

Environmental

Untargeted screening for volatile PFAS indoor in air using thermal desorption-GC Orbitrap mass spectrometry

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Keywords

Polyfluoroalkyl substances (PFAS), indoor air monitoring, thermal desorption, TD100-xr, gas chromatography-mass spectrometry, GC-MS, Orbitrap Exploris GC, HRAM, TRACE 1610 GC, EI, CI, ddMS², Compound Discoverer software, elemental composition, FreeStyle software

Goal

The purpose of this application note is to demonstrate thermal desorption sampling coupled with the Thermo Scientific Orbitrap™ Exploris™ GC Mass Spectrometer and Thermo Scientific™ Compound Discoverer™ Software for effective and simple identification/screening of untargeted volatile PFAS in indoor air.

Introduction

Per- and polyfluoroalkyl substances (PFAS) consist of one or more alkyl residues where all hydrogen atoms have been replaced by fluorine atoms. PFAS, often referred to as “forever chemicals,” are used for their surfactant properties.¹ Volatile PFAS are also found in indoor air as they are widely used in consumer cleaning products and applied to fabrics and upholstery for surface protection. PFAS are known to cause a range of health problems. Neutral PFAS species (n-PFAS), such as fluorotelomer alcohols (FTOHs), fluorotelomer carboxylic acids (FTCAs), and perfluorooctanesulfonamides (FOSA), can degrade within the body and in the environment to form perfluorooctanoic acid (PFOA), which has been linked to cancer, reproductive and immune system toxicity, and other diseases at low concentrations.²

The thermal desorption (TD) technique provides an efficient way to conduct air monitoring. Stainless-steel tubes packed with sorbent sampling media can preconcentrate volatile species from several liters of air to be directly analyzed by GC-MS without any additional sample preparation prior to analysis.³ Full scan data acquisition

with HRAM allows all ions to be acquired at high mass selectivity and accuracy across the entire scan range. This provides a simple method setup to conduct untargeted compound screening with retrospective data mining capabilities.⁴

Non-targeted screening combined with HRAM GC-MS and TD represents a fast and broad analytical approach for providing a comprehensive picture of indoor air quality. Combined with Compound Discoverer software for data mining, this approach simplifies monitoring of thousands of organic contaminants in air, including volatile PFAS species. Analysis within this study investigated indoor air from three different locations (carpeted, non-carpeted, and cleaning supplies storage closet) in our facility located in San Jose, California. We demonstrated the simplicity and the potential of the untargeted screening workflow for volatile PFAS illustrated in Figure 1.

Experimental design and workflow

Sampling system

A Markes International™ TD100-xr™ Advanced thermal desorber with electronic flow control, equipped with a Markes International™ Internal Standard Addition / Dry Purge (ISDP) accessory for automated addition of gaseous internal standard, was used. The TD100-xr thermal desorption unit offers sequential, unattended analysis of up to 100 samples. Due to the use of Peltier cooling for refocusing in the trap, the TD100-xr eliminates both the cost and hassle of using a cryogenic fluid. Markes' systems also allow samples to be split and re-collected onto a clean sorbent tube at the tube desorption and/or trap

desorption stages, providing “insurance” against failed runs and simplifying demonstration of complete analyte transfer and absence of analytical bias. Re-collection also allows for sample backup for storage purposes. The re-collection feature was used for replicate injections for samples to be run twice without the need for new spiked sorbent tubes during method optimization as well as for confirmation.

Standard and sample preparation

Native PFAS standards—procured from Wellington Laboratories Inc., Cat. No. EPA-1633stk, and AccuStandard, Inc., Cat. No. FTOH-MIX-001 (Fluorotelomer Alcohols Mix 1), Cat. No. FTOH-004S (1:3 FTOH), Cat. No. M-1633-2/3A-CN-10X (EPA 1633 perfluorosulfonic acids and perfluorosulfonamides), and Cat. No. CLP-PS-3-10X (Toluene-d8)—were used for method optimization and for building the in-house Thermo-SJ-PFAS HRAM EI database and mass lists for the Thermo Scientific™ TraceGOLD™ TG-200MS GC Column used for this study.

PFAS Standard mix (1 ng/μL) was prepared in methanol and 5 μL was spiked on to the sorbent tubes using a Calibration Solution Loading Rig (CSLR™) purged with nitrogen.

Markes International™ PFAS Extended volume tubes (Thermo Fisher Cat. No. 76473-0942) were used for spiking standards and indoor air sampling. Markes International™ ACTI-VOC PLUS™, fast-flow pump kit was used for sampling indoor air into sorbent tubes for TD analysis. Pumped sampling is one of the most versatile methods for sampling VOCs and SVOCs. Using ACTI-VOC PLUS, precise volumes from 20 mL to

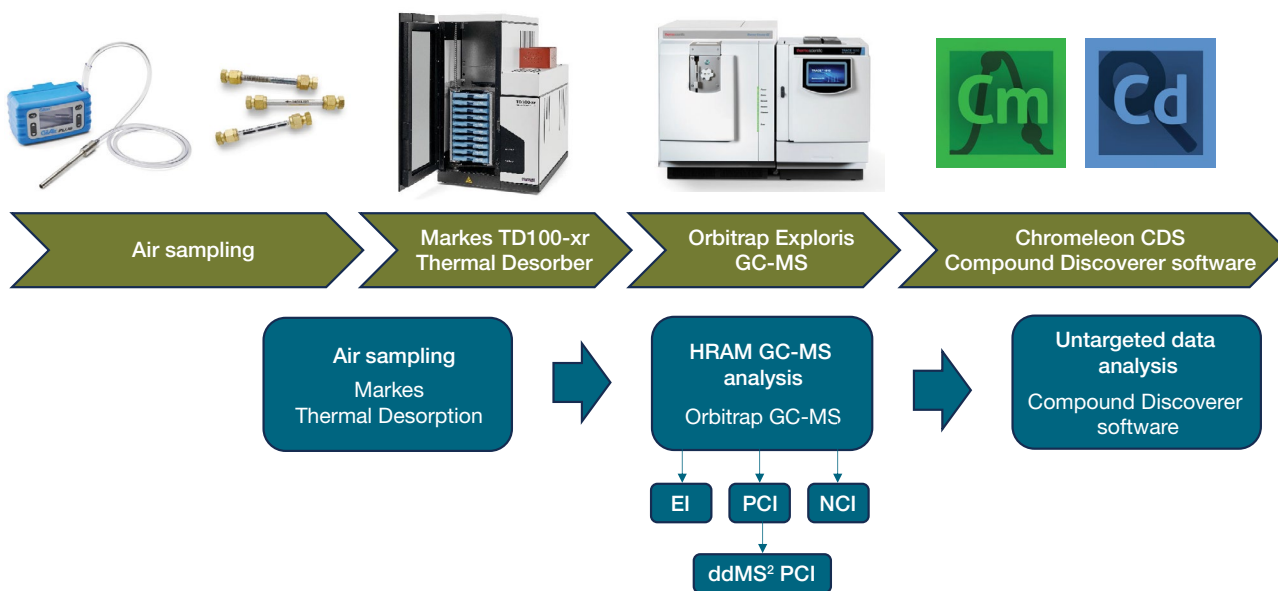


Figure 1. TD-GC-HRMS workflow for untargeted PFAS analysis in air.

several hundred liters can be drawn through the tubes, allowing analytes over a wide concentration range to be sampled and analyzed. Thirty-five liters of indoor air were sampled from the three different locations (carpeted, non-carpeted, and cleaning supplies storage closet).

