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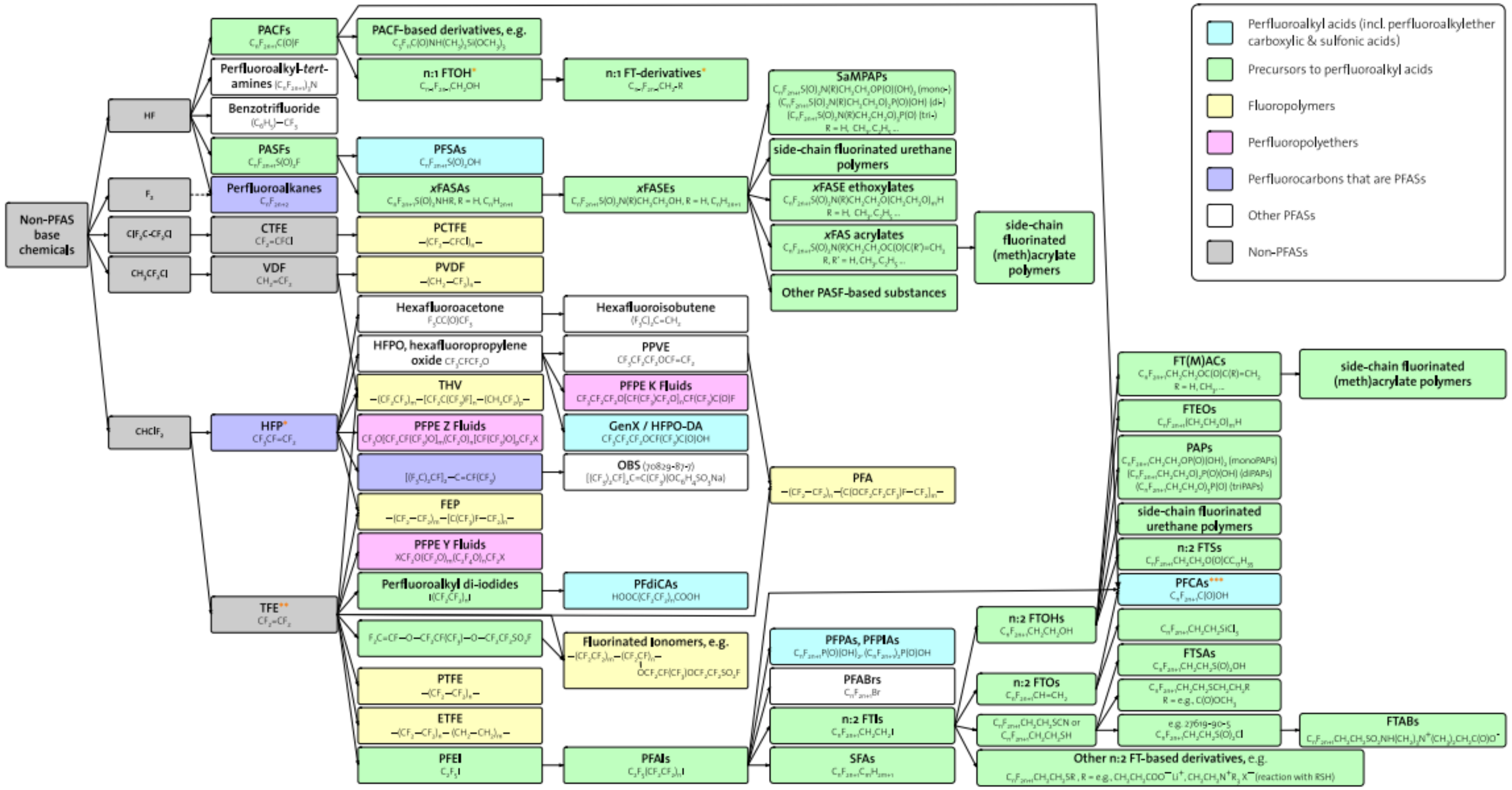
Excellence in Science

Emerging Methods for the Analysis of Volatile PFAS in Water: HS-SPME-GC/MS

Andy Sandy, Yoshiyuki Okamura, Evelyn Wang,
Alan Owens, Ruth Marfil-Vega

The PFAS universe



* Strictly speaking, these substances are not fluorotelomers, as they are not derived from the telomerization process. Despite this, they are termed here "n:1 fluorotelomer-based" substances for readability. Future work may consider to identify more proper terminology for this group of PFASs.
** Note that for many compounds such as HFP and TFE, there are different synthesis routes with different starting materials, and here shows only one of them.
*** Note that there are three synthesis routes shown here for manufacturing of PFCAs, from PACFs, PFAIs and n:2 FTIs. Note that different synthesis routes may generate PFCAs with different perfluorocarbon chain lengths.

Sources: (1) Siegemund G, Schwertfeger W, Feiring A, Smart B, Behr F, Vogel H, McKusick B. *Fluorine Compounds, Organic*, 3rd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; Vol. 33. (2) Banks RE, Smart BE, Tatlow JC. Organofluorine Chemistry: Principles and Commercial Applications. New York: Plenum, 1994. (3) Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SPJ. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integr Environ Assess Manag* **2011**, 7 (4), 513–541. (4) Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbühler K. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ Int* **2014**, *70*, 62–75. (5) Moffett RH, Howell JL, Hoerter JM, Shtarov AB, Jannerfeldt G, Johnston SB, Keenan J, Warriner C, Closser DM. *Perfluoroalkylpolyethers* in *Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology* (third edition), Edited by Rudnick LR. 2020. CRC Press. ISBN: 978-1-138-06821-6. (6) Grot W. *Fluorinated Ionomers*. William Andrew 2011. ISBN: 978-1-437-74457-6.

Figure 10. An overview of some common synthesis routes of different individual or groups of PFASs based on publicly accessible source

The analytical instrumentation universe for PFAS

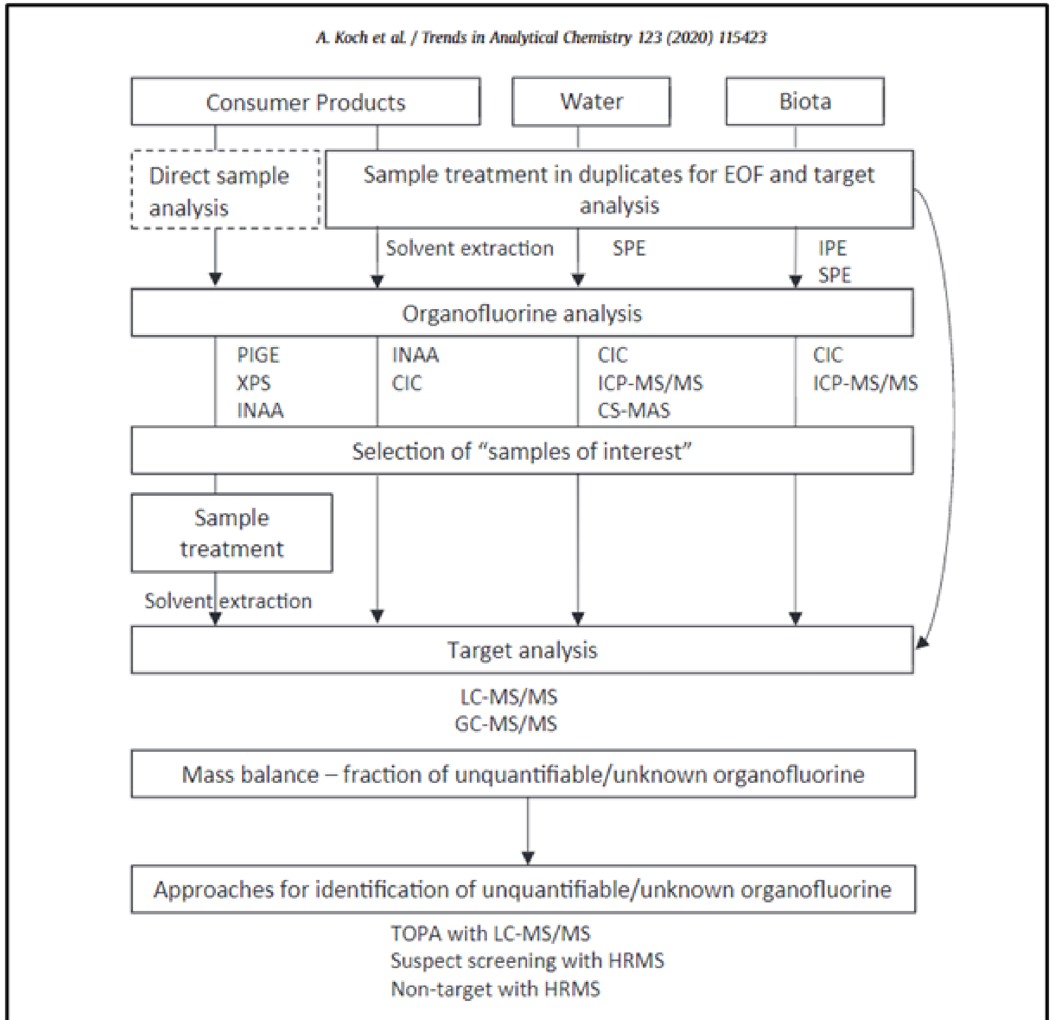
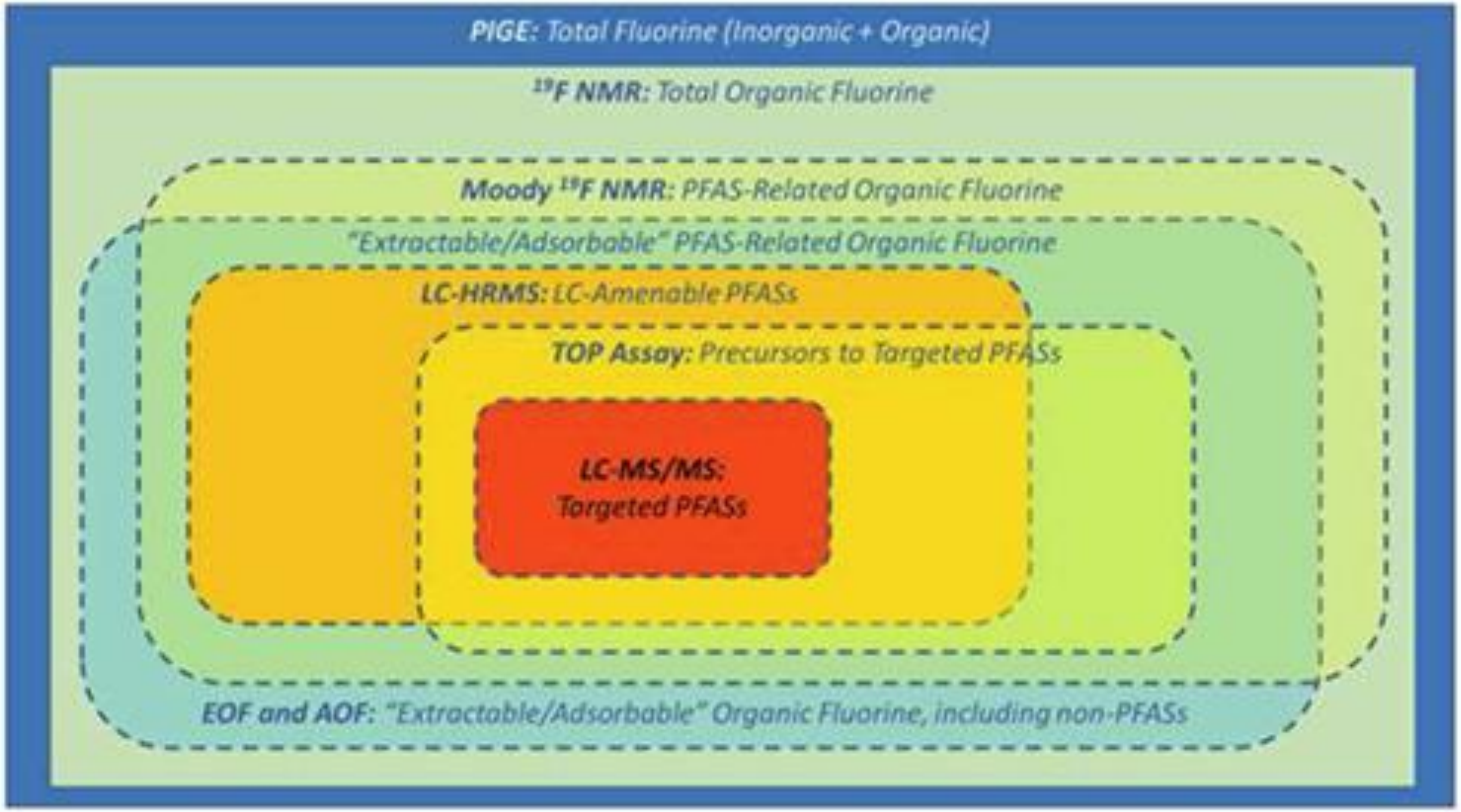


