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Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?

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S *Supporting Information*

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) represent a class of more than 4000 compounds. Their large number and structural diversity pose a considerable challenge to analytical chemists. Measurement of total fluorine in environmental samples and consumer products is therefore critical for rapidly screening for PFASs and for assessing the fraction of unexplained fluorine (i.e., fluorine mass balance). Here we compare three emerging analytical techniques for total fluorine determination: combustion ion chromatography (CIC), particle-induced γ-ray emission spectroscopy (PIGE), and instrumental neutron activation analysis (INAA). Application of each method to a certified reference material (CRM), spiked filters, and representative food packaging samples revealed good accuracy and precision. INAA and PIGE had the advantage of being nondestructive, while CIC displayed the lowest detection limits. Inconsistencies between the methods arose due to the high aluminum content in the CRM, which precluded its analysis by INAA, and sample heterogeneity (i.e., coating on the surface of the material), which resulted in higher values from the surface measurement technique PIGE compared to the values from the bulk volume techniques INAA and CIC. Comparing CIC-based extractable organic fluorine to target PFAS measurements of food packaging samples by liquid chromatography–tandem mass spectrometry revealed large amounts of unidentified organic fluorine not captured by compound-specific analysis.
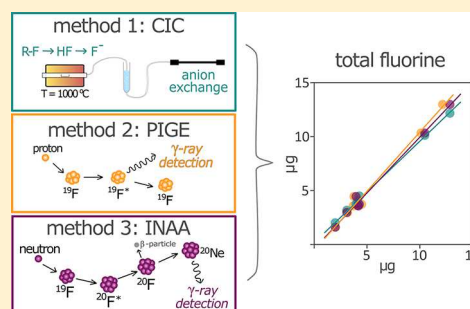
1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are a class of ubiquitous chemicals that have found innumerable industrial and consumer applications over the past seven decades.[1] PFASs can be categorized as polymeric or nonpolymeric,[2] collectively amounting to more than 4700 CAS-registered substances according to the OECD.[3] Environmental concerns pertaining to PFASs are centered primarily on the perfluoroalkyl acids (PFAA), a subclass of PFAS which display extreme persistence and chain-length-dependent bioaccumulation and adverse effects in biota.[2]

The water- and grease-repellent properties of PFASs have led to their extensive use in food contact paper and packaging. Concentrations in the range of 1.0−1.5% per fiber dry weight are typical in most finished products.[4] Historically, most fluorinated coatings for paper and board were based on perfluorooctanesulfonate (PFOS) precursors, such as *N*-ethyl perfluorooctane sulfonamido alcohol-based phosphate diesters (SamPAPs).[5,6] However, as a consequence of the phase-out of PFOS and its precursors by 3M in 2001, most contemporary formulations are now based on acrylate polymers with fluorotelomer or sulfonamido alcohol side chains or perfluoro-

polyether-based polymers (PFPEs).[4,7] Several peer-reviewed studies have reported the occurrence of PFAAs, polyfluoroalkyl phosphates (PAPs), fluorotelomer alcohols, and saturated and unsaturated fluorotelomer acids in various types of food packaging materials.[5,8−13] While the importance of PFASs in food packaging as a human exposure source remains unclear, some PFASs have been shown to migrate from food packaging into food.[14,15] In response to concerns surrounding PFASs, several states in the United States have implemented bans on the use of these chemicals in food packaging,[16] and the Danish Ministry of the Environment and Food has established a total fluorine indicator value of 0.1 μg/cm^2 in food packaging.[17]

Given their vast number and structural diversity, a comprehensive characterization of PFASs in consumer products represents a considerable analytical challenge.[18] Typically, a limited number of PFASs are quantified using a

