



Investigation of pH-dependent extraction methods for PFAS in (fluoropolymer-based) consumer products: A comparative study between targeted and sum parameter analysis

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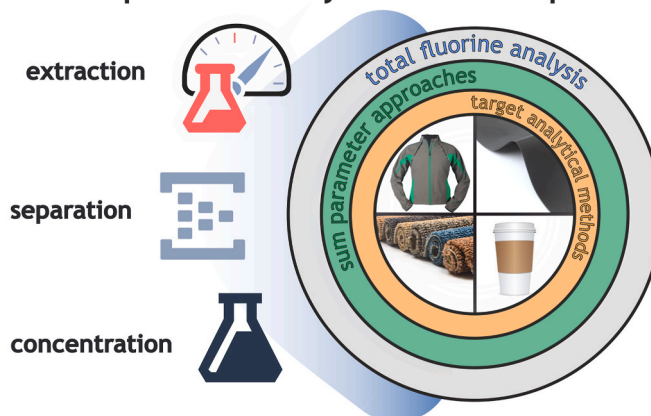
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HIGHLIGHTS

- A hydrolytic extraction protocol for sum parameter analysis of PFAS in consumer goods was developed.
- First analysis for the sum parameter "hydrolyzable organic bound fluorine" (HOF) by combustion ion chromatography (CIC).
- Basic hydrolysis yields higher HOF values compared to classical EOF for fluoropolymer-based consumer products.
- The fluorine mass balance approach was conducted to assess the efficiency of the extraction methods.
- Depending on the type of consumer good, target analysis methods can provide accurate fluorine recovery values or no results.

GRAPHICAL ABSTRACT

PFAS sum parameter analysis of consumer products



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ABSTRACT

Here, we report a comparative study of different sum parameter analysis methods for the extraction of per- and polyfluoroalkyl substances (PFAS) from manufactured consumer products, which can be measured by combustion ion chromatography (CIC). Therefore, a hydrolysis-based extraction method was further developed, which accounts for the addition of hydrolyzable covalently bound polyfluoroalkylated side-chain polymers (SFPs) to the extractable organic fluorine portion of the mass balance proposed as "hydrolyzable organically bound fluorine" (HOF). To test this hypothesis, the method was applied to 39 different consumer products containing fluoropolymers or monomeric PFAS taken from four different categories: outdoor textiles, paper packaging, carpeting, and permanent baking sheets. We also evaluated the method's efficiency by extracting four

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Solid-liquid extraction
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synthesized fluorotelomer polyacrylate reference compounds. The total fluorine (TF) and extractable organically bound fluorine (EOF) values were measured through CIC using established protocols. The TF values ranged from sub-ppb to %-levels, depending on the compound class. All samples showed results for hydrolyzed organofluorine (HOF) between 0.03 and 76.3 $\mu\text{g/g}$, while most EOF values were lower ($<\text{LOD}$ to 58.1 $\mu\text{g/g}$). Moreover, the methods were contrasted with the "total hydrolyzable precursor" (THP) assay analyzed using gas-chromatography coupled mass spectrometry (GC-MS), which yielded concentrations of 6:2–10:2 fluorotelomer alcohols ($<\text{LOD}$ -568 $\mu\text{g/g}$) for textile and paper samples. Furthermore, targeted analytical investigation of 25 compounds via liquid chromatography coupled tandem mass spectrometry (LC-MS/MS) was conducted and accounted for significantly lower sum amounts ($<\text{LOD}$ -0.98 μg PFAS/g). To estimate the fluorine mass balance of all methods, the fluorine levels of target analytical data were calculated and compared to the sum parameter values and evaluated. Finally, the efficiency of the extraction method was approximated by the recovery analysis of four selected SFP model compounds compared to their TF values, yielding 36.7–74.0% after extraction and 3.8–36.3% after processing the extract for the HOF sum parameter.

1. Introduction

The totality of per- and polyfluoroalkyl substances (PFAS) is a chemically synthesized class of more than 7 million compounds specifically designed for their application as grease, water and stain repellent material coatings or as additives used in a wide variety of industrial applications and products of daily use (Glüge et al., 2020; Schymanski et al., 2023). Due to the increasing number of critical scientific reports over the last decade regarding their persistence, environmental effects and potential carcinogenic properties, PFAS have rapidly emerged as a major area of interest and research for industrial, regulatory and scientific research stakeholders worldwide (Chohan et al., 2021; Fenton et al., 2021; Ng et al., 2021; Pelch et al., 2022; Rodgers et al., 2022). Nonetheless, only few governmental restrictions have been enacted to date, mainly resulting in the discontinuation of production and use of certain PFAS in consumer products with a slightly shifted range of chemical compounds (Brennan et al., 2021; Post, 2021). As an example, the European chemical legislation CLP (classification, labelling and packaging) solely prohibits perfluorononanoic acid, perfluorodecanoic acid and perfluorooctanesulfonic acid (PFNA, PFDA and PFOS) regarding production and use (REGULATION, 2008). In addition, a total of nine compounds are currently labeled as "substances of very high concern" and another group of three "restricted substances" are banned via REACH Annex XVII (PFOA, PFNA and PFDA), with four more compounds potentially added in the future (Europa, 2023). In 2023, the European Chemical Agency (ECHA) published a proposal to ban all non-essential use of all PFAS (ECHA, 2023). Given the vast number of produced and applied PFAS, PFAS regulations need to be updated regularly. The fast alteration of compound design leads to a much more demanding assessment of hazardous chemicals, which is already time-consuming and limited by analytical approaches (Bock and Laird, 2022; Tyrrell, 2023).

