

PAPER

View Article Online
View Journal | View Issue



Cite this: *Environ. Sci.: Processes Impacts*, 2024, 26, 82

Identification and quantification of fluorinated polymers in consumer products by combustion ion chromatography and pyrolysis-gas chromatography-mass spectrometry†

Lisa Skedung,^{‡*a} Eleni Savvidou,^{‡*c} Steffen Schellenberger,^b Anders Reimann,^a Ian T. Cousins^{‡c} and Jonathan P. Benskin^{‡*c}

Total fluorine was determined in 45 consumer product samples from the Swedish market which were either suspected or known to contain fluorinated polymers. Product categories included cookware (70–550 000 ppm F), textiles (10–1600 ppm F), electronics (20–2100 ppm F), and personal care products (10–630 000 ppm F). To confirm that the fluorine was organic in nature, and deduce structure, a qualitative pyrolysis-gas chromatography-mass spectrometry (pyr-GC/MS) method was validated using a suite of reference materials. When applied to samples with unknown PFAS content, the method was successful at identifying polytetrafluoroethylene (PTFE) in cookware, dental products, and electronics at concentrations as low as 0.1–0.2 wt%. It was also possible to distinguish between 3 different side-chain fluorinated polymers in textiles. Several products appeared to contain high levels of inorganic fluorine. This is one of the few studies to quantify fluorine in a wide range of consumer plastics and provides important data on the concentration of fluorine in materials which may be intended for recycling, along with insights into the application of pyr-GC/MS for structural elucidation of fluorinated polymers in consumer products.

Received 9th October 2023
Accepted 5th December 2023

DOI: 10.1039/d3em00438d

rsc.li/espi

Environmental significance

Due to their unique physical–chemical properties, per- and polyfluoroalkyl substances (PFAS) are used across a wide range of consumer products. PFAS may be released into the environment over the course of a product's lifecycle (including during manufacture, use and disposal). While class-wide regulation to mitigate PFAS exposure is currently under consideration, appropriate analytical tools are still needed to support enforcement. The present work determined total fluorine across four different product categories (cookware, textiles, electronics and personal care products), and compared these levels to proposed regulatory guidelines. Thereafter, a new approach based on pyrolysis gas chromatography-mass spectrometry was validated for identifying the nature (*i.e.*, organic or inorganic) and structure of the fluorine. In addition to providing new measurements of total fluorine in consumer products suitable for inventories and environmental emission estimates, this study lays the groundwork for new analytical approaches for identifying PFAS in consumer products which may be suitable for future regulatory enforcement.

Introduction

Per- and polyfluoroalkyl substances (PFAS) encompass a diverse class of over 12 000 chemicals containing at least one per-fluoromethyl (CF₃) or methylene (–CF₂–) group.^{1,2} Collectively, these chemicals span a wide range of physical–chemical

properties, from low molecular weight, highly polar, water-soluble acids (*e.g.* trifluoroacetic acid) to high molecular weight, water- and oil-repelling polymers (*e.g.* polytetrafluoroethylene (PTFE)). The unique properties of PFAS have led to their widespread use in materials such as food packaging, paper, textiles, plastics, and cosmetic products.³ However, PFAS are also highly persistent and have been linked to adverse effects in humans and in animal models⁴ as well as in wildlife.⁵ This is particularly concerning considering that PFAS already contaminate the global environment,^{6,7} and occur in the tissues of humans and wildlife everywhere.⁸

As a result of their widespread occurrence and problematic risk profile, efforts to restrict the use of PFAS have ramped up over the last 2 decades. In 2020, the EU's Chemicals Strategy for Sustainability indicated that use of PFAS should be phased out

^aRISE Research Institutes of Sweden, Department Materials and Surface Design, Stockholm, Sweden. E-mail: lisa.skedung@ri.se

^bRISE Research Institutes of Sweden, Unit Environment and Sustainable Chemistry, Stockholm, Sweden

^cStockholm University, Department of Environmental Science, Stockholm, Sweden. E-mail: Eleni.Savvidou@aces.su.se; Jon.Benskin@aces.su.se

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3em00438d>

‡ Shared first authorship.



Pyrolysis-gas chromatography-mass spectrometry (pyr-GC/MS) is a commonly used method for identifying plastic and plastic additives,²⁵ and involves pyrolyzing a sample directly (*i.e.* without extraction) at temperatures between 250–1000 °C, followed by online analysis of the degradation products.²⁵ Pyr-GC/MS has been successfully applied for distinguishing PTFE from SFPs in textiles of firefighter turnout gear¹⁸ and for studying

The objectives of the present work were to carry out a broad survey of fluorine content in consumer products from the Swedish Market using CIC and evaluate the potential of pyr-GC/MS for characterizing the nature of the fluorine. Collectively, these data represent the most extensive survey of fluorine content in materials and provide important information on both the concentration and identity of PFAS in these products. This work offers a new means of screening polymeric PFAS in consumer products that may be suitable for enforcing the EU-wide PFAS restriction proposal, when it comes into force.

