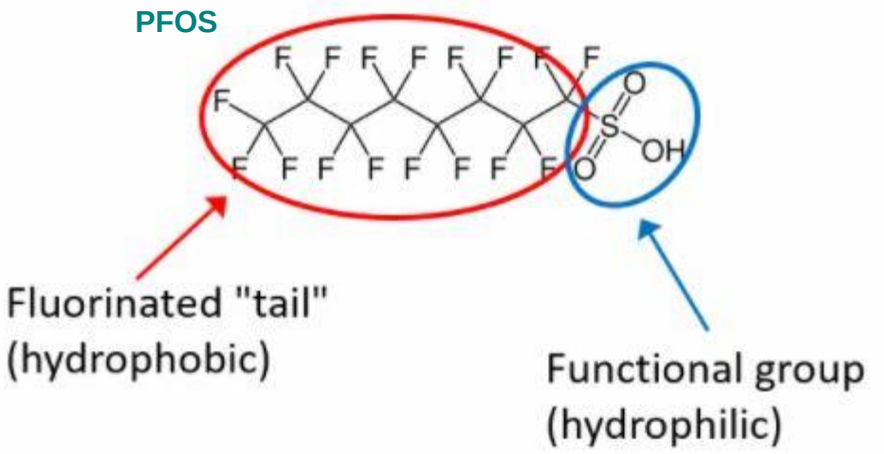
WISSEN
TECHNIK
LEIDENSCHAFT

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) – an Analytical Challenge!

Milica Jovanovic MSc
Erich Leitner Prof. Dr.
Institute of Analytical Chemistry and Food Chemistry
Graz University of Technology

What are PFAS?