Despite being challenging, numerous extraction protocols for PFAS in consumer samples were established based on analysis via liquid chromatography coupled mass spectrometry (LC-MS/MS), which allows for identification of up to 50 compounds but is limited by the availability of isotopically labeled analysis standards (Kotthoff et al., 2015; Bokkers et al., 2019; Dueñas-Mas et al., 2023; Zhou et al., 2023). To avoid these limitations, alternative sum parameter approaches were developed: The "total oxidizable precursor" (TOP) assay was invented to quantify precursor molecules such as alcohols and esters as their oxidized products using available standards and LC-MS/MS (Houtz and Sedlak, 2012). Originally designed for a high range of environmental and product matrices, the method was later refined as "direct TOP" (dTOP) assay (Göckener et al., 2022) and "photochemically induced TOP" (photo-TOP) assay (Zweigle et al., 2022), respectively. In 2021, Nikiforov introduced a hydrolysis-based extraction method and exclusive quantification of four fluorotelomer alcohols (FTOHs) via gas chromatography coupled mass spectrometry (GC-MS), to propose a sum parameter for

non-extractable side-chain fluorinated polymers (SFPs), "total hydrolyzable precursors" (THP) (Nikiforov, 2021), also adapted by others (Schwartz-Narbonne et al., 2023; Zweigle et al., 2023). Among supplementary non-targeted and suspect screening approaches which allow identification of unknown single compounds in PFAS-treated consumer products (Harris et al., 2022; Schwartz-Narbonne et al., 2023), further combustion-based sum parameters such as "total fluorine" (TF) and "extractable organically bound fluorine" (EOF) methods have raised attention in the last years (Herkert et al., 2022; Lauria et al., 2022; Winkens Pütz et al., 2022). Being independent from isotopic standard availability and enabling a high matrix tolerance, combustion ion chromatography (CIC) or high resolution-continuum source-graphite furnace molecular absorption spectrometers (HR-CS-GF-MAS) allow for relatively fast detection of organofluorine molecules from a high variety of sample types (Gehrenkemper et al., 2021; Simon et al., 2022). Although highly requested by environmental protection and health stakeholders, standardized extraction protocols and analytical methods for PFAS monitoring and control in consumer samples are still lacking. Advanced TOP-assay approaches can overcome the problems of target analytical methods and occasionally achieve sum parameter values but are limited to standard availability, thus are not competitive with respect to novel, unregulated PFAS formulations (Zweigle et al., 2023). In the past, numerous TF and EOF measurements were successfully conducted on PFAS analysis for consumer goods, such as cosmetic products (Whitehead et al., 2021; Winkens Pütz et al., 2022), durable professional gear (Liagkouridis et al., 2021; Muensterman et al., 2022) or surface treatment products (Fredriksson et al., 2022; Herkert et al., 2022). TF measurements can be advantageous for quantifying PFAS in product samples, but results can be affected by the presence of inorganic fluorides. Currently, only liquid extraction methods are reliable for separating PFAS from inorganic fluorides before measurement. Therefore, a more comprehensive extraction protocol is required that allows for the inclusion of insoluble PFAS in the sum parameter analysis.

In this study, we investigate the performance of two different liquid extraction methods (alkaline (HOF) and acidic (EOF)) for various PFAS-containing product samples optimized for sum parameter analysis via CIC. Therefore, a hydrolysis extraction procedure was developed and PFAS in liquid extracts were determined as sum parameter values which we suggest as "hydrolyzable organically bound fluorine" (HOF). More specifically, the study focuses on the potential for inclusion of non-extractable organic fluorine compounds, such as those found in SFPs, to the sum parameter approach. We compare the results to TF values obtained from total combustion of every samples. To determine the amount of FTOHs released by hydrolysis from each sample, we included additional quantification by GC-MS spectrometry via the THP-assay. Eventually, all sum parameter methods were compared to standardized target analytical approaches via LC-MS/MS and evaluated via a fluorine mass balance approach.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used in the extraction processes and synthesis of polymers were purchased prior to conducting the experiments, used upon receipt and stored according to the manufacturer's specifications: methanol (99.98 %, Rotisol, LC-MS grade, Roth), acetone (99.5 %, p.A., Chemsolute), methyl-*tert*-butylether (MTBE, Emplura grade, Merck), *n*-hexane (puriss, Merck), 1-4-dioxane (reagent grade, Roth), petroleum ether (40–60 °C, p.A., Chemsolute), azobisisobutyronitrile (AIBN, 98%, SigmaAldrich), acetic acid (>99.8 %, p.A., Chemsolute), NaOH (99.5 %, p.A., Chemsolute), HCl (37 %, p.A., Chemsolute), NH₄F•0.5H₂O (99.995 %, Puratronic®, AlfaAesar), 1*H*,1*H*,2*H*,2*H*-nonafluorohexan-1-ol (4:2-FTOH, 97 %, BLD pharm), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (6:2-FTOH, 97 %, AlfaAesar), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanol (8:2-FTOH, 97 %, SigmaAldrich), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-dodecanol (10:2-FTOH, 97 %, SigmaAldrich), 2-(perfluorobutyl)ethylacrylate (4:2-FTAcrylate, 97 %, abcr), 1*H*,1*H*,2*H*,2*H*-perfluorooctylacrylate (6:2-FTAcrylate, 97 %, abcr), 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate (8:2-FTAcrylate, 97 %, abcr), 2-(perfluorodecyl)ethylacrylate (10:2-FTAcrylate, 97 %, abcr), 2-(perfluorobutyl)ethyl methacrylate (4:2-FTMethacrylate, 95 %, abcr), 1*H*,1*H*,2*H*,2*H*-perfluorooctylmethacrylate (6:2-FTMethacrylate, 95 %, abcr), 1*H*,1*H*,2*H*,2*H*-perfluorodecylmethacrylate (8:2-FTMethacrylate, 98 %, abcr), 2-(perfluorodecyl)ethylmethacrylate (10:2-FTMethacrylate, 97 %, abcr). A MilliQ IQ 7000 system (Merck) generating ultra-pure water (<0.06 µS/cm, TOC ≤5 ppb) was used for sample extraction and dilution.

All GC-MS extracts were produced using the aforementioned solvents methanol, methyl-*tert*-butylether and hexane. All native unlabeled analytical standards used for GC-MS analysis were purchased from known chemical suppliers and used without further purification steps (97–99 % purity).