Samples

Textiles. A total of 13 individual textile products were examined in the present work. Three products (shade sail, tablecloth, and backpack) did not include any information about the coating. The remaining 10 textiles consisted of 5 fabric types (nylon, polyester with polyurethane laminate, polyamide, and polyester textile with polyester laminate, and

cotton), which, according to the suppliers, were treated with commercial PFAS-free (coded as “C0-finish”) or C6-SFP (coded as “C6-finish”) durable water repellent (DWR) coatings. Textiles were sub-sampled using scissors that were pre-cleaned with methanol. The samples were stored in PP tubes prior to analysis. Further, three pieces of each fabric (8.6–59 cm²) were weighed for density estimation.

Instrumental analysis

Total fluorine determination by combustion ion chromatography (TF-CIC). TF measurements were carried out on all samples using a Thermo-Mitsubishi combustion ion chromatograph (CIC) using a previously established method (Schultes *et al.* 2018). Between 0.1 and 0.9 mg of sample material (depending on expected fluorine concentrations) was weighed into a pre-baked ceramic boat. The samples were combusted in a furnace (HF-210, Mitsubishi) at 1100 °C under a flow of oxygen (400 mL min⁻¹) and argon mixed with water vapor (200 mL min⁻¹) for approximately 5 minutes. Combustion gases were absorbed in MilliQ water during the entire length of the combustion process using a gas absorber unit (GA-210, Mitsubishi). An aliquot of the absorption solution (50 µL) was injected onto an ion chromatograph (Dionex Integrion HPIC, Thermo Fisher Scientific) equipped with an anion exchange column (Dionex IonPac AS19 2 × 50 mm guard column and 2 × 250 mm analytical column, 7.5 µm particle size) operated at 30 °C. Chromatographic separation was achieved by running a gradient of aqueous hydroxide mobile phase ramping from 8 mM to 60 mM at a flow rate of 0.25 mL min⁻¹. Fluoride was detected using a conductivity detector.

Structural elucidation by pyrolysis GC-MS (pyr-GC/MS). Pyrolysis was carried out on a subset of samples (33 in total, see Table S1†) using a PYROLA 2000 filament pulse pyrolyzer (Pyrol AB, Lund, Sweden). The pyrolysis chamber (165 °C) was purged with helium gas and thereafter ~0.5 mg of sample was pyrolyzed at approximately 700 °C (determined from initial testing with cookware products). The GC/MS system consisted of an Agilent 8890 GC coupled to an Agilent 5977B MSD mass spectrometer. Chromatography was achieved on a 30 m × 0.25 mm i.d. Agilent HP-5MS Ultra Inert (Chrompack) column. The temperature programme started at 50 °C (hold for 2 min), then increased at 21 °C min⁻¹ to 325 °C (hold for 12 min). The mass spectrometer was operated in electron impact (EI) mode.

While pyr-GC/MS is a well-established technique, it has not been widely adopted for structural elucidation of PFAS in consumer products. In order to examine the potential of PFAS to form “fingerprint-like” pyrolysis products suitable for identification in consumer products, we examined the pyrolysis GC(EI) MS spectra produced from authentic standards of perfluorohexanoate (PFHxA), perfluorooctanoate (PFOA), and perfluorohexane sulfonate (PFHxS) purchased from Sigma-Aldrich, and perfluorobutane sulfonate (PFBS) purchased from Dyneon (Belgium) as well as four reference polyamide textiles (one uncoated, one coated with C₄F₉SO₂N– “C4-SFP”, one with C₆F₁₃C₂H₂– “C6-SFP”, and one with C₈F₁₇C₂H₂– “C8-SFP”) that were prepared in-house¹⁴ (for details see Fig. S2†). Two

cookware products known to contain a PTFE coating (C2 and C11) and one baking plate (C1) known to contain a ceramic Si-based coating were also used as references. Finally, pure polymer granulates of fluorinated ethylene propylene (FEP) and perfluoroalkoxy alkanes (PFA) which were kindly donated by a Swedish cable producer were analyzed.

Quality control

We previously demonstrated that fluorine measurements on our CIC were F-specific.³⁰ Moreover, a series of internal validation and interlaboratory comparisons have confirmed total fluorine measurements to be accurate, reproducible, and in good concordance with other laboratories across a wide range of matrices.^{16,17,22,31} Ongoing QC in the present work involved (at minimum) triplicate combustions of boat blanks, a PFOS/PFOA standard and a certified reference material (CRM, BCR-461, fluorine in clay) for each batch of samples. Measurements of the CRM showed good agreement with the reference value (568 ± 60 mg of F kg⁻¹), with an average recovery of 91 ± 8%, indicating good method accuracy and precision. Around 30% of the samples in each batch were measured in duplicates. Finally, analysis of 16 samples by PIGE (see ESI and Fig. S1†), showed no statistical difference (Wilcoxon-test; *p* > 0.05) and a reasonable correlation with data produced by CIC (*r*² > 0.71). Limits of detection (LODs) were estimated using the mean concentration measured in boat blanks plus 3 times the standard deviation. To avoid carryover, two to three boat blanks were measured after samples where high F content was expected. The average LOD for all analyzed batches was 22 µg F g⁻¹.