Method setup

Spiked standard tubes and indoor air samples were thermally desorbed, cryo-focused, and trapped at -28 °C onto the Markes International PFAS focusing trap (Thermo Fisher Cat. No. 76473-0940), which was desorbed at 250 °C for 8 min onto the GC analytical column. The focusing trap was heated to 300 °C for 3 min between injections to avoid carry-over.

Table 1. TRACE 1610 GC - Orbitrap Exploris GC parameter settings.

TRACE 1610 GC parameters	
Injection mode	Splitless
GC aux heater (°C)	250
Carrier gas, flow (mL/min)	He, 1.2
Oven temperature program	
Temperature (°C)	40
Hold time (min)	2.0
Rate (°C/min)	15
Temperature 2 (°C)	250
Hold time (min)	3
Rate 2 (°C/min)	50
Temperature 3 (°C)	300
Hold time 2 (min)	3
GC run time (min)	23
Analytical column	
TraceGOLD TG-200MS	30 m × 0.25 mm × 1 µm (Cat. No. 26084-2960)
Orbitrap Exploris GC mass spectrometer parameters	
EI mode	
Transfer line temperature (°C)	250
Ion source type and temperature (°C)	Thermo Scientific™ ExtractaBrite™ electron ionization source, 250
Aquisition mode	Full Scan
Mass range (<i>m/z</i>)	50–700
Resolution	60,000
Internal mass calibration	On
CI mode	
Transfer line temperature (°C)	250
Ion source type and temperature (°C)	ExtractaBrite, 150
CI gas type and flow (mL/min)	Methane, 1.75
Internal mass calibration	Off
CI ddMS ² mode	
Scan range	90–700
Full Scan → ddMS ²	4 scans

Standards and samples were analyzed using the Thermo Scientific™ TRACE™ 1610 Series GC coupled to the Orbitrap Exploris GC mass spectrometer. Chromatographic separation was achieved on a TraceGOLD TG-200MS capillary column 30 m × 0.25 mm × 1.0 µm (Cat. No. 26084-2960). The trifluoropropylmethylpolysiloxane stationary phase of the TraceGOLD TG-200MS column provides an exceptionally inert phase for improved thermal stability, low column bleed, and reliable run-to-run and batch-to-batch reproducibility.³ Its mid-polarity can resolve compounds that phenyl and cyano phases cannot due to fluorine in its stationary phase. GC-HRMS conditions are summarized in Table 1, while Table 2 shows the TD-100-xr parameters.

Data acquisition

Data acquisition was carried out in full scan analysis. Additional MS method parameters for both EI and CI modes are summarized in Table 1. External mass calibration was performed prior to analysis, while characteristic ions representing column bleed were used as lock masses when scanning in EI to perform internal mass calibration. Sample acquisition and qualitative processing were performed using the Thermo Scientific™ Chromeleon™ version 7.3.2 Chromatography Data System (CDS) and Thermo Scientific™ FreeStyle™ Software, an application to view and qualitatively analyze raw MS data. Indoor untargeted air screening data full processing was done using Compound Discoverer software along with the Thermo Scientific™ Orbitrap™ GC-MS HRAM Contaminants Library, GC Orbitrap™ PFAS EI Database by the U.S. Environmental Protection Agency (EPA), and in-house curated PFAS HRAM EI database and mass list.

Table 2. Markes International TD100-xr parameters (2-3 Stage Tube Desorb settings).

Parameter	Value
Tube type	PFAS Extended volume tubes (Cat. No. 76473-0942)
Split flow	10 mL/min
Flow path temperature	150 °C
Minimum carrier pressure	5 psi
Automatic dry purge	1 min at 50 mL/min
Tube desorption	250 °C for 10 min at 50 mL/min
Trap purge	1 min at 50 mL/min
Focusing trap	PFAS focusing trap (Cat. No. 76473-0940)
Focusing trap low temperature	-28 °C
Elevated trap purge temperature	25 °C
Trap high temperature	250 °C (8 min)
Trap heat rate	28 °C/s
Split flow	2 mL/min

Results and discussion

The Orbitrap Exploris GC-MS was used for accurate mass measurements in full-scan mode at 60,000 mass resolution (FWHM at m/z 200). Variable electron voltage (VeV) is an effective technique that can be implemented in the high-resolution, accurate-mass (HRAM) Orbitrap Exploris GC-MS Series. This highly efficient technology enables lower eV settings for electron ionization, essentially soft EI as previously described, and routinely delivers very robust tuning results. The softer EI technique promotes higher mass signals and increases sensitivity for compounds prone to extensive fragmentation.⁵ Using the VeV technique, electron energy at 50 eV was optimal for PFAS analysis in EI mode.

Table 3 reports the list of PFAS compounds included in the standard mixture, and the corresponding EIC of MS quantitation peaks are shown in Figure 2. By thermally desorbing the PFAS compounds, we are able to trap and detect very volatile compounds that would be otherwise elute in the solvent front with liquid injections.

The Chromeleon CDS data file for the PFAS standard mix (5 ng) was imported as a raw data file in FreeStyle software. Mass spectra of each PFAS standard were curated by subtracting the background and checking the elemental composition and mass accuracy of the EI fragments (Appendix Figure A3). Spectra can be imported for library construction to non-target screening applications. These libraries can then be used by the Compound Discoverer software for identification of PFAS compounds.

Indoor air analysis

Thirty-five liters of indoor air from three different locations—namely carpeted, non-carpeted, and a cleaning supplies storage closet in our facility—were collected at 300 mL/min using the ACTI-VOC low-flow pump into Markes PFAS Extended volume tubes. Pumped sampling tubes were desorbed and HRAM data was collected in both EI and CI ionization modes. Example of TIC chromatograms in EI and CI modes are shown in Figures A1 and A2 in the Appendix.

Table 3. Component table of PFAS standard mix.

