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Detection of Per- and Polyfluoroalkylated Substances by ASTM 8591-24 Using Agilent Thermal Desorption Tubes on a TD-GC-MS/MS

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Introduction

Volatile and semi-volatile neutral per- and polyfluoroalkyl substances are increasingly recognized as an important class of airborne contaminants in indoor environments. Accurate measurement of these compounds requires sampling and analytical approaches that address compound volatility, persistence, and susceptibility to laboratory background contamination. In this study, ASTM D8591-24 was evaluated using Agilent UltiMetal PFAS thermal desorption tubes, analyzed on a Markes TD100-xr thermal desorber, an Agilent 8890 gas chromatography system, and an Agilent 7000E triple quadrupole mass spectrometer. In addition to the four fluorotelomer alcohols specified in ASTM D8591-24, the method was expanded to include fluorinated acrylates, perfluoroalkyl sulfonamides, and sulfonamide ethanols. Furthermore, this work demonstrates low-level detection capabilities for the expanded analyte list, highlighting the applicability of TD-GC/MS/MS for both trace-level analysis and routine monitoring applications.

Experimental

Target analytes are listed in Table 1. To create calibration curves, two solutions were created. The ISTD, MFDET, was added into a stock solution of 5 µg/mL and then diluted to 1 µg/mL or 1000 pg/µL. All target analytes and the RCS, MFOET, were added into a stock solution of 5 µg/mL, and then diluted to create individual solutions ranging from 10 – 2500 pg/µL.

Table 1. Compound name, abbreviation, and CAS number for all target analytes.

Compound	Abbreviation	CAS
1H,1H,2H,2H-Perfluoro-1-hexanol	4:2 FTOH	2043-47-2
1H,1H,2H,2H-Perfluoro-1-octanol	6:2 FTOH	647-42-7
1H,1H,2H,2H-Perfluoro-1-decanol	8:2 FTOH	678-39-7
1H,1H,2H,2H-Perfluoro-1-dodecanol	10:2 FTOH	865-86-1
2-Perfluorooctyl (1,1-2H2,1,2-13C2)ethanol	MFOET	872398-73-7
2-Perfluorodecyl (1,1-2H2,1,2-13C2)ethanol	MFDET	872398-74-8
1H,1H,2H,2H-Perfluorodecyl acrylate	8:2 ACR	27905-45-9
1H,1H,2H,2H-Perfluorododecyl acrylate	10:2 ACR	17741-60-5
N-Methylperfluoro-1-octanesulfonamide	MeFOSA	31506-32-8
N-Ethylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2
2-(N-Methylperfluoro-1-octanesulfonamido)ethanol	MeFOSE	24448-09-7
2-(N-Ethylperfluoro-1-octanesulfonamido)ethanol	EtFOSE	1691-99-2

Instrument method parameters can be found by scanning the QR code. The Agilent Ultimate Plus deactivated fused silica tubing was used in the Markes TD100-xr as the transfer line to complement the Agilent Inert Flow Path. In addition, it is recommended to use the 6 mm extraction lens for TD analysis.

Results and discussion

Chromatography

ASTM D8591-24 specifies the use of a nitroterephthalic acid–modified polyethylene glycol (PEG) column, or an equivalent phase. The Agilent equivalent to this specified column chemistry is the Agilent J&W DB-FFAP. Performance was compared with that of the Agilent J&W DB-WAX UI, Ultra Inert column. DB-WAX UI employs a novel technology that gives this PEG column better inertness across a wider range of analyte functionalities and stabilizes the phase during high temperature analysis, giving the column improved longevity. Overall chromatographic separation was similar, but the DB-WAX UI, produced improved peak shapes and reduced tailing (Figure 1).