Results and discussion

Pyrolysis GC/MS method validation

Perfluoroalkyl acid (PFAA) standards. Pyr-GC/MS analysis of authentic standards of PFBS, PFHxA, PFHxS, and PFOA revealed a single peak eluting early in each of the total ion chromatograms, which was only observable after removing the mass spectrometer's solvent delay. As expected, retention times increased with increasing perfluoroalkyl chain length (*i.e.* 1.41 min, 1.42 min, 1.44 min and 1.48 min, for PFBS, PFHxA, PFHxS, and PFOA, respectively; Fig. 1). Unfortunately, most information on the original structure contained in the pyrolysis products was lost during EI ionization, resulting in highly fragmented mass spectra (Fig. 1). As observed previously for PFOA,²⁶ the perfluoroalkyl carboxylates (PFHxA and PFOA) produced major ions at *m/z* 131 ([C₃F₅]⁺) and *m/z* 69 ([CF₃]⁺), followed by lower abundance ions at *m/z* 181 ([C₄F₇]⁺), 51 ([CF₂H]⁺), 93 ([C₃F₃]⁺), 100 ([C₂F₄]⁺), and 119 ([C₂F₅]⁺). In comparison, the most abundant ion produced by the perfluoroalkane sulfonates (PFBS and PFHxS) occurred at *m/z* 69, followed by lower abundance ions at *m/z* 48 ([SO]⁺), 50 ([CF₂]⁺), 64 ([SO₂]⁺), 81 ([C₂F₃]⁺), 93, 100, 119, 131, 169 ([C₃F₇]⁺), and 181 ([C₄F₇]⁺). Slight differences in the relative abundance of ions formed from PFBS and PFHxS were observed (*e.g.* PFBS produced a much stronger signal at *m/z* 131 compared to PFHxS), but no ions appeared to be specific to either substance.



Overall, these data indicate that perfluoroalkane sulfonates can be differentiated from perfluoroalkyl carboxylates based on differences in mass spectra, but that information on the chain length of the pyrolyzed substance requires the retention time of an authentic standard and cannot be deduced from the mass spectra alone, at least when using EI ionization.

Side-chain fluorinated polymer reference materials. Analysis of the three SFP-coated polyamide reference textiles revealed significantly more complex total ion chromatograms compared to the PFAA standards, with many different peaks originating from the textile. Considering the results obtained from the PFAA standards, we anticipated that the major fluorinated peaks would elute early (*i.e.* ~ 1 – 2 min) in the SFP chromatograms. Indeed, high intensity peaks were observed at 1.28 (C4), 1.52 (C6), and 1.97 (C8) min which were made up of

characteristic fluorinated ions (*i.e.* m/z 51 ($[\text{HCF}_2]^+$), 69, 77 ($[\text{C}_3\text{H}_3\text{F}_2]^+$), 100, 119, 131, 150, and 169; Fig. 2). Slight differences in the relative abundance of ions within these peaks were observed for each SFP. For example, m/z 69 was the major ion observed for the C4-SFP, whereas m/z 77 was the major ion for C6- and C8-SFPs. Importantly, no peaks were observed between 1.3 and 2 min in the total ion chromatogram of the uncoated (*i.e.* blank) polyamide textile, confirming that this retention time region is useful for monitoring the presence of SFPs in textiles. However, given that none of the ions making up these early eluting peaks provided information on the length of the side chain, the use of SFP reference textile materials for confirmation is recommended to confirm the exact retention time for a specific instrument (as was performed in the present study).



Fig. 1 Total ion chromatograms and mass spectra (inset) of the major peak for the individual PFAA standards PFBS (A), PFHxA (B), PFHxS (C), and PFOA (D).

