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Assessing TD-GC-MS/MS for the Measurement of PFAS in Air and From Consumer Products

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Caroline Widdowson
Specialist in trace chemical characterisation - Chair of BSi committee EH2/5 Indoor Air Quality - Market Development Professional

PFAS monitoring in the gas phase

When should you use GC?

LC

- ✓ Perfluorinated sulfonic acids
- ✓ Perfluorinated carboxylic acids
- ✓ Ionic species
- ✓ Semi-volatile species (>C8)
- × Volatile species
- × Neutral species

GC (with Thermal desorption)

- ✓ Volatile fluorinated compounds (VFCs)
- ✓ Neutral PFAS species
  - ✓ FTOH, FTAcr, FTCA, FOSA, FOSE
- ✓ Perfluorinated carboxylic acids (with caveats)
- × Perfluorinated sulfonic acids
- × Ionic species

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- × Perfluorinated sulfonic acids
- × Ionic species

These are the species that are “volatile” enough to be the gas phase.

Where is this methodology being used?

Gas phase – Trace PFAS Analysis

Industrial emissions

Ambient Air

Landfill gas

Food contact

Indoor Air

PFAS destruction

AFFF

Material emissions

Methods for monitoring VOCs

1 Particulate sampling

Direct desorption of filters

2 Gas phase sampling

A Pumped sampling onto sorbent tubes

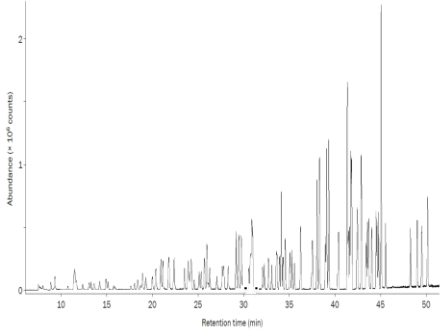
B Passive sampling onto sorbent tubes

C Canisters and bags

D On-line monitoring

3 Material sampling

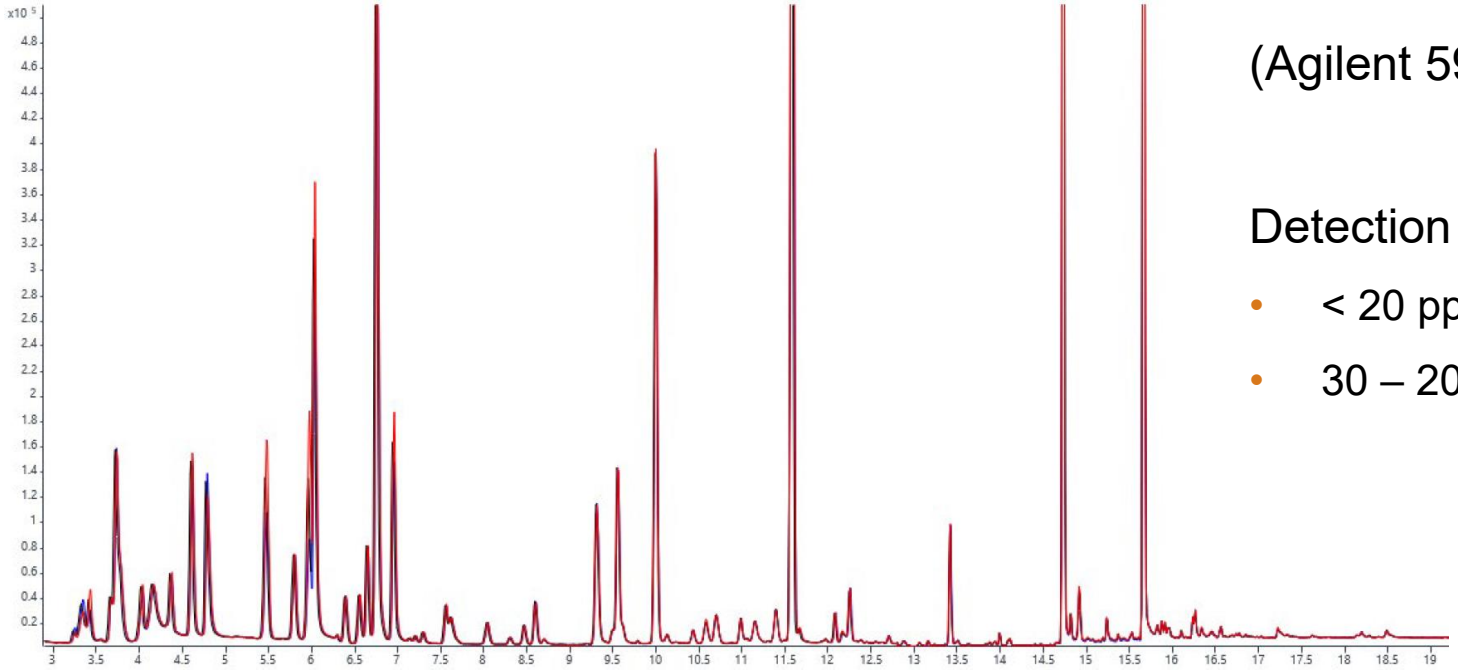
Chamber emission testing



The main sampling approaches used to monitoring VOCs and SVOCs in air from the environment are all compatible with TD

Typical Air Monitoring

Typical air sampling – sample size 0.2L – 10L using Single Quad



0.5L real air sample

(Agilent 5977 MSD)

Detection limits:

- < 20 pptv
- 30 – 200 pg/L (ng/m^3)