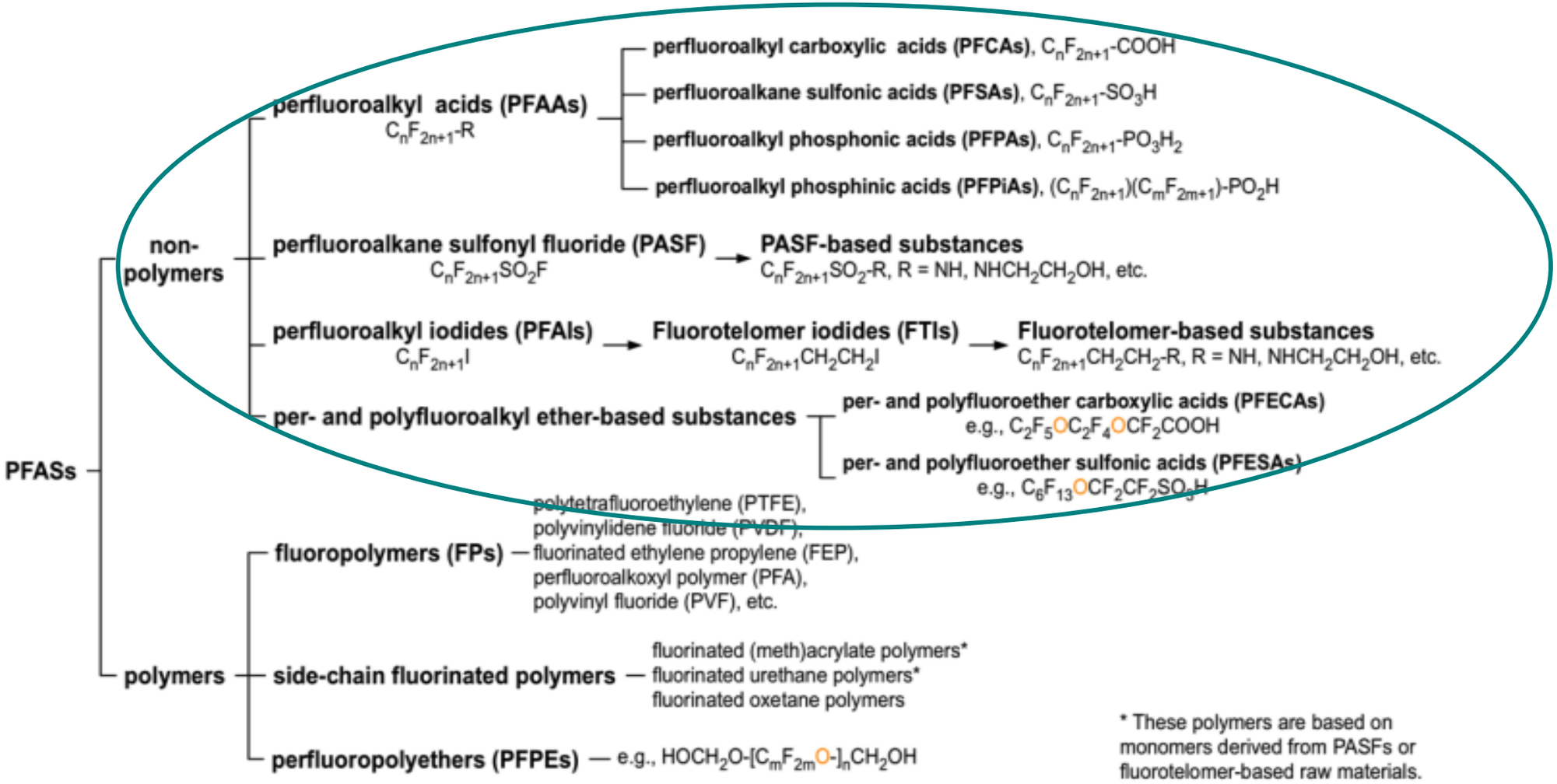
Poly and PerFluoro Alkyl Substances



- C-F bond is one of the strongest chemical bonds known
- Repel water, fat and dirt

- Resistant towards aggressive chemicals and physical strain
- Persistent, Bioaccumulative and Toxic
- Widely detected in wildlife and humans

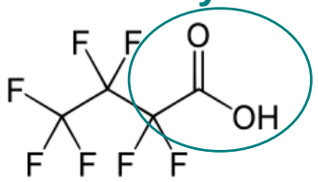
Per- and polyfluoroalkyl substances (PFASs)



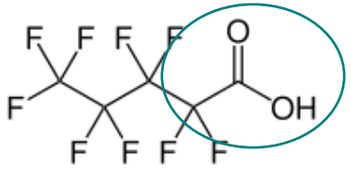
* These polymers are based on monomers derived from PASFs or fluorotelomer-based raw materials.

Our Focus…

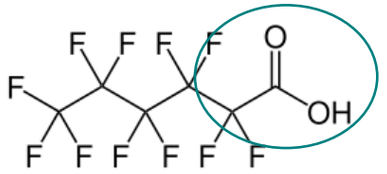
Perfluoroalkyl carboxylic acids – C4 – C14



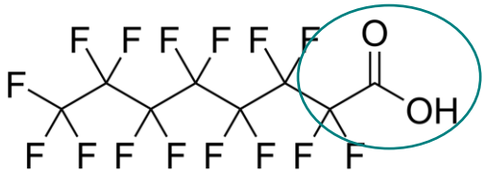
PFBA - Perfluorobutanoic acid



PFPeA - Perfluoropentanoic acid



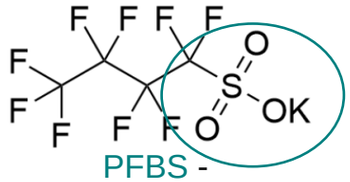
PFHxA - Perfluorohexanoic acid



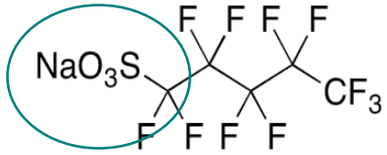
PFOA - Perfluorooctanoic acid

...

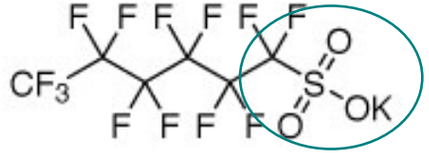
Perfluoroalkyl sulfonates – C4 – C10



PFBS - perfluorobutanesulfonate



PFPeS - perfluoropentanesulfonate

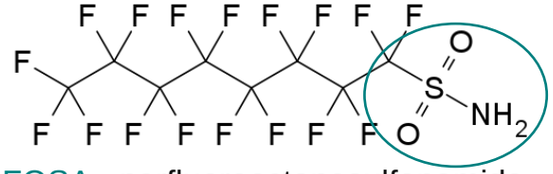


PFHxS - perfluorohexanesulfonate

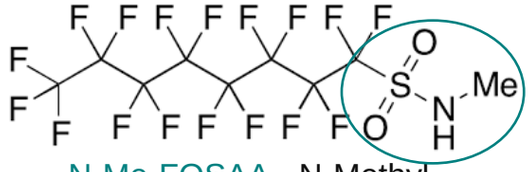
PFOS - perfluorooctanesulfonate

...