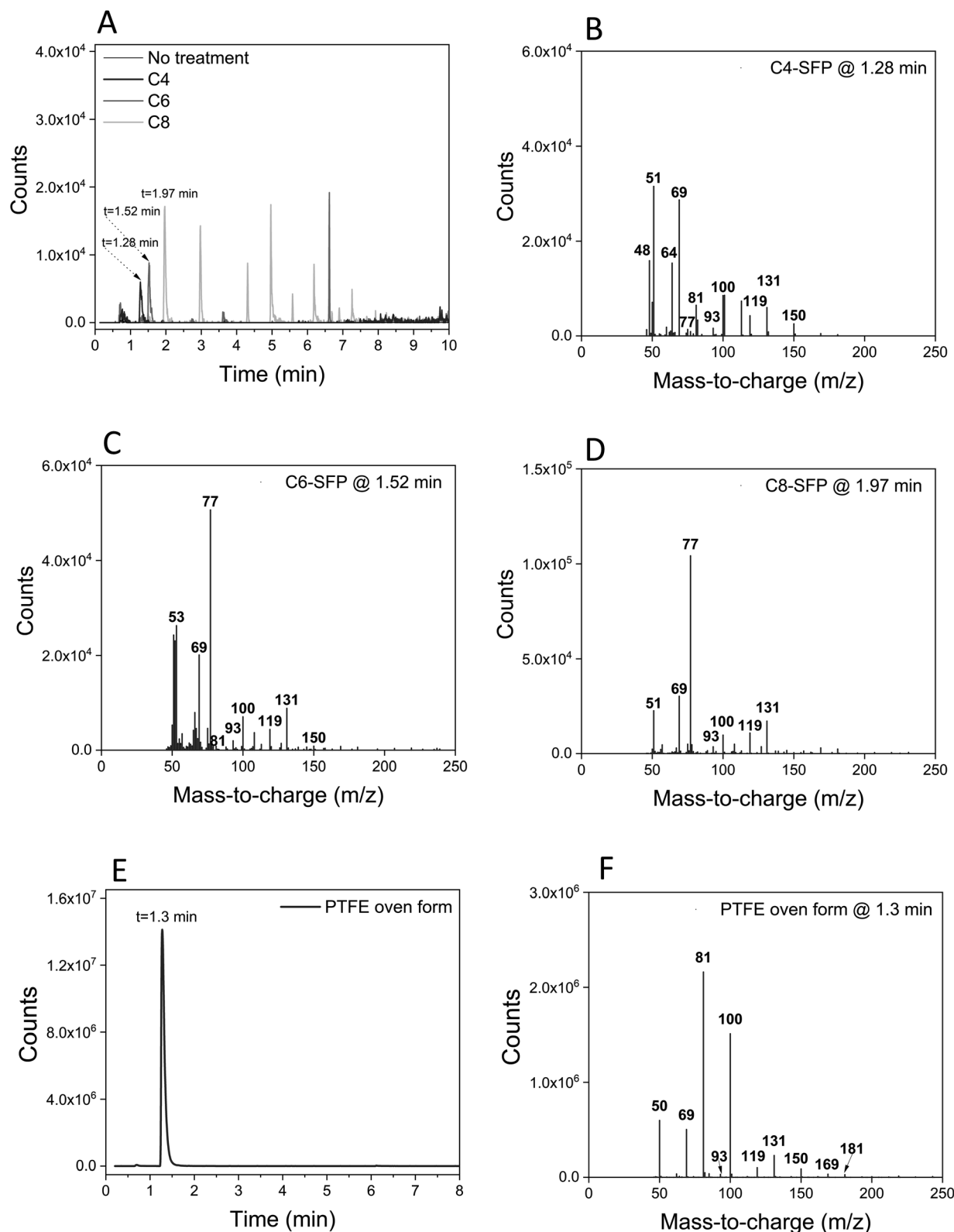


Fig. 2 Extracted ion chromatograms (m/z 131) for C4, C6, and C8 reference textiles (panel (A)) and the associated mass spectra for the first peak in each chromatogram (panels (B)–(D)). Panel (E) shows the total ion chromatogram for the PTFE-coated oven form, while the mass spectrum associated with the single peak at 1.3 min is provided in panel (F).

We also examined later eluting peaks in the chromatograms, which we hypothesised could contain higher molecular weight pyrolysis products suitable for *de novo* structural elucidation of

SFPs. For the C4-SFP, a peak at 9.23 min contained a potentially diagnostic ion at m/z 341 (tentatively $[C_4F_9SO_2NC_3H_8]^+$), along with characteristic fluorinated ions at m/z 69, 100, and 131,





Fig. 3 (A) Total fluorine concentrations in electronics, relative to the 50 ppm regulatory limit. The polymer listed above each bar indicates the identity of the organofluorine determined by pyr-GC/MS. (B) Overview of coffee maker parts analyzed for total fluorine. (C) Extracted ion chromatogram (m/z 100) for the plastic wireless headphone case E38 with a PTFE peak at 1.3 min and a methyl methacrylate peak at 2.4 min. (D) Mass spectrum of PTFE with the characteristic m/z peaks. Bars of the same colour indicate that subsamples were obtained from the same product. Error bars represent standard deviation.

confirming the occurrence of a fluorinated pyrolysis product at this retention time. Likewise, a peak at 6.62 min in the C6-SFP chromatogram contained an ion at m/z 434 (tentatively $[C_6F_{13}-C_2H_4OC_4H_7O]^+$) along with a number of typical fluorinated ions (m/z 51, 69, 77, 100, 119 and 131). Finally, examination of the C8-SFP chromatogram revealed a peak at 6.19 min (m/z 505; tentatively $C_{12}H_{11}F_{13}O_2$) which again contained characteristic fluorinated ions (m/z 51, 69, 77, 100, 119, 131 and 169). In comparison, none of the aforementioned ions were observed at the same retention times in the uncoated textile. In fact, the only peak observed in the uncoated textile that risked triggering a false positive eluted very late in the program (10.66 min), and only contained two ions (m/z 77 and 131) in common with fluorinated ions. Confirmation of the presence of a SFP should therefore require positive matches for more than two typical PFAS ions (Table S2[†]) eluting at the same retention time.