Fig. 2. Proposed workflow for a comprehensive organofluorine assessment.

https://doi.org/10.1016/j.trac.2019.02.024

Historically, focus on ionic PFAS



https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7584354/

Growing interest in neutral and volatile PFAS

- Diverse sample types
- New methods being published by EPA and other standardization organizations
- LCMS can be used… but GCMS is most suitable

Sample introduction for GCMS

Sample Introduction Technique	Sensitivity (GC-MS)	Extraction Mode
SHS	ppb~ppm level	Static equilibrium gas extraction
DHS	ppt~ppb level	Dynamic non-equilibrium gas extraction
SPME	ppt~ppb level	Sorptive extraction
TD	ppt~ppb level	Sorptive extraction
Direct-TD	ppt~ppm level	Direct thermal extraction
Liq	ppb level	-
Py	µg level	Destructive thermal decomposition
DI	ng level	-

SHS	Static Headspace	Direct TD	Direct Thermal Desorption
DHS	Dynamic Headspace (Purge & Trap)	Liq	Liquid Injection
SPME	Solid Phase Microextraction	Py	Pyrolisis
TD	Thermal Desorption	DI	Direct Injection

Sample introduction for GCMS

Environmental Compliance

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Sample introduction for GCMS

Environmental Compliance | Emerging

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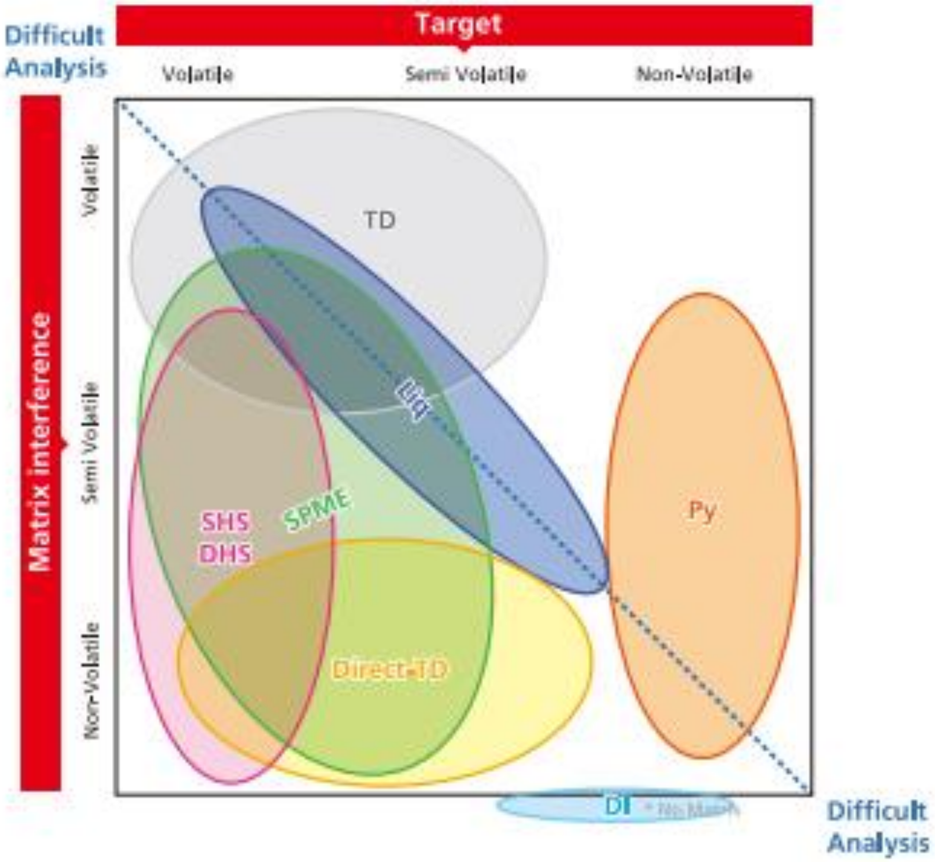
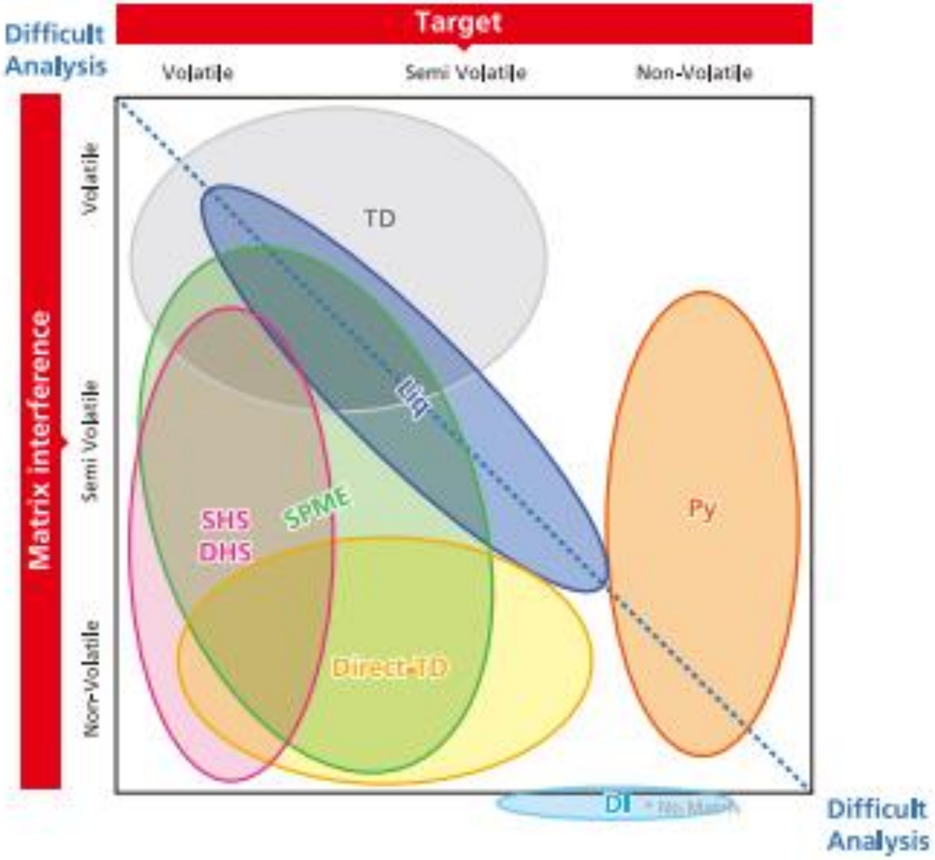
Comparison of techniques



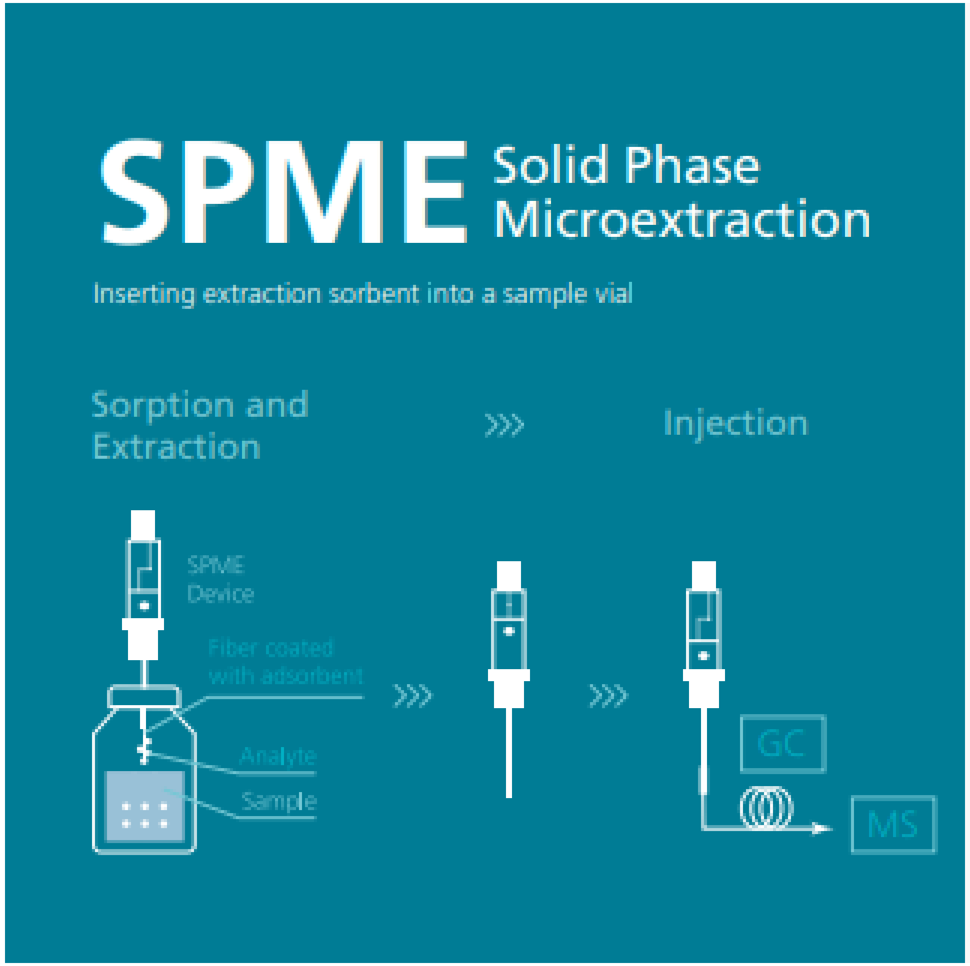
Comparison of techniques for PFAS analysis



Most commonly used

- Liquid injection
- Thermal Desorption

What about Headspace and SPME?