LC-MS/MS analysis was performed using methanol (Chemsolute, LC-MS grade) and ammonium acetate (ULC/MS Optigrade, LGC Standards). All native PFAS standards were included in the PFAC30PAR standard-mix which was purchased by Wellington Laboratories, Canada. The ¹³C-isotopically labeled internal standard mixture MPFAC-24ES was obtained from the same supplier as a prepared solution at a concentration of 1000 ng/mL. More detailed information is provided in the SI.

2.2. Sample collection and preparation

All textile samples originate from used trademarked impregnated outdoor apparel (jackets, trousers, coats), donated during the course of several weeks by colleagues at our research institution. Food contact materials (paper-based plates, bowls, cups, wrappers) were collected from various vendors in Berlin, Germany between 2021 and 2022. All carpet samples were taken from manually selected fitted carpet pieces purchased from a local hardware store in Berlin. The baking sheet samples were taken from fluoropolymer-based permanent baking and barbecue sheets preselected and purchased from several online vendors.

All product samples were placed in sealed PP-bags and stored in a dry place under light exclusion at ambient temperature. Prior sample extraction, uniformly shaped disks (Ø = 3.17 cm) of all materials were punched out with the help of a hydraulic press.

2.3. Total fluorine (TF) analysis via combustion ion chromatography (CIC)

For TF analysis, 5–10 mg samples of all consumer products were directly combusted and subsequently analyzed via CIC, following the protocols of previous work (Zweigle et al., 2023). All samples were analyzed in triplicate to account for possible material inhomogeneities. More detail on the analytical process and quality control is provided in the SI.

2.4. Sample extraction methods (for sum parameter analysis)

For all extraction processes analyzed via CIC, uniformly disk-shaped sample pieces were manually cut with methanol rinsed scissors to smaller pieces (<1 cm) and subsequently weighed in 15 mL PP-centrifugal tubes. Due to the different nature of the materials and individual PFAS concentrations, optimized amounts of sample cut-outs were used for the extractions: textile samples (2 disks), food contact materials (4 disks), carpetry (1 disk), baking sheets (1 disk). For this study, all samples were extracted in triplicates.

2.4.1. Alkaline hydrolysis extraction procedure (hydrolyzable organically bound fluorine HOF method)

Inspired by previous work by Nikiforov and Simon et al., an improved extraction protocol was developed for sum parameter analysis via CIC (Nikiforov, 2021; Simon et al., 2022). The description given here accounts for one single sample extraction but may be extended to multiple samples. A schematic overview as well as a detailed description of the standard extraction procedure is provided in *Scheme S1* (see SI). The use of strong alkaline conditions in the extraction process allows for inclusion of hydrolyzable precursors to be included in the sum parameter value (extraction). At the same time highly inert per- and poly-fluorinated polymers such as polytetrafluoroethylene (PTFE) and polyvinylidene difluoride (PVDF) remain undissolved, thus are not interfering with the analysis. As a drawback, high amounts of alkaline cations need to be removed via precipitation from the analyte solution prior to combustion (separation), to avoid fast degeneration of the quartz reactor. Eventually, the solution requires pre-concentration in order to detect sub-ppb-levels of analyte.

2.4.2. Acidic extraction procedure (extractable organically bound fluorine EOF method)

Consistent with the alkaline extraction protocol, uniformly sized samples were taken for this comparative extraction method. The samples were weighed in 15 mL PP-centrifugal tubes and extracted with 0.5 % acetic acid in methanol according to the extraction protocol reported by Simon and co-workers (Simon et al., 2022).

2.5. EOF and HOF analysis by CIC

Similar to previously reported work (Roesch et al., 2021), liquid PFAS extracts from all samples were quantified by CIC. Aliquots of all samples (250 µL) were injected via automated syringe from fluorine-free PP-screw neck vials (1.5 mL, Macherey-Nagel, Germany) into a quartz wool-filled ceramic boat prior to measurement by CIC. All samples were measured in triplicates to survey instrumental deviations. To quantify the correct absorbance, an internal standard of known concentration was added to the absorbance solution prior to each combustion step. Sample quantification was performed using an 11-point calibration curve from 1 to 20 µg fluoride/L (R² = 0.995) for low fluoride samples and a 6-point calibration curve from 10 to 500 µg fluoride/L (R² = 0.999) for detection of higher fluoride levels. Calibration solutions were prepared from aqueous NH₄F stock solution and calibration was performed by combustion of corresponding aliquots using the CIC instrument. All sum parameter values are expressed in µg/g dry weight. More detailed information is provided in the SI.

2.6. Sample extraction and targeted analysis of FTOHs via GC-MS spectrometry (THP)

All samples were extracted according to a modified protocol published by Nikiforov (2021). In contrast to the HOF-protocol, the THP-assay requires no further pre-concentration steps and is determined directly from a hexane-MTBE-extract after workup. To obtain a more consistent extraction data set for the different types of sample matrices, the extraction solution volume was quadrupled. The weighed sample

masses ranged from 50 to 70 mg depending on the density of the material. All sample extracts were screened for fluorotelomer alcohols and quantified via liquid injection gas chromatography coupled mass spectrometry using the selected ion monitoring (SIM) mode. To increase accuracy, all samples were extracted and measured in duplicates. Further details on the instrumental and methodical details are provided in the SI.

2.7. Sample extraction and targeted analysis via LC-MS/MS spectrometry

All individual samples were extracted according to standard procedure DIN EN 17681–1:2022–11 (German Institute for Standardization, 2022). The selected targeted analyte standards were based on the PFAC30PAR standard mixture by Wellington Laboratories. For each individual sample, uniformly sized pieces of cut material were weighed into PP Falcon tubes (15 mL), spiked with 100 μL of ^{13}C -labeled internal standard mixture and made up with 5 mL of pure methanol. The tubes were then placed in an ultrasonic bath at 60 °C for 2 h and the extract concentrated with a gentle nitrogen stream to a volume of 500 μL . The solutions were transferred to Eppendorf® vials and diluted with 500 μL of ultrapure water (Milli-Q). After vortexing, all samples were filtered through 0.45 μm nylon syringe filters. To receive data precision, all samples were extracted and measured in duplicates. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis was performed on an Agilent 1290 Infinity II-UHPLC in negative ion mode using multiple reaction monitoring (MRM). A more detailed description of the applied LC-MS/MS methods and all investigated target samples can be reviewed in the SI (Table S14).