combination of solvent extraction and either liquid chromatography–tandem mass spectrometry (LC–MS/MS; ionic PFASs) or gas chromatography–mass spectrometry (GC–MS; semivolatile PFASs). These methods cannot capture all PFASs, and even when high-resolution MS is employed (i.e., suspect or nontarget screening), a lack of authentic standards precludes unequivocal identification and quantification. As a result, questions about how many PFASs are missed during routine analysis remain. Several analytical approaches have emerged for quantifying total fluorine (TF) regardless of chemical structure or molecular weight (reviewed by McDonough et al.[19]). These approaches can be used for rapid screening of PFASs or in combination with targeted analyses (i.e., LC–MS/MS or GC–MS) to assess the fluorine mass balance in a sample. Combustion ion chromatography (CIC) is the most common method and was first used for fluorine mass balance experiments in 2007 by Miyake et al.[20] Since then, there have been several applications of CIC for determination of TF in environmental samples and consumer products.[21−24] Another method, particle-induced γ-ray emission (PIGE) spectroscopy, is a long-established ion beam technique used for analysis of solid materials.[25−28] The approach was recently applied to papers and textiles by Robel et al., who showed that ΣPFAS concentrations accounted for a mere 0.2–14% of the TF content.[29] Lastly, instrumental neutron activation analysis (INAA) is another nuclear technique with widespread uses,[30−32] with one recent application involving measurement of fluorine in biological and environmental matrices.[33] The current paper reports the first application of INAA to consumer products. Other approaches for measuring TF exist, such as inductively coupled plasma (ICP) MS,[34] molecular absorption spectroscopy,[35] and X-ray photoelectron spectroscopy;[36] only the latter has recently been applied to fluorine mass balance experiments in consumer products. The data produced by these approaches have not yet been compared. This is clearly needed, given the growing interest in fluorine mass balance experiments and the use of TF for regulation of PFASs in consumer products.

The objectives of this study were (1) to compare the accuracy, precision, linearity, and detection limits of TF measurements by CIC, PIGE, and INAA, (2) to assess the limitations of each approach, and (3) to assess the fluorine mass balance in several food packaging materials from the Swedish market using LC–MS/MS and CIC.

2. MATERIALS AND METHODS

2.1. Sample Collection and Preparation. Total fluorine measurements from three different laboratories were compared using (a) a certified reference material (CRM), (b) PFOA-spiked cellulose filters, and (c) a variety of food packaging materials (Table S1). CIC analysis was carried out at Stockholm University (SU); PIGE analysis was carried out at the University of Notre Dame (UND), and INAA was carried out at the University of Missouri Research Reactor (MURR). The CRM (BCR-461, fluorine in clay) was purchased from Sigma-Aldrich and subsampled at SU into 13 mL polypropylene tubes prior to being shipped to UND and MURR for direct analysis. Cellulose filter papers (Whatman) were prepared by UND by spiking perfluorooctanoic acid (PFOA) solutions (prepared in methanol with food coloring to determine the area with which the standard was applied) with total masses of 0, 1.9, 3.8, 9.5, 19.1, and 38.2 μg of PFOA. The methanol was evaporated to dryness prior to analysis.

Triplicates of each PFOA-spiked filter were sealed in individual zip-lock bags and shipped to SU and MURR for analysis. Finally, three french-fry bags (FF1−FF3) and six microwave popcorn bags (MP1−MP6) purchased in Sweden in 2012 were selected for analysis in this study. Pieces (2 cm × 2 cm) of each sample were cut and sealed in individual zip-lock bags and shipped to UND and MURR for analysis.

2.2. Extraction of Food Packaging. For targeted PFAS analysis, food packaging samples were extracted according to a Gebbink et al.[37] In short, samples (5 cm × 5 cm) were cut into small pieces, fortified with internal standards (0.5 ng each), and stirred in 40 mL of methanol at room temperature for 8 h. The extract was concentrated under a stream of nitrogen to approximately 1 mL, cleaned up using EnviCarb, and fortified with a recovery standard (0.5 ng). For analysis of total extractable organic fluorine (EOF), the extraction procedure was modified slightly by omitting the addition of internal and recovery standards and cleanup by EnviCarb.

2.3. Instrumental Analysis. Detailed descriptions of instrumental analysis and quantification for CIC, PIGE, and INAA can be found in the Supporting Information. A brief overview is provided here.

2.3.1. TF and EOF Analysis by CIC. TF and EOF were analyzed according to the method described by Schultes et al.[24] Briefly, samples (neat samples and extracts) were placed directly onto a ceramic boat that was introduced into a combustion oven (HF-210, Mitsubishi) heated to 1100 °C under an atmosphere of argon (carrier gas) and oxygen (combustion gas) for ~5 min. All gases were collected in Milli-Q water (GA-210, Mitsubishi). Ions were separated on an ion exchange column and measured by conductivity detection.

