Defluorination and Derivatization of Fluoropolymer for Determination of Total Organic Fluorine in Polyolefin Resins by Gas Chromatography

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Supplementary Information:

Figure S1. Comparison of reaction yields obtained for defluorination and derivatization of PFOA at 100 ppm w/w in various solvents.

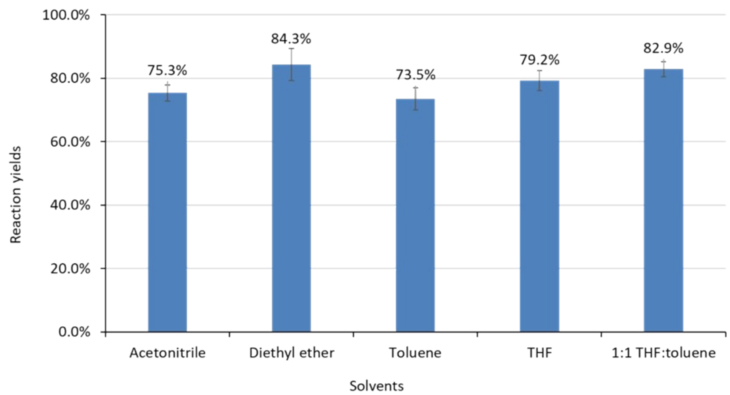


Figure S2. Comparison of reaction yields obtained for various PFAS model compounds at a concentration of 100 ppm w/w in diethyl ether.

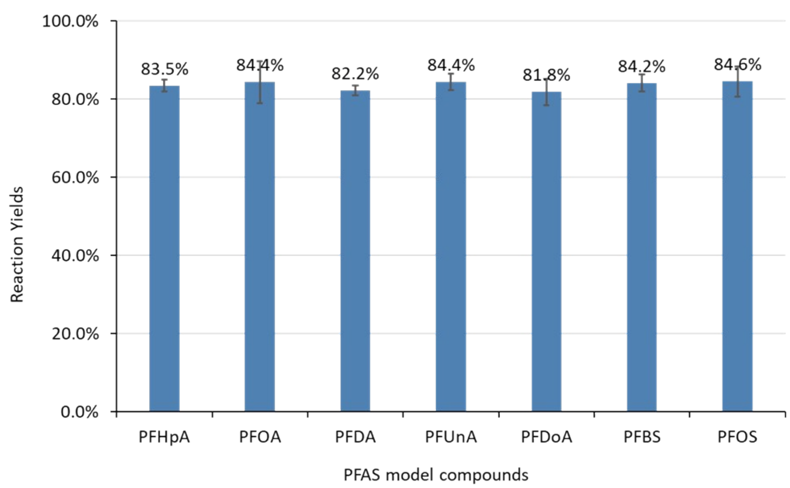


Figure S3. (a) Total ion chromatogram of a 100 ppm w/w PVDF-HFP in THF standard after defluorination and derivatization, (b) Mass spectrum of TPSiF peak at 17.1 min. Conditions: Inlet 250 °C, split ratio 200:1, oven temperature programing 40 °C (1 min) to 280 °C at 15 °C/min, column 30 m × 0.25 mm × 1 µm CP-Sil 5 CB, column flow 1mL/min helium, transfer line 300 °C, ion source 220 °C, mass range from 29-400 Da.

