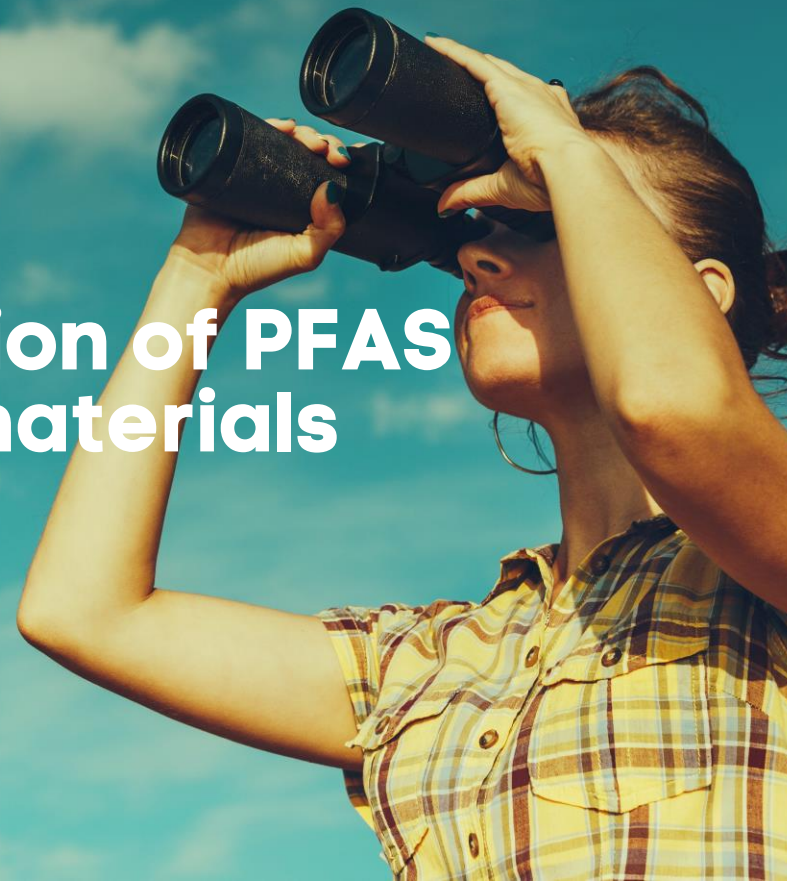


Screening and identification of PFAS in textiles, food contact materials and electronics

Lisa Skedung, lisa.skedung@ri.se
2024-09-02



Outline

Main message 1:
There are analytical methods that captures polymeric PFAS!

Main message 2:
It is possible to enforce a universal PFAS restriction!

