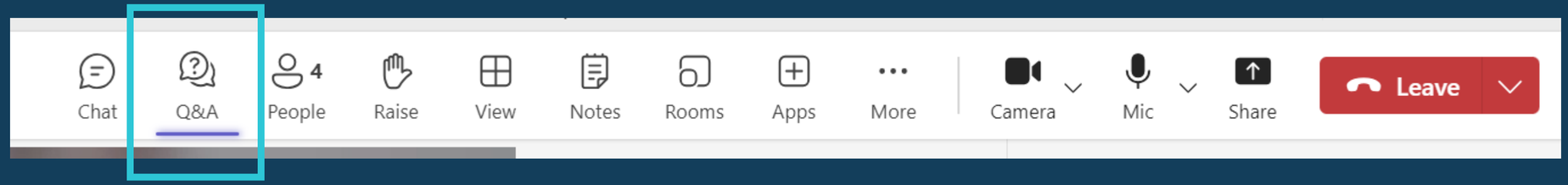
Build the Right Analytical Toolbox
There is no single best method for all PFAS; the most effective strategy is to choose the right combination of tools for the job.

- For instrumentation, LC-MS is the standard for ionizable PFAS, while GC-MS excels for the neutral and volatile species that LC can miss.
- For sample preparation, the mascara study showed that SPME offers a simpler, filtration-free workflow ideal for hydrophilic PFAS, while automated µSPE provides higher sensitivity for hydrophobic ones.

Importantly, all sample preparation aspects can be automated.



Q&A



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Ingenious sample handling

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9. Shimadzu Scientific Instruments, Application Note GCMS-2402, "Analysis of Volatile PFAS in Water Using HS-SPME-GC/MS".

PAL System Resources

- PAL SPME Arrow: Discover the Power of SPME and the Benefits of SPME Arrows
- PAL µSPE: Micro-SPE - A Green Extraction technique in modern laboratories
- Upgrade Kits for PFAS Analysis: PFAS Analysis - Equip your PAL System for PFAS Analysis
- PAL System Content Hub: PAL Content Hub - Search our Library