Successful analysis of PFAS by HS-GCMS

Henry's Law constants of 15 per- and polyfluoroalkyl substances determined by static headspace analysis

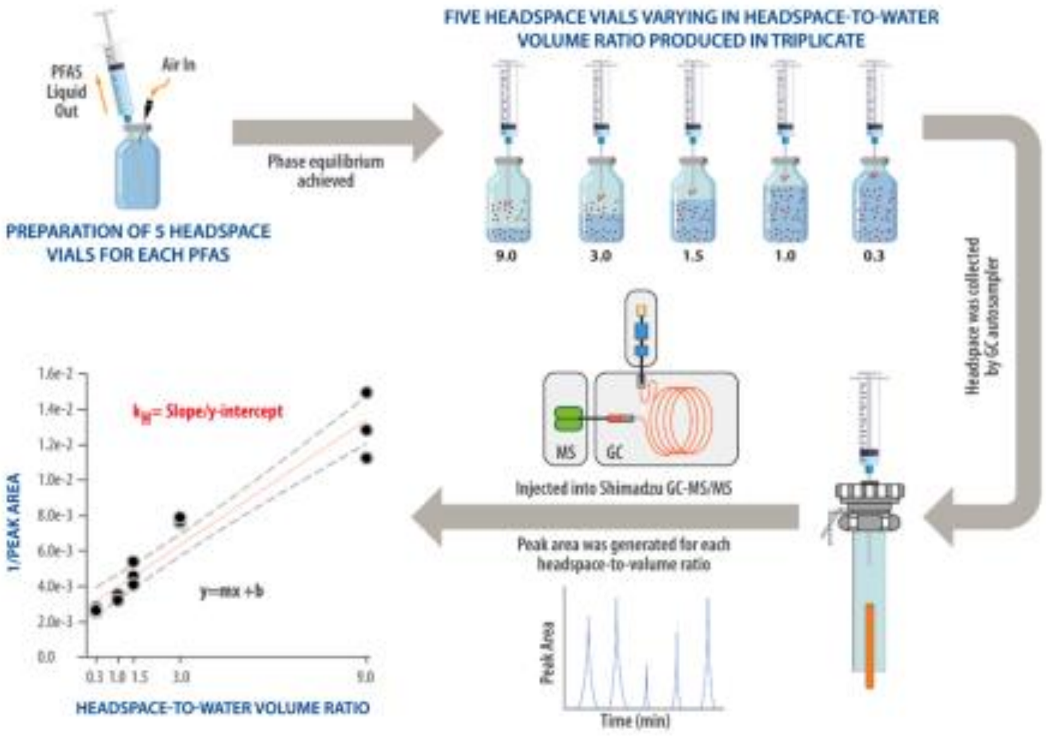


Fig. 1. Schematic of the method of preparing and analyzing headspace samples by GC-MS/MS for the determination of the k_H of PFAS.

Abusallout et al. 2022

https://doi.org/10.1016/j.hazl.2022.100070

Successful analysis of PFAS by HS-GCMS

PFAS	k_H	Slope	Intercept	R^2	pH
4:2 FTOH	0.31 ± 0.07	2.77 ± 0.39 × 10^{-5}	8.91 ± 1.70 × 10^{-5}	0.920	6.59 ± 0.29
6:2 FTOH	1.26 ± 0.40	5.18 ± 0.29 × 10^{-6}	4.12 ± 1.20 × 10^{-6}	0.986	6.55 ± 0.08
8:2 FTOH*	1.98 ± 0.69	1.51 ± 0.06 × 10^{-5}	7.66 ± 2.60 × 10^{-6}	0.993	6.74 ± 0.17
10:2 FTOH*	2.82 ± 1.12	6.92 ± 0.22 × 10^{-4}	2.45 ± 0.96 × 10^{-4}	0.995	6.69 ± 0.26
4:2 FTS	0.09 ± 0.02	4.11 ± 0.88 × 10^{-4}	4.33 ± 0.38 × 10^{-3}	0.833	5.66 ± 0.02
6:2 FTS	0.16 ± 0.01	2.37 ± 0.17 × 10^{-4}	1.48 ± 0.08 × 10^{-3}	0.976	5.70 ± 0.01
8:2 FTS	0.18 ± 0.02	8.55 ± 0.65 × 10^{-5}	4.75 ± 0.28 × 10^{-4}	0.975	5.84 ± 0.03
PFHxI	1.01 ± 0.46	4.70 ± 0.47 × 10^{-7}	4.66 ± 2.01 × 10^{-7}	0.956	6.90 ± 0.01
6:2 FTUI	0.48 ± 0.10	4.41 ± 0.39 × 10^{-6}	9.27 ± 1.70 × 10^{-6}	0.966	6.39 ± 0.01
6:2 FTI	0.30 ± 0.07	1.32 ± 0.19 × 10^{-6}	4.39 ± 0.85 × 10^{-6}	0.910	6.71 ± 0.08
N-EtFOSA-M	0.43 ± 0.12	1.18 ± 0.15 × 10^{-3}	2.77 ± 0.68 × 10^{-3}	0.927	6.33 ± 0.16
N-MeFOSA-M	0.92 ± 0.48	2.03 ± 0.26 × 10^{-3}	2.21 ± 1.11 × 10^{-3}	0.933	6.24 ± 0.07
6:2 FTO	3.86 ± 1.49	4.40 ± 0.18 × 10^{-7}	1.14 ± 0.43 × 10^{-7}	0.987	6.23 ± 0.02
8:2 FTCA	0.69 ± 0.07	8.18 ± 0.26 × 10^{-5}	1.19 ± 0.11 × 10^{-4}	0.995	5.66 ± 0.28
8:2 FTAC	0.32 ± 0.11	3.09 ± 0.06 × 10^{-3}	9.75 ± 2.61 × 10^{-4}	0.858	6.58 ± 0.05

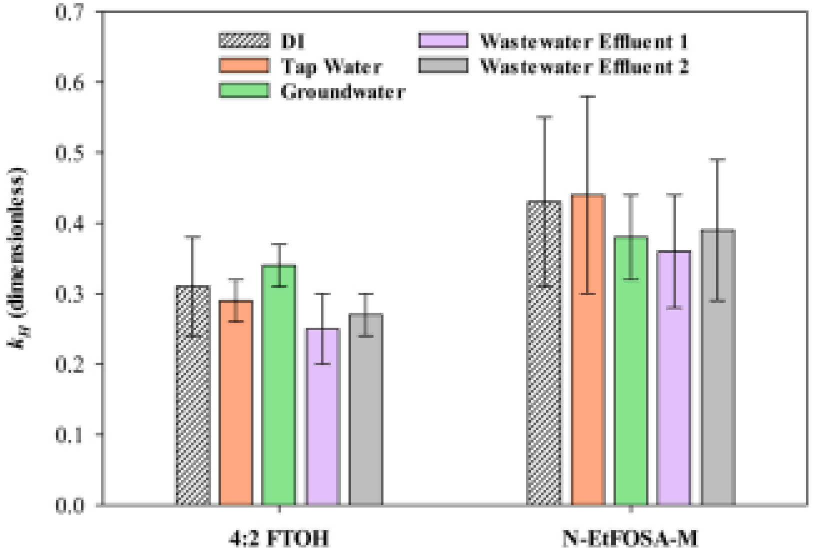


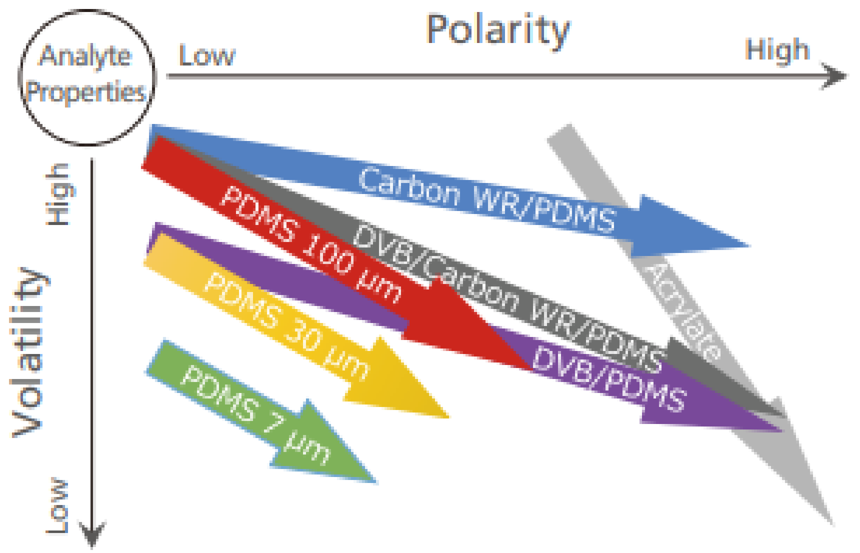
Fig. 3. k_H of 4:2 FTOH and *N*-EtFOSA-M in varying water matrixes.