Name	Retention time (min)	CAS #	Chemical formula	MS quant. peak	MS conf. peak 1	MS conf. peak 2	MS conf. peak 3
1:3 FTOH	2.92	461-18-7	C ₄ H ₇ F ₃ O	77.0197	68.9947	91.0354	107.0303
5:1 FTOH	3.07	423-46-1	C ₆ H ₃ F ₁₁ O	91.0542	130.9915	68.9947	162.997
d8-Toluene	3.08	2037-26-5	C ₆ D ₅ CD ₃	98.098	100.1122	–	–
4:2 FTOH	3.50	2043-47-2	C ₆ H ₅ F ₉ O	95.0102	130.9915	127.0166	68.9947
5H4:1 FTOH	3.95	355-80-6	C ₅ H ₄ F ₈ O	130.9915	95.0103	113.0009	68.9947
7:1 FTOH	4.58	307-30-2	C ₈ H ₃ F ₁₅ O	130.9914	68.9946	99.993	180.9883
PFBS(Perfluorobutanesulfonic acid)	4.93	375-73-5	C ₄ HF ₉ O ₃ S	162.9977	68.9947	113.0009	130.9915
6:2 FTOH	5.08	647-42-7	C ₈ H ₅ F ₁₃ O	95.0102	127.0165	68.9946	296.0054
8:1 FTOH	5.35	423-56-3	C ₉ H ₅ F ₁₇ O	130.9914	68.9947	180.9883	99.993
PFPS (Perfluoropentanesulfonic acid)	5.71	2706-91-4	C ₅ HF ₁₁ O ₃ S	180.9883	68.9947	162.9977	130.9915
6:3FTOH	6.33	80806-68-4	C ₉ H ₇ F ₁₃ O	130.9914	68.9947	180.9883	115.0542
8:2 FTOH	6.54	678-39-7	C ₁₀ H ₅ F ₁₇ O	130.9914	68.9947	180.9883	95.0103
9ME-8:2FTOH	7.30	31200-98-3	C ₁₁ H ₅ F ₁₉ O	130.9914	68.9947	180.9883	95.0102
10:2 FTOH	7.80	865-86-1	C ₁₂ H ₅ F ₂₁ O	130.9914	68.9947	180.9883	95.0102
12:2FTOH	8.96	39239-77-5	C ₁₄ H ₅ F ₂₅ O	130.9914	68.9947	180.9883	95.0103
N-MeFBSE	9.95	34454-97-2	C ₇ H ₈ F ₉ NO ₃ S	325.989	68.9947	130.9915	262.0273
N-me-PFOSA	10.03	31506-32-8	C ₉ H ₄ F ₁₇ NO ₂ S	93.9956	68.9947	280.9818	130.9915
1:8:1FTdiOH	10.12	754-96-1	C ₁₀ H ₆ F ₁₆ O ₂	130.9914	68.9947	180.9883	95.0102
PFOSA	10.15	754-91-6	C ₈ H ₂ F ₁₇ NO ₂ S	79.9801	68.9947	230.9853	130.9915
Sulfuramid	10.34	4151-50-2	C ₁₀ H ₆ F ₁₇ NO ₂ S	447.9987	68.9947	108.0114	130.9915
Et-FOSA-AcOH	11.94	2991-50-6	C ₁₂ H ₈ F ₁₇ NO ₄ S	134.962	68.9947	146.962	130.9915

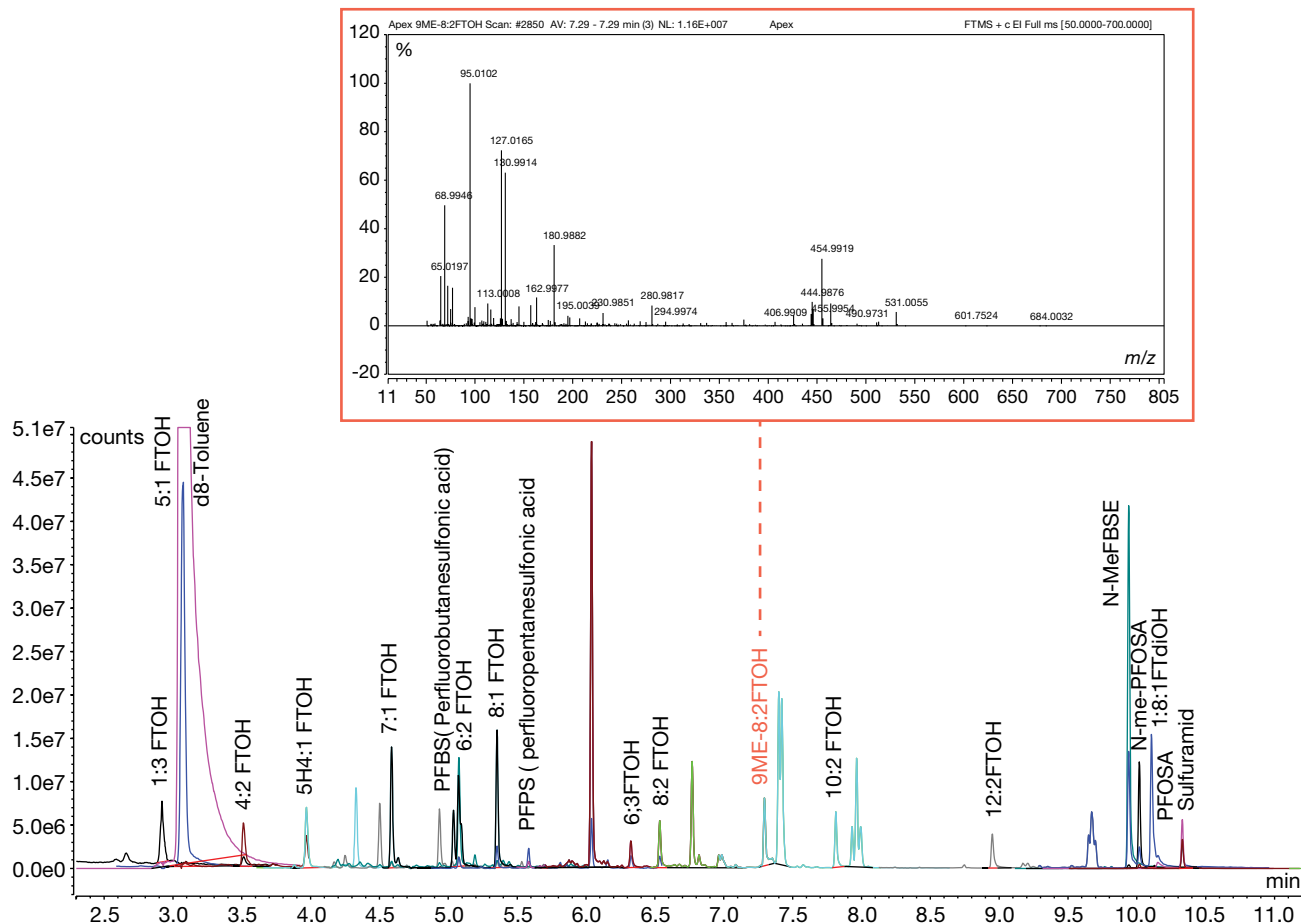


Figure 2. Extracted ion chromatogram (EIC) of PFAS standards mix (5 ng) on a TraceGOLD TG-200MS column in Full-scan EI mode. The inset shows the HRAM spectrum for 9ME-8:2FTOH.