The isotopically labeled internal standard species were obtained from Wellington Laboratories as a prepared solution at a concentration of 1000 ng/mL with an uncertainty of $\pm 5\%$. All organic solvents, reagents and modifiers used for extraction and LC-MS/MS analysis were tested for potential blanks before used. All dilution and spiking steps were gravimetrically controlled.

3. Results and discussion

3.1. Total fluorine (TF) determination

Depending on the type of material investigated, the TF values exhibited a significant variability in magnitude (see table S3, SI). For the textile samples, the TF values ranged between 81.9 and 788 $\mu\text{g/g}$, whereas both food contact paper samples and carpet samples gave TF values between 4.1 and 28.6 $\mu\text{g/g}$. Previous studies have shown that outdoor apparel is often covered via surface modified fluorinated side chain polymer coatings, thus a higher fluorine content is expected (Schellenberger et al., 2022). Other studies have reported similar values when investigating organofluorine impregnated textile samples (Liagkouridis et al., 2021; Xia et al., 2022). In contrast, food contact material and carpets are known to be impregnated via fluorinated alkyl phosphate esters and other monomeric FTOH derivatives, thus lower TF concentrations can be explained (Wu et al., 2020, 2021; Glenn et al., 2021; Duenas-Mas et al., 2023; Schwartz-Narbonne et al., 2023). The final product group studied in this work – the baking sheets – yielded very high TF values, given the fact that the majority of samples consist of a fluoropolymer base-layer (predominantly polytetrafluoroethylene (PTFE)). Consequently, the latter showed values reaching from 146 to 567 mg/g (14.6–56.7 %). Only two samples exhibited deviating TF values of 230 and 2158 $\mu\text{g/g}$ (BS8 and BS6), respectively, indicating that they were composed of a lower molecular weight fluoropolymer coated on a silicone rubber base material instead. Values of good agreement were published recently (Skedung et al., 2024). The presence of inorganic fluorides was investigated via analysis of aqueous extracts of selected samples via standard ion chromatography but was found to be negligible. All detected TF values were regarded as maximum detectable level of PFAS per compound and serve as a reference value for all liquid extraction methods investigated in this work.

3.2. Comparison of extractable organically bound fluorine (EOF) and hydrolyzable organically bound fluorine (HOF)

Both HOF and EOF values were determined from samples extracted according to their respective protocols (see section 2.4.1 and 2.4.2). The determined sum parameter data are shown in figure S1 and table S3. For the textile samples TX1-8 EOF values between 1.32 and 58.1 $\mu\text{g/g}$ could be identified, while the respective absolute HOF numbers showed up to ten times higher values after hydrolytic extraction (1.38–76.3 $\mu\text{g/g}$). Both sum values gave results in the range of previous analysis of textile samples (Herkert et al., 2022; Zweigle et al., 2023). A different scenario was monitored when paper and carpet samples were investigated. The overall EOF values for the paper (PA1-7) and carpet (CP1-10) samples yielded significantly lower values, 0.06–2.34 $\mu\text{g/g}$ and 0.1–0.34 $\mu\text{g/g}$, respectively. The hydrolysis extraction of the same compounds yielded similar HOF values from 0.08 to 19.7 $\mu\text{g/g}$ for the paper samples and 0.03–0.18 $\mu\text{g/g}$ for the carpet samples, respectively. While the EOF extraction appears to be more efficient for the PFAS composition in the paper products, the overall low amounts of PFAS in the carpet samples revealed the limits of both sum parameter approaches. Minet et al. recently concluded that food contact materials predominantly rely on both polymeric and monomeric PFAS coatings such as mono- and di-PAPs as well as fluorotelomer sulfonate derivatives (Minet et al., 2022). Both EOF and HOF sum values of the carpet samples were a little lower in concentration but generally in agreement with previously analyzed target analysis sum amounts by (Wu et al., 2020). In contrast to their samples, the carpet trials used in this work were unused and never came into contact with external PFAS contamination such as anti-staining products. Nevertheless, the overall PFAS concentrations were significantly lower for both product categories, compared to functional textiles.

In contrast, both extraction approaches behave differently upon analysis of the fluoropolymer-based baking sheet sample extracts. While the EOF values vary between 0.05 and 4.47 $\mu\text{g/g}$ per sample, the HOF sum parameter yielded values up to seven times higher (7.78 $\mu\text{g/g}$ in maximum) for the sheet samples. These results clearly indicate that the amount of extractable PFAS is limited in these products, the amount of polymer based PFAS is significantly higher. Both silicone-based materials BS6 and BS8 showed the lowest values for both sum parameter approaches, which correlates well with the TF measurements.

Moreover, we compared the data as natural logarithmic functions with the respective TF values in Fig. 1 to clarify their correlation.

Depending on the class of materials the correlation values show lower or greater deviation for linear fit calculation ($R^2 = 0.003\text{--}0.703$). This can be explained by the very different PFAS concentrations that were analyzed in this study as well as the uncertain number of fluorinated species that were not covered by both methods. The textile samples yield overall slightly better correlation for the HOF concentrations compared to the EOF values, but both methods showed values in a similar concentration range. Fig. 1b and c depict the relatively low fluoride to TF ratio of both extraction methods for paper and carpet samples. While the EOF/TF correlation exceeds the HOF/TF values for paper samples, both sum parameter extraction methods show an overall equal performance for the carpet samples. In case of the highly perfluorinated sheet samples, the ln-correlation analysis yields a significantly better performance of the hydrolysis method as depicted in Fig. 1d. Although high levels of HOF over EOF values could be identified in the textile and sheet products, there is still a significant uncertainty towards the TF values identified. Nonetheless, the data allows for the assessment of the method performance with respect to substrate choice. The use of the basic extraction protocol allows for a higher fluorine recovery in sum parameter analysis when fluoropolymer-based compounds need to be investigated.