- Contribution to closing the mass balance of PFAS in the environment:
  - Simplified analytical method
  - Determination of physico-chemical properties

Abusallout et al. 2022

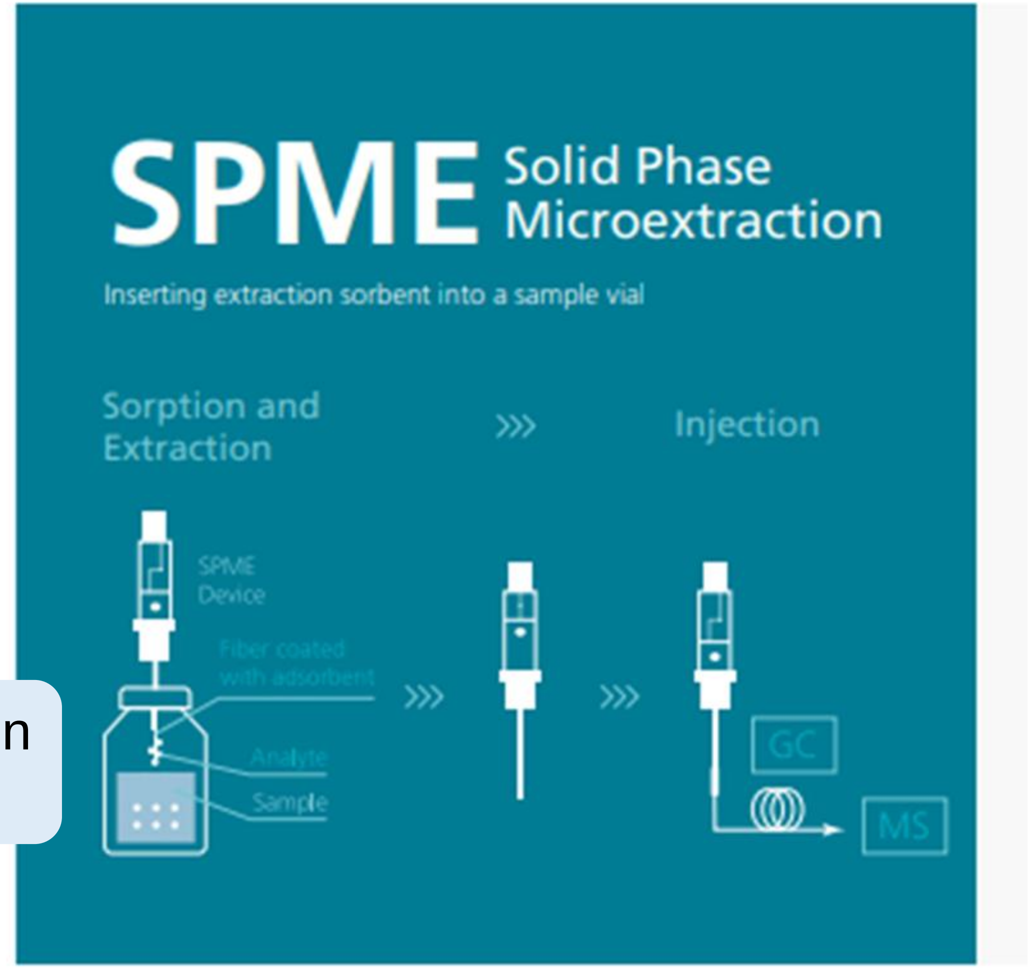
https://doi.org/10.1016/j.hazl.2022.100070

More about SPME

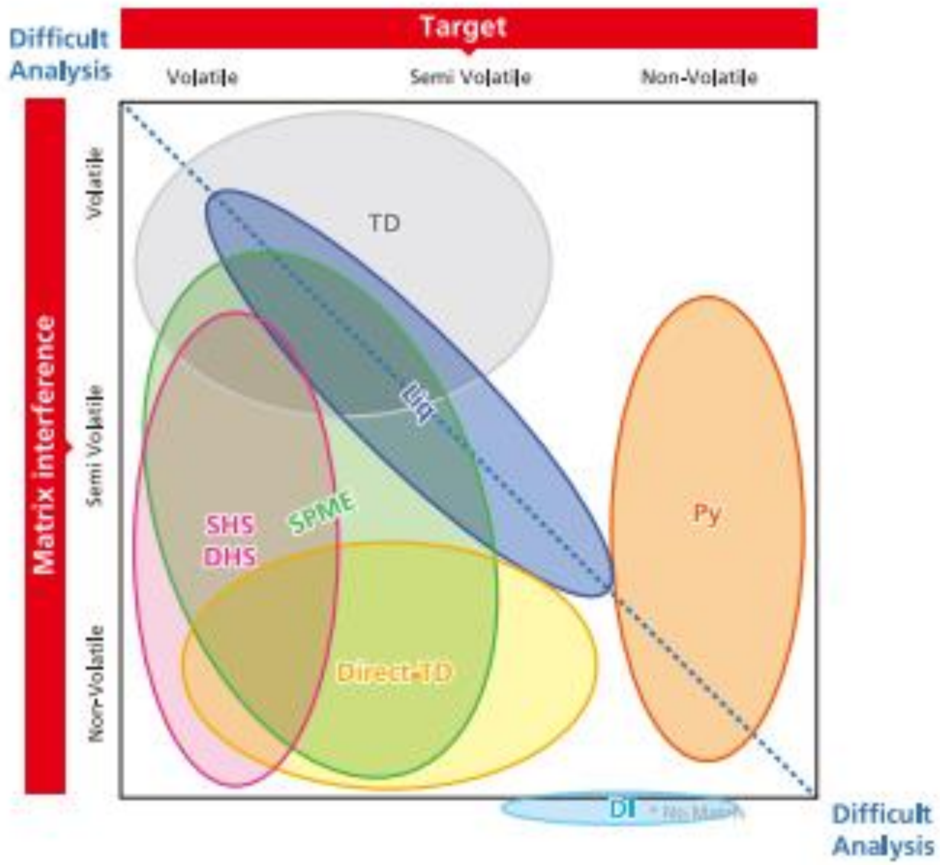


Compatibility of SPME fiber coatings with analyte properties
(PDMS = polydimethylsiloxane, DVB = divinylbenzene, Carbon WR = Carbon Wide Range)

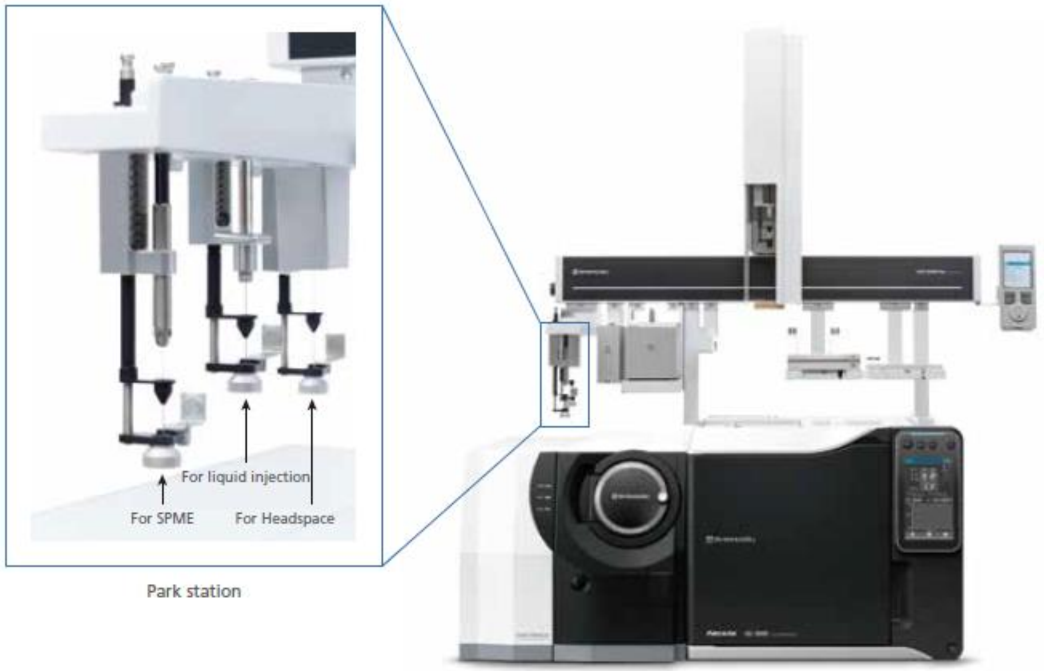
- Direct immersion
- Head Space



HS-SPME-GCMS



Occurrence of volatile PFAS in **liquid** and solids samples of diverse origin (**environmental**, food, consumer products) with same set-up



Instrumentation and targets

Shimadzu's GCMS QP-2020NX

Shimadzu's GCMS TQ-8040

Chemical Class	Compound	Acronym	CAS Number
Perfluoroalkyl iodides (PFIs)	Perfluorohexyl iodide	PFHxI	355-43-1
	Perfluorooctyl iodide	PFOI	507-63-1
(n:2) Fluorotelomer iodides (FTIs)	4:2 Fluorotelomer iodide	4:2 FTI	2043-55-2
	6:2 Fluorotelomer iodide	6:2 FTI	2043-57-4
	8:2 Fluorotelomer iodide	8:2 FTI	2043-53-0
(n:2) Fluorotelomer acrylates (FTACs)	6:2 Fluorotelomer acrylate	6:2 FTAC	17527-29-6
	8:2 Fluorotelomer acrylate	8:2 FTAC	27905-45-9
	1H,1H,2H,2H-Perfluoro-n-octyl acrylate-d3	*6:2 FTAC d3*	*7527-29-6*
(n:2) Fluorotelomer methacrylates (FTMACs)	6:2 Fluorotelomer methacrylate	6:2 FTMAC	2144-53-8
	8:2 Fluorotelomer methacrylate	8:2 FTMAC	1996-88-9
(n:2) Fluorotelomer alcohols (FTOHs)	8:2 Fluorotelomer alcohol	8:2 FTOH	678-39-7
	10:2 Fluorotelomer alcohol	10:2 FTOH	865-86-1
	2-perfluorooctyl-[1,1-2H2-1,2- 13C2]-ethanol	*8:2 FTOH $^{13}C2$*	*872398-73-7*
	2-perfluorodecyl-[1,1-2H2-1,2- 13C2]-ethanol	*10:2 FTOH $^{13}C2$*	*865-86-1*
Perfluoroalkane sulfonamides (FASAs)	N-Methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8
	N-Ethyl perfluorooctane sulfonamide	EtFOSA	4151-50-2
	n-ethyl-d5-perfluoro-1-octanesulfonamide	*EtFOSA d5*	*936109-40-9*