Untargeted screening of indoor air for PFAS using Compound Discoverer software

Compound Discoverer software is a powerful platform providing a comprehensive solution for the untargeted analysis including PFAS in complex matrices. The GC-EI or CI workflows contain a pre-assembled combination of customizable interconnected nodes with parameters optimizable for the analysis of PFAS (Figure 3). These workflows leverage formula prediction based on HRAM and spectral best fit. Descriptive statistics and differential analysis nodes enable the visualization of statistical differences seen in different PFAS species amongst the three different locations of sampled indoor air in our study. The result exporter node is used to export results from Compound Discoverer software in text as well as csv file formats. These files can be imported into Chromeleon CDS for setting up targeted analysis.

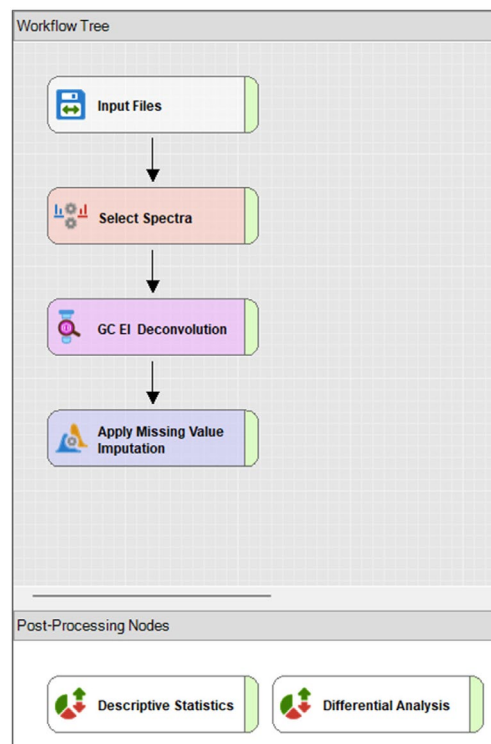
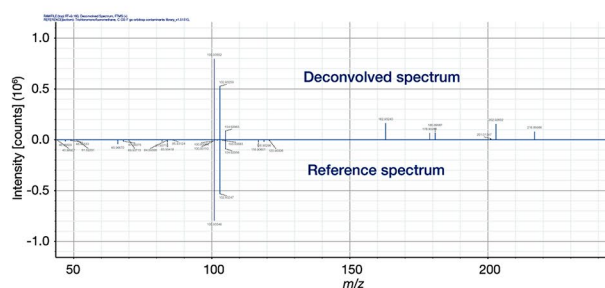
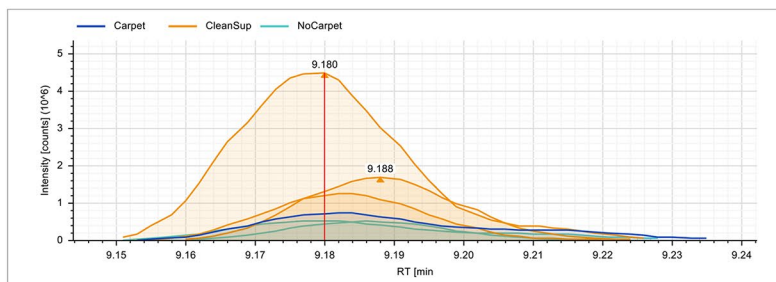


Figure 3. GC-EI workflow in Compound Discoverer software.

GC-EI results can be filtered for PFAS-specific compounds by applying a filter to the library hit formula that specifically contains fluorine. Formula prediction is constrained by a maximum of 50 fluorine atoms to provide optimal coverage for the observable chemical space where PFAS reside.⁶ More than 2,000 compounds were identified in the present indoor air study, which

was shortlisted to 100 compounds by adding a fluorine filter to the NIST library hit formula. Other filters like total score, high resolution filtering (HRF) score, and search index (SI) score can be applied to further simplify the compound list. Figure 4 (A,B) shows GC-EI results filtered for fluorine.

A



GC EI Compounds														
Checked	Tags	Comments	Name	CAS Num	Calc. MW	RT [min]	Reference m/z	Avg TIC	NIST Lib Hit Formula	NIST Theo. Mol. Mass	Total Score	HRF Score	SI	Calculated RI
<input type="checkbox"/>			8_2 Fluorotelomer Alcohol		503.10812	9.539	326.96585	32633015	C10 H5 F17 O	464.00635	63.7	17.7	829	1142
<input checked="" type="checkbox"/>			Trichloromonofluoromethane	75-69-4	201.01402	9.180	102.93259	2196001	C Cl3 F	135.90441	85.5	72.4	827	1095
<input type="checkbox"/>			(Perfluorobutyl)-2-thenoylmethane		140.02966	8.725	110.98992	6986507	C10 H5 F7 O2 S	321.98930	87.1	76.9	815	1036
<input type="checkbox"/>			(Perfluorobutyl)-2-thenoylmethane		125.13303	8.065	111.99327	8092902	C10 H5 F7 O2 S	321.98930	81.2	62.3	811	955
<input type="checkbox"/>			8_2 Fluorotelomer Alcohol		415.03720	7.202	326.96585	41852435	C10 H5 F17 O	464.00635	68.4	30.9	804	856
<input type="checkbox"/>			1,1-Difluoroethane	75-37-6	259.01709	4.019	115.01655	87465	C2 H4 F2	66.02756	81.5	64.8	780	
<input type="checkbox"/>			Trichloromonofluoromethane	75-69-4	100.93607	2.443	102.93259	1260715	C Cl3 F	135.90441	83.2	69.9	760	
<input type="checkbox"/>			Flamprop-isopropyl	52756-22	120.05748	7.685	105.03336	86479403	C19 H19 Cl F N O3	363.10320	95	99.7	756	912
<input type="checkbox"/>			Flamprop-isopropyl	52756-22	138.14090	10.760	106.03708	18552767	C19 H19 Cl F N O3	363.10320	93.3	95.8	747	1315
<input type="checkbox"/>			Bifenthrin	82657-04	164.06267	11.124	166.07780	4633965	C23 H22 Cl F3 O2	422.12549	90.8	100.0	738	1368
<input type="checkbox"/>			(Perfluorobutyl)-2-thenoylmethane		224.04376	8.067	126.01343	4265913	C10 H5 F7 O2 S	321.98930	82.5	69.5	733	956

GC EI Compounds per File														
Checked	Name	CAS Num	Formula	Total Score	HRF Score	RHRF Score	SI	RSI	Elements Found[%]	Molecular Weight	Theo. Mol. Mass	Library	Library Hit key	Library ID Number
<input type="checkbox"/>	Dichlorodifluoromethane	75-71-8	C Cl2 F2	86.0	72.4	0.0	851	999	100.0	119.93451	119.93396	gc-orbit	gc-orbitrap contaminar	1498
<input checked="" type="checkbox"/>	Trichloromonofluoromethar	75-69-4	C Cl3 F	85.5	72.4	100.0	827	971	100.0	135.90496	135.90441	gc-orbit	gc-orbitrap contaminar	1510
<input type="checkbox"/>	1,1,2-Trichloro-1,2,2-trifluor	76-13-1	C2 Cl3 F3	81.8	72.4	100.0	643	755	100.0	185.90177	185.90122	gc-orbit	gc-orbitrap contaminar	1486
<input type="checkbox"/>	1,1-Dichloro-1-fluoroethane	1717-00-6	C2 H3 Cl2 F	81.0	72.4	0.0	851	999	75.0	115.95958	115.95904	gc-orbit	gc-orbitrap contaminar	1487