Clearly, late eluting peaks in the chromatogram can aid in structural elucidation, but we note that these peaks are typically much less intense than the early eluting peaks in the chromatogram and may therefore be more difficult to detect. Overall, we recommend the use of m/z 131 as a first step in screening for SFPs in textiles. With few exceptions, this ion is both sensitive and highly specific to SFPs and provided much less interference compared to the total ion chromatogram. Although ion m/z 77 is more intense, it is a common ion for many pyrolysis products and less specific to PFAS.

Fluoropolymer reference materials. Pyrolysis of PTFE obtained from two reference cookware products (C2 and C11) produced a single chromatographic peak at 1.3 min (Fig. 2). Many of the ions in this peak were consistent with those observed from pyrolysis of the PFAA standards (*i.e.* m/z 69, 81, 100, 119, 131), but at different relative abundances (*e.g.* m/z 81





Fig. 4 (A) Total fluorine concentrations in personal care products relative to the 50 ppm regulatory limit. The polymer listed above each bar indicates the identity of the organofluorine determined by pyr-GC/MS. (B) Extracted ion chromatogram (m/z 100) for the dental floss products H74 and H79 with a PTFE peak at 1.3 min. (C) Mass spectrum of PTFE with the characteristic m/z peaks illustrated for sample H79. Error bars represent standard deviation.

and 100 were the major ions produced from PTFE compared to m/z 131 and 69 for the PFAA standards). The exceptions were m/z 50 ($[\text{CF}_2]^+$) and 150 ($[\text{C}_3\text{F}_6]^+$), which were only observed following pyrolysis of PTFE. These results are largely consistent with Muensterman *et al.* (2022),¹⁸ who reported the same ions at similar ratios following pyrolysis of a textile containing PTFE. Thus, m/z 100 ($[\text{C}_2\text{F}_4]^+$), m/z 50 ($[\text{CF}_2]^+$) and 150 ($[\text{C}_3\text{F}_6]^+$) occurring at 1.3 min initially appeared useful to screen for PTFE. However, subsequent pyrolysis of the fluoropolymers PFA and FEP revealed chromatograms with a peak eluting at the same retention time (after accounting for a retention time shift due to the use of a new GC column; Fig. S2†) and mass spectra which were indistinguishable from those of PTFE (Fig. S2†). This is perhaps not surprising considering their structural similarities. Since non-stick coating formulations commonly use a mixture of all three polymers,³² observation of a signal at 1.3 min from m/z 50, 100, and 150 should be considered a general indicator for the occurrence of PTFE and its co-polymers, rather than

specifically for PTFE. For this reason, detection of PTFE in consumer products (see below) refers to “PTFE-related” polymers rather than specifically to PTFE.

A ceramic baking plate was also included as a reference material to verify the absence of typical PFAS ions (Fig. S3†). Indeed, none of the characteristic ions previously observed for PTFE or the PFAA standards were observed at 1.3 min for the ceramic baking plate, confirming the utility of this region for monitoring PTFE-related polymers (see *e.g.* Fig. S3† vs. Fig. 1). However, the observation of environmentally persistent cyclic siloxane pyrolysis products was notable (Fig. S3†) and requires further investigation when considering the life-cycle of Si-based alternatives.

Electronics

Total fluorine concentrations in electronics ranged from <22–3040 $\mu\text{g F g}^{-1}$, with 12 out of 15 samples exceeding the 50 $\mu\text{g F g}^{-1}$ (ppm) regulatory limit suggested in the recent class-wide





Fig. 5 (A) Total fluorine concentrations in cookware, relative to the 50 ppm regulatory limit. The polymer listed above each bar indicates the identity of the organofluorine determined by pyr-GC/MS. (B) Extracted ion chromatogram (m/z 100) where PTFE is observed at 1.3 min with only for the air fryer (C9). (C) Mass spectrum of PTFE with the characteristic m/z peaks illustrated for sample C9. Error bars represent standard deviation.