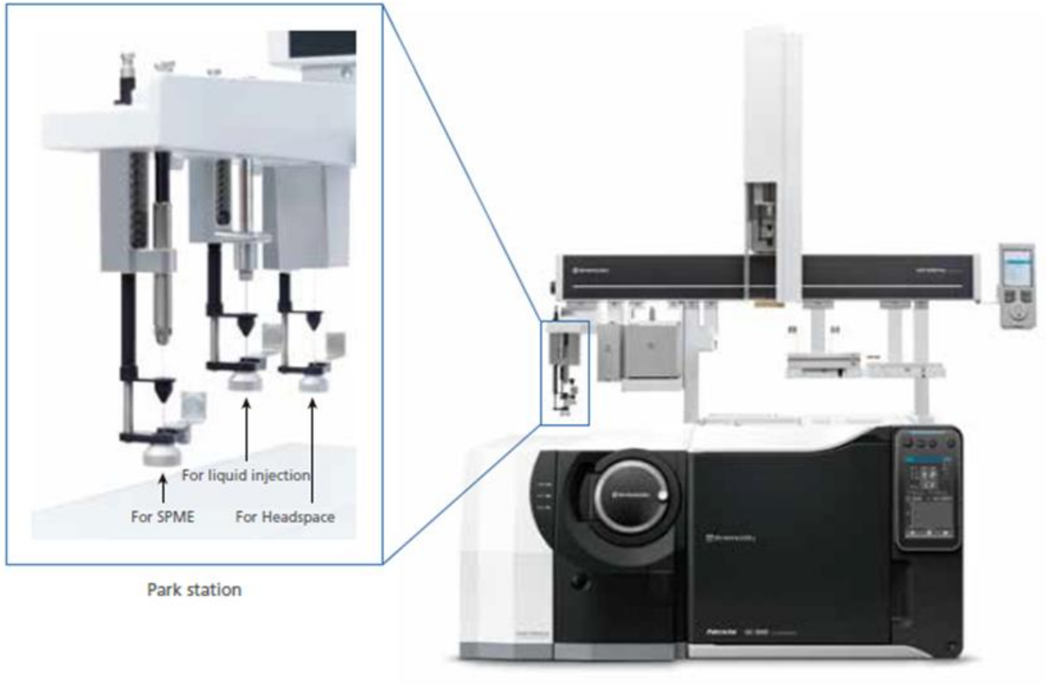
Optimized method conditions

Gas Chromatography	Nexis GC-2030
Injection mode	Splitless
Carrier gas	Helium
Injection port temperature (°C)	240
High pressure injection	Auto, 250 kPa, 1 min
Column	SH-I-624Sil MS Capillary, 30 m x 0.25 mmID x 1.40 um
Flow control mode (cm/sec)	Linear velocity, 44.4
Total flow (mL/min)	50
Oven temperature	40°C (7 min.), 5°C/min. to 188°C (0 min.), 40°C/min. to 300°C, (5 min.)
SPME analysis	**AOC-6000 Plus**
SPME Fiber	50/30 μm DVB/CAR/PDMS
Incubation time (min)	5
Extraction time (min)	30
Desorption time (min)	7
Agitation speed (rpm)	300
Extraction temperature (°C)	50
Sample volume (mL)	10
Desorption temperature (°C)	240
Sampling salinity	2 % NaCl (w/v)

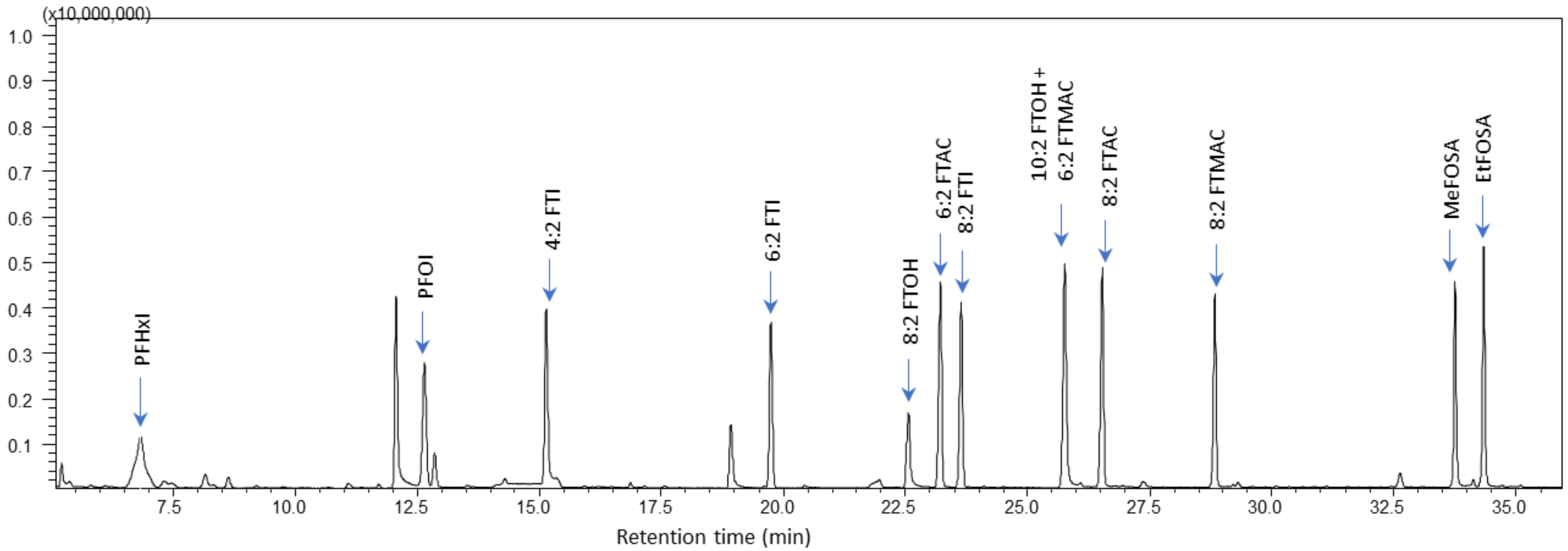
Mass Spectrometer	Common Parameters
Interface temperature (°C)	280
Ion source temperature (°C)	200
Detector voltage (kV)	Relative to Tune 0.4
Threshold	0
Mass Spectrometer	**QP-2020NX**
Acquisition mode	Qualitative analysis: Full scan: m/z 50 to 600 Quantitative analysis: SIM, Event time 0.3 sec.
Tuning mode	High Sensitivity
Mass Spectrometer	**TQ-8040**
Acquisition mode	Acquisition mode: MRM, Loop time: 0.3 sec.
Tuning mode	Normal mode

Experimental plan

- Chromatographic and MS methods, by liquid injection
  - Single Quadrupole
  - Triple Quadrupole
- SPME parameters - optimization
- Calibration curve and linear range
- Carry-over
- PFAS in the background
- Analysis of environmental samples
  - Low system background
  - Precision and accuracy
  - Matrix effects