B

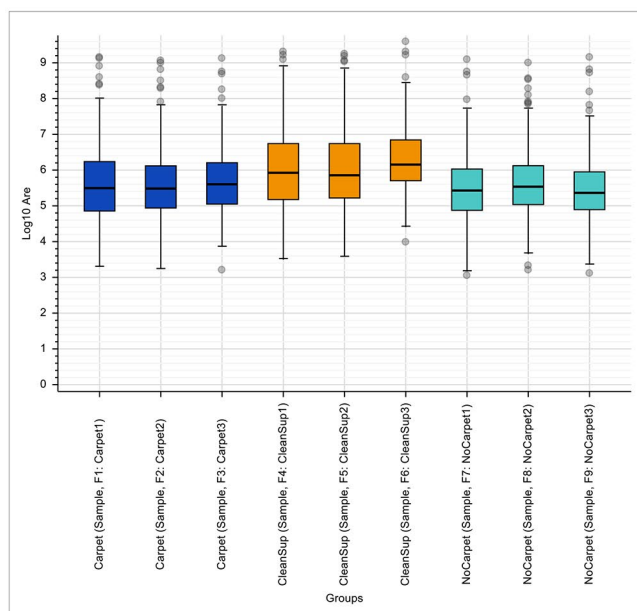


Figure 4. (A) GC-EI results in Compound Discoverer software filtered for fluorine; (B) GC-EI results in Compound Discoverer software showing filter and differential analysis between sample groups.

The PCI workflow in Compound Discoverer software, schematized in Figure 5, is used to confirm the compounds identified in the EI workflow. All nodes can be customized depending on which library or identification route the user chooses to employ.⁷ The GC-CI workflow can also be used to process PCI dd-MS² data acquisition. The built-in CI workflow enabled searching our PCI dd-MS² data against online databases like the Thermo Scientific™ mzCloud™ mass spectral fragmentation library and ChemSpider. The structure proposal capability enabled applying a Fragment Ion Search, or FISh, score by performing *in silico* fragmentation of the proposed compound, critical to pinpoint the right hit from similar *m/z*.

As shown in Figure 6, 6:2 FTOH was identified at RT 5.08 min based on the library hit formula. Despite the library match, several ions missing from the experimental spectra result in low SI score. This can be attributed to the low concentration of the detected analyte as well as co-elution of background matrix compounds present at higher concentrations.

To address this challenge, Compound Discoverer software uses the HRF score, which represents the percentage of the spectrum that is explained by the chemical formula proposed by the library hit. In this example, a HRF score of 98.2 is achieved.

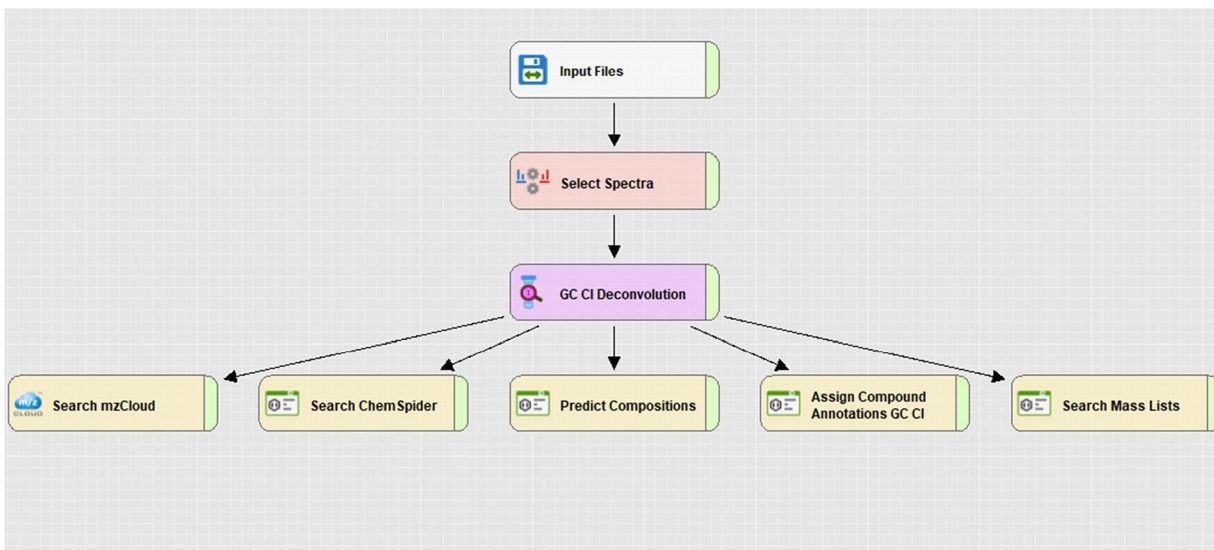
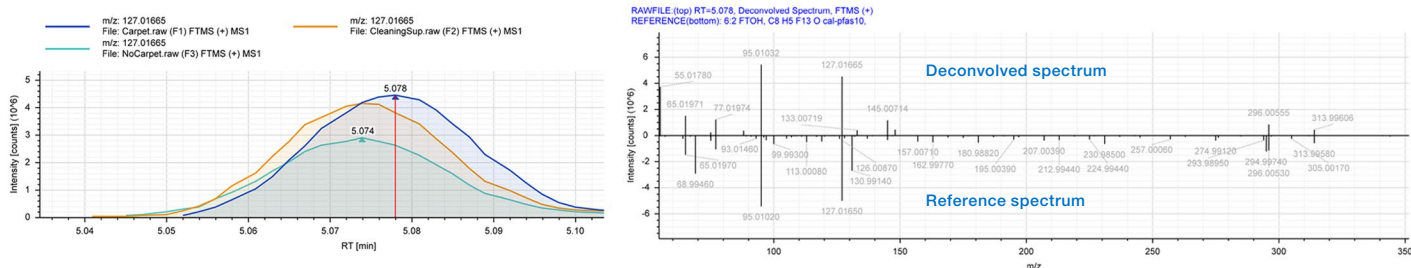


Figure 5. PCI workflow in Compound Discoverer software.