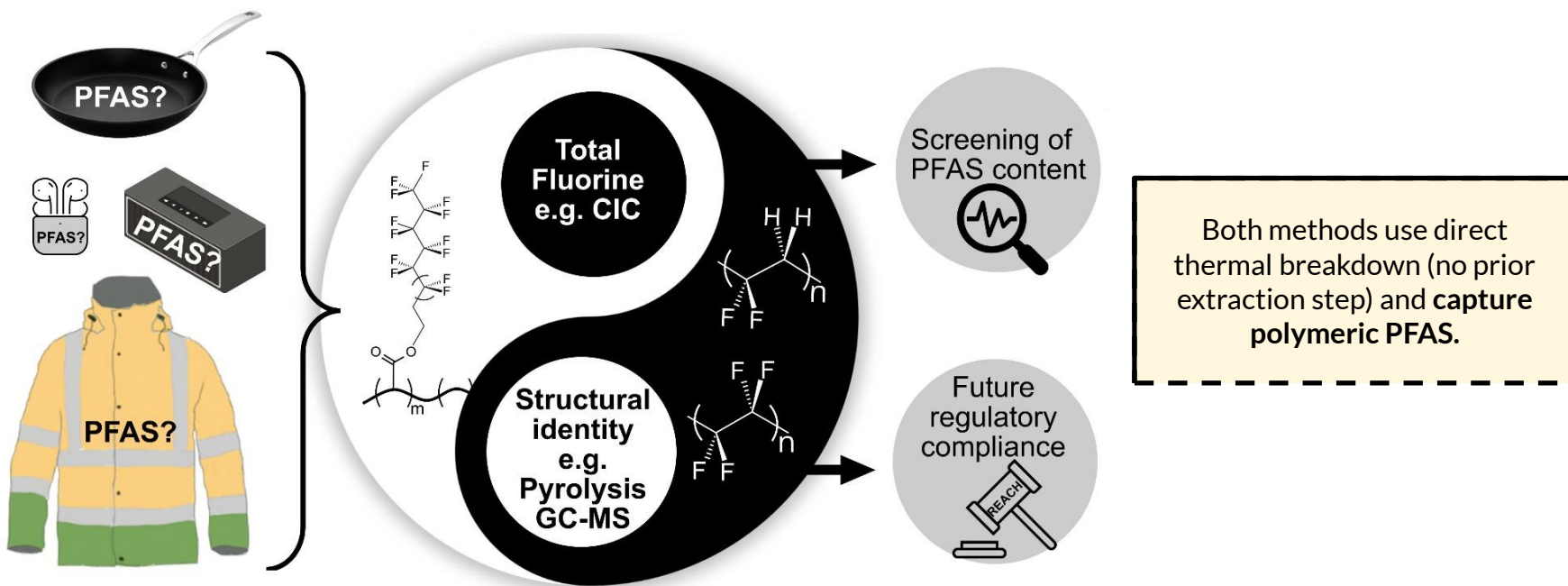


- Background to proposed systematic workflow for analysis of PFAS in products
- Case studies implementing the workflow



Analysis of PFAS in products

Combustion ion chromatography and pyrolysis-GC/MS are two complimentary techniques



Skedung, L., Savvidou, E., Schellenberger, S., Reimann, A., Cousins, I. T., & Benskin, J. P. (2024). Identification and quantification of fluorinated polymers in consumer products by combustion ion chromatography and pyrolysis-gas chromatography-mass spectrometry. *Environmental Science: Processes & Impacts*, 26(1), 82-93.

Possible enforcement of a universal PFAS restriction

Environmental Science & Technology >

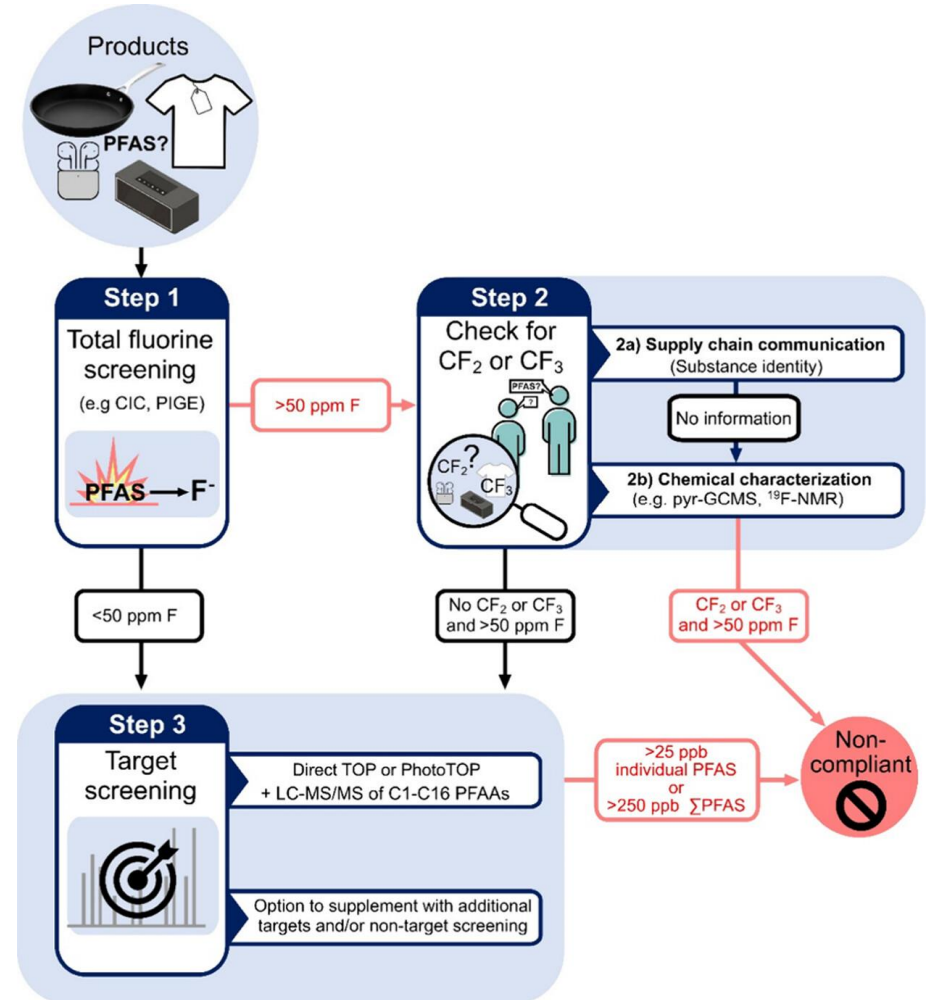
ASAP > Article

Open Access

VIEWPOINT | August 14, 2024

A Systematic Workflow for Compliance Testing of Emerging International Classwide Restrictions on PFAS