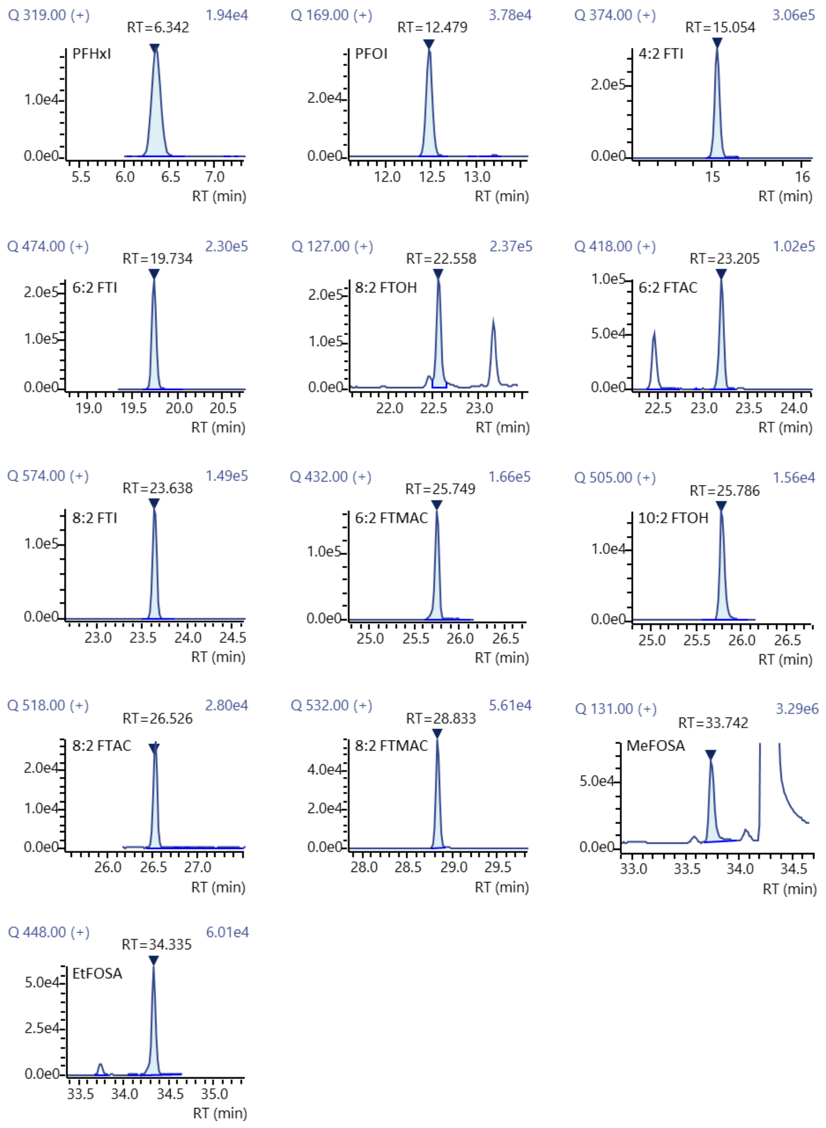


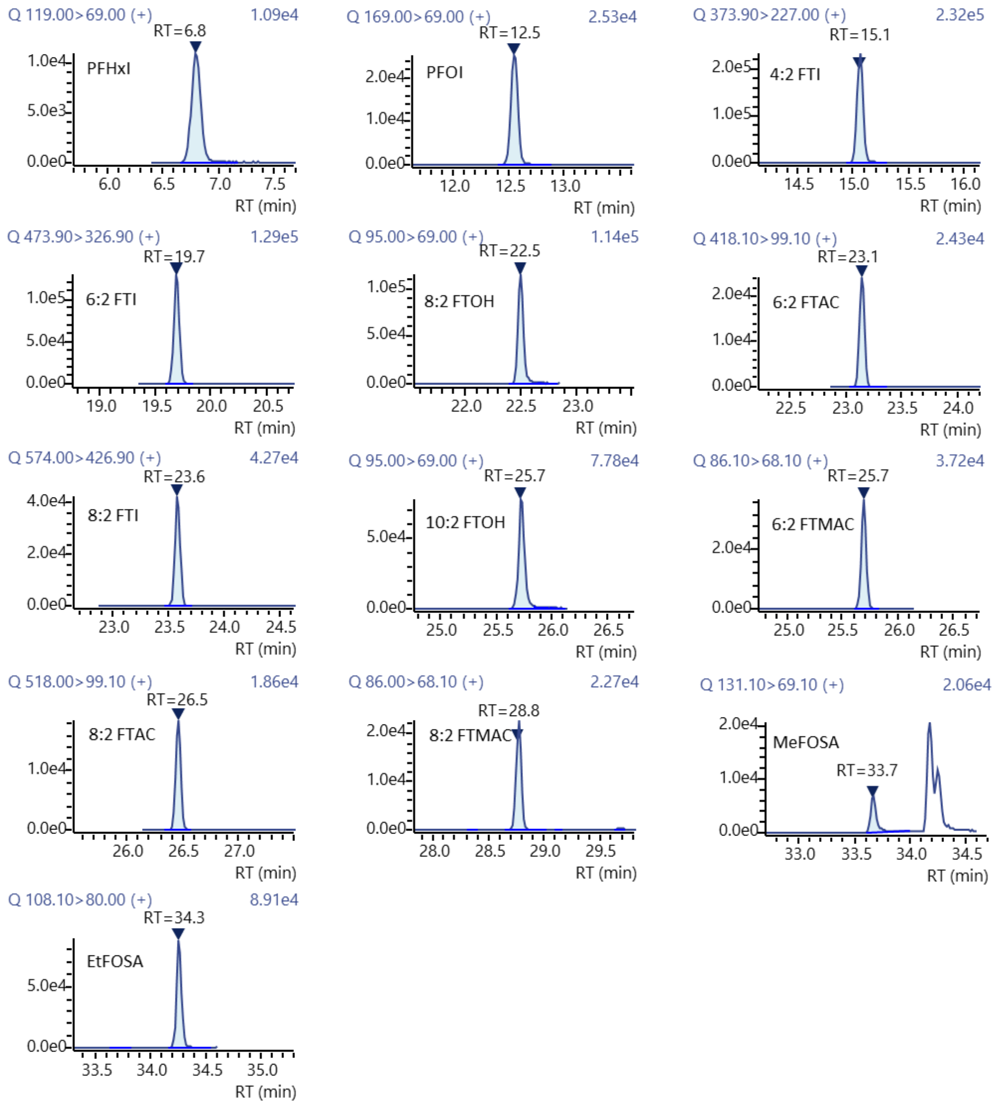
Results - Chromatography



TIC chromatogram of the 13 targeted PFAS compounds at 5 mg/L

SIM and MRM





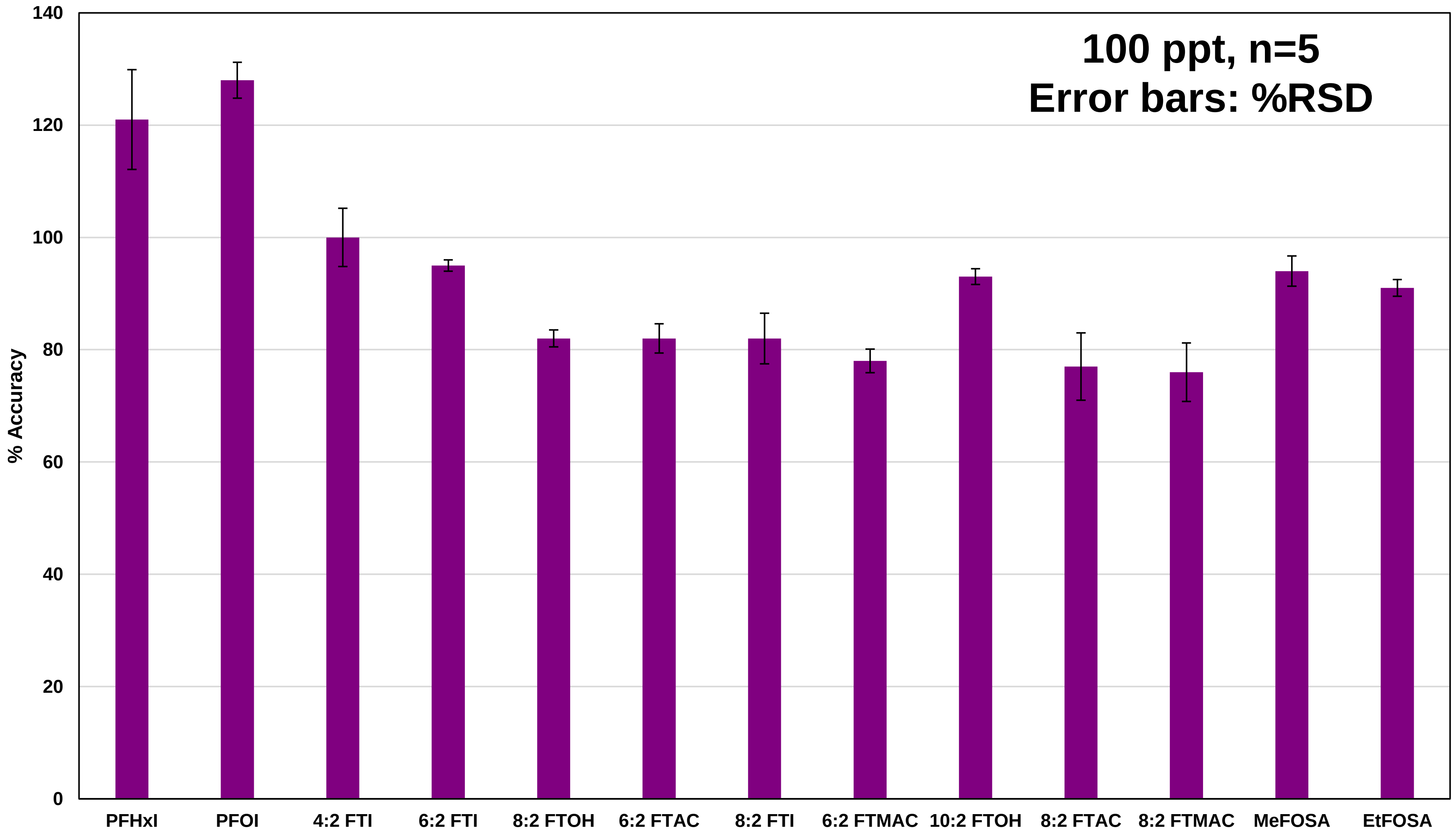
PFAS compounds at 100 ng/L in ultrapure water

Calibration curve

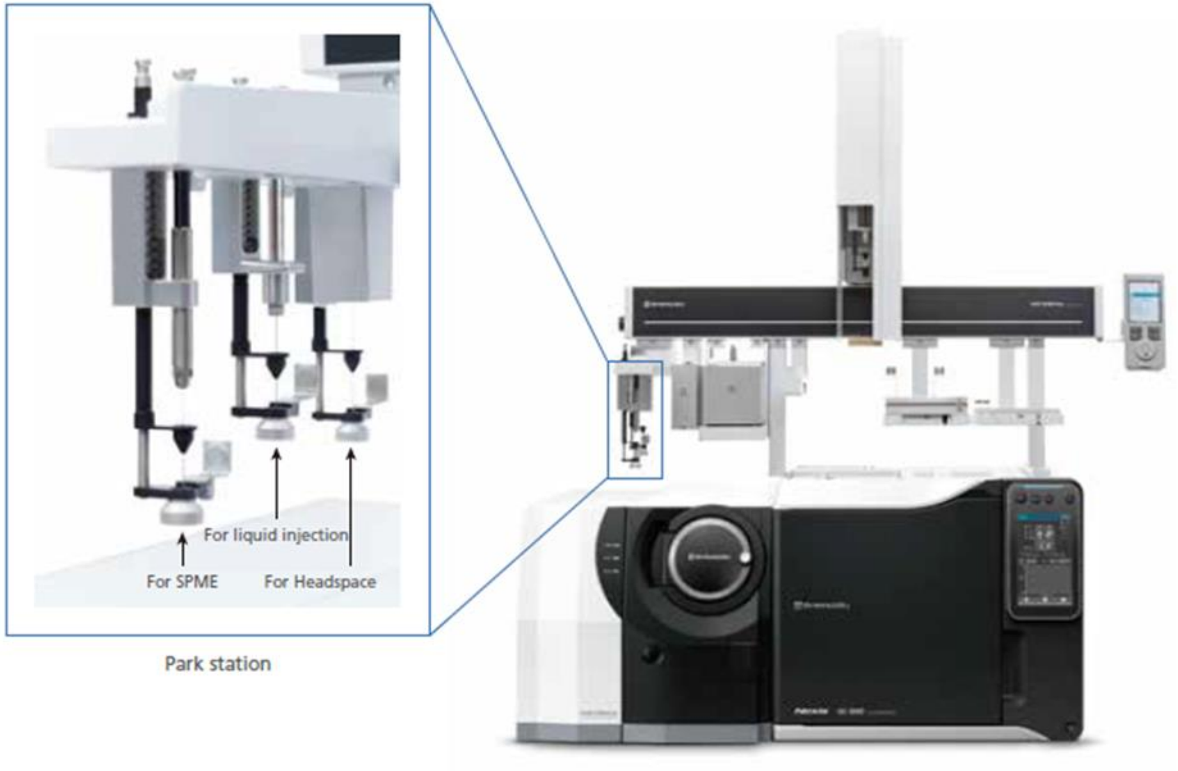
	QP-2020NX			TQ-8040		
Compound	Calibration Range (ng/L)	R2	RF (Response Factor) %RSD	Calibration Range (ng/L)	R^2	RF (Response Factor) %RSD
PFHxI	2.5-2000	0.993	10.89	2.5-2000	0.999	13.68
PFOI	2.5-2000	0.997	10.26	2.5-1000	0.998	18.94
4:2 FTI	2.5-800	0.993	8.28	2.5-2000	0.997	9.30
6:2 FTI	25-800	0.994	13.53	1-2000	0.998	17.18
8:2 FTOH	25-2000	0.997	5.37	2.5-2000	>0.999	6.31
6:2 FTAC	25-2000	0.998	19.87	2.5-2000	0.998	4.03
8:2 FTI	2.5-800	0.996	13.59	2.5-2000	0.999	9.05
10:2 FTOH	2.5-2000	0.999	10.38	2.5-2000	>0.999	6.45
6:2 FTMAC	2.5-800	0.995	12.43	2.5-2000	0.998	10.41
8:2 FTAC	5-250	0.995	14.81	2.5-2000	0.999	11.32
8:2 FTMAC	2.5-250	0.998	19.51	2.5-2000	0.999	9.98
MeFOSA	5-2000	>0.999	17.79	2.5-2000	0.999	6.85
EtFOSA	10-2000	0.999	11.40	1-2000	>0.999	7.17

The linear range of each PFAS target includes at least seven calibration levels
Results showed a good linear fit for all compounds with R2 ≥ 0.993 and RF %RSD < 20.

%Accuracy and precision with TQ-8040



What about PFAS in the background?