restriction proposal. Ten of these products were further characterized by pyr-GC/MS. Surprisingly, the plastic headphone cases (E38 and E39) and loudspeaker plastic back plate (E25-5) showed relatively high fluorine concentrations (1595, 1641 and 2064 $\mu\text{g F g}^{-1}$). Pyr-GC/MS analysis of these samples revealed a peak with a retention time (1.3 min) and fragment ions (m/z 69, 81, 100, 131) which were characteristic of PTFE-related polymers (Fig. 3). The highest concentrations of fluorine were observed in the two glass fibre cables of the coffee maker (E18-6: 3043 $\mu\text{g F g}^{-1}$ and E18-7: 2121 $\mu\text{g F g}^{-1}$). Within the coffee maker, high concentrations occurred in the papermetal sheet (E18-1; 1580 $\mu\text{g F g}^{-1}$), another glass fibre cable (E18-2b; 957 $\mu\text{g F g}^{-1}$) and a coating (E18-4; 198 $\mu\text{g F g}^{-1}$), while the other plastic cable (E18-2a), the plastic tube (E18-3a) and the plastic holder (E18-5) contained low levels of fluorine (38–53 $\mu\text{g F g}^{-1}$). Follow-up analysis of the papermetal sheet (E18-1), heat plate coating (E18-4), and glass fibre cables (E18-2b and E18-6) by pyr-GC/MS revealed no evidence of organofluorine. For the former two samples, we speculate that the fluorine may be from mica, an inorganic pigment/filler that is commonly used in cookware to provide pearlescent aesthetics and for heat protection in high-

temperature applications. As for the glass fibre cables, the total ion chromatograms indicate a silicone coating, but we could not determine the origin of the fluorine. Clearly, all four products require further investigation to identify the structure of the fluorine measured in them. We speculate that analysis of the ash leftover after pyrolysis, for example by scanning electron microscopy and/or energy-dispersive X-ray spectroscopy (SEM-EDS), may offer a means of confirming the presence of inorganic fluorine, but this requires further investigation.

Personal care products

Total fluorine concentrations in the nine personal care products ranged from <22–630 000 $\mu\text{g F g}^{-1}$ (Fig. 4), with two products exceeding the proposed 50 $\mu\text{g F g}^{-1}$ regulatory limit. The first product, floss picks (H74; 632 670 $\mu\text{g F g}^{-1}$), contained PTFE according to the packaging, which was ultimately confirmed by pyr-GC/MS. The second product, dental floss (H79; 573 835 $\mu\text{g F g}^{-1}$), not only contained fluoride according to the packaging, but also PTFE, according to pyr-GC/MS analysis. These data highlight the importance of follow-up analysis by pyr-GC/MS for confirming the nature of total fluorine measurements. While





Fig. 6 (A) Total fluorine concentrations in textiles based on weight (light purple) and area (dark purple). (B) Extracted ion chromatogram (m/z 131) of the shade sail textile (T20) and the backpack (T22) where the presence of PFAS was initially unknown with the specific eluting retention times (1.96, 2.97 and 4.97 min). (C) The corresponding mass spectra containing typical m/z peaks suggest that T22 contains a C8-SFP. Error bars represent standard deviation.

the exact proportion of total fluorine attributed to PTFE *vs.* fluoride remains unclear, we can reasonably assume that most is from PTFE, since this appears to comprise the entirety of the floss material (the fluoride, in comparison, appears to be a coating on the floss).

Cookware

All analyzed cookware coatings contained fluorine concentrations (range 70–550 000 $\mu\text{g F g}^{-1}$) which exceeded the 50 ppm limit suggested in the restriction proposal. The highest fluorine concentrations were observed in oven form C2, frying pan C11,

and air fryer C9 (553 064 $\mu\text{g F g}^{-1}$, 335 127 $\mu\text{g F g}^{-1}$, and 22 723 $\mu\text{g F g}^{-1}$, respectively), which had concentrations several orders of magnitude higher than the other products. For C2 and C11, high concentrations were expected due to the known PTFE coating (see prior section on pyr-GC/MS method validation). For the remaining five products (*i.e.* air fryer C9, bake form C4, hamburger press C17, air fryer C19 and air fryer C72) the coating was unknown. These products were therefore all subjected to further analysis by pyr-GC/MS. Note that the bake plate C1 was not analyzed with CIC due to the challenges of removing and collecting the extremely fine powder formed when trying to scrape off the coating.



original draft, writing – review and editing; Steffen Schellenberger: visualization, investigation, writing – original draft, writing – review and editing; Anders Reimann: investigation, writing – review and editing; Ian Cousins: writing – original draft, writing – review and editing, funding acquisition; Jon Benskin: conceptualization, investigation, visualization, writing – original draft, writing – review and editing.

Conflicts of interest

There are no conflicts of interest to be declared.

Acknowledgements

The project received funding from POPFREE Industry – Towards a PFAS-free and circular industry, VINNOVA (grant number 2021-04200), Swedish Research Council FORMAS (grant number 2020-01978). Graham Peaslee and Seán Roche from the University of Notre Dame are thanked for carrying out the PIGE analysis. The POPFREE Industry partners are acknowledged for providing most of the samples for the study.