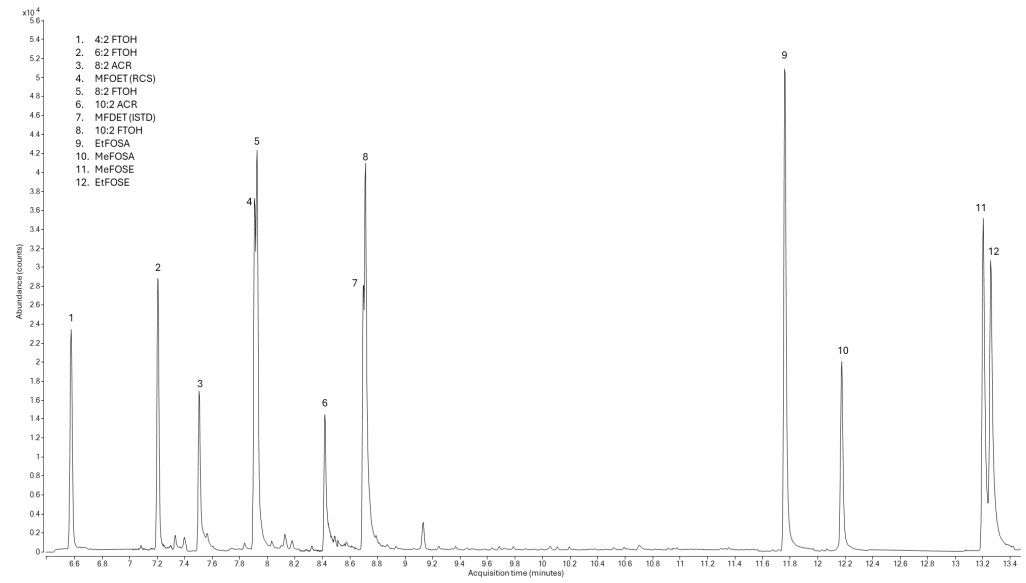

Figure 1. Chromatogram TIC at 1000 pg on tube of target analytes.

Inter- and intra-day repeatability

A preliminary assessment of inter- and intra-day repeatability, focused on the FTOHs listed in ASTM D8591-24, was performed using the UltiMetal PFAS TD tubes. Seven tubes were each spiked with 1 µL of a 5 ng/µL standard solution across four separate days. On days 1 to 3, tubes were spiked and then immediately analyzed. On day 4, tubes were spiked, capped with press-fit DiffLok™ caps, and then held on the bench for 72 hours before analysis. Excellent inter- and intra-day repeatability was observed for all FTOHs, where all %RSDs were < 6% (Table 2).

Table 2. Inter- and intraday %RSD (n = 7) of target analytes listed in D8591 at 5 ng on tube.

Target Analyte	Intra-day %RSD				Inter-day %RSD
	Day 1	Day 2	Day 3	Day 4	
4:2 FTOH	2.25	3.58	4.84	3.09	3.74
6:2 FTOH	3.36	4.11	4.78	1.94	3.95
MFOET (RCS)	4.33	4.13	4.90	2.08	4.28
8:2 FTOH	4.29	4.05	5.14	2.02	4.32
MFDET (ISTD)	3.57	3.96	5.66	2.23	4.58
10:2 FTOH	3.25	3.61	5.71	2.68	4.62

Expansion of ASTM D8591

ASTM D8591-24 permits the expansion of the target analyte list beyond the four FTOHs specified in the method, provided that all the performance criteria outlined in the standard are met. The objective of this application note was to demonstrate that six additional analytes, 8:2 ACR, 10:2 ACR, MeFOSA, EtFOSA, MeFOSE, and EtFOSE, also fulfill these criteria. ASTM D8591-24 further allows calibration ranges to be adjusted to concentrations relevant to the study objectives. In this work, emphasis was placed on achieving sensitive, low-level detection of PFAS.

To assess method performance, a five-point calibration curve was constructed over a range of 0.1 to 2.5 ng on tube (Figure 2). The AVG RF %RSD values ranged from 3.3% to 8.8%, while precision values for target analytes ranged from 3% to 11% (Table 3). Calculated IDLs spanned 13 to 39 pg per tube. Overall, the method met the performance criteria specified in ASTM D8591-24, which requires both AVG RF %RSD and precision (%RSD) to be less than 25%.

Table 3. AVG RF %RSD, %RSD (n = 8) at 250 pg on tube, IDLs (n = 8), and the concentration of replicate IDL samples for PFAS target analytes.