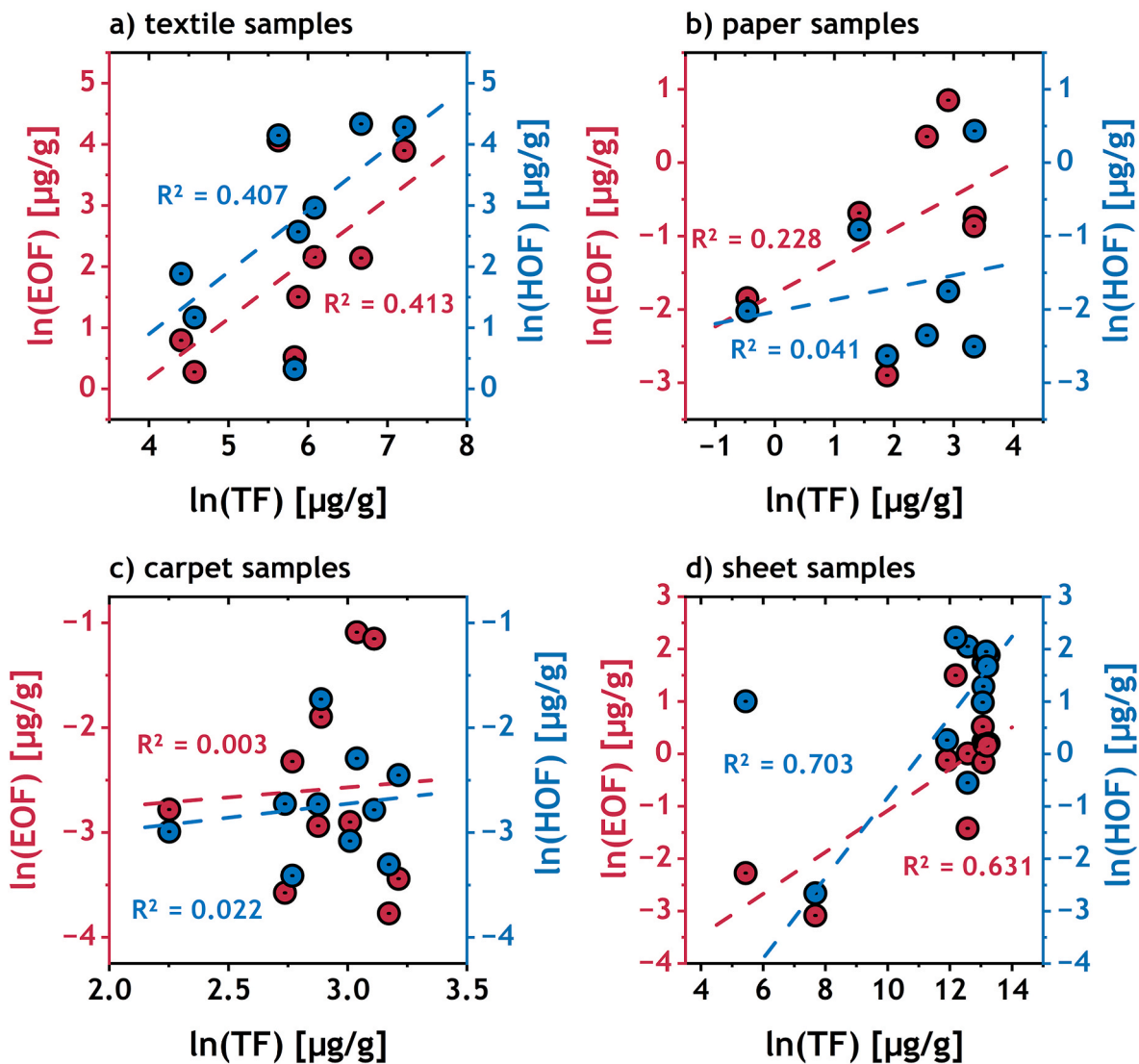


Fig. 1. Correlation of natural logarithmic functions (\ln) of fluoride concentration EOF (red) and HOF (blue) over TF values grouped by the investigated product categories: textiles (a), paper (b), carpet (c) and permanent baking sheets (d).

