**Text Supplemental Information (SI)**

**Text SI 1. Materials.** Deactivated, Qsert, Amber screw cap vial with cap (product # 186001130DV) and screw cap blue PTFE/Silicone Septa (product # 51903156) were purchased from Agilent Technologies (Santa Clara, CA). Dichloromethane analytical standard HPLC grade (product # [270997](https://www.sigmaaldrich.com/US/en/product/sial/270997)), ethyl alcohol ACS spectrophotometric grade 95% (product # [493511](https://www.sigmaaldrich.com/US/en/product/sial/493511)), alkane standard mixture for performance tests of GC-systems C10 - C40(all even), 50 mg/L each dissolved in n-heptane (product # 68281), HPLC grade acetone (product # 650501) was purchased from Sigma Aldrich (St. Louis, MO).

The following PFAS were commercially procured from Sigma Aldrich: 1H,1H,2H-perfluoro-1-hexene (99%) (product #371459) , 1H,1H,2H,2H-perfluorohexan-1-ol (97.00%) (product # 532770), perfluorohexanoic acid (≥ 98.0%) (product # 43809), undecafluoro-2-methyl-3-oxahexanoic acid (≥96%) (product # 018340), 1H,1H,2H-perfluoro-1-octene (99%) (product # [371459](https://www.sigmaaldrich.com/US/en/product/aldrich/371459)) , 1H,1H,2H,2H-perfluoro-1-octanol (97%) (product #370533), and 1H,1H,2H-perfluoro-1-decene (99%) (product # 370576).

The heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (97%) (product # 2107312) and 1H-perfluoroheptane (97%) (product # 1100375) was purchased from SynQuest Laboratories located (Alachua, FL). The 1H,1H,2H-perfluoro-1-dodecene (> 98%) (product # FC021025) was purchased from Fluoryx Labs (Carson City, NV).

**Text SI 2. Challenge Sample Creation.** PFAS compounds were selected for the challenge sample to represent a diverse mix of PFAS with different functional groups as well as varying difficulties of identification. For example, some compounds were present in the custom database as well as external databases while others were only present in external databases. One compound was not present in the custom database or external databases. Furthermore, two fluoroteleomer alcohols were used (4:2 Fluorotelomer Alcohol and 6:2 Fluorotelomer Alcohol) to test the workflow’s ability to differentiate compounds in a homologous series.

**Text SI 3. Standard and Sample Storage and Runs.** The standards and samples were stored at -80 °C to reduce solvent evaporation between runs. Before vortexing, the samples were allowed to thaw for at least 30 minutes at ambient room temperature. Before each analysis, the amber vials containing the PFAS chemicals were shaken by hand for 15 seconds and vortexed for 20 seconds. Between every 10 PFAS chemicals, ethanol blanks were run. For each sample run, external n-alkane standards were used for the determination of retention time indices for the PFAS (see **SI 7** for specifics). These standards were run following ethanol blanks at the beginning and end of the sequence runs. After each run, the PTFE/silicone caps were replaced with new PTFE/silicone caps to prevent solvent evaporation.

**Text SI 4. Settings for the TriPlus RSH Autosampler.** For the general setting, the injection port was set at B (SSL), and the type was put as single. The injection mode was basic, with rapid mode injection disabled. The sampling volume was set at 1 µL, with 3 plunger strokes, with an auto and filling mode. The injection depth was standard, with no pre-injection or post-injection dwell time. The sampling depth in the vial was 30 mm. The samples were non-viscous.

For washes of the syringe, there were multiple solvents from the standard wash station. For pre-injection, there were 3 cycle rinses with solvent A (methanol) with a solvent volume of 1 µL, followed by 3 cycle rinses with solvent B (acetone) with a solvent volume of 1 µL. The rinse with the samples was set at 2, with a solvent volume of 1 µL. Post-injection, there were 10 cycle rinses with solvent A (methanol) with a solvent volume of 1 µL, followed by 10 cycle rinses with solvent B (acetone) with a solvent volume of 1 µL. The GC synchro start setting was set at standard.

**Text SI 5. Custom PFAS Database.** Using PFAS chemicals, a custom database was constructed with EI, PCI, and NCI data. Peaks were manually selected using Freestyle 1.8 SP2 program. Background-subtracted spectra were exported to the NIST software and added to the custom PFAS database. In the NIST program under spectrum import options, the settings were changed; under Tandem Spectrum accuracy, precursor ion *m/z*, decimal places were set to 5. The product ion *m/z* decimal places were set to 5. The in-source/EI accurate ion *m/z* was set to 5 decimal places. Adding spectra to spec list was prepended (add to the top) to the library. The spectra without precursor ion *m/z* value was set to accurate *m/z*. The RI type was set at unspecified. An image capture of the import options chart is located in **Figure SI 3**.

**Text** S**I 6. Retention Indexes (RIs). Table SI 4** lists predicted and experimental RIs for the 141 PFAS chemicals used to build the custom database. **Tables SI 6 and SI 8** include RIs for other PFAS and fluorinated compounds from the NIST and Wiley databases, when available.“Estimated RI” refers to values that exist in the NIST and Wiley databases that are predicted based on molecular structure. The NIST database offers a second predicted RI value from an artificial intelligence algorithm, and this is referred to as “AI RI”. The NIST and Wiley databases also contain some RIs calculated from experimental data, which we refer to as “Database Experimental RI”. Finally, the RIs calculated based on our experimental data for a given sample set are referred to as Calculated RI. Calculated RIs are calculated in Compound Discoverer 3.3 by inputing observed retention times for n-alkanes which were run at the directly after sample analysis.

**Text SI 7. Identification Workflow.** For analysis of the PFAS challenge sample and incineration samples taken in EI mode, Compound Discoverer 3.3 was used.

For the samples analyzed in EI mode, the study type was set for GC and the Processing Workflow chosen was: WorkflowTemplates\GC\GC EI\Core GC EI – Before Reprocessing. Some of the advanced parameter settings were changed in the GC EI deconvolution workflow as follows: The RT Tolerance [sec] was changed from 5 to 10. The setting of “Use Reverse Search” was changed from “False” to “True”. Smoothing was changed from “9” to “5”. Two types of analysis were performed using different libraries. The first analysis was performed using the EI custom PFAS database. The next analysis was performed using qed nist library, replib, W11del, W11main1, W11main2, and W11rep. The analysis was run in bulk and not by individual file. See **Figure SI 3** for an image capture of the settings.