Target Analyte	AVG RF %RSD	%RSD (250 pg)	IDL (pg)	IDL Level (pg)
4:2 FTOH	3.3	8.0	19	100
6:2 FTOH	5.3	5.0	21	100
8:2 ACR	4.9	6.1	16	100
MFOET (RCS)	7.4	3.0	24	100
8:2 FTOH	6.1	4.3	21	100
10:2 ACR	3.7	6.0	14	100
10:2 FTOH	3.3	5.0	22	100
EtFOSA	3.8	6.0	13	100
MeFOSA	4.9	6.8	15	100
MeFOSE	8.8	11.0	39	250
EtFOSE	8.2	9.0	32	250

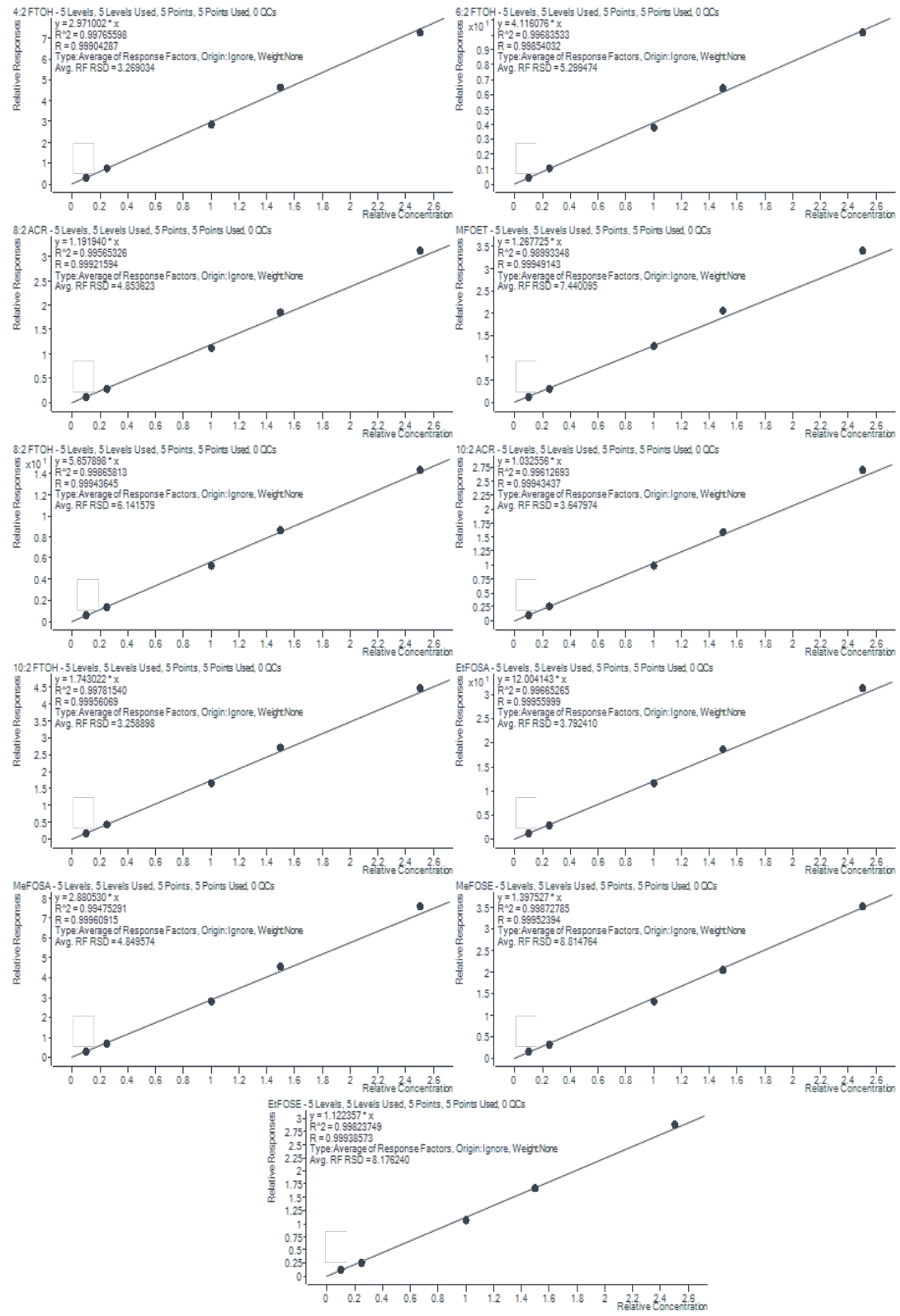

Figure 2. Calibration curves ranging from 0.1 to 2.5 ng on tube for all PFAS target analytes.