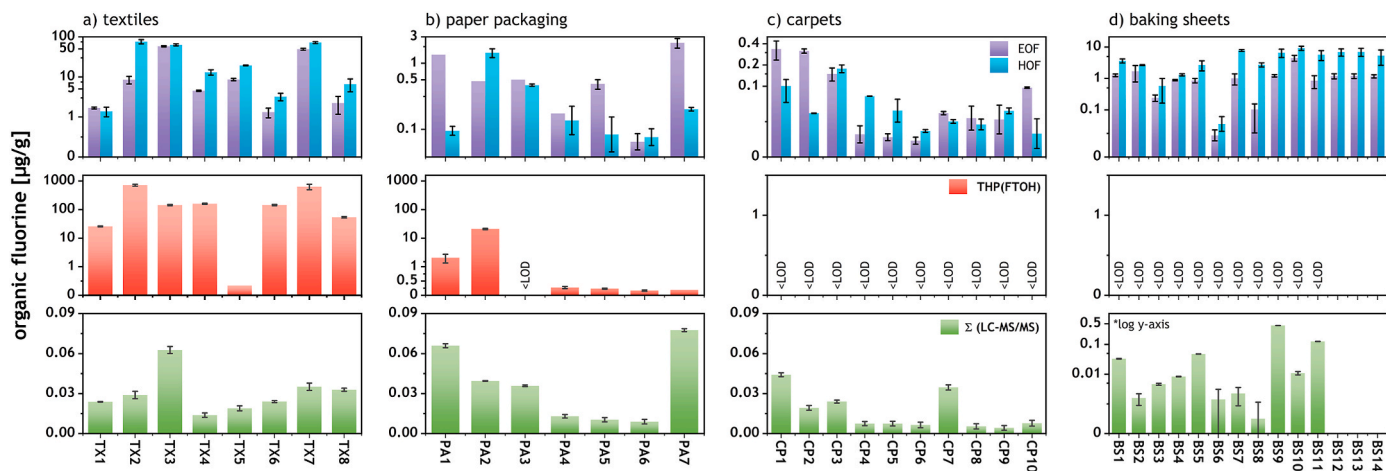


Fig. 2. Comparison of CIC-measured sum parameters EOF (purple) and HOF (blue), as well as calculated fluorine sum values of THP(FTOH) (red) and $\Sigma(\text{LC-MS/MS})$ (green) measurements for all samples: a) textiles, b) paper packaging, c) carpet and d) baking sheet samples. GC-MS data that were below the limit of detection were highlighted accordingly. Note that some scales are partly in logarithmic form to facilitate data view. No target analytical data were recorded for samples BS12-14.

3.3. Total hydrolyzable precursor (THP)-assay and GC-MS analysis

For comparison of the sum parameter methods, all samples were additionally analyzed for fluorotelomer alcohol (FTOH) precursor concentrations via GC-MS based on the literature known THP-assay (Nikiforov, 2021). All measured PFAS values were calculated to their respective fluorine equivalents and depicted in Fig. 2 as well as Table S4. For the SFP-based textile samples the THP-assay showed the highest values between 0.34 and 721 $\mu\text{g/g}$ depending on the type of sample, mainly contributed by high amounts of the 6:2- and 8:2-FTOH precursors. In most of the samples 10:2-FTOH could be identified only in smaller amounts. Similar results were recently observed for textile samples (Zweigle et al., 2023). The PFAS-treated paper samples showed a completely different result. With the exception of PA2 (20.9 $\mu\text{g/g}$), the THP values for all other paper samples were mostly below 0.5 $\mu\text{g/g}$. The fluorine sum value was predominantly contributed by 6:2-FTOH as well as minor amounts of 10:2-FTOH. The precursor 8:2-FTOH could not be detected. Moreover, no 4:2-FTOH precursors could be identified in any of the investigated samples. In contrast to the first two sample types, no FTOH-values could be identified for the carpet and baking sheet samples above the detection limit. This finding might be explained by the absence of fluorotelomer-containing PFAS (such as SFPs) in the coating of both carpet and baking sheet samples.

3.4. Target analysis via LC-MS/MS

In addition to sum parameter analysis, standardized target analytical measurements were performed. The method comprises 25 compounds including classical PFAAs and PFASs with chain length $\text{C}_4\text{--C}_{12}$. All recorded target analysis data are summarized in figure S2 and table S5. Calculated fluorine equivalents of all values are depicted in Fig. 2.

The overall detected sum concentrations PFAS ranged from 1.22 to 1062 ng/g. Some compounds as perfluorobutyl sulfonic acid (PFBS) could be identified in almost all investigated product samples (37 out of 39 samples), whereas perfluoroundecanoic acid (PFUDA) was not found in a single sample.

For the textile samples sum PFAS values between 21.6 and 97.9 ng/g were identified. Due to the fact that the majority of the textile samples were utilized in outdoor garments at the end of their lifespan, the occurrence of phased-out perfluorooctanoic acid (PFOA) and perfluoro sulfonic acid (PFOS) was expected. In fact, the analysis revealed the presence of both compounds in all textile samples with relatively low values of <LOD-27.9 ng/g and 1.93–10.9 ng/g, respectively. Except of one sample, all textile samples showed low levels of perfluorobutanoic acid (PFBA) 2.56–11.4 ng/g and elevated perfluorohexanoic acid values (PFHxA) 4.04–26.7 ng/g, which is in good conformance with previous studies on PFAS in textiles (Muensterman et al., 2022; Xia et al., 2022).

The major analytes in all paper materials were PFBA, yielding values between 4.11 and 55.5 ng/g, PFBS (6.03–50.3 ng/g) and PFOS (3.74–31.3 ng/g). All compounds showed elevated values, given the rather low total fluorine content of the paper samples. While PFBA and PFBS were previously identified in food packaging samples within former studies (Dueñas-Mas et al., 2023; Schwartz-Narbonne et al., 2023), PFOS was rarely found in food contact materials after the market ban in Europe 2010 (Chinthakindi et al., 2021). Interestingly, no PFOA was identified in any of the food contact material samples.

The lowest targeted sum PFAS concentrations of all samples were measured for the carpet samples (6.60–68.9 ng/g). Besides PFBA and PFOS, hexafluoropropylene oxide dimer acid (HFPO-DA) was the most abundant target identified in all except one carpet samples (0.50–10.8 ng/g). The frequent occurrence of HFPO-DA may be attributed to the industrial transition to a substitute compound, resulting from the European ban on PFOA in 2020. Besides, almost all carpet sample extracts yielded significant amounts of 4:2-, 6:2- and 8:2-fluorotelomersulfonic acid (X:2-FTSA). The latter gave values between < LOD and 7.08 ng/g which is in good agreement with other studies on carpet samples (Wu et al., 2020).

Compared to their determined HOF values, only little PFAS sum amounts could be identified via target analysis of the baking sheet samples. Although the measured sum target values range from <LOD to 1062 ng/g, the median amount is only 8.37 ng/g. Again, PFBA and PFBS were identified among the major targeted PFAS contributors in almost all samples (<LOQ-123 ng/g; <LOQ-17.9 ng/g). Among all baking sheet samples BS9 yielded the highest sum concentration which could be attributed predominantly to PFOS (989 ng/g), which presumably was used as an additive in the production of the PTFE fibers. Moreover, PFOS was only detected in lower concentrations in the extracts of samples BS5 and BS11.