Checked	Tags	Comments	Name	CAS Num	Calc. MW	RT [min]	Reference m/z	Avg TIC	NIST Lib Hit Formula	NIST Theo. Mol. Mass	Total Sci	HRF Score	SI
<input type="checkbox"/>	○○○○○		Perfluorooctane sulfonamide amine		477.00146	10.116	152.06209	15904992	C13 H13 F17 N2 O2	584.04208	91.7	99.7	589
<input type="checkbox"/>	○○○○○		Flamprop-isopropyl	52756-22	152.06262	11.303	105.03336	48755636	C19 H19 Cl F N O3	363.10320	91.5	100.0	572
<input type="checkbox"/>	○○○○○		Perfluorooctane sulfonamide amine		366.97964	5.606	68.99467	2482325	C13 H13 F17 N2 O2	584.04208	91.3	100.0	562
<input type="checkbox"/>	○○○○○		Flamprop-isopropyl	52756-22	205.15927	11.363	105.03336	33312268	C19 H19 Cl F N O3	363.10320	91.2	98.0	599
<input type="checkbox"/>	○○○○○		1H,1H-Perfluoro-3,6,9-trioxadecan-1		166.99338	4.432	118.99155	11183551	C7 H3 F13 O4	397.98183	91.1	96.2	630
<input type="checkbox"/>	○○○○○		Bifenthrin	82657-04	181.10167	11.504	180.08929	1905141	C23 H22 Cl F3 O2	422.12549	91.1	100.0	556
<input type="checkbox"/>	○○○○○		Flamprop-isopropyl	52756-22	105.03390	11.488	175.05774	8131146	C19 H19 Cl F N O3	363.10320	91	93.6	680
<input type="checkbox"/>	○○○○○		Perfluorooctanamide		413.97763	2.864	130.99147	42206253	C8 H2 F15 N O	412.98914	90.7	92.2	689
<input checked="" type="checkbox"/>	○○○○○		6:2 FTOH	647-42-7	75.00465	5.078	127.01665	16923172	C8 H5 F13 O	364.01273	90.7	98.2	573
<input type="checkbox"/>	○○○○○		Flamprop-isopropyl	52756-22	132.09393	6.414	105.03336	46919274	C19 H19 Cl F N O3	363.10320	90.5	100.0	694
<input type="checkbox"/>	○○○○○		Bifenthrin	82657-04	178.07828	11.506	152.06207	29776744	C23 H22 Cl F3 O2	422.12549	90	98.3	532

Figure 6. Example of PFAS data mining using library match for indoor air samples.

Excessive fragmentation in EI analysis can hinder detection of the molecular ion. Confirmation of the molecular ion can be performed through PCI analysis along with additional structural information using ddMS² data. Using our previous example of 6:2 FTOH, the exact mass of its molecular ion (*m/z* 364.0369) was confirmed with a mass error of 1.12 ppm using both M+H and

respective methane reagent adduct ions (Figure 7). In addition, the structure proposal generated from the MS² data was used in *in silico* fragmentation. Comparison of the experimental and expected fragmentation of the molecular ion produced a FISH coverage score of 80% to the expected fragmentation pattern.

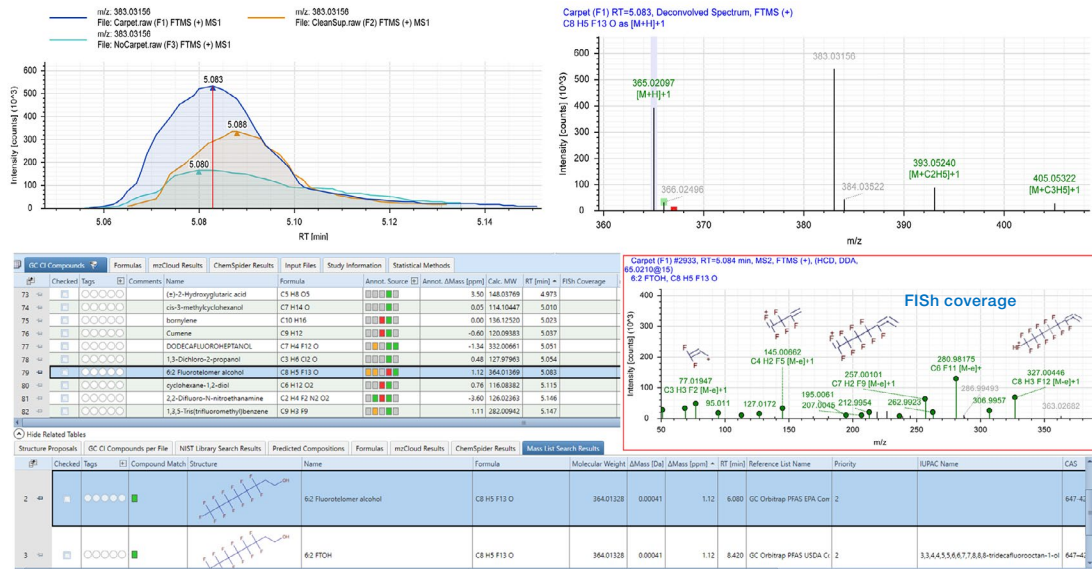


Figure 7. Identification of 6:2 FTOH using PCI ddMS² data, accurate *m/z* 364.0369, and FISH coverage.

Compounds that were not present in our PFAS library were also identified through the Compound Discoverer workflow. An example of this is parachlorobenzotrifluoride, eluting at 4.525 min, tentatively identified through the ChemSpider database search. The compound with accurate *m/z* 179.9953 was PCI amenable and displayed respective M+H ion and methane adducts.

A FISH score of 26 was obtained through fragment matching, highlighting the need for further investigation (Figure 8). Using the information obtained in PCI on the molecular ion and proposed chemical formula, revisiting data collected in EI can provide further insight.

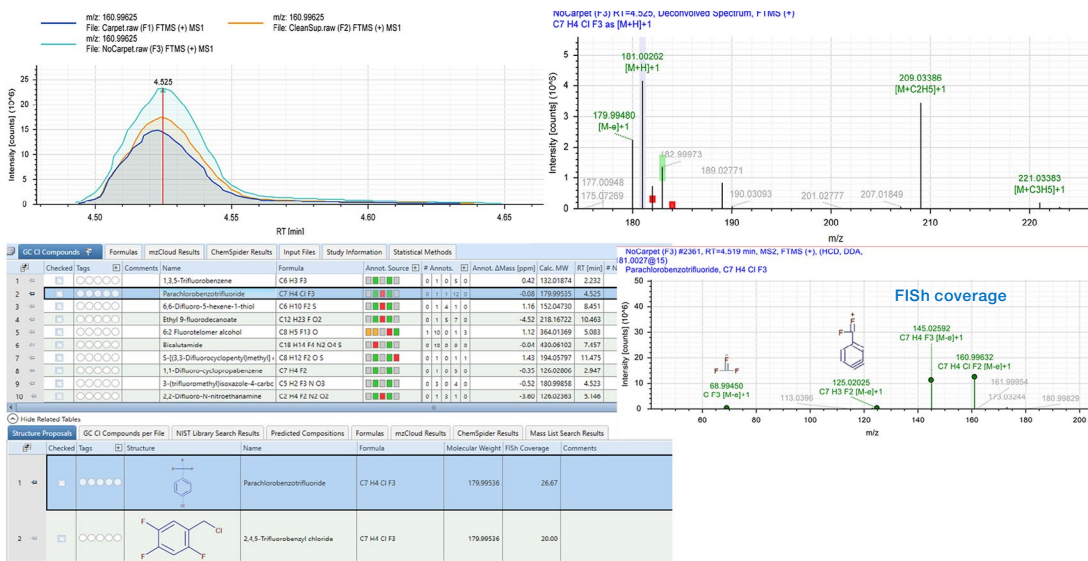


Figure 8. Example of PFAS data mining for unknowns in indoor air samples using ChemSpider match and FISH coverage.