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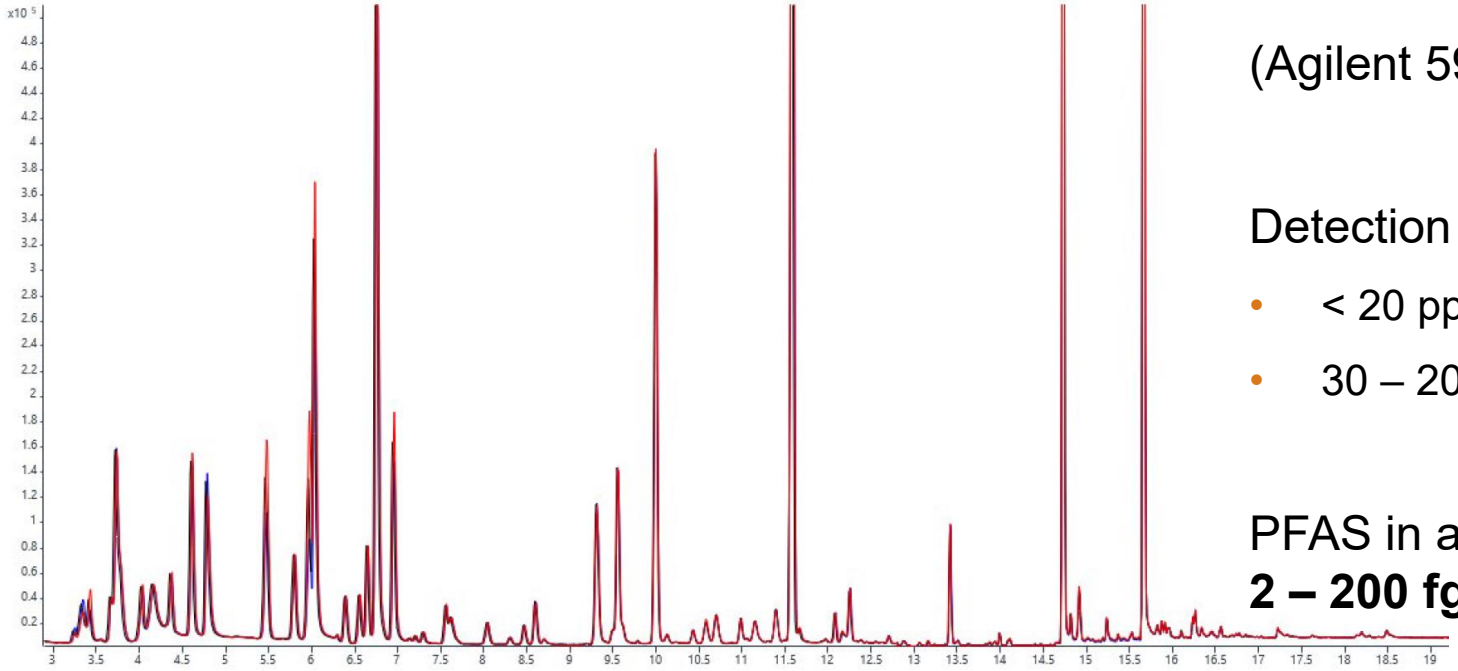

0.5L real air sample

(Agilent 5977 MSD)

Detection limits:

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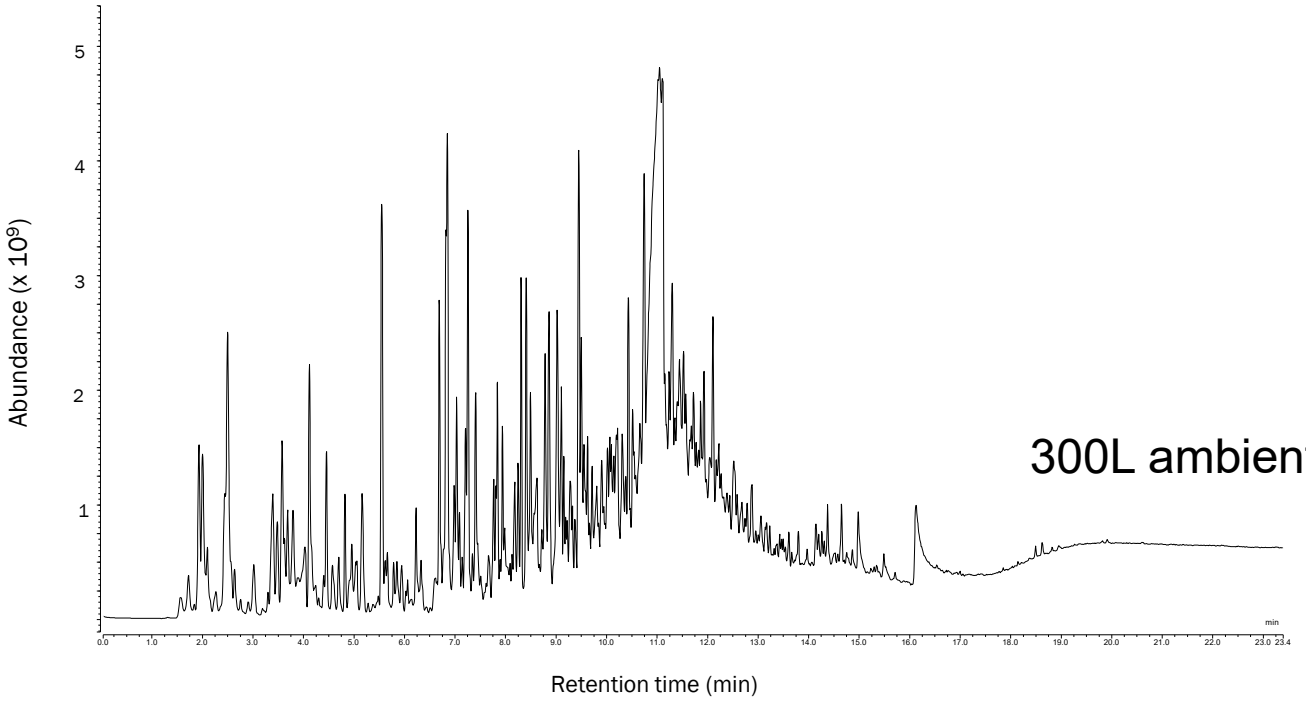
PFAS in ambient air is at:

2 – 200 fg/L (pg/m^3)