Robin Vestergren*, Anders Appelblom, Simona A. Bălan, Sicco H. Brandsma, Thomas A. Bruton, Ian T. Cousins, Jeremy R. Gauthier, Audun Heggelund, Jenny Ivarsson, Anna Kärman, Lisa Melymuk, Chijioke Olisah, Amanda Rosen, Eleni K. Savvidou, Steffen Schellenberger, Lisa Skedung, Petteri Talasniemi, Tonie Wickman, Jonathan Zweigle, Christian Zwiener, and Jonathan P. Benskin*



PFAS restriction proposal

PFAS shall not be manufactured, used or placed on the market as substances on their own; nor not be placed on the market in another substance, as a constituent; in a mixture, or in an article in a concentration of or above:

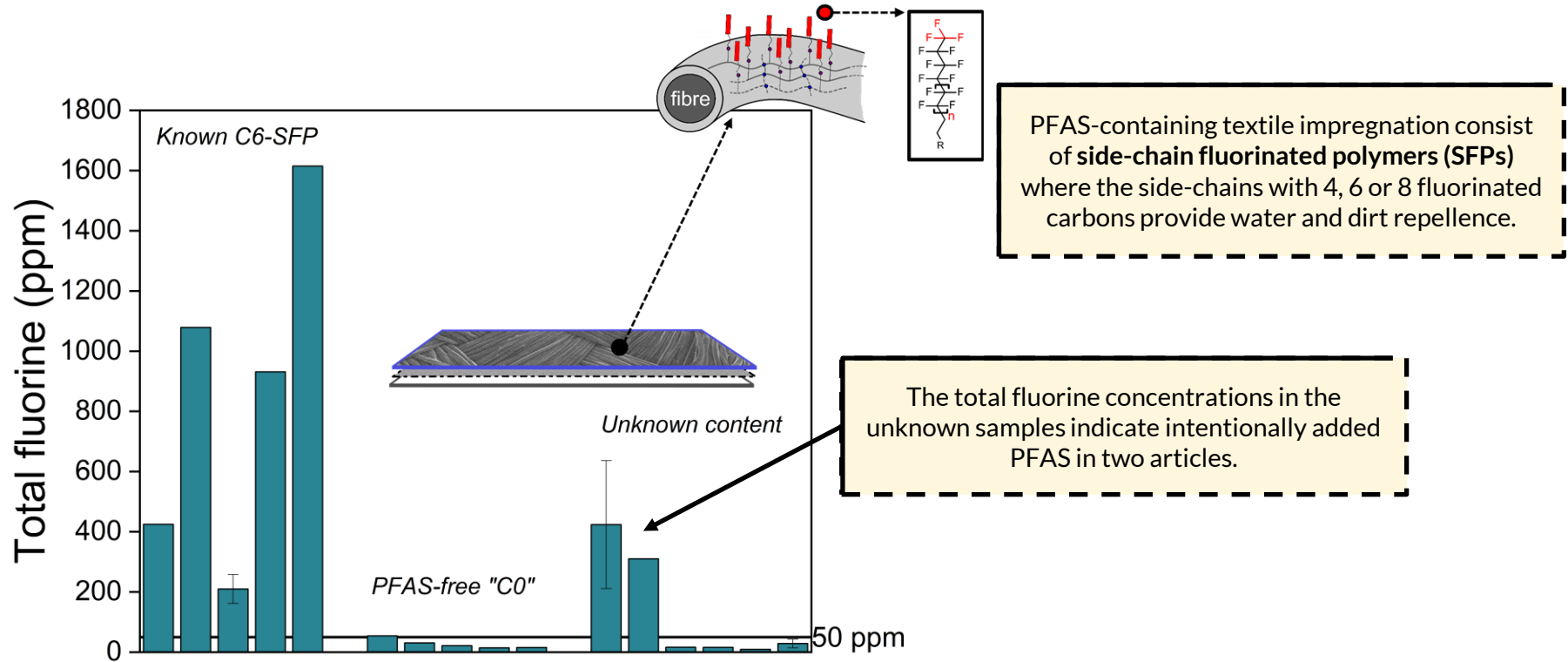
- 25 ppb for any PFAS
- 250 ppb for the sum of PFASs
- **50 ppm** for PFASs (polymeric PFASs included)

If total fluorine exceeds 50 mg F/kg the manufacturer, importer or downstream user shall upon request provide to the enforcement authorities a proof for the fluorine measured as content of either PFASs or non-PFASs.