References

- 1 *CompTox Chemicals Dashboard*, <https://comptox.epa.gov/dashboard/chemical-lists/pfasmaster>, (accessed 15 November 2022).
- 2 Z. Wang, A. M. Buser, I. T. Cousins, S. Demattio, W. Drost, O. Johansson, K. Ohno, G. Patlewicz, A. M. Richard, G. W. Walker, G. S. White and E. Leinala, A New OECD Definition for Per- and Polyfluoroalkyl Substances, *Environ. Sci. Technol.*, 2021, **55**, 15575–15578.
- 3 J. Glüge, M. Scheringer, I. T. Cousins, J. C. DeWitt, G. Goldenman, D. Herzke, R. Lohmann, C. A. Ng, X. Trier and Z. Wang, An overview of the uses of per- and polyfluoroalkyl substances (PFAS), *Environ. Sci.: Processes Impacts*, 2020, **22**, 2345–2373.
- 4 S. E. Fenton, A. Ducatman, A. Boobis, J. C. DeWitt, C. Lau, C. Ng, J. S. Smith and S. M. Roberts, Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research, *Environ. Toxicol. Chem.*, 2021, **40**, 606–630.
- 5 G. T. Ankley, P. Cureton, R. A. Hoke, M. Houde, A. Kumar, J. Kurias, R. Lanno, C. McCarthy, J. Newsted, C. J. Salice, B. E. Sample, M. S. Sepúlveda, J. Steevens and S. Valsecchi, Assessing the Ecological Risks of Per- and Polyfluoroalkyl Substances: Current State-of-the Science and a Proposed Path Forward, *Environ. Toxicol. Chem.*, 2021, **40**, 564–605.
- 6 J. W. Washington, K. Rankin, E. L. Libelo, D. G. Lynch and M. Cyterski, Determining global background soil PFAS loads and the fluorotelomer-based polymer degradation rates that can account for these loads, *Sci. Total Environ.*, 2019, **651**, 2444–2449.
- 7 D. Muir and L. T. Miaz, Spatial and Temporal Trends of Perfluoroalkyl Substances in Global Ocean and Coastal Waters, *Environ. Sci. Technol.*, 2021, **55**, 9527–9537.
- 8 A. O. De Silva, J. M. Armitage, T. A. Bruton, C. Dassuncao, W. Heiger-Bernays, X. C. Hu, A. Kärrman, B. Kelly, C. Ng, A. Robuck, M. Sun, T. F. Webster and E. M. Sunderland, PFAS Exposure Pathways for Humans and Wildlife: A Synthesis of Current Knowledge and Key Gaps in Understanding, *Environ. Toxicol. Chem.*, 2021, **40**, 631–657.
- 9 European Commission, *Chemicals Strategy for Sustainability*, <https://circabc.europa.eu/ui/group/8ee3c69a-bccb-4f22-89ca-277e35de7c63/library/dd074f3d-0cc9-4df2-b056-dabcacfc99b6/details?download=true>, (accessed 21 September 2023).
- 10 European Chemicals Agency, *ANNEX XV RESTRICTION REPORT-Per- and Polyfluoroalkyl Substances (PFAS), Proposal for a Restriction*, <https://echa.europa.eu/documents/10162/1c480180-ecce9-1bdd-1eb8-0f3f8e7c0c49>, (accessed 21 September 2023).
- 11 European Chemicals Agency, *The PFAS Restriction Proposal - Media Briefing Brussels*, 2023, https://echa.europa.eu/documents/10162/2082415/2023-02-07_pfas+media+briefing_en.pdf/1661579d-353a-2fb0-1062-38fc3eb4bd78?t=1675849038730 (accessed 21 September 2023).
- 12 R. C. Buck, J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury and S. P. van Leeuwen, Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins, *Integr. Environ. Assess. Manage.*, 2011, **7**, 513–541.
- 13 B. Améduri, The Promising Future of Fluoropolymers, *Macromol. Chem. Phys.*, 2020, **221**, 1900573.
- 14 S. Schellenberger, P. Gillgard, A. Stare, A. Hanning, O. Levenstam, S. Roos and I. T. Cousins, Facing the rain after the phase out: Performance evaluation of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics, *Chemosphere*, 2018, **193**, 675–684.
- 15 A. E. Robel, K. Marshall, M. Dickinson, D. Lunderberg, C. Butt, G. Peaslee, H. M. Stapleton and J. A. Field, Closing the Mass Balance on Fluorine on Papers and Textiles, *Environ. Sci. Technol.*, 2017, **51**, 9022–9032.
- 16 L. Schultes, G. F. Peaslee, J. D. Brockman, A. Majumdar, S. R. McGuinness, J. T. Wilkinson, O. Sandblom, R. A. Ngwenyama and J. P. Benskin, Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?, *Environ. Sci. Technol. Lett.*, 2019, **6**, 73–78.
- 17 M. Z. Lauria, A. Naim, M. Plassmann, J. Fäldt, R. Sühling and J. P. Benskin, Widespread Occurrence of Non-Extractable Fluorine in Artificial Turfs from Stockholm, Sweden, *Environ. Sci. Technol. Lett.*, 2022, **9**, 666–672.
- 18 D. J. Muensterman, I. A. Titaley, G. F. Peaslee, L. D. Minc, L. Cahuas, A. E. Rodowa, Y. Horiuchi, S. Yamane, T. N. J. Fouquet, J. C. Kissel, C. C. Carignan and J. A. Field, Disposition of Fluorine on New Firefighter Turnout Gear, *Environ. Sci. Technol.*, 2022, **56**, 974–983.
- 19 K. W. Pütz, S. Namazkar, M. Plassmann and J. P. Benskin, Are cosmetics a significant source of PFAS in Europe? product inventories, chemical characterization and