Increasing Sample volume

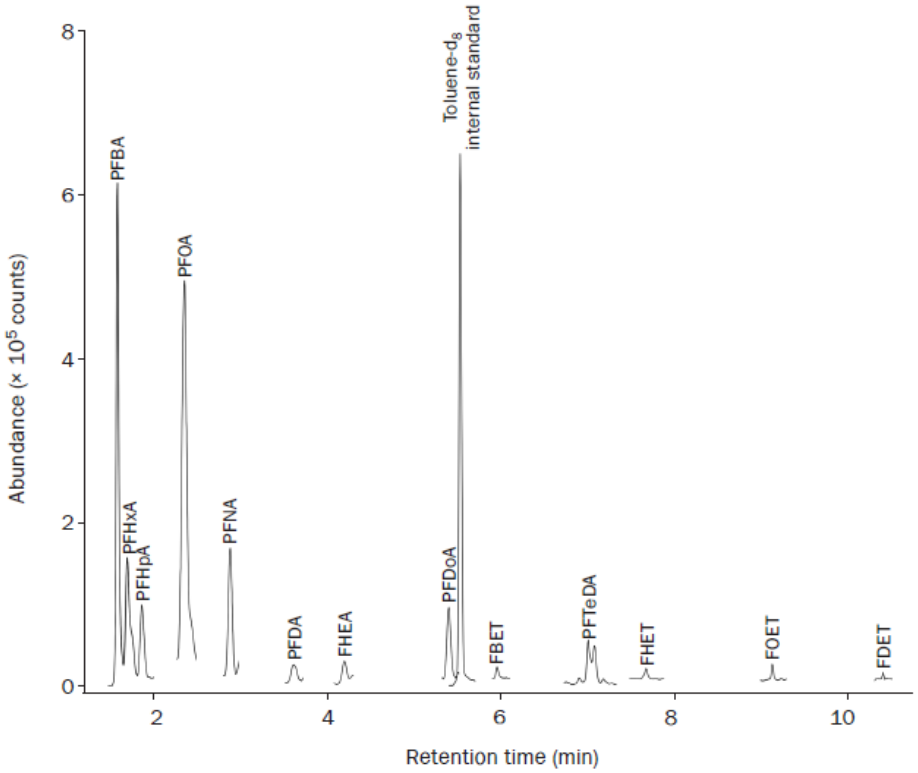
Bigger sample size = more background



300L ambient air sample (TIC)