Also applies to imported goods and recycled materials!

Total fluorine in textile samples

The 50 ppm level in the restriction proposal makes sense

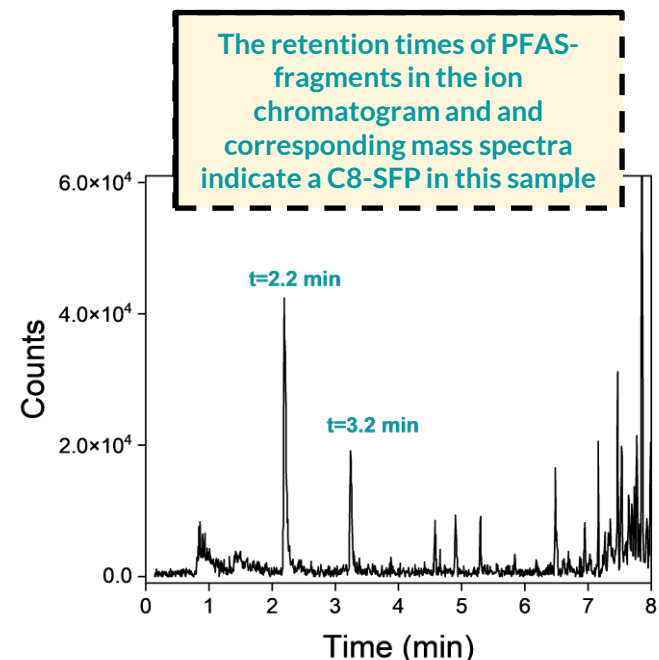
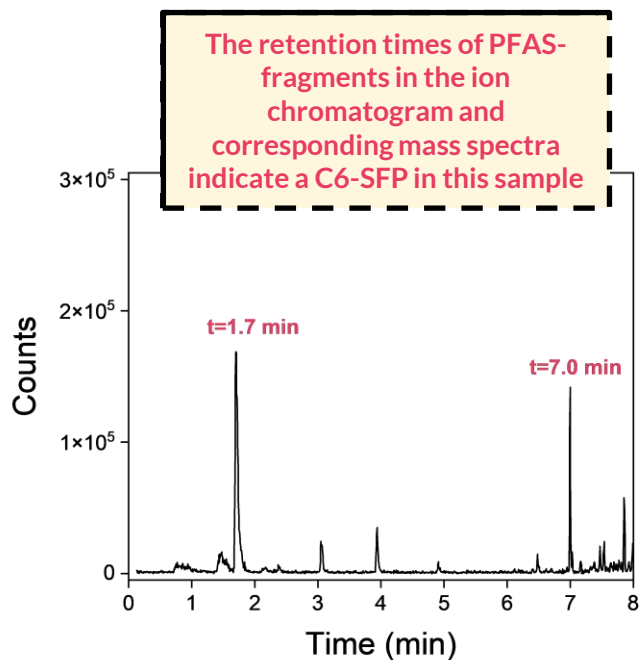
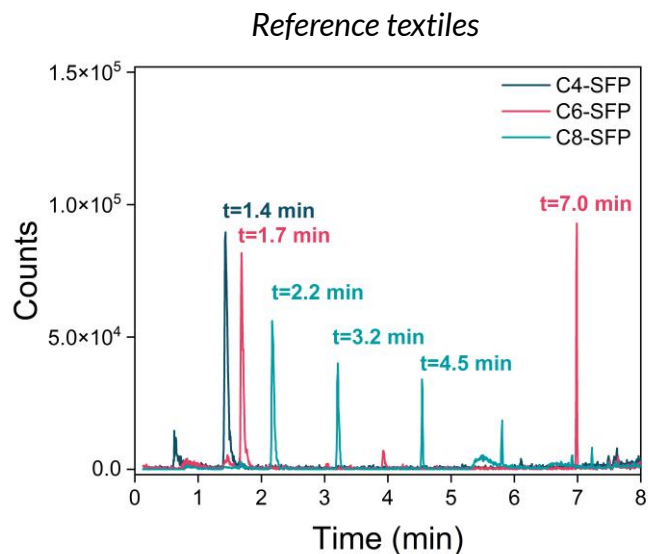


PFAS-containing textile impregnation consists of side-chain fluorinated polymers (SFPs) where the side-chains with 4, 6 or 8 fluorinated carbons provide water and dirt repellence.

The total fluorine concentrations in the unknown samples indicate intentionally added PFAS in two articles.