2.3.2. TF Analysis by PIGE. TF was analyzed according to the method described by Ritter et al.[28] Briefly, samples were mounted across a stainless steel target frame and bombarded with a 3.4 MeV beam of protons (~50 nA for 180 s) to produce γ-rays, which were measured using a high-purity germanium detector (HPGe, Canberra, 20%) located at approximately 75° to the beam. The combined number of counts of two γ-rays characteristic of the decay of the ^{19}F nucleus at 110 and 197 keV/μC of beam delivered is proportional to the TF. The beam intensity was measured in a suppressed Faraday cup before and after each 3 min run and normalized to a current measured in a tantalum collimator near the beam exit window. For the powdered CRM material, replicate targets were prepared by hydraulically compressing the powder into a self-supporting pellet at approximately 350 bar for 30 s and then taped onto target frames.

2.3.3. TF Analysis by INAA. Samples were analyzed according to the method described by Spate et al.[32] Briefly, samples were weighed into 0.5 mL high-density polyethylene (HDPE) vials. The vials were encapsulated in HDPE "rabbits" for irradiation in the pneumatic tube irradiation position of the MURR at a neutron flux of 5.5×10^{13} n cm^{-2} s^{-1}. Samples were irradiated for 7 s, decayed for 11 s, and were counted for 30 s using an HPGe detector (Canberra, 20%). The ^{20}F decays (11.03 s half-life) by β-particle emission with a characteristic γ-ray at 1633.6 keV. A correction was made for the fast neutron reaction ^{23}Na(n,α)^{20}F using a single-element Na standard irradiated and counted under the same conditions. The neutron activation product ^{24}Na emits a characteristic γ-ray at 1368.6 keV. The measured ratio of the 1633.6 keV/1368.6 keV γ-ray in the single-element standards is used to correct interference in the samples based on the measured 1368.6 keV

γ-ray. The correction in samples analyzed in this study was <1%.

2.3.4. Target PFAS Analysis by UHPLC–MS/MS. Target PFASs, including perfluoroalkyl carboxylic acids (PFCAs, C4–C15), perfluoroalkyl sulfonic acids (PFSAs, C4, C6, C8, and C10), perfluorooctane sulfonamide (FOSA), perfluoroalkane sulfonamidoacetic acids, fluorotelomer sulfonates (4:2, 6:2, and 8:2 FTSAs), fluorotelomer carboxylic acids (5:3, 7:3, and 9:3), ADONA, F53-B, and polyfluoroalkyl phosphoric acid mono- and diesters (mono- and diPAPs, respectively), were analyzed using a Waters Acquity UHPLC instrument coupled to a Xevo TQ-S triple-quadrupole mass spectrometer according to the methods described by Vestergren et al.[38] and Gebbink et al.[37] Instrumental parameters are listed in Table S2. Limits of detection (LODs) for individual PFASs are based on the average concentration in the extraction blank plus 3 times the standard deviation. In the absence of a blank signal, the LOD was based on the concentration of the lowest calibration standard at a minimum signal-to-noise ratio of 3. Individual LODs are listed in Table S8.

2.4. Fluorine Mass Balance Calculations. To compare PFAS concentrations (C_{PFAS}, nanograms of PFAS per gram) derived from UHPLC–MS/MS analysis to EOF and TF (C_{F_EOF} and C_{F_TF}, respectively; nanograms of F per gram) measured by CIC, molecular PFAS concentrations are converted to fluorine equivalents using the following equation:

$$C_{F\_PFAS} = n_F \times A_F / MW_{PFAS} \times C_{PFAS} \qquad (1)$$

where C_{F_PFAS} (nanograms of F per gram) is the corresponding fluorine concentration of a given PFAS, n_F is the number of fluorine atoms on the molecule, MW_{PFAS} is the molecular weight of the PFAS, and A_F is the atomic weight of fluorine.

The total known extractable fluorine concentration (ΣC_{F_PFAS}, nanograms of F per gram), which is the sum of all individual C_{F_PFAS} values, can be related to C_{F_EOF} by eq 2:

$$C_{F\_EOF} = \Sigma C_{F\_PFAS} + C_{F\_extr.unknown} \qquad (2)$$

where $C_{F\_extr.\ unknown}$ (nanograms of F per gram) is the total concentration of unidentified, extractable organic fluorine.