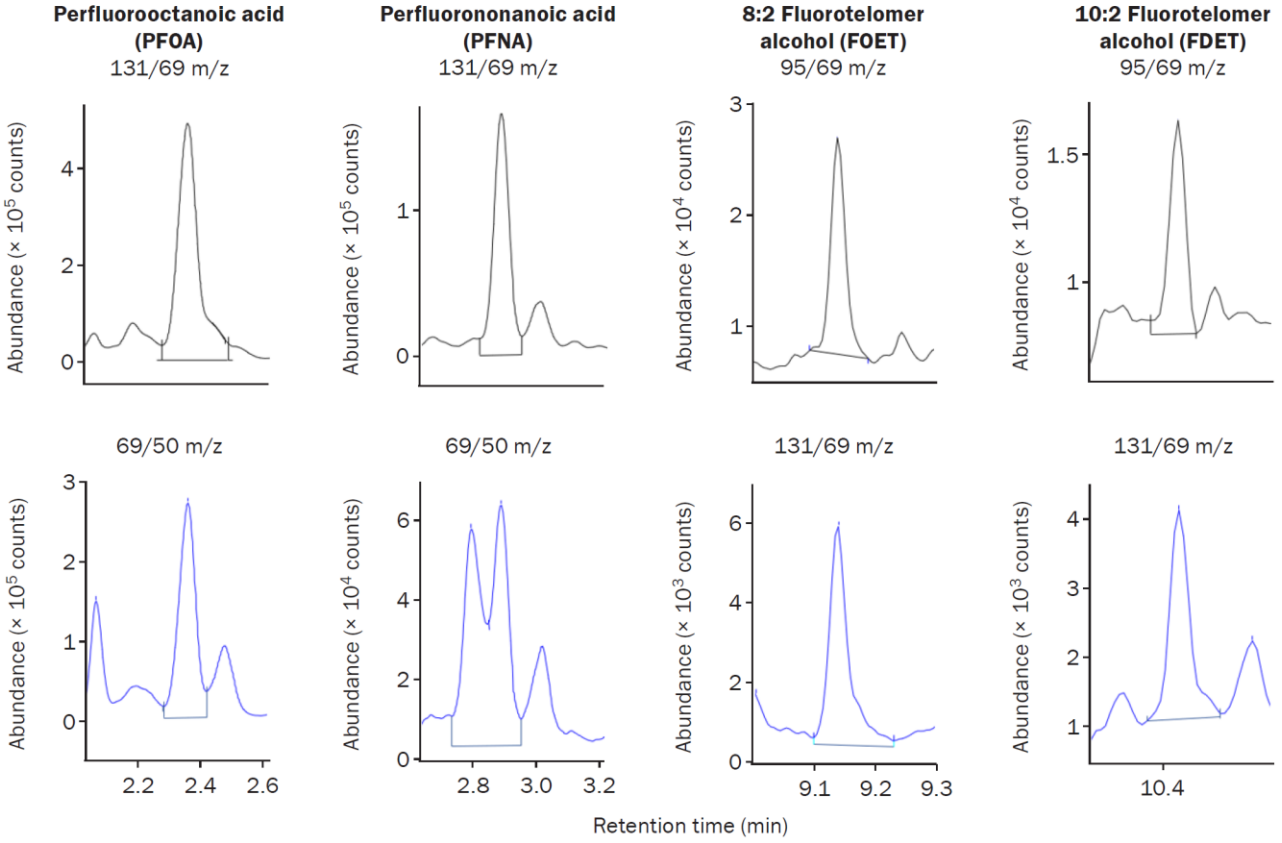
Increasing Detector capabilities

Triple Quad for confident quantitation



300L ambient air sample

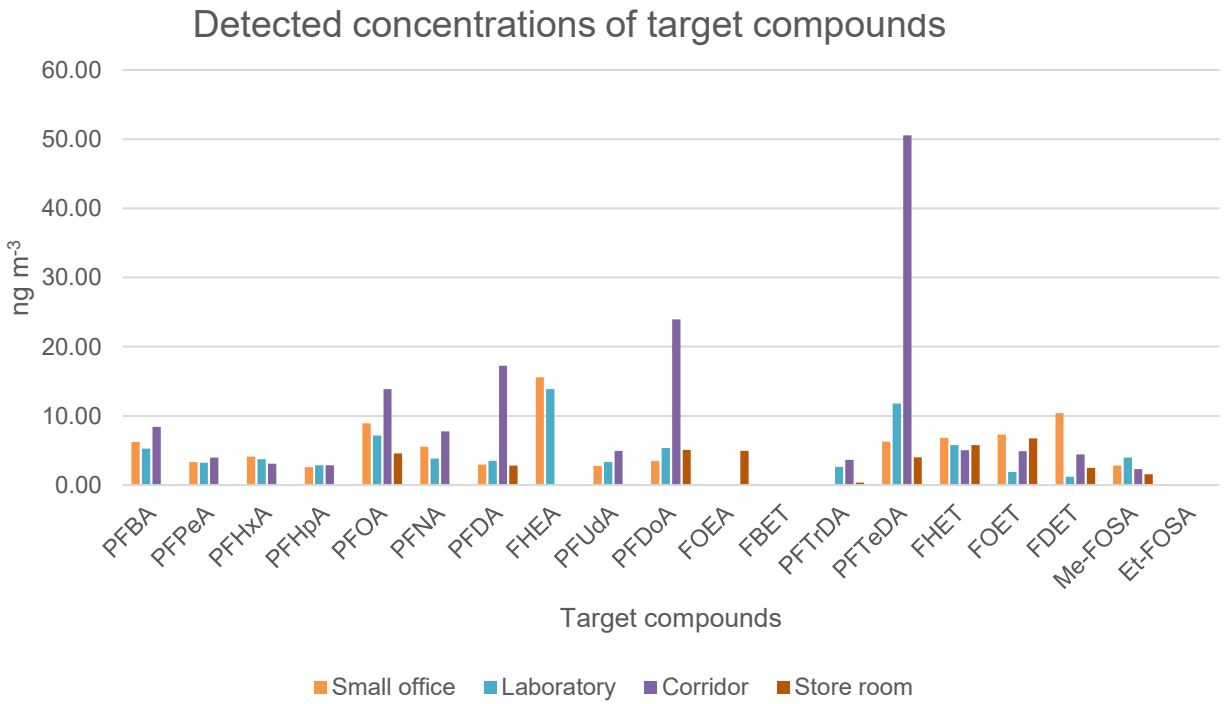
Quantitation transitions



Indoor air monitoring and material emissions

Workplace air

Comparison of environments 20L



Total PFAS

Office
89 ng m^{-3}

Lab
79 ng m^{-3}

Corridor
157 ng m^{-3}

Store
38 ng m^{-3}

Material off gassing - Basic method workflow

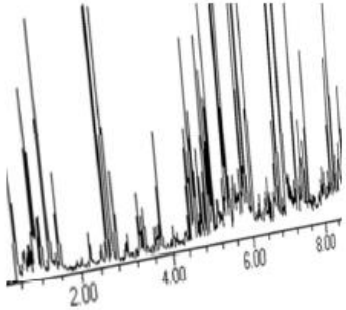
Chambers sampling

1 Load the material

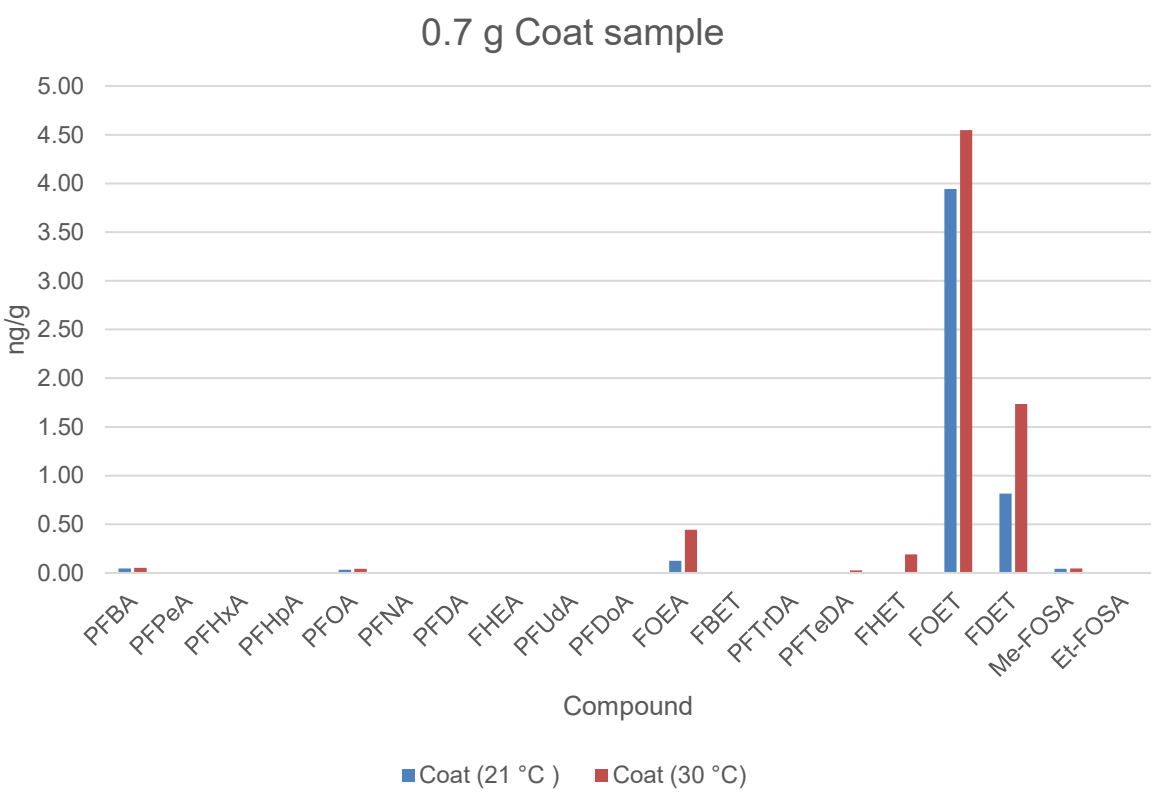
2 Set the conditions

3 Collect the volatiles

4 Analyse the sample



New coat smell



Total PFAS
(ng g^{-1})

21 ° C
5 ng g^{-1}

30 ° C
7 ng g^{-1}

Emission rates
(ng g^{-1} min^{-1})

21 ° C
0.084 ng g^{-1} min^{-1}

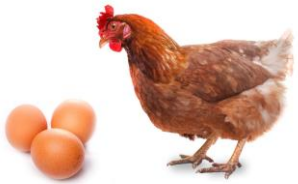
30 ° C
0.119 ng g^{-1} min^{-1}

Regulations and standard methods

Relevant regulations likely to necessitate TD-GC-MS/MS methods:

We are expecting regulation to come into force in the following areas:

- PFAS emissions from manufacturing
- PFAS emissions from destruction/disposal
- Vapour intrusion from PFAS impacted sites
- PFAS emissions from materials/consumer goods



Current focus is around the carboxylic and sulfonic acids.