Pyrolysis-GC/MS for verification

The fluorinated side-chain seem to be kept intact providing structural information



CASE STUDY

Textile articles

PFAS in 57% of the articles

Total fluorine (TF) concentrations of 13/23 articles in the range 65 ppm - 1450 ppm



Presence of PFAS was verified in the 13 articles with pyrolysis-GC/MS.

C6-SFP was found in 10 of the samples and C8-SFP was found in 3 of the articles.

Comparison analytical techniques

Method	Sample A	Sample B	Proposed regulatory threshold
Σ PFAS22 (LC-MS/MS)	15 ppb	150 ppb	250 ppb
Σ PFAS22 (LC-MS/MS) after oxidation (TOP)	28 400 ppb	500	250 ppb?
Total fluorine (CIC)	1 450 000 ppb (1 450 ppm)	275 000 ppb (275 ppm)	50 ppm

Concentrations under the proposed regulatory threshold with target analysis.

Oxidation significantly increases Σ PFAS in the target analysis. This is why we propose oxidation (direct TOP) in step 3 before target analysis.

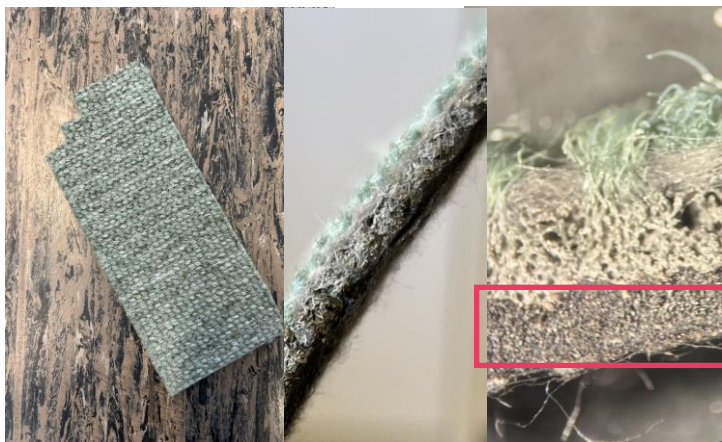
The total fluorine concentrations clearly indicate PFAS and non-compliance with future universal PFAS restriction.



Analysis of a carpet

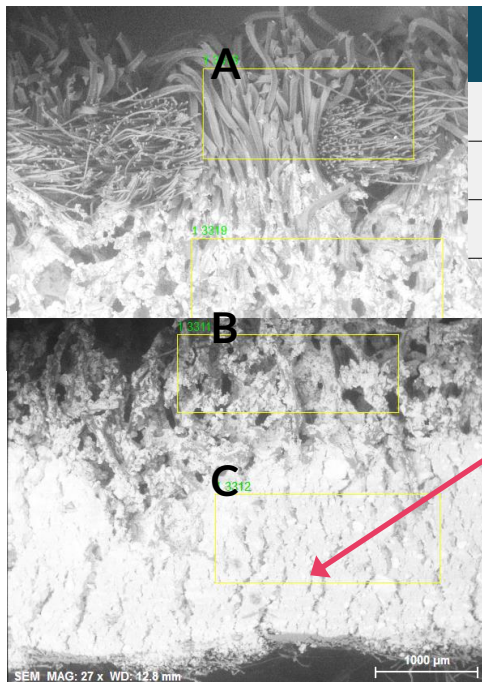
Elemental analysis with SEM-EDS*

Table shows atomic %



Total fluorine: **440 ppm** (mg/kg)
All layers included in the analysis.

No PFAS detected with pyrolysis-GC/MS in neither of the five layers.



Spectrum	C	O	F	Al	Si	S	Ca	Ti
A	81	18	-	0.34	0.02	0.05	0.46	0.05
B	58	31	-	0.03	0.08	0.27	10	
C	61	24	0.49	-	0.04	8	6	

Example where quantified fluorine is inorganic (not PFAS).
Pyrolysis-GC/MS is useful to avoid “false positives”.