3.5. Data comparison and fluorine mass balance: sum parameter values vs target analysis

Assessing a fluorine mass balance approach that relies on a combination of determined and calculated data sources is critical. While CIC enables direct quantification of inorganic fluoride converted from an organic source, targeted analytical methods such as LC and GC-MS spectrometry provide quantification of individual molecular amounts. The calculated fluorine mass balance for all four sample groups is shown in figures S3-S4 (more details on calculation in SI chapter 1.5 and in table S6). The textile samples showed an overall high value for TF which can be explained by the highly fluorinated polymer-based coating of the textile products. The HOF measurements yielded values from 0.4 to 22.7 % fluorine recovery post CIC-analysis related to the TF values. Except for TX1, the comparable EOF approach yielded smaller fluorine recovery values between 0.49 and 20.9 %. In comparison, the THP-assay showed significantly higher fluorine sum values for the textile samples, ranging from 7.5 to 96.9 % recovery. Only two out of eight samples deviated in values (TX5: 0.1 %, TX6: 149 %). This finding indicates a high appearance of FTOH-based fluoropolymer coating in the textile samples, that can be represented by the hydrolysis-assay. The classical target analysis approach based on 25 standard PFAS barely represents the total fluorine composition with values < 0.4 % recovery.

Both paper and carpet samples showed significantly lower TF values (0.63–28.6 % for paper, 9.51–24.9 % for carpet). Both CIC sum parameter values show similar performances within the mass balance. The HOF values range from 0.29 to 20.9 % fluorine recovery for the paper and 0.15–1.0 % for the carpet products. In comparison, the EOF approach showed a slightly better outcome with 0.84–24.9 % recovery for the paper products and 0.1–1.61 % for carpets. Again, the paper sample mass balance was slightly better represented by the THP values with recovery values between 0.82 and 73.3 %, when FTOH were identified. For PA3 no FTOHs could be detected. In case of the carpet samples, the hydrolysis-assay was not effective, since all target values were below the detection limit. This might be explained by the limited use of fluorotelomer-based surfactants on carpets. In contrast, the LC-MS/MS target analysis sum values yield 0.04–2.05 % fluorine recovery for paper samples and 0.02–0.36 % for the respective carpet samples.

Compared to the other samples, the baking sheet samples represent an extremely different material, since most of the samples are based on fluorinated polymeric materials such as PTFE that cannot be dissolved under hydrolytic lab extraction conditions. In consequence, the total fluorine values for the sheet samples were several orders of magnitudes higher and gave %-values of fluorine, thus only very low fluorine recovery values can be achieved. Nonetheless, the HOF values showed the highest recovery percentage of all compared methods with 0.0006–1.19 %. The EOF values were significantly lower and reached only up to 0.04 % of TF. As observed before, the THP could not identify any FTOH precursors in the fluoropolymer materials, thus no contribution to the fluorine mass balance was made. The LC-MS/MS sum amounts for the baking sheet samples could only identify fluorine values in the sub ppm-range of the TF values. Based on our data, the larger the TF value, the less accurate and more error-prone the estimation of the other sum parameter values, and thus the fluorine mass balance, becomes. This might be explained by the high amount of

insoluble, chemically stable organofluorine polymers present in predominantly textile and sheet samples.

3.6. Method quality validation – analysis of model compound extraction

In order to estimate the extraction potential of all extraction methods and the subsequent analysis via CIC and GC-MS, fluorotelomer alcohol substituted polyacrylate polymer samples were used as model substrates. Therefore, four different homopolymerized fluorotelomer polyacrylates (N:2-FT-PAC; N = 4, 6, 8, 10) were synthesized via radical polymerization reaction (detailed description in SI). Defined amounts of all four model polymers were first extracted according to both extraction methods and subsequently analyzed via CIC analysis as described earlier (see 2.4). To estimate the unaffected extraction potential of the hydrolytic solvent mix, samples were additionally analyzed directly from unworked extraction solutions (HOF-direct). For comparison, the FTOH content of all model compounds were determined via the THP-assay implementing targeted GC-MS spectrometry. The experiments were conducted in order to evaluate and validate the extraction potential of every single extraction method. As point of reference, the TF value of every single polymer mixture was determined via direct combustion with CIC. The extraction potential is depicted in Fig. 3.

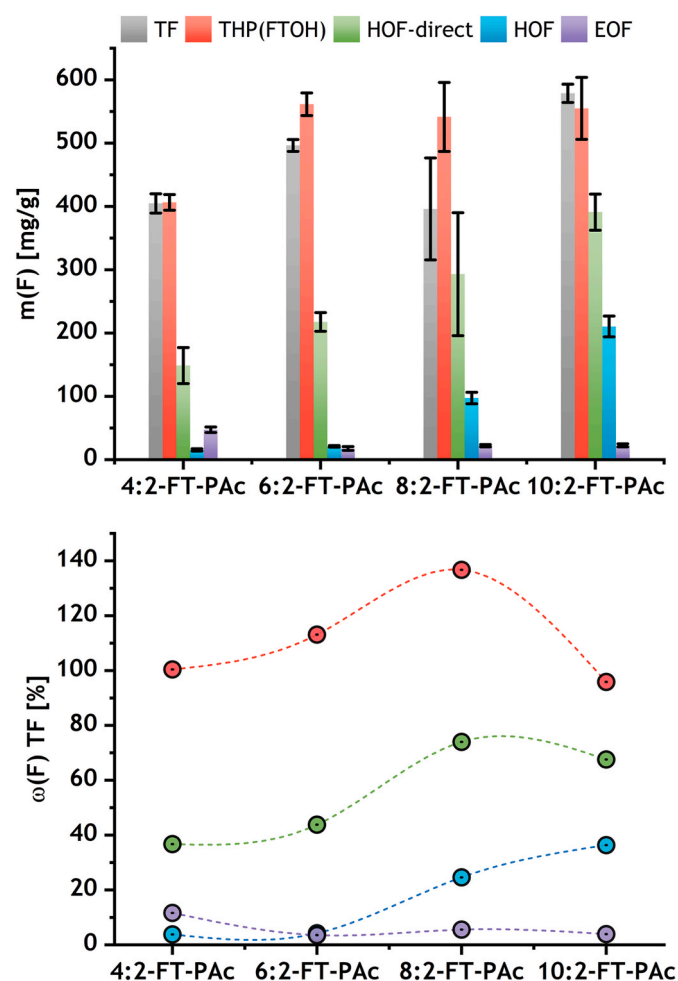


Fig. 3. Comparison of average fluorine sum parameter amounts TF, EOF and HOF (pre- and post-work-up) as well as target analysis data THP(FTOH) of fluoropolymer models (N:2-FT-PAC; N = 4, 6, 8, 10) (top); compared average extraction efficiency in mass-% of hydrolysis and standard EOF approach with regard to fluoropolymer model compounds (bottom). All samples were measured in duplicates. The error bars represent standard deviations of the total measurements.