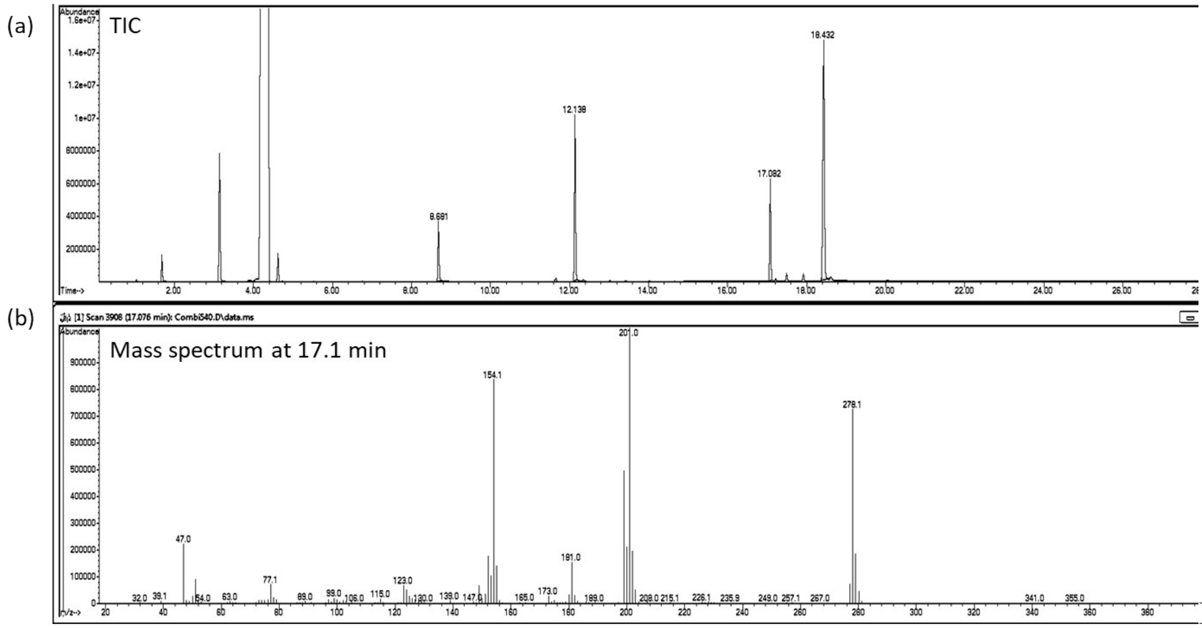


Figure S4. Comparison of chromatograms of method blanks obtained from (a) solvent blank of heptane, (b) DI water blank with the derivatization process, (c) THF blank with defluorination and derivatization.

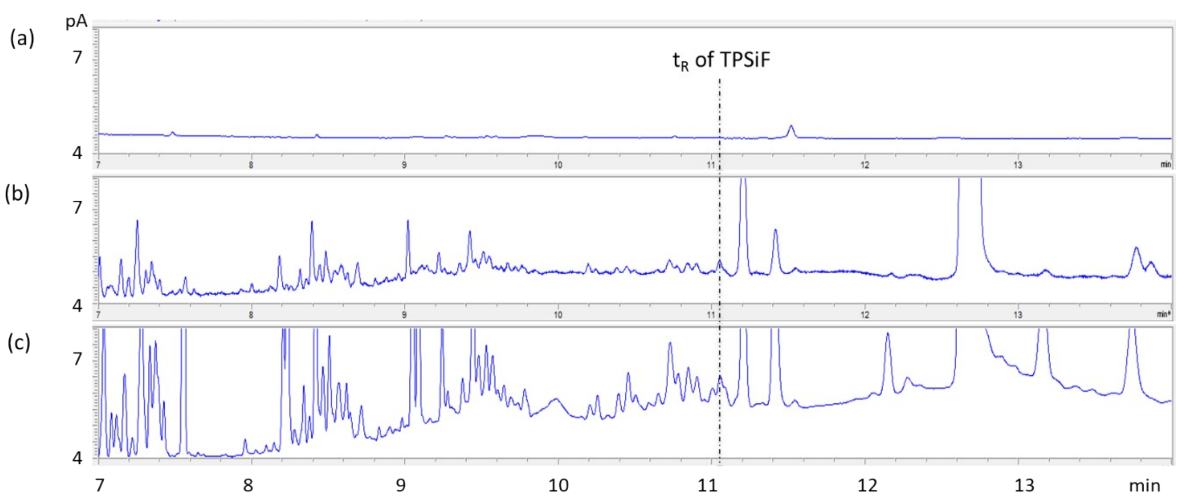
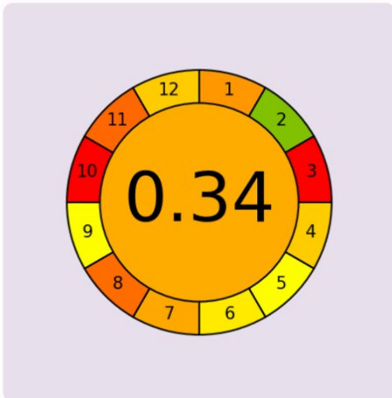