- emission estimates, *Environ. Sci.: Processes Impacts*, 2022, **24**, 1697–1707.
- 20 J. Zweigle, B. Bugsel and C. Zwiener, Efficient PFAS prioritization in non-target HRMS data: systematic evaluation of the novel MD/C-m/C approach, *Anal. Bioanal. Chem.*, 2023, **415**, 1791–1801.
 - 21 K. Rankin and S. A. Mabury, Matrix Normalized MALDI-TOF Quantification of a Fluorotelomer-Based Acrylate Polymer, *Environ. Sci. Technol.*, 2015, **49**, 6093–6101.
 - 22 I. Liagkouridis, R. Awad, S. Schellenberger, M. M. Plassmann, I. T. Cousins and J. P. Benskin, Combined Use of Total Fluorine and Oxidative Fingerprinting for Quantitative Determination of Side-Chain Fluorinated Polymers in Textiles, *Environ. Sci. Technol. Lett.*, 2022, **9**, 30–36.
 - 23 J. Zweigle, B. Bugsel, C. Capitain and C. Zwiener, PhotoTOP: PFAS Precursor Characterization by UV/TiO₂ Photocatalysis, *Environ. Sci. Technol.*, 2022, **56**, 15728–15736.
 - 24 V. A. Nikiforov, Hydrolysis of FTOH precursors, a simple method to account for some of the unknown PFAS, *Chemosphere*, 2021, **276**, 130044.
 - 25 F. Akoueson, C. Chbib, S. Monchy, I. Paul-Pont, P. Doyen, A. Dehaut and G. Duflos, Identification and quantification of plastic additives using pyrolysis-GC/MS: A review, *Sci. Total Environ.*, 2021, **773**, 145073.
 - 26 F. Xiao, P. C. Sasi, B. Yao, A. Kubátová, S. A. Golovko, M. Y. Golovko and D. Soli, Thermal Stability and Decomposition of Perfluoroalkyl Substances on Spent Granular Activated Carbon, *Environ. Sci. Technol. Lett.*, 2020, **7**, 343–350.
 - 27 A. Alinezhad, P. Challa Sasi, P. Zhang, B. Yao, A. Kubátová, S. A. Golovko, M. Y. Golovko and F. Xiao, An Investigation of Thermal Air Degradation and Pyrolysis of Per- and Polyfluoroalkyl Substances and Aqueous Film-Forming Foams in Soil, *ACS ES&T Engg*, 2022, **2**, 198–209.
 - 28 A. Alinezhad, H. Shao, K. Litvanova, R. Sun, A. Kubatova, W. Zhang, Y. Li and F. Xiao, Mechanistic Investigations of Thermal Decomposition of Perfluoroalkyl Ether Carboxylic Acids and Short-Chain Perfluoroalkyl Carboxylic Acids, *Environ. Sci. Technol.*, 2023, **57**, 8796–8807.
 - 29 POPFREE Industry – Towards a PFAS-free and circular industry, <https://www.ri.se/en/popfree/popfree-industry>, accessed 13 December 2022.
 - 30 K. M. Spaan, B. Yuan, M. M. Plassmann, J. P. Benskin and C. A. de Wit, Characterizing the Organohalogen Iceberg: Extractable, Multihalogen Mass Balance Determination in Municipal Wastewater Treatment Plant Sludge, *Environ. Sci. Technol.*, 2023, **57**, 9309–9320.
 - 31 A. Kärman, L. W. Y. Yeung, K. M. Spaan, F. Thomas Lange, M. Anh Nguyen, M. Plassmann, C. A. de Wit, M. Scheurer, R. Awad and J. P. Benskin, Can determination of extractable organofluorine (EOF) be standardized? First interlaboratory comparisons of EOF and fluorine mass balance in sludge and water matrices, *Environ. Sci.: Processes Impacts*, 2021, **23**, 1458–1465.
 - 32 P. Thomas, The use of fluoropolymers for non-stick cooking utensils, *Surf. Coat. Int. (1991-2000)*, 1998, **81**, 604–609.