The TF values varied between 396 and 578 mg/g due to different densities and molecular weight distributions among the four polymers. The HOF-direct fluoride values represent the amount of organic fluorine dissolved in the extraction solution separated from the solids. As shown in Fig. 3, values between 148 and 391 mg/g could be recovered via CIC analysis. These values equal a fluoride recovery of 36.7–74 % compared to the respective TF values. Due to the high concentration of sodium hydroxide (1 mol/l), routine analysis of extraction solution via CIC without further workup is not practicable. The analysis was repeated after implementation of the hydrolysis process described in 2.4.1 for all four model compounds. Compared to the HOF-direct, the values exhibited for HOF lay significantly lower between 15 and 210 mg/g (3.8–36.3 % fluorine recovery), indicating a loss of analytes during the workup process. This correlates to a loss of SPF analyte post-extraction of ~90 % for 4:2-FT-PAC and 6:2-FT-PAC, ~66 % for 8:2-FT-PAC and ~46 % for 10:2-FT-PAC, respectively. Additionally, all four model compounds were extracted according to the EOF procedure described in 2.4.2. The measured post-extraction EOF values lay between 17 and 47 mg/g and were significantly lower compared to the HOF values. The TF recovery numbers were 11.7 % for 4:2-FT-PAC and 3.5–5.6 % for the other analytes. Overall, the extraction potential of the EOF method is significantly lower compared to the hydrolysis method. The total loss during the EOF process ranges from ~66 % (4:2-FT-PAC) to >90 % for the resumming analytes.

The THP-assay of all four model compounds revealed very individual results for each compound. Whereas the hydrolysis products 4:2- and 10:2-FTOH gave recovery values close to 100 % (after recalculation of the fluoride concentration), the long chain alcohols 6:2- and 8:2-FTOH showed significant overestimation after work-up with 114 and 140 %, respectively (s. Fig. 3). These variations suggest that even if a method is optimized for a specific compound class, like the hydrolysis assay, recovery bias cannot be excluded. For both sum parameter extraction methods EOF and HOF starting from FT-acrylates, the recovery of the shorter chain compounds 4:2- and 6:2-FTOH was insufficient throughout the whole process, which is in agreement with previous work on volatile PFAS (Pan and Helbling, 2023). Compared to the longer chain hydrolysis products, 4:2- and 6:2-FTOHs are more reactive in solution, thus might re-react faster and precipitate from solution. In case of the hydrolytic extraction process, long-lasting concentration steps during workup might potentially contribute to the loss of the more volatile compounds. For the same reason, the longer chain hydrolysis products 8:2- and 10:2-FTOH showed significantly higher recovery values. Here, the difference between strong alkaline extraction conditions and acidic methanol is particularly visible and speaks in favor of the HOF sum parameter approach. Nonetheless, it must be emphasized that the comparison between HOF-direct, HOF and EOF values only account for the selected model compounds and cannot be transferred to any other PFAS analyte without further investigation.

4. Conclusions

To summarize, we were able to quantify total fluorine sum values in all consumer product samples investigated through combustion-IC analysis. Moreover, two different pH-depending liquid extraction protocols for consumer products by CIC analysis were successfully conducted and assessed for potential improvements. On the one hand, the hydrolytic sum parameter HOF showed better extraction performance for consumer product samples based on fluoropolymer coatings/materials (textiles, sheets), but on the other hand, samples with a higher monomeric PFAS concentration showed slightly more effective extraction by classic EOF approach (paper, carpet). The higher the fluorine content of the sample, the more accurate the HOF approach. Overall, the use of sum parameter approaches provided a more comprehensive overview of PFAS analysis in consumer goods than standardized target analytical methods, which should be considered as complementary in future PFAS studies.

The THP-assay was very accurate in terms of fluorine recovery for SFP-based textile samples and some paper products but unsuitable for the carpet and sheet samples. This observation clearly indicates the limitation of the assay in absence of fluorotelomer-based analytes. In terms of fluorine mass balance, only the GC-MS-method yielded satisfactory fluorine recovery values for the textile samples. Extraction-based sum parameters HOF and EOF showed lower fluorine recovery values, which might be explained by higher insolubility during the extraction or the loss of analytes during the workup process. This finding was also indicated after the assessment of the model-polymer study, which demonstrated the advantageousness of the THP-assay over other extraction protocols (HOF, EOF). Compared to the targeted analytical methods, CIC measurements lack internal standards and analytical precision, and therefore still require preconcentration steps that are more prone to error during workup. In consequence, future method improvements should predominantly focus on lossless workup processes, which enable a higher fluorine recovery independent from analyte concentration and composition. Until then, TF analysis via CIC remains the only highly reproducible, sample-independent, and accurate method for PFAS analysis of fluoropolymer-based consumer products.

CRediT authorship contribution statement

Philipp Roesch: Writing – original draft, Visualization, Validation, Investigation, Data curation, Conceptualization. **Andrea Schinnen:** Writing – review & editing, Validation, Methodology, Investigation. **Maren Riedel:** Writing – review & editing, Validation, Resources, Investigation. **Thomas Sommerfeld:** Writing – review & editing, Validation, Resources, Investigation. **George Sawal:** Writing – review & editing, Supervision, Project administration. **Nicole Bandow:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Christian Vogel:** Writing – review & editing, Supervision. **Ute Kalbe:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Franz-Georg Simon:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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