Trace-level analysis of target analytes

Calculated IDLs from the current study demonstrate that target analytes can be detected as low as 13 pg. Thus, an investigation of observed detection limits was of interest. Three replicates at concentrations of 10, 25, and 50 pg on tube were analyzed. Calibration curves were extended down to 10 pg to investigate average response factor RSDs of the calibration curve. Table 4 shows AVG RF %RSD ranging from 7% to 19.8% and R2 values were all > 0.999. Integrated peaks at 25 pg on tube are shown in Figures 3.

The instrument configuration and method presented in this study can detect and calibrate target analytes down to 10 pg. However, additional investigation is required to determine if such low limits will meet the criteria for D8591-24, as it was beyond the scope of this study to fully demonstrate robustness and repeatability at such low levels.

Flow path inertness and surface deactivation

The chemical inertness of the analytical flow path plays a critical role in achieving accurate quantitation of volatile and semi-volatile PFAS. The Agilent UltiMetal PFAS thermal desorption tubes used in this study incorporate Agilent's UltiMetal Plus deactivation chemistry; a proprietary chemical vapor deposition (CVD) process applied to stainless steel surfaces. The treatment forms a high-purity, inert layer that passivates active sites, such as metal oxide sites, commonly present on untreated stainless-steel surfaces. These sites are known to catalyze degradation or absorb polar and reactive analytes, including alcohols, acids, and sulfonamides, leading to peak tailing, reduced recovery, and elevated background levels.