This is expected to shift over time to volatile species.

Regulations and standard methods

USA – ASTM & EPA Methods/Practices

Standard methods for GC:

- **ASTM D8560:** Standard Guide for Determination of Airborne PFAS in the Indoor Air Environment
- **ASTM D8591:** Standard Test Method for Determination of Fluorotelomer Alcohols in Test Chamber Air by Thermal Desorption-Gas Chromatography-Triple Quadrupole Tandem Mass Spectrometry (TD-GC-MS/MS)

ASTM INTERNATIONAL

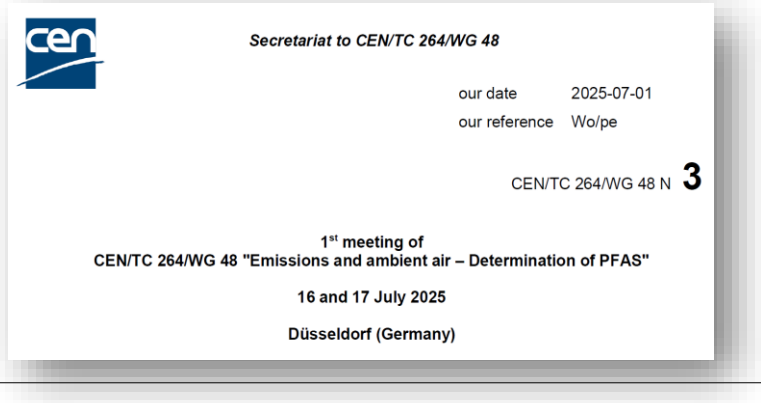
- **US EPA OTM-50:** Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters (TD-GC-MS)

Regulations and standard methods

European Methods/Practices

European Committee for Standardization (**CEN**, French: *Comité Européen de Normalisation*).

- CEN/TC 264 ‘Air Quality’(CEN Technical Committee 264) is a technical decision-making body within the CEN system working on standardization in the field of air quality in the European Union.
- WG48: Emissions & Ambient Air - Determination of PFAS



Secretariat to CEN/TC 264/WG 48

our date 2025-07-01
our reference Wo/pe

CEN/TC 264/WG 48 N **3**

1st meeting of
CEN/TC 264/WG 48 "Emissions and ambient air – Determination of PFAS"

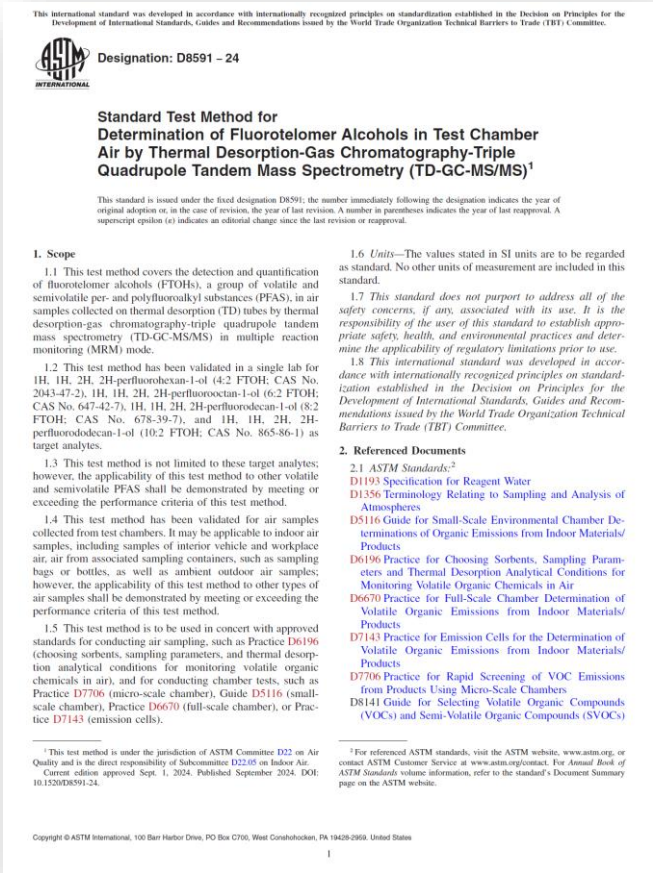
16 and 17 July 2025

Düsseldorf (Germany)

MARKES international

ASTM D8591 (ILS)

Standard Test Method for Determination of Fluorotelomer Alcohols in Test Chamber Air by Thermal Desorption-Gas Chromatography-Triple Quadrupole Tandem Mass Spectrometry (TD-GC-MS/MS)



This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D8591 – 24

Standard Test Method for Determination of Fluorotelomer Alcohols in Test Chamber Air by Thermal Desorption-Gas Chromatography-Triple Quadrupole Tandem Mass Spectrometry (TD-GC-MS/MS)[1]

This standard is issued under the fixed designation D8591; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the detection and quantification of fluorotelomer alcohols (FTOHs), a group of volatile and semivolatile per- and polyfluoroalkyl substances (PFAS), in air samples collected on thermal desorption (TD) tubes by thermal desorption-gas chromatography-triple quadrupole tandem mass spectrometry (TD-GC-MS/MS) in multiple reaction monitoring (MRM) mode.

1.2 This test method has been validated in a single lab for 1H, 1H, 2H, 2H-perfluorohexan-1-ol (4:2 FTOH; CAS No. 2043-47-2), 1H, 1H, 2H, 2H-perfluorooctan-1-ol (6:2 FTOH; CAS No. 647-42-7), 1H, 1H, 2H, 2H-perfluorodecan-1-ol (8:2 FTOH; CAS No. 678-39-7), and 1H, 1H, 2H, 2H-perfluorododecan-1-ol (10:2 FTOH; CAS No. 865-86-1) as target analytes.

1.3 This test method is not limited to these target analytes; however, the applicability of this test method to other volatile and semivolatile PFAS shall be demonstrated by meeting or exceeding the performance criteria of this test method.

1.4 This test method has been validated for air samples collected from test chambers. It may be applicable to indoor air samples, including samples of interior vehicle and workplace air, air from associated sampling containers, such as sampling bags or bottles, as well as ambient outdoor air samples; however, the applicability of this test method to other types of air samples shall be demonstrated by meeting or exceeding the performance criteria of this test method.