Lastly, C_{F_EOF} and C_{F_TF} are related to each other via the total nonextractable fluorine concentration ($C_{F\_non\ extr.}$, nanograms of F per gram) according to eq 3:

$$C_{F\_TF} = C_{F\_EOF} + C_{F\_non\ extr.} \qquad (3)$$

2.5. Quality Assurance and Quality Control. Accuracy and precision were assessed through (a) replicate ($n = 3$) spike–recovery experiments using printer paper fortified with 36 native PFASs (targeted analysis) and (b) comparison of replicate ($n = 8$) measurements of the CRM to certified concentrations (TF analysis). Extraction blanks were processed in every batch to monitor for background contamination, while solvent blanks were injected intermittently during UHPLC–MS/MS and CIC analysis to monitor for carryover. Statistical analysis was carried out at an $\alpha = 0.05$ confidence level in all instances.

3. RESULTS AND DISCUSSION

3.1. Total Fluorine Method Comparison. A comparison of the measured ($n = 8$) versus certified concentrations (568 ± 60 μg/g) of CRM BCR-461 revealed no statistically significant differences for CIC ($p = 0.18$) or PIGE ($p = 0.84$) [one-sample t tests (Figure 1a and Table S3)], indicating good accuracy
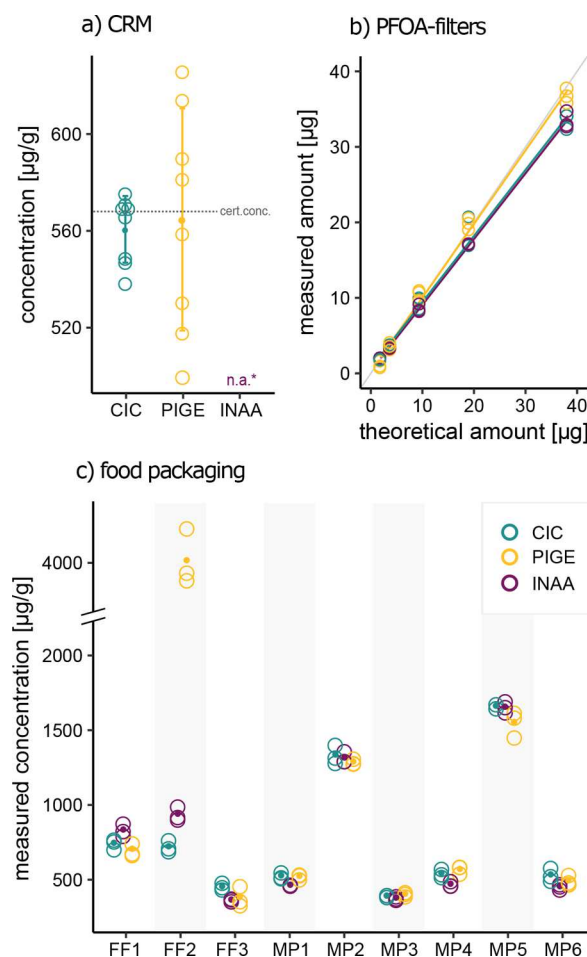

Figure 1. Comparison of TF methods (CIC, PIGE, and INAA) by means of (a) certified reference material (CRM) measurements ($n = 8$; circles) and means (dots) (the error bar represents the standard deviation, and the gray line indicates the certified concentration), (b) PFOA-spiked filter measurements vs theoretical concentrations (the gray line indicates slope = 1 and intercept = 0), and (c) food packaging samples (circles, data points; dots, means). Note the discrepancy in FF2 by PIGE due to the thickness and heterogeneity of this paperboard sample. *n.a., not analyzed due to interference.

for both methods. Precision was also reasonable for both approaches but slightly better for CIC (2.5% CV) than for PIGE (8.1%; $p = 0.005$; F-test). INAA was unable to measure F in the CRM due to the high Al content. The ^{27}Al captures a neutron, yielding unstable ^{28}Al, which decays by β-emission with a characteristic γ-ray at 1779 keV. The high levels of Al in geological materials result in detector dead times of >90% for the F analysis. Thus, INAA was deemed unsuitable for this matrix.