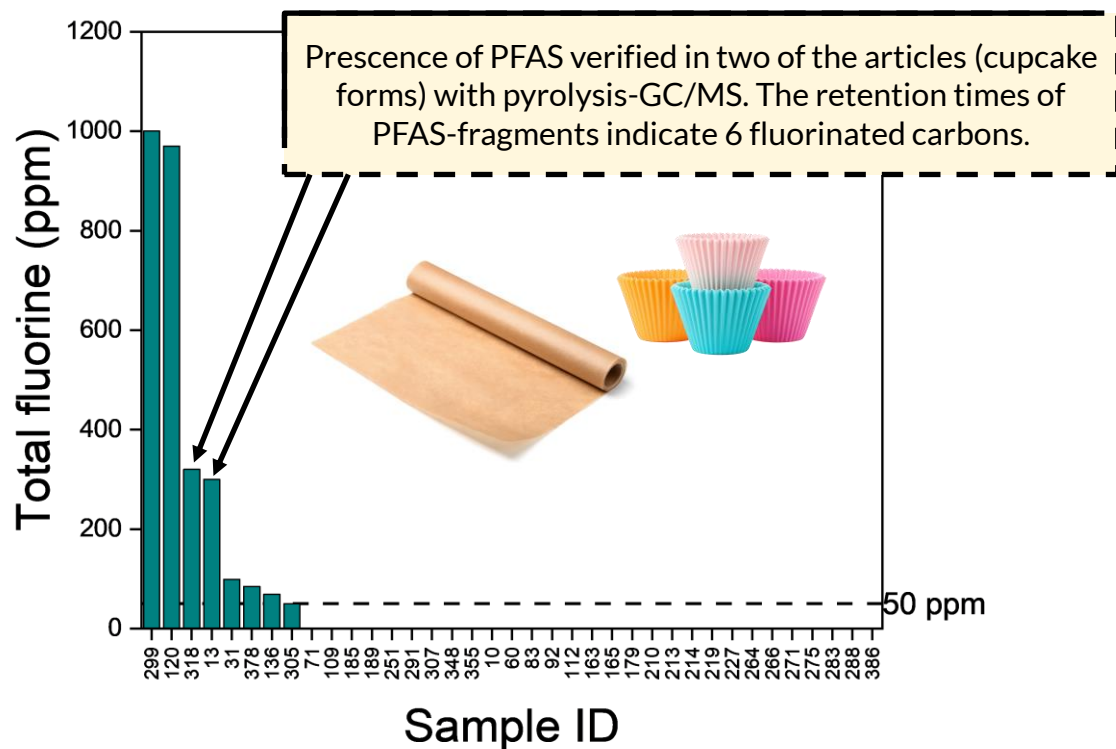


CASE STUDY

Food contact materials

PFAS in 5% of the analysed articles

Total fluorine (TF) concentrations of 8/37 articles in the range 50 ppm - 1000 ppm



Presence of PFAS could not be verified in the other samples with a TF-concentration > 50 ppm.

Neither PFAS nor silicone chemistry are found in the two samples with highest TF concentration. We believe this is another example where the fluorine is inorganic (not PFAS).

ΣPFAS increases with oxidation (TOP)

Method	299	120	318	13	31	378	136	305	71	109	185	189	251	291	307	348	355
ΣPFAS22 (LC-MS/MS)	1.3	1.0	49	5.0	2.4	1.7	28	0.79	34	1.5	0.7	0.05	0.11	54	2.1	1.6	0.43
ΣPFAS22 (LC-MS/MS) after oxidation (TOP)	n/a	n/a	17 000	20 700	n/a	n/a	n/a	n/a	5.5	n/a	n/a	n/a	n/a	210	n/a	n/a	n/a

n/a - all analysed PFAS-substances under LOQ for the TOP-method

ΣPFAS under the proposed 250 ppb regulatory threshold with target analysis for all articles including those where PFAS-chemistry was confirmed.

A significant increase in ΣPFAS in the TOP-analysis for the same two samples where presence of PFAS was verified with pyrolysis-GC/MS.



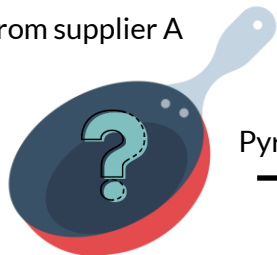
Ceramic non-stick coatings

Is the coating free from PFAS?



Contamination?

From supplier A



Pyrolysis-GC/MS



From supplier A



Pyrolysis-GC/MS

PFAS-chemistry verified in final article AND the paint.

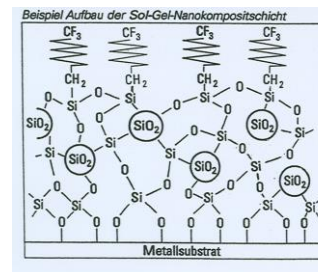
PFAS-chemistry in the inorganic/organic network?