In our EI analysis, several co-eluted peaks were identified at the same retention time (Figure 9A). The peak at 4.52 min was further investigated using the FreeStyle software. The match formula proposed from ChemSpider in our PCI analysis was used

to confirm elemental composition and mass accuracy of the EI fragments. Elemental composition analysis confirmed that the compound is indeed a PFAS, and EI fragments observed are part of the compound identified in PCI.

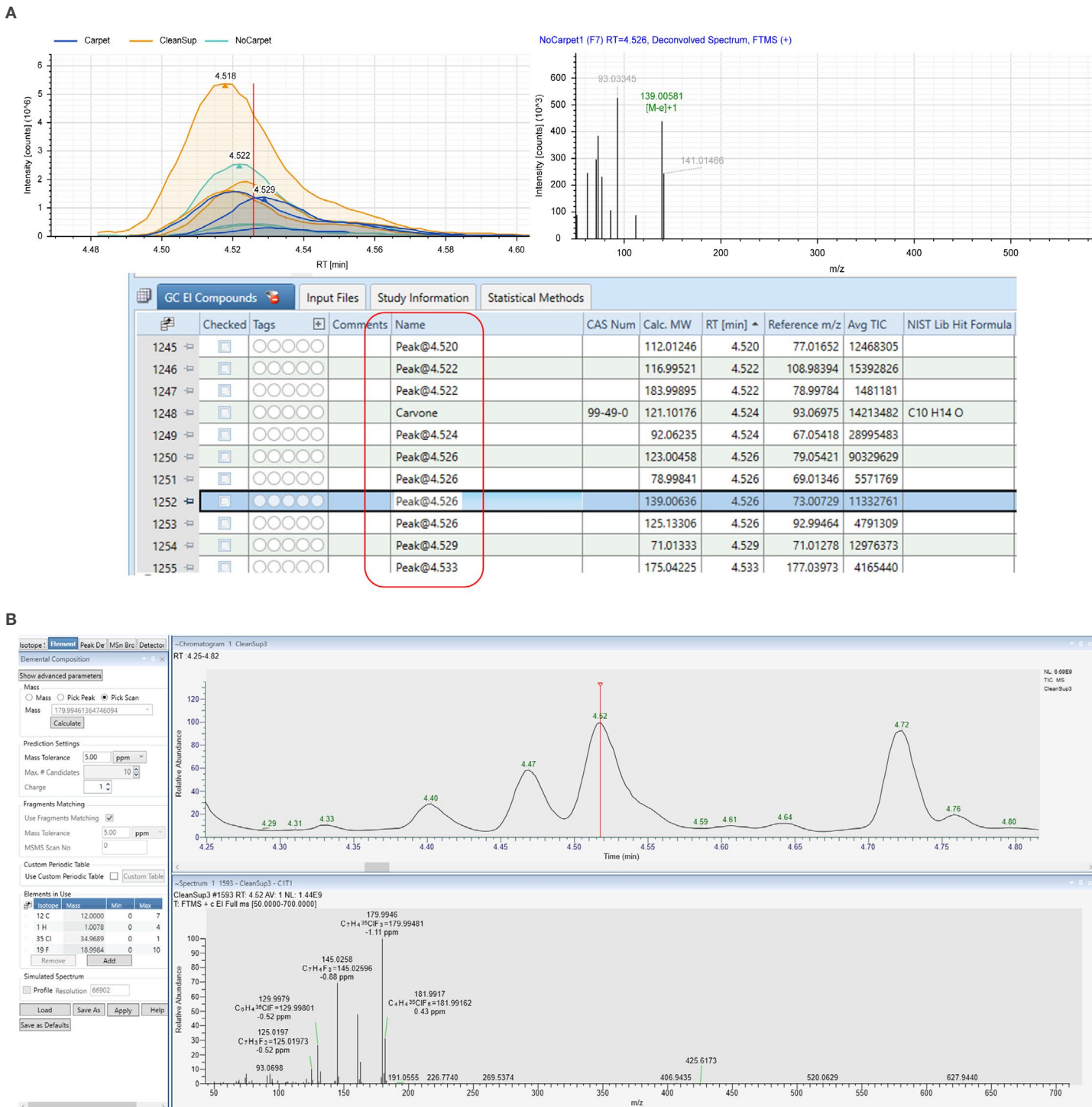


Figure 9. (A) EI data with co-eluted peaks at 4.526 min that were present in all indoor air samples; (B) elemental composition of the peak at 4.52 min from an indoor air sample analyzed in Freestyle software confirms the PFAS compound.

Conclusions

This study successfully demonstrated the effectiveness of thermal desorption (TD) coupled with high-resolution accurate-mass (HRAM) gas chromatography - Orbitrap mass spectrometry (GC-MS) as a powerful approach for untargeted screening of volatile PFAS in indoor air. Thermal desorption, while reducing the need for complex extraction and sample preparations, boosted sensitivity by concentrating volatile PFAS present in air. HRAM delineated target compounds from background noise or matrix interference for precise measurements.

Untargeted PFAS screening was performed by using a top-tier ensemble of Thermo Scientific™ software entailing Chromeleon CDS for instrument control and acquisition combined with FreeStyle software and Compound Discoverer software for data analysis for a simplified screening approach. Qualitative data analysis was facilitated by FreeStyle software through data visualization and HRAM data curation. Compound Discoverer software streamlined compound identification and comparative analyses, and provided extensive filtering and data graphics display capabilities. Also, the built-in EI/CI workflows for GC-MS together with variable electron voltage (VeV) for softer ionization provided complementary fragmentation information enhancing confidence of PFAS identification. Integrated libraries, databases, and robust statistical analysis tools available in Compound Discoverer software enabled rapid and precise insights to the untargeted screening approach, greatly simplifying interpretation.

Data demonstrate the presence of many volatile PFAS in indoor air. Air samples analyzed from the three areas under study—carpeted, non-carpeted, and cleaning supplies storage closet—represent common areas with exposure to consumer cleaning products. Occurrence of volatile PFAS in indoor air confirms the off-gassing and persistence of these “forever chemicals” resulting from use of consumer cleaning products. As expected, indoor air from the carpeted and cleaning closet had the largest

amount of these chemicals with concentrations ≤ 0.01 - 0.03 ppt. PFAS detected were predominantly fluoropolymers containing fluorotelomer or fluoroalkyl sulfonate moieties.