Consumables and reagents

- SPME vials
- SPME fibers
- Salt
- Solvents
- Commercial standards

No fluorinated components
in sample flow path

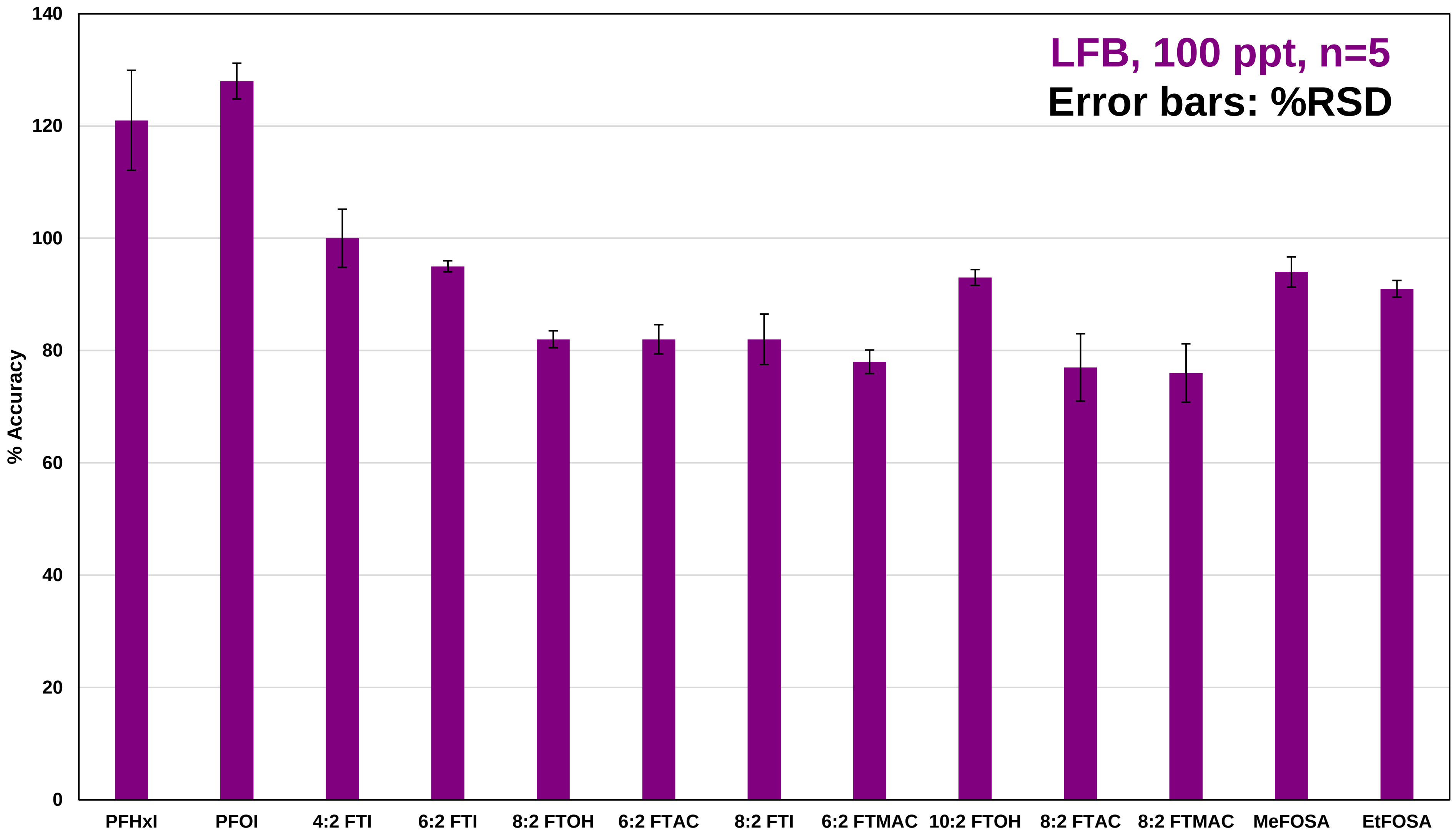
Background and carryover

- None of the target PFAS in the laboratory blank samples showed quantifiable results

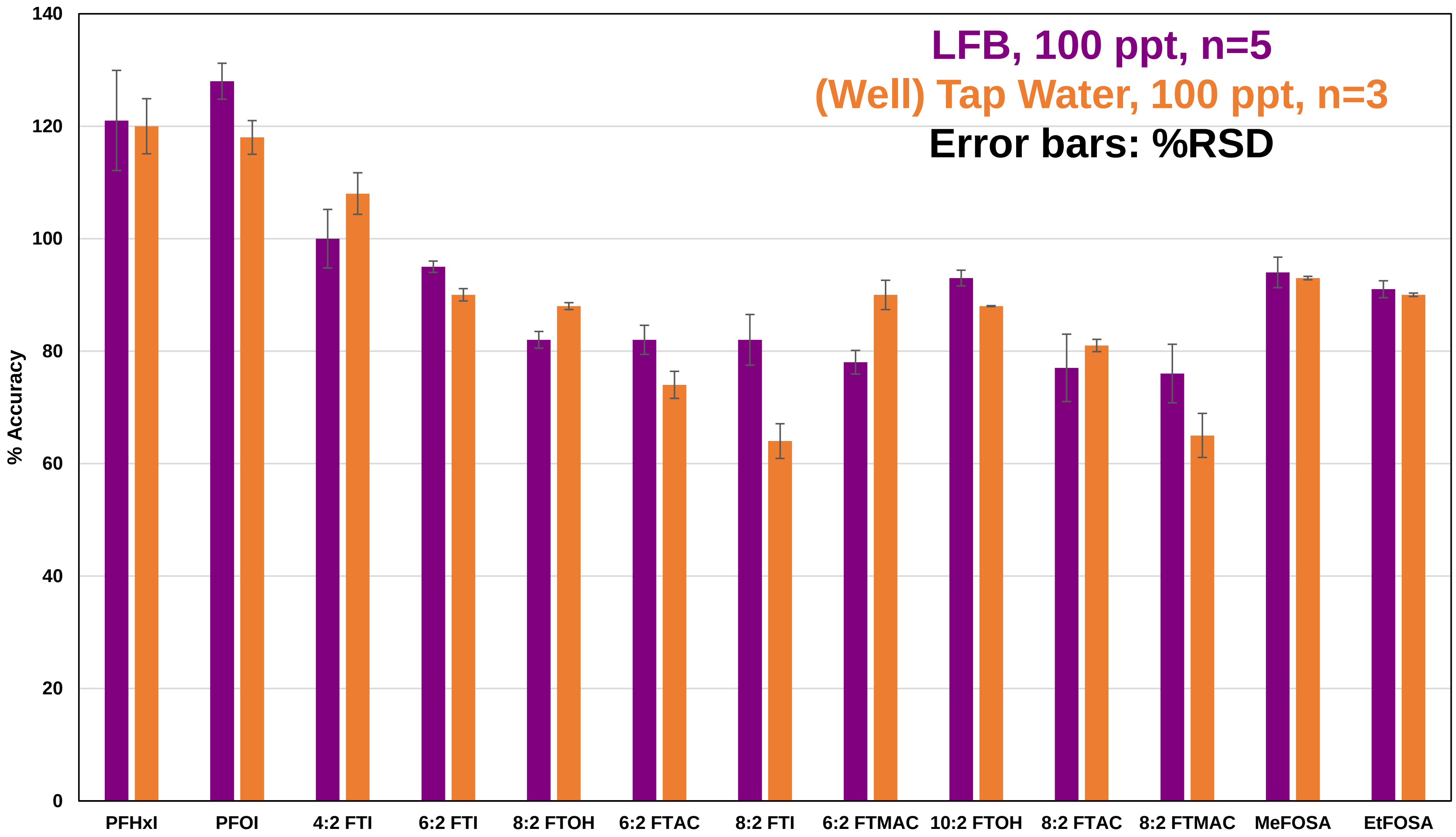
- The area of peaks of in the blanks were less than 1/5 of the lowest calibration standard

- The carryover effect was evaluated by analyzing a blank immediately after the highest calibration standard: <0.2%