From supplier B



Pyrolysis-GC/MS

No PFAS-chemistry

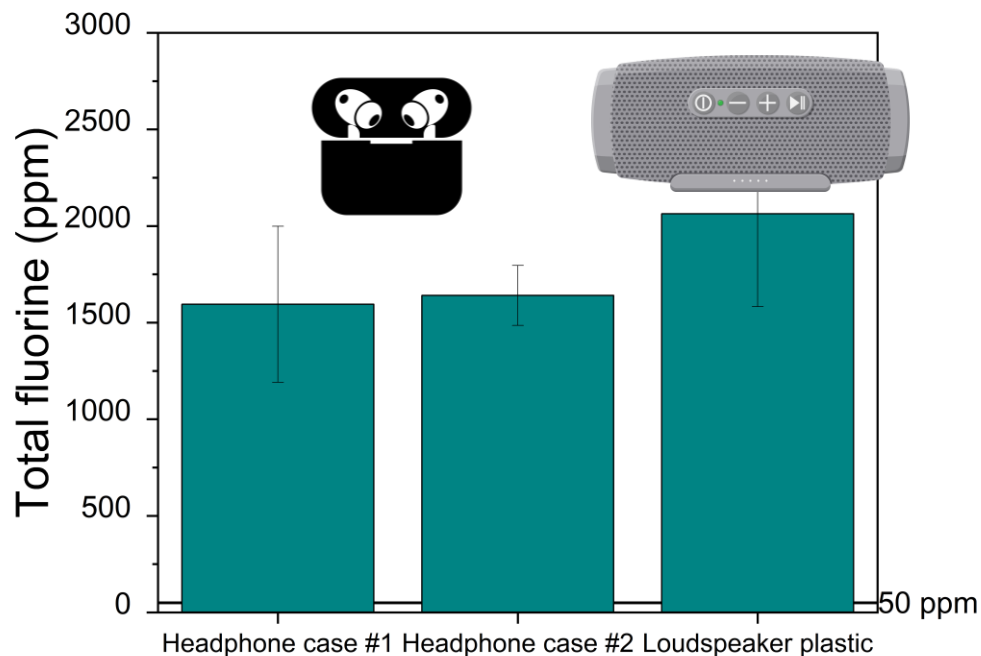




CASE STUDY

Electronic products

PTFE as an additive in plastic



Pyrolysis-GC/MS verifies that the quantified fluorine originates from the fluoropolymer PTFE.

Pyrolysis-GC/MS also verified PTFE in the construction plastic in my computer power cable.



Study with European Outdoor Group



Illustrative photos of analysed articles



- Disassembling of products
- Analysis of selected components based on function and higher probability of finding PFAS
- Analysis with pyrolysis-GC/MS
- Target analysis (PFAS22) of displays and printed circuit boards

Summary of analyses

X = Analysed part
 ✓ = Presence of PFAS

Product type	PCB	Display	Cables	Outside battery/Battery case	Plastic	Textile part	Charging cable	Transparent lamp
Led vest ¹	X			✓		X		
Headlamp ²	X, X		X	X, ✓	X	X, X		
Headlamp ²	X, X			✓				X
Headlamp ²	X		X, X, ✓	X, ✓	X			
Headlamp ²	X		X	X				X
Avalanche beacon ²	X, X, X, X	X, X, X, X, X, X	X, X	X	X			
Avalanche beacon ¹	X	X		X				
Battery pack ²	X			X, X, X			X, X, X, X	

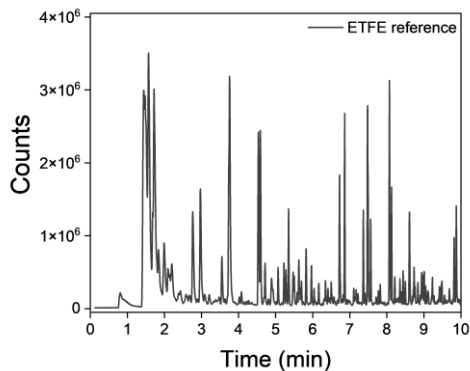
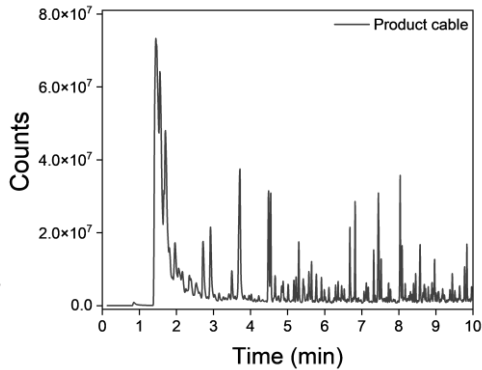
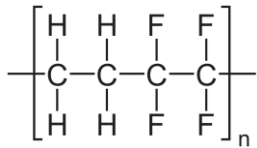
¹Driven by non-rechargeable alkaline batteries