1.5 This test method is to be used in concert with approved standards for conducting air sampling, such as Practice D6196 (choosing sorbents, sampling parameters, and thermal desorption analytical conditions for monitoring volatile organic chemicals in air), and for conducting chamber tests, such as Practice D7706 (micro-scale chamber), Guide D5116 (small-scale chamber), Practice D6670 (full-scale chamber), or Practice D7143 (emission cells).

1.6 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D5116 Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products
D6196 Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air
D6670 Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products
D7143 Practice for Emission Cells for the Determination of Volatile Organic Emissions from Indoor Materials/Products
D7706 Practice for Rapid Screening of VOC Emissions from Products Using Micro-Scale Chambers
D8141 Guide for Selecting Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs)

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.
Current edition approved Sept. 1, 2024. Published September 2024. DOI: 10.1520/D8591-24.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Basic method workflow

Chambers used for material testing

Micro-chamber: screening, R&D, product development

1m^3 chambers and larger : product validation for regulation

Basic method workflow

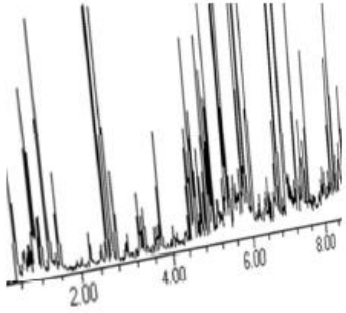
Chambers sampling

1 Load the material

2 Set the conditions

3 Collect the volatiles

4 Analyse the sample



Basic method workflow

Analysis by TD-GC-MS/MS

- Three Samples provided, to be run in triplicate

- Four target species:
  - 4:2 FTOH
  - 6:2 FTOH
  - 8:2 FTOH
  - 10:2 FTOH

- Analytical system:
  - Markes TD100-xr Advanced
    - PFAS Sorbent Tubes and Focusing Traps
  - Agilent 8890 GC
  - Agilent 7000E MS/MS

How is the TD100-xr optimized for PFAS analysis?

TD100-xr Automated Thermal Desorption System

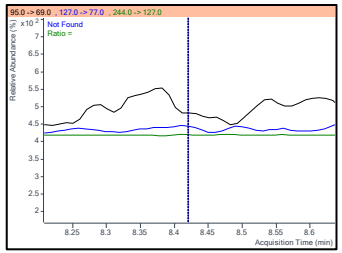
- No PFAS background
  - Proven in multiple independent studies
- High capacity autosampler
  - 100 tubes as standard
- Sample re-collection ability
  - Proven to be a benefit to users running PFAS

Background and Interferents

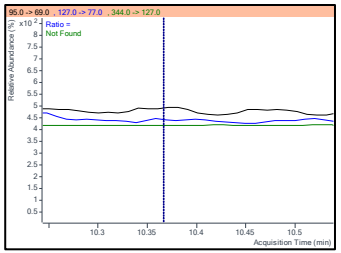
Instrument is clean and free from PFAS

Background investigation is a must

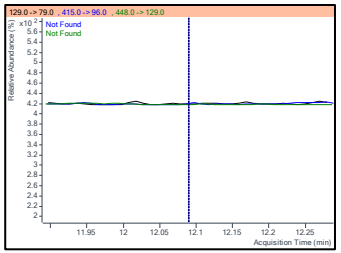
- Instrument background has been proven to be free from target PFAS compounds – Blank Tube
- Results from a tube blank shown below with quantifier and qualifiers overlaid
- No peaks observed for any target PFAS



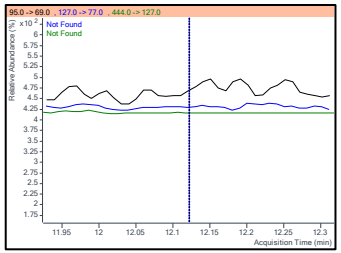
4:2 FTOH



6:2 FTOH



8:2 FTOH RCS



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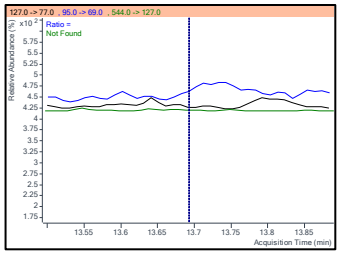


10:2 FTOH

ASTM Method Criteria

Target compounds and QC checks

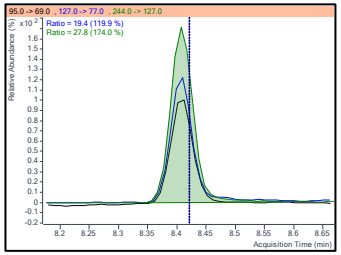
- **Daily Calibration Check (DCC):** *Cal 3 (mid-level) 5ng/uL*
- **Internal Audit Protocol (IAP):** *Mid-level concentration (5ng/uL) from alternative supplier*
- **Recovery Check Standard (RCS):** *8:2 FTOH M+4, at 2ng/uL*
- **Internal Standard (IS):** *10:2 FTOH M+4, at 10ng/uL*

Compound	
4:2 FTOH	Target
6:2 FTOH	Target
8:2 FTOH	Target
10:2 FTOH	Target
8:2 FTOH M+4	RCS
10:2 FTOH M+4	IS

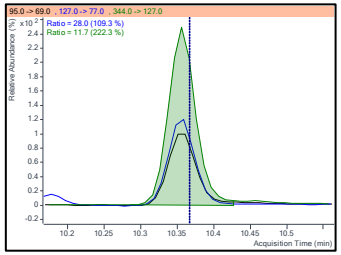
Results

Data Quality Checks and Results

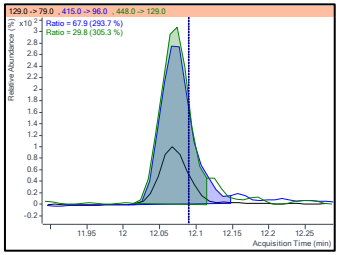
- QC checks all pass criteria
  - No exceptions
- Gaussian peak shapes achieved for all targets and QC compounds
- MDLs also reported – in accordance with US 40 CFR Part 136
  - Requirement to be below the lowest calibrant