PFOA-fortified filters (six fortification levels, including a blank, each prepared in triplicate) were measured by CIC, PIGE, and INAA (Figure 1b and Table S4). The blank filters were below the LOD for all methods and therefore excluded from statistical analysis. Concentrations measured by CIC were, on average, 2.1% higher than those from PIGE and 4.1% higher than those from INAA, while those from PIGE were 1.9% higher than those from INAA. Repeated t tests with Bonferroni correction revealed that these differences were not statistically significant (for individual p values, see Table S6). All methods displayed good linearity ($r^2 > 0.99$) and precision
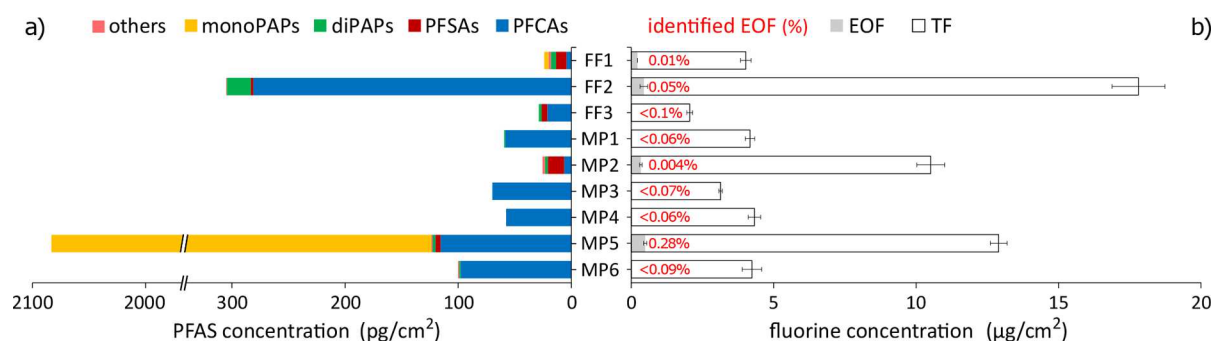
Figure 2. Fluorine mass balance in food packaging samples comprising (a) PFAS concentrations displayed as the sum of each class (in picograms per square centimeter) as measured by UHPLC−MS/MS and (b) total fluorine and extractable organic fluorine contents (error bars represent the standard deviation of triplicate measurements) in micrograms per square centimeter as measured by CIC. The percentage of EOF identified by the sum of target PFAS (ΣC_{F_PFAS}) is indicated in red.

[CV; 3−12% (CIC), 3−39% (PIGE), and 2−6% (INAA)] over the range of concentrations on the filters.

Nine food packaging materials were analyzed in triplicate by CIC, PIGE, and INAA (Figure 1c and Table S5). It is important to note that while measurement replicates were obtained for PIGE and INAA, the destructive nature of CIC requires technical replicates to assess precision. Another difference between methods arises from the fraction of the sample that contributes to the fluorine signal. For example, depending on the penetration depth of the PIGE particle beam, only the surface F content is measured in thick samples; in contrast, CIC and INAA measure the F content of the entire sample independent of material thickness. As a result, TF measurements determined by PIGE will be higher than those determined by INAA and CIC for surface-coated products when expressed on a weight basis. This difference is clearly demonstrated through measurements of FF2, which was the only thick paperboard material analyzed in this work and was over-reported by PIGE relative to CIC and INAA. When FF2 was excluded, CIC produced TF concentrations that were, on average, 2.4% higher than those produced by PIGE and 7.3% higher than those produced by INAA, while PIGE measurements were an average of 4.9% higher than INAA measurements. These differences were not statistically significant [two-way analysis of variance with replication (p = 0.39)]. All methods showed good precision [CV; 2−8% (CIC), 1−8% (PIGE), and 1−6% (INAA)]. Assuming a 10 mg sample size, detection limits were lowest for CIC (0.8 μg/g), followed by INAA (20 μg/g) and PIGE (38 μg/g).

3.2. Fluorine Mass Balance of Food Packaging Samples. *3.2.1. Target PFAS Analysis.* A total of 22 of 44 target PFASs were detected in the food packaging materials investigated here with Σ_{44}PFAS concentrations ranging from 23.9 to 2220 pg/cm^2 (Figure 2a and Table S8). Spike−recovery experiments demonstrated good accuracy and precision of the targeted PFAS analysis (see Table S7). PFTeDA, PFDoDA, PFHpA, 6:2 diPAP, PFHxA, 6:2/8:2 diPAP, and 8:2 diPAP were detected in >50% of the samples. 10:2 monoPAP was detected at by far the highest concentration (2100 pg/cm^2) but only in a single sample (MP5). In all other samples, the contribution of PFAA precursors was minor. PFCAs were the major compound class in 6 samples (FF2, FF3, MP2−MP4 and MP6), with PFHxA (<0.37−160 pg/cm^2) accounting for 53−90% of Σ_{44}PFAS concentrations in these samples. PFOA was detected in only FF2 and MP5 (4.32 and 22.4 pg/cm^2, respectively), possibly

reflecting the shift among industries from C8 to C6 chain lengths.