Results and Discussion

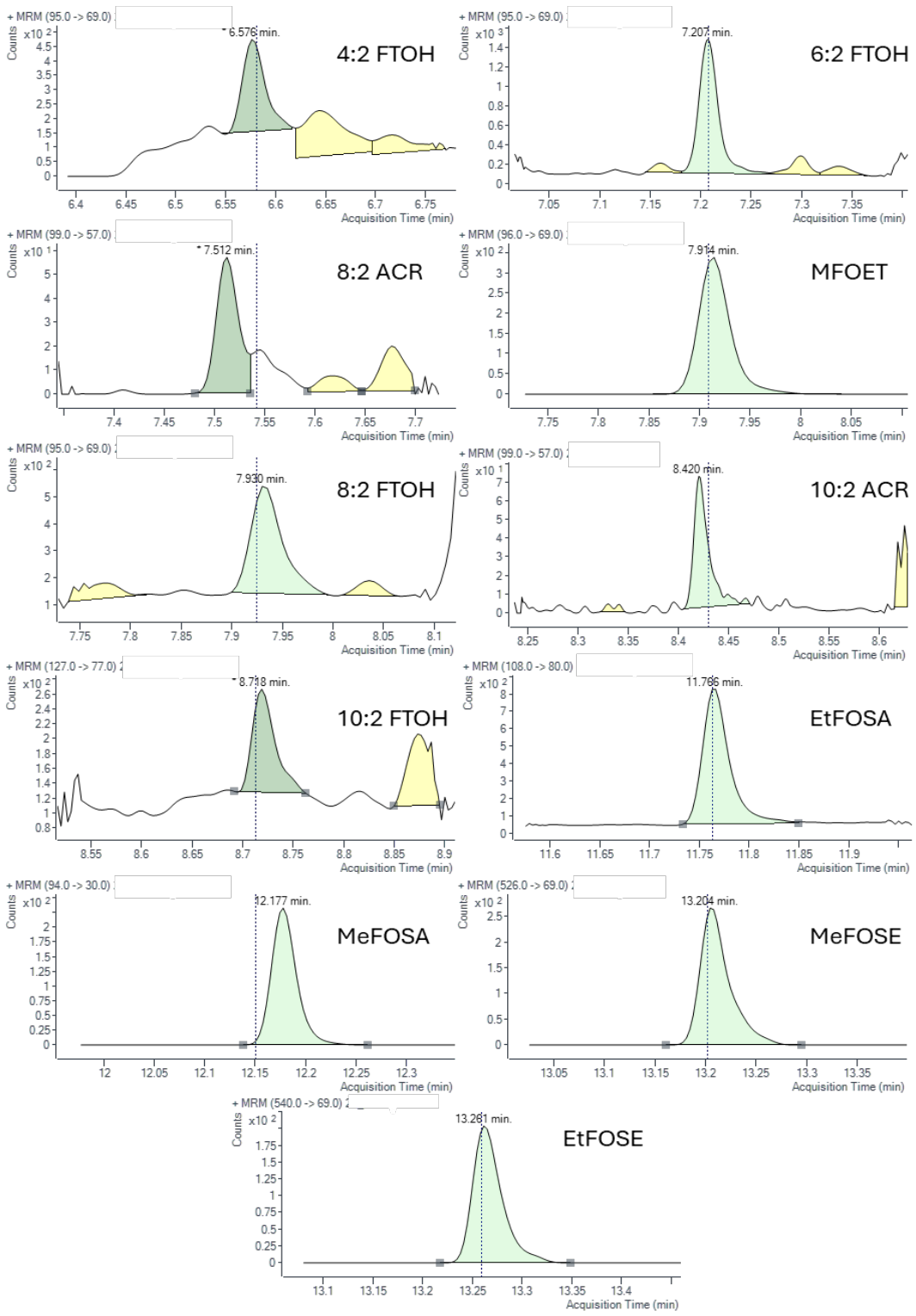

Figure 3. Quantified peaks at 25 pg on tube of PFAS target analytes.

Flow path inertness and surface deactivation (cont'd)

The UltiMetal Plus coating mitigates these effects by minimizing compound-surface interactions, thereby improving peak shape, enhancing linearity of response, and enabling lower detection limits. These benefits are particularly important for trace-level PFAS analysis, where analytical sensitivity and reproducibility are essential. The UltiMetal Plus-treated tubes demonstrated excellent performance across all target analytes, with no measurable background contamination observed in instrument blanks. Furthermore, the coating exhibits thermal stability up to 400 °C and hydrophobic surface properties, contributing to consistent analyte recovery and reduced carryover. These characteristics support the suitability of the UltiMetal Plus-treated TD tubes for routine monitoring of volatile PFAS in air.

Table 4. AVG RF %RSD and coefficient of determination (R2) of calibration curves ranging from 0.01 to 2.5 ng on tube for PFAS target analytes.

Target Analyte	AVG RF %RSD	R^2
4:2 FTOH	12.5	0.9992
6:2 FTOH	12.7	0.9992
8:2 ACR	19.8	0.9994
MFOET (RCS)	9.8	0.9998
8:2 FTOH	11.8	0.9998
10:2 ACR	19.8	0.9999
10:2 FTOH	9.1	0.9998
EtFOSA	7.1	0.9999
MeFOSA	7.0	0.9999
MeFOSE	15.2	0.9998
EtFOSE	14.6	0.9996

Conclusions

- A reliable and sensitive TD GC/MS/MS method was demonstrated for determination of volatile and semi volatile PFAS in air down to 100 pg using Agilent UltiMetal PFAS thermal desorption tubes, meeting ASTM D8591 24 performance criteria.
- The method was successfully extended beyond the four fluorotelomer alcohols specified in ASTM D8591 24 to include fluorinated acrylates, sulfonamides, and sulfonamide ethanols.
- Five point calibration curves (100–2500 pg) met ASTM requirements, with average response factor %RSDs of 3.3–8.8% and precision at 250 pg on tube of 3–11%.
- Use of UltiMetal PFAS TD tubes with rigorous contamination control yielded excellent intra day and inter day repeatability (%RSD < 6%), addressing a key challenge in PFAS air analysis.
- Instrument detection limits of 13–39 pg on tube, with verified detection at 10, 25, and 50 pg levels, demonstrate suitability for trace level PFAS measurements.

More information

https://explore.agilent.com/asms-2026

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