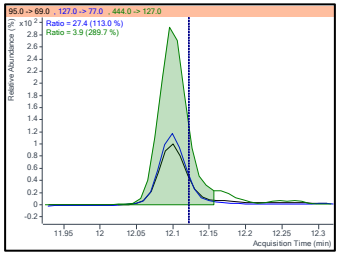
4:2 FTOH



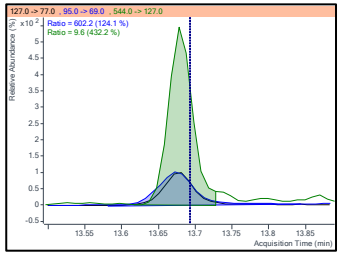
6:2 FTOH



8:2 FTOH RCS



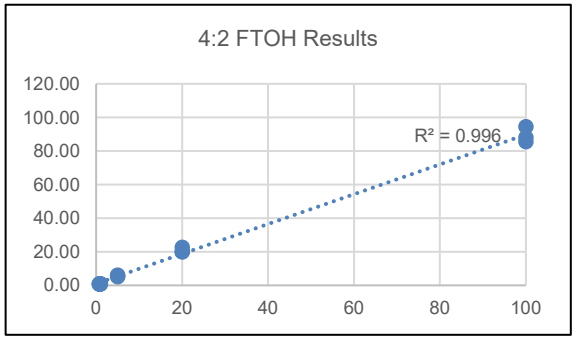
8:2 FTOH

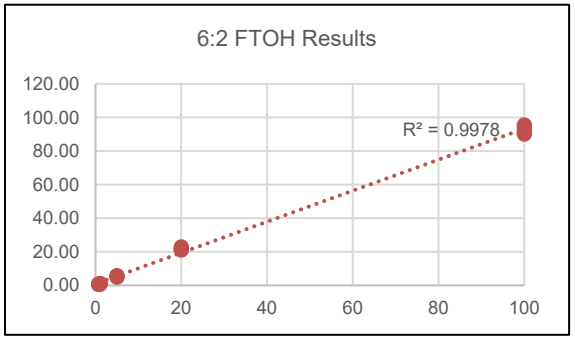


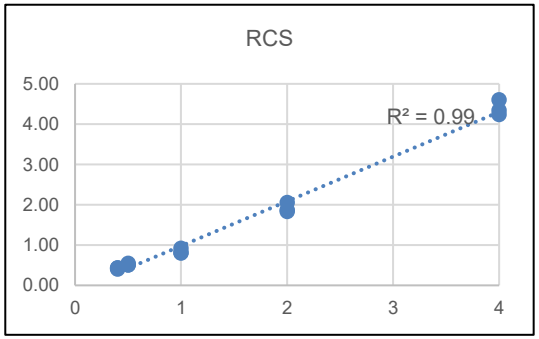
10:2 FTOH

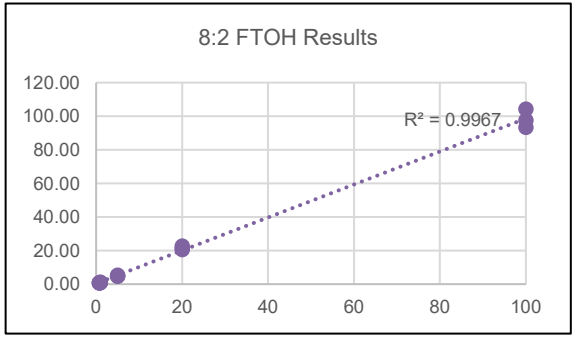
Results

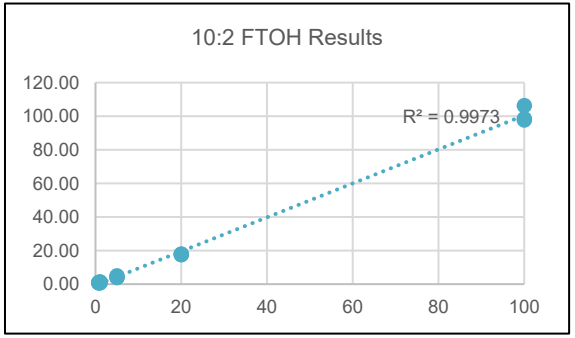
Linearity plots











- Excellent linearity results observed with all compounds passing RRF with <25%RSD – highest value was 16.6%RSD

Results

Data Quality Summary

- Linearity passes with excellent results
  - All RRF passes with <25%
- All QC checks pass
  - IAP <25%RSD
  - DCC within ±25%
  - RCS within ±25% and <25%RSD

Compound	%RSD RRF	IAP <25%RSD	DCC within +/- 25%	RCS within +/- 25%
4:2 FTOH	11.6	Pass	Pass	N/A
6:2 FTOH	9.1	Pass	Pass	N/A
8:2FTOH M+4 (RCS)	9.5	Pass	Pass	Pass
8:2 FTOH	10.3	Pass	Pass	N/A
10:2 FTOH	16.6	Pass	Pass	N/A

Results

Samples and outcome

	Concentration (ng/tube)					% Recovery of RCS
Sample	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH	RCS	
Replicate 1	0.32	3.19	1.76	14.29	1.86	96%
Replicate 2	0.28	3.11	1.62	14.14	1.63	84%
Replicate 3	0.28	3.02	1.63	14.66	1.69	87%

- Example of sample results shown above
  - Excellent repeatability for each compound including RCS
  - Recovery of RCS between 75-125% in every analysis
- ASTM confirmation that Markes-Agilent passed the ILS, with 8 other laboratories - so the method has been fully validated
- Paper in Review (June 2025)
- Markes-Agilent application brief to be published

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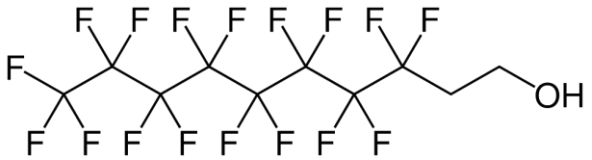
Application Development

Challenges and Resolutions

Challenges and Resolutions

Tips and Tricks for Best Results

- Compound availability and make up of standards
- Standard spiking
  - Multiple standards
  - Internal standard normalisation
- Background and various contributions from external sources