Figure S5. Results of AGREE analysis for the CDD-GC method.



The CDD-GC method was assessed with the Analytical GREEnness calculator (AGREE) [34], where various aspects of an analytical method were evaluated including the amounts and toxicity of reagents, generation of waste, the safety of the analysts, the number of procedure steps, and energy consumption. The assessment criteria were based on the 12 principles of green analytical chemistry (SIGNIFICANCE) [35] and each of the 12 input criteria was converted into a score of 0−1 range. The output is presented as a clock-like graph where the performance of each principle reflected with red-yellow-green color scale, and the overall score and color representation in the middle. The AGREE analysis result for the CDD-GC method was presented in Figure S4. In summary, the procedure involves external sample treatment with reduced number of steps (principle 1), and 0.5 g of resin sample is required (principle 2). The measurement is off-line (principle 3), and the procedure involves six distinct steps (principle 4). The procedure is manual and can be considered as miniaturized (principle 5). Derivatization agent is used in the analysis (principle 6). The total amount of waste is about 15 g, including the sample itself, solvent and reagent, pipette tips, microcentrifuge tubes (principle 7). Since only total fluorine is measured, the number of analytes determined in a single run is considered to be one and the sample throughput is ~2.5 samples/hour (principle 8). The most energy demanding technique is GC (principle 9). None of the reagents is from bio-based sources (principle 10), the volume of toxic reagents is ~10 mL (principle 11). THF and heptane is highly flammable and toxic to aquatic life, 70% perchloric acid is corrosive (principle 12). The results show a generally low overall AGREE score of 0.34, some of the weak points identified are the multiple sample preparation steps involved which negatively affects the sample throughput, the use of various reagents and subsequent waster generation.

Figure S6. BAGI index pictogram for the CDD-GC method.

This BAGI tool focuses mainly on the practical aspects and evaluates ten main attributes including the type of analysis, the number of analytes that are simultaneously determined, instrumentation, the number of samples that can be simultaneously treated, sample preparation scale, the number of samples that can be analysed per hour, types of reagents and materials, the requirement for preconcentration, the automation degree, and the amount of sample. Through the evaluation of these attributes, discrete scores of 10, 7.5, 5.0, and 2.5 points are assigned with 10 being high compliance and 2.5 being no compliance. The results are then presented as an asteroid pictogram where discrete hues of dark blue, blue, light blue, and white are used to represent the individual scores from 10 to 2.5 for each attribute. The overall score was in the center, ranging between 25–100, with 25 being the worst method performance and 100 being the best. It is recommended that a minimum of 60 points for a method to be considered as "practical". The BAGI analysis result for the CDD-GC method was depicted in Figure S5. In summary, the method is quantitative and is considered as a single-element analysis since only total fluorine is measured. The method uses simple instrumentation that is available in most labs (GC-FID) and commercially available reagents. Conventional sample preparation which involves multiple steps such as solvent extraction and derivatization is required. Simultaneous sample preparation of around 20 samples can be conducted which require a time span of 120 min, followed by a GC analysis time of 16 min, resulting in a sample throughput of 2.5 h^{-1}. No preconcentration was required to meet the current regulatory requirements. Sample preparation is manual, but analysis is done with GC autosampler, therefore, the process is semi-automated. 0.5 g of sample is required for the analysis. The total BAGI score for the developed method is 67.5, demonstrating its applicability.