Overall, the proposed approach delivers high analytical confidence, simplified workflow integration, and the ability to uncover emerging or unexpected PFAS species, providing environmental and industrial laboratories with a valuable tool for air quality monitoring.

Acknowledgment

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Appendix

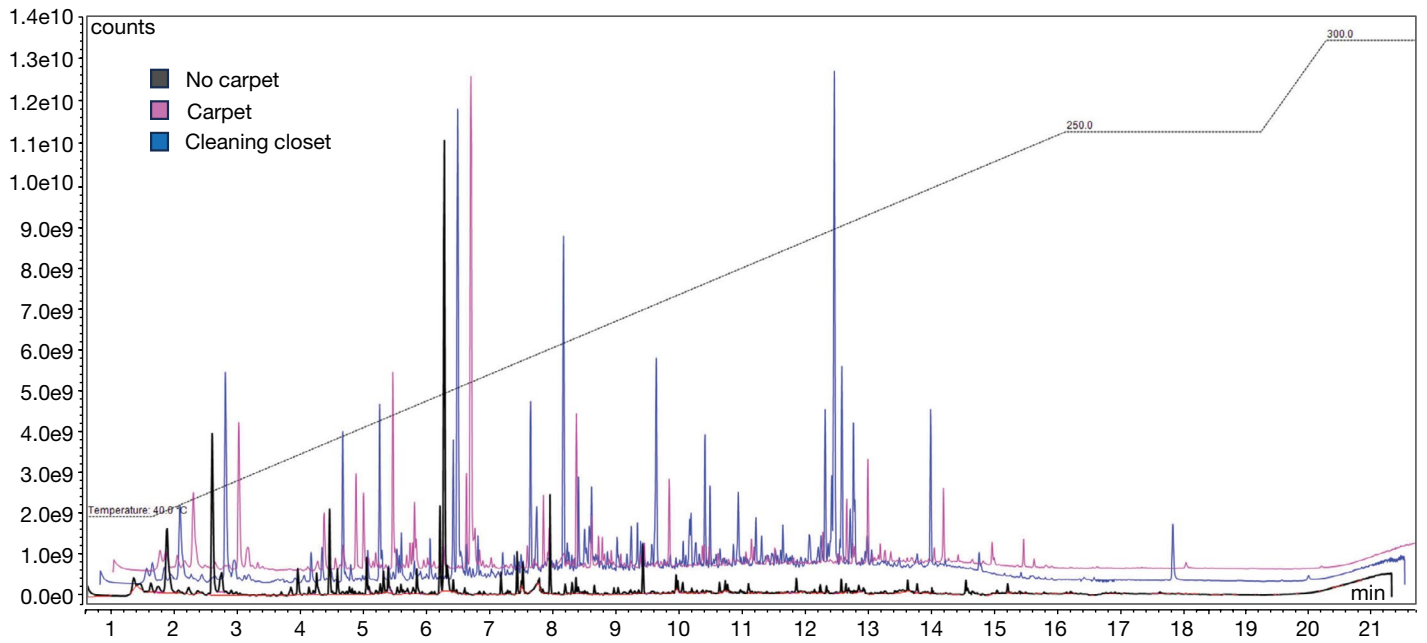


Figure A1. Total ion chromatogram of three different indoor air samples in EI Full Scan mode.

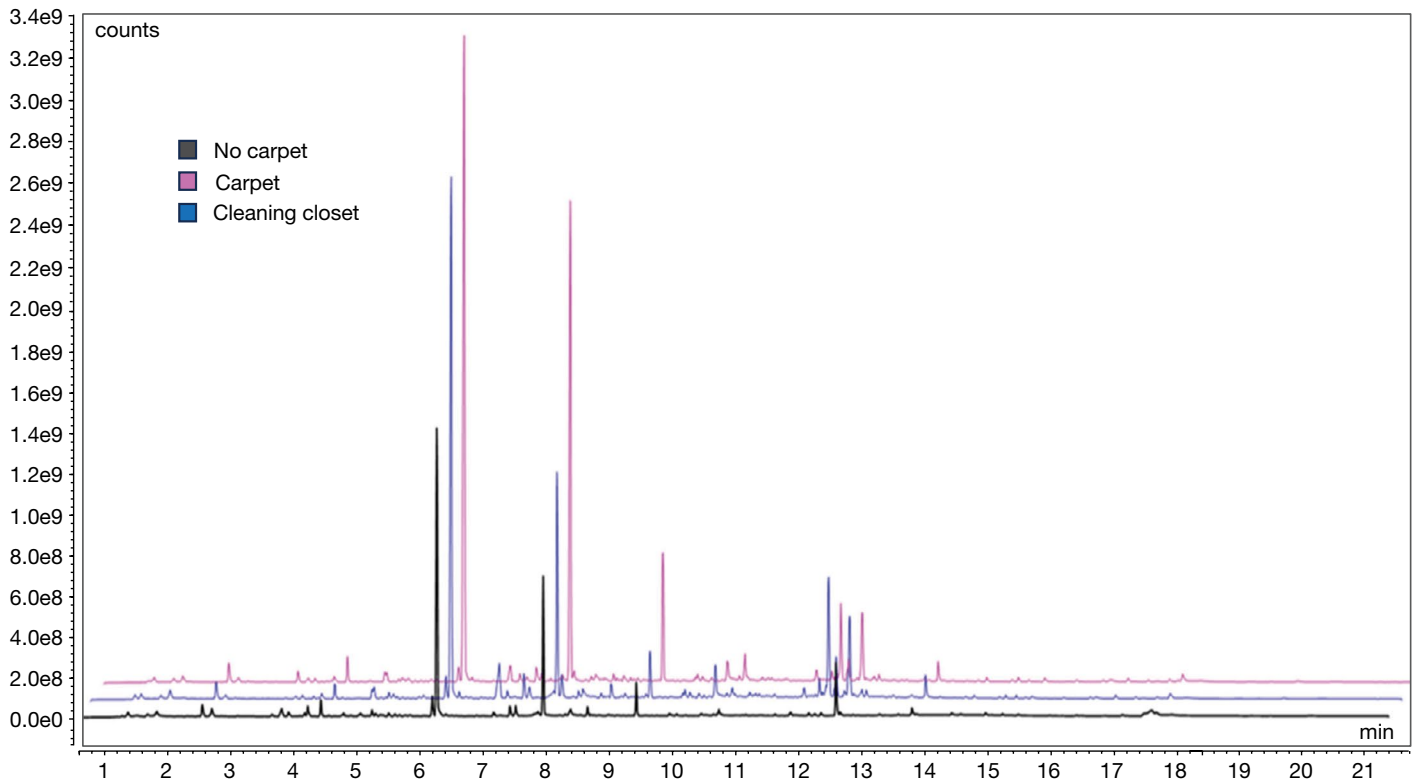


Figure A2. Total ion chromatogram of three different indoor air samples in positive CI mode (Full Scan filter from a PCI ddMS² method). Note fewer peaks as compared to EI acquisition in Figure A1.