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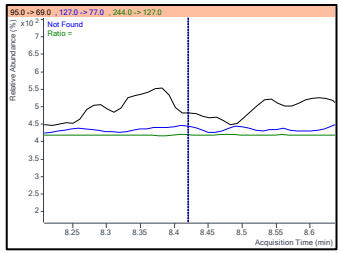
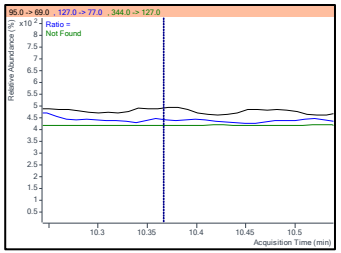
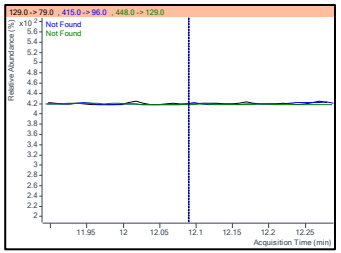


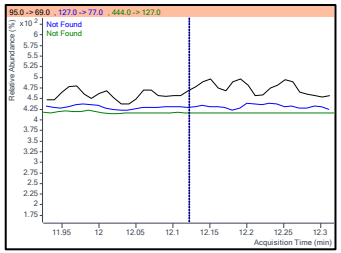
4:2 FTOH



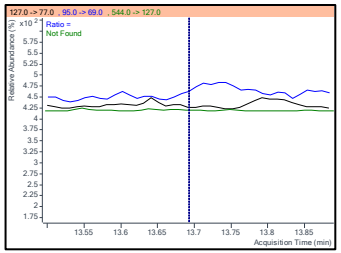
6:2 FTOH



8:2 FTOH RCS



8:2 FTOH



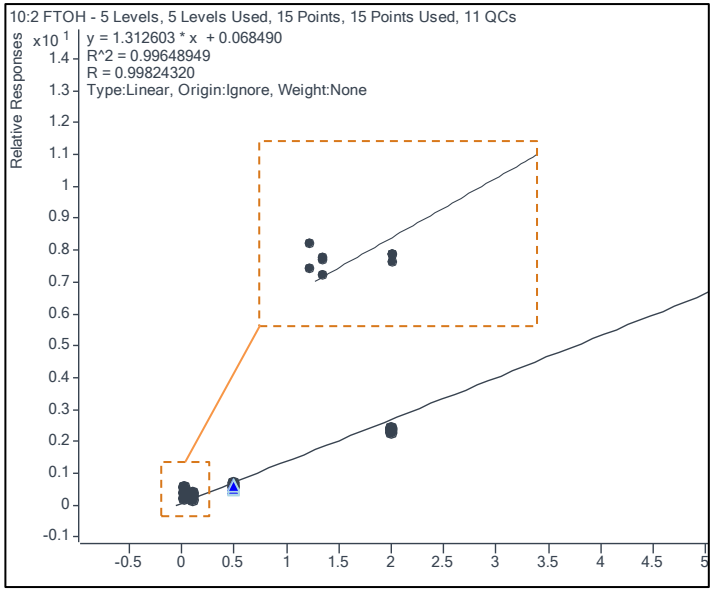
10:2 FTOH

Background and Interferents

Low level interference can be present from external sources

- Interference seen at low levels which has affected the calibration
  - Lowest levels most affected
  - Higher results skew the linearity and although the R2 passes, RRF values are >25%RSD

- Example shown for 10:2 FTOH
  - R2 of 0.9965



Background and Interferents

ASTM Blanks Criteria and Potential Sources

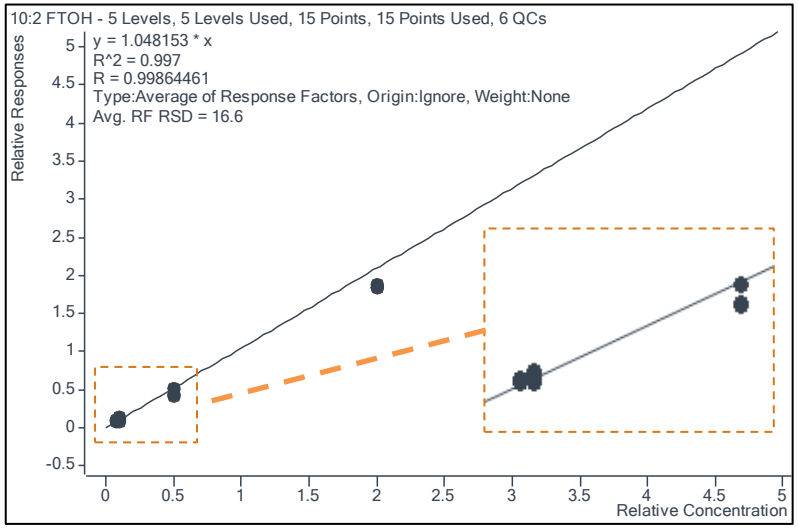
> ***6. Interferences***
>
> *Interferences because of PFAS contamination are of concern during the entire analytical process (see EPA OTM-45, EPA OTM-50, and ref. 20). The following items shall be verified to be free of PFAS: Polypropylene bottles, vials, caps, and disposable pipette tips, lab materials and supplies such as reagents and solvents, glassware, tubing, gloves, and lab coats. This verification shall be done via laboratory blank analysis by rinsing them with methanol, spiking the methanol onto TD tubes and then analyzing the spiked tubes under the same conditions as the samples, or by including process blanks in each analysis batch, depending on the nature of the item of concern.*

- Most contributions come from sources external to the instrument
  - Solvents and glassware
  - Gas lines and connections
  - Syringes and pipette tips
  - Gloves and lab wear
  - Other consumables like septa on CSLR
  - Sorbent tubes

Background and Interferents

Optimised protocols produced desired results

- Stringent cleaning process and quarantined items for PFAS analysis – SOP controls implemented
- Dedicated syringes to minimise cross contamination
  - Additional flushing of syringes and pipette tips required
- Regular updating of consumables
- Enables interferences to be removed and ensuring accurate calibrations can be achieved



Summary

- ASTM D8591 is a robust method for the analysis of fluorotelomer alcohols
  - Forms an excellent basis for analysis of ambient and indoor air, and in the emissions from materials.
- Using as a template, many more neutral/volatile PFAS species could be assessed in a variety of matrices using the same methodology.
- TD100-xr coupled to 8890/7000E performed excellently for the method
- Markes consumables and sampling accessories (available via Agilent) provide a full PFAS sampling workflow as well as the analytical
  - ACTI-VOC for air sampling
  - Micro-Chamber for materials sampling
  - Sorbent tubes and traps validated for PFAS

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