²Driven by rechargeable batteries

Fluoropolymer PTFE was found in the outside battery/battery case in 4 products.
Fluoropolymer ETFE found in 1/9 analyzed cables.
 PPT-levels (extremely low) of specific PFAS quantified in the printed circuit boards and displays

Cables

Fluoropolymer ETFE found in one of nine analysed cables

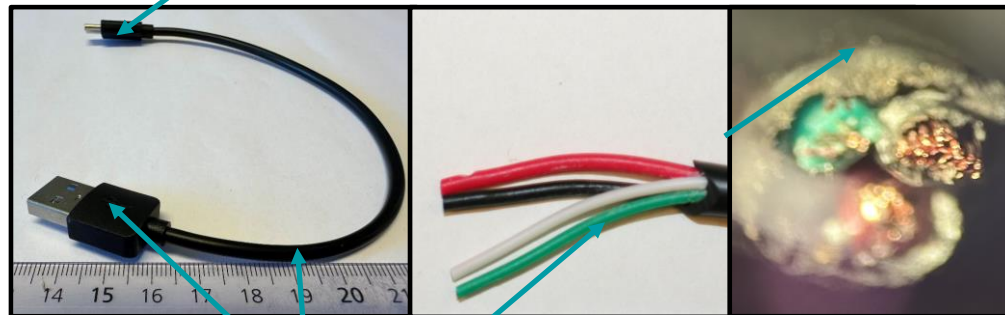


Fluoropolymers have high dielectric strength and temperature resistance and may be used in cables for electrical insulation.

Other cable materials in analysed products:

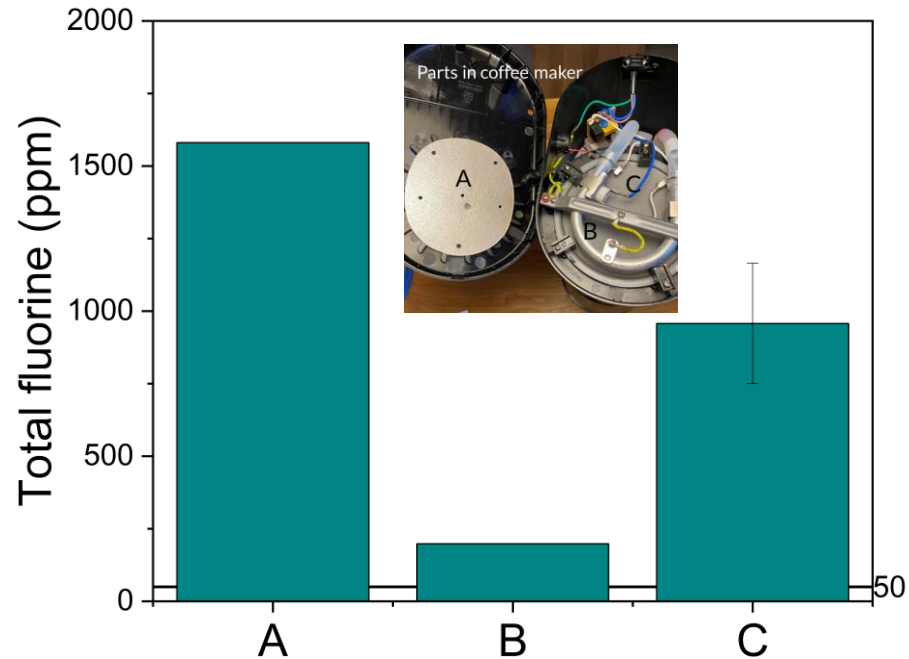
Polyethylene (PE)
Polyvinyl chloride (PVC)
Glass fibres
Polyurethane

PP & styrene



PVC + phthalates

Quantified fluorine may not be PFAS



Some parts in an analysed coffee maker showed a total fluorine concentration > 50 ppm.

The presence of PFAS in A, B and C could not be confirmed with pyrolysis-GC/MS.

MICA used for fire protection and isolation is a possible source of fluorine in electronic products



To summarise

Conclusions

Main message 1:
There are analytical methods that captures polymeric PFAS!

Main message 2:
It is possible to enforce a universal PFAS restriction!



- Proposed workflow for PFAS-analysis works in practice and on many different types of products.
- Pyrolysis-GC/MS complements fluorine quantification, confirming organic nature (PFAS).
- Target analysis with oxidation (TOP) is recommended in stage 3 (higher chance to detect PFAS).
- Direct thermal breakdown is key to detect polymeric PFAS.
- Analysis on component level in complex products.



RI.
SE

Acknowledgements

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Thank you!

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