3.2.2. Fluorine Mass Balance. CIC-based C_{F_TF} concentrations in food packaging [2.05−17.8 μg/cm^2 (Figure 2b)] were high relative to the Danish Ministry of the Environment and Food indicator value of 0.1 μg/cm^2. This value was established as a means of differentiating between intentionally added and background PFASs in food packaging.[39] The C_{F_EOF} was greater than the method detection limit (MDL) (0.04−0.07 μg/cm^2) in four samples, but low (0.22−0.49 μg/cm^2) compared to C_{F_TF} (accounting only for 0−5.5%). No significant correlations were observed among C_{F_TF}, C_{F_EOF}, and ΣC_{F_PFAS}. According to eq 3, $C_{F\_non\ extr.}$ was high in all samples, ranging from 94.5 to 99.9%. These findings affirm the presence of polymeric coatings [e.g., perfluoropolyethers and fluorotelomer (meth)acrylate-based side-chain fluorinated polymers] on these papers and paperboards, as polymers have low solubility in most nonfluorinated solvents.[40] Furthermore, the fractions of C_{F_TF} and C_{F_EOF} explained by ΣC_{F_PFAS} were negligible in all samples [means of 0.002 and 0.08%, respectively (Table S9)], leaving the majority of TF and EOF unattributed. Therefore, we assume that our UHPLC−MS/MS method does not capture the PFASs intentionally used in these products. Here it is germane to note that possible degradation products and/or unreacted monomers of the aforementioned polymeric coatings [e.g., FTOHs, fluorotelomer olefins, or fluorotelomer (meth)acrylates] were not included in our targeted analysis.

Previous reports on TF in food packaging align well with concentrations reported in our study. Robel et al. measured concentrations from below the LOD to 8.17 μg/cm^2, and Schaider et al. concentrations of ≤15.2 μg/cm^2 in U.S. fast food packaging.[13,29] To the best of our knowledge, no prior studies have performed direct quantification of EOF in food packaging. While Robel et al. analyzed TF by PIGE in packaging samples before and after extraction, thereby indirectly measuring EOF, the differences were not statistically significant.[29] This is a general problem arising when comparing two large numbers, whereby a small difference easily lies within the error bounds. In our study, that problem is avoided by direct measurement of EOF. Similar to our results, Robel et al. report that the sum of ionic PFASs accounted for only 0−0.03% of the TF.

3.3. Implications. The results of the method comparison revealed excellent agreement among all three total fluorine methods. However, technical differences help determine their

applicability domains. For example, the rapid and non-destructive nature of PIGE and INAA allows for quick screening applications, as for example for regulatory purposes. CIC on the other hand excels at sensitivity and versatility, with lower detection limits and the possibility for direct IC analysis for determination of inorganic fluoride. All three methods can be used to analyze solid and liquid samples, although preconcentration methods are used to increase sensitivity for PIGE, which are not required for INAA and CIC.

In the case of food packaging materials, all three methods prove to be applicable. Because of the limited penetration depth of the particle beam, PIGE can distinguish between coated and uncoated surfaces. Most fluorine was persistent on the paper and paperboards after methanol extractions, as determined by comparably low EOF and target PFAS concentrations. More broadly, the cross-validation of these three TF methods means that they can be used as a complement to high-specificity targeted analysis. The mass balance measurements demonstrated in this work are critical in fate and transport studies of PFASs in the environment, such as those that can be found in the end-of-life options for paper packaging. For example, regardless of whether PFAS-treated paper decays in a landfill, is composted and used as fertilizer, or is recycled directly into more paper, these TF methods can be used to study the environmental release of all PFASs over a broad range of samples, disposal conditions, and locations. Such a broad question could not be answered in a timely manner with compound-specific analysis, yet LC−MS/MS identification of PFASs will remain an essential complement to these robust TF methods.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.es-tlett.8b00700.

> Additional information about food packaging samples, instrumental methods, target PFAS compounds, quality assurance and quality control results, p values for statistical analysis, and tabular overviews of CIC, PIGE, INAA, and LC−MS/MS results (PDF)

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Notes
The authors declare no competing financial interest.

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