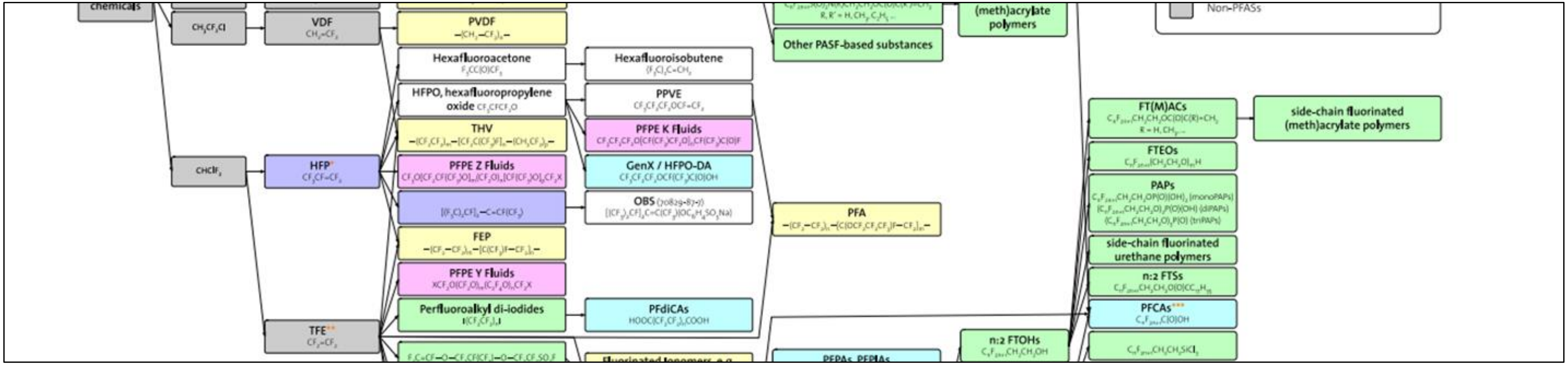
More results - Samples

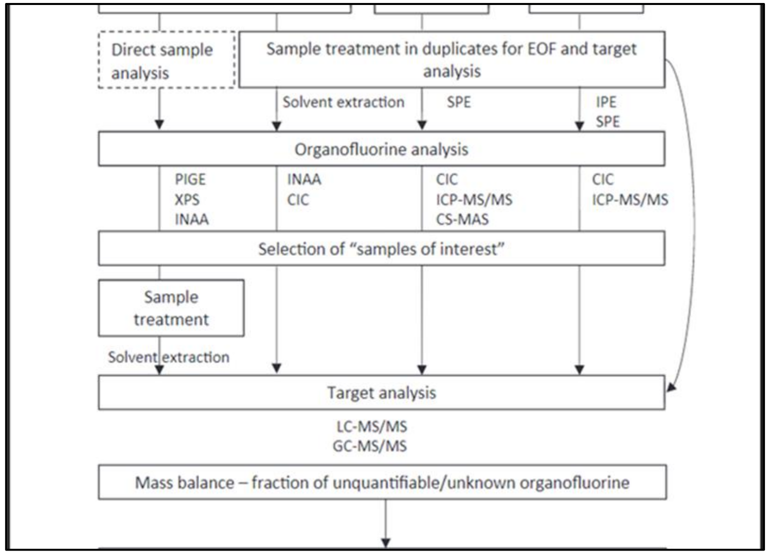


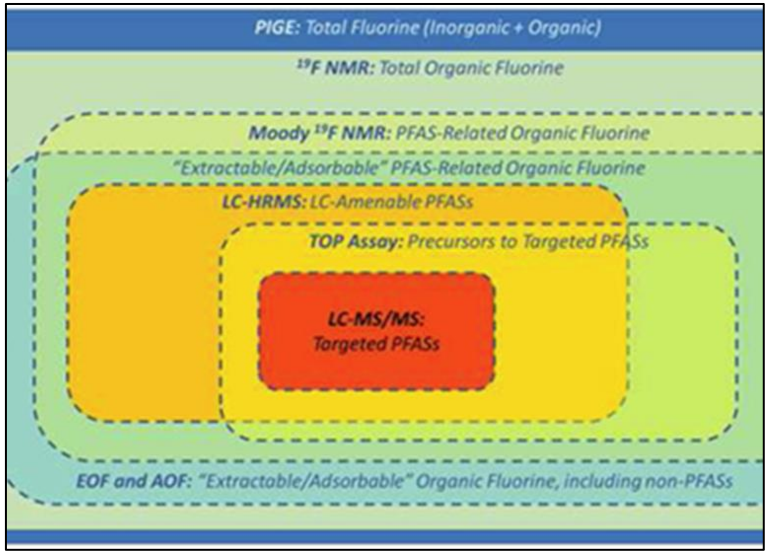
More results - Samples



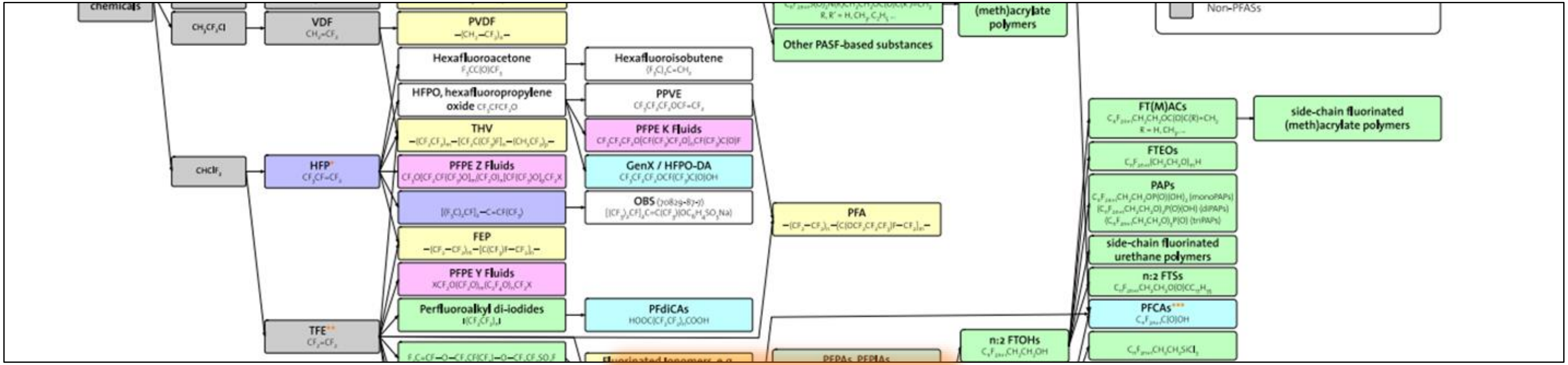
Take home messages

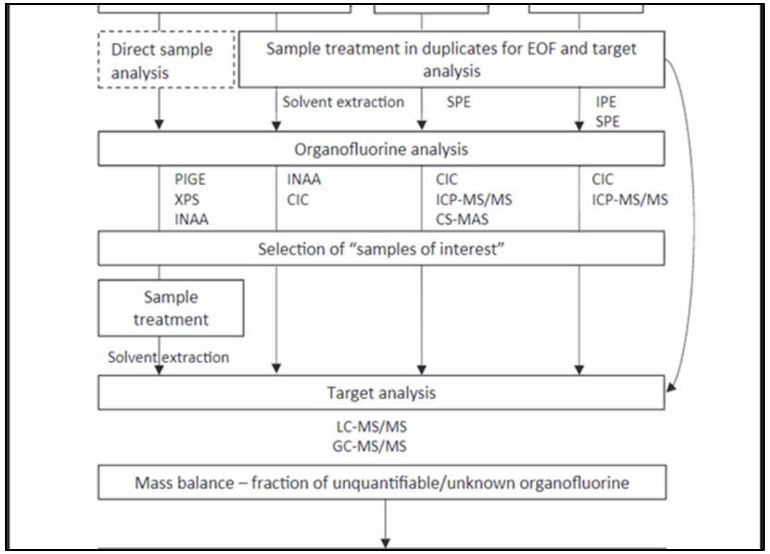


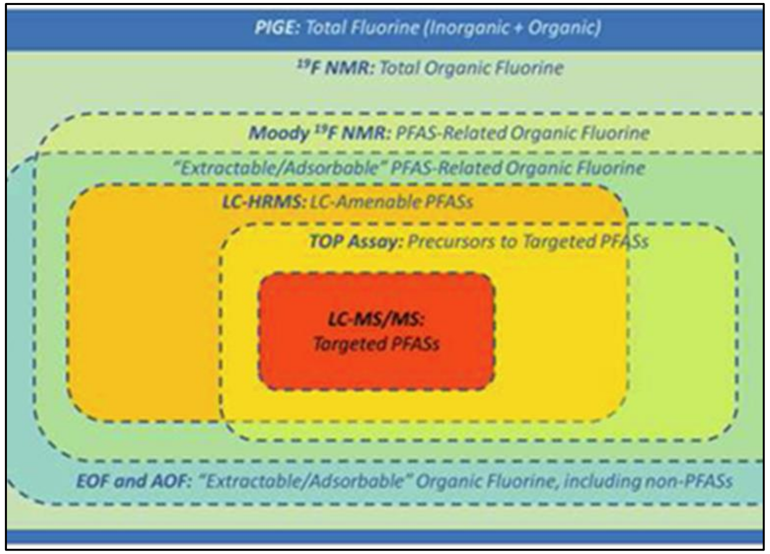




Take home messages

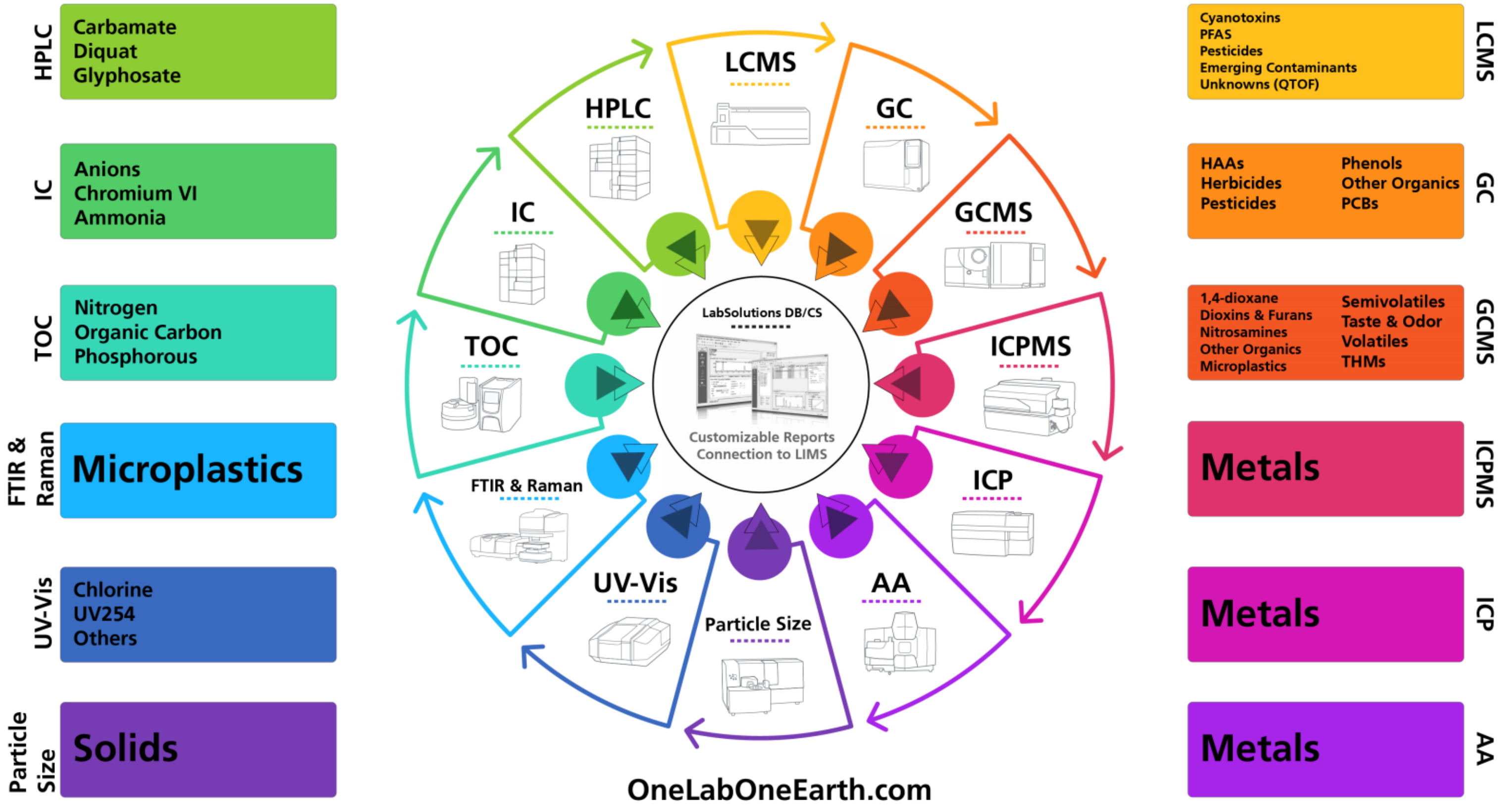






Take home messages

- Demonstrated the suitability of HS-SPME-GCMS for the analysis of selected classes of volatile PFAS in environmental liquid samples, without the need of extensive sample preparation
  - Sensitivity:
    - SQ: 2.5 - 25 ppt
    - TQ: 1 – 2.5 ppt
  - Minimal sources of PFAS in background
- More work on-going…



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