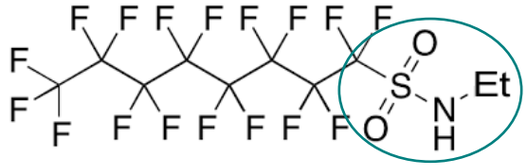
Perfluoroalkyl sulfonamides



FOSA - perfluorooctanesulfonamide

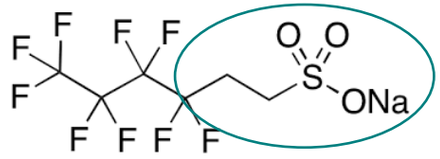


N-Me-FOSAA - N-Methyl-Perfluoroctanesulfonamido acetic acid

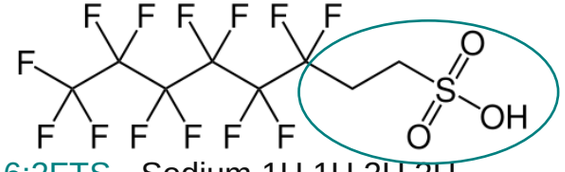


N-Et-FOSAA - N-Ethyl-Perfluoroctanesulfonamido acetic acid

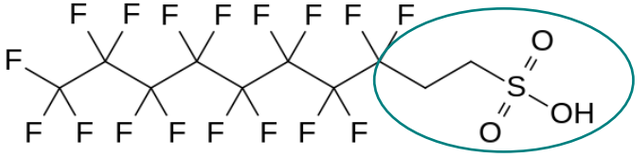
Telomer sulfonates



4:2FTS - Sodium 1H,1H,2H,2H-perfluorohexane sulfonate



6:2FTS - Sodium 1H,1H,2H,2H-perfluorooctane sulfonate



8:2FTS - Sodium 1H,1H,2H,2H-perfluorodecane sulfonate

Current situation:

- Complicated
- Various regulatory initiatives specify their acceptable levels in environmental matrices
- EPA – nonbinding advisory threshold for PFOA and PFOS in water of 70 ng/l
- REACH - The EU has decided to ban 200 PFAS substances in phases, starting February 2023

MEDIA RELEASE / JANUARY 13, 2021

McDonald's announces global ban of toxic chemicals in food packaging

Company eliminating PFAS in packaging materials by 2025

Source: safechemicals.org

NEWS | June 17, 2021

Burger King plans to remove PFAS from food packaging

Research suggests that certain PFAS can lead to increased cholesterol level, kidney and liver problems among other issues.

Burger King plans to eliminate PFAS chemicals from food packaging by the end of the year. Credit: JBers / Flickr.

Source: packaging-gateway.com

PFAS Levels in Different Matrices

Compound	Paper & board (ng/g)		Food stuff (ppt)	Aqueous matrices (ng/L)			
				Ground water (military bases)	Bottled water	Tap water	Surface water
PFBA	3.2 - 290	1.8 - 820	42.9 - 220	3.400 - 57.000	1.3	3.6	13.7 - 98.8
PFPeA	37 - 130	3.2 - 73	78.8 - 89	12.000 - 120.000	1.1	2.7	24.6 - 74.1
PFHxA	2.2 - 405	0.6 - 811	98.6 - 108	19.000 - 350.000	0.58	4.5	1.47 - 12.8
PFHpA	1.3 - 320	3.9 - 15	30 - 46.9	3.300 - 45.000	1.1	3.2	0.12 - 2.23
PFOA	0.1 - 290	2.2 - 56	29 - 169	12.000 - 220.000	3.0	4.9	4.26 - 15.4
PFNA		7 - 9	1400	40 - 390	0.05	4.5	0.022 - 0.64
PFDA	4.3 - 140	2.8 - 44	760 - 3400		0.69	1.0	0.22 - 0.27
PFUdA			990 - 6540		0.39	1.6	
PFDoA			1100		2.9	1.1	0.048 - 1.11
PFTrDA					0.17	0.94	0.09 - 0.28
PFTe[illegible]					0.08	0.62	0.03 - 0.78
L-[illegible]			69	7.100 - 150.000	1.6	1.1	0.95 - 12.6
L-[illegible]			76				
L-PF[illegible]			1270	36.000 - 360.000	0.67	1.0	0.087 - 1.58
L-PFHp[illegible]			181	3.700 - 11.000			
L-PFOS			20.9 - 5000	15.000 - 78.000	0.67	4.1	
L-PFDS						1.5	0.023 - 0.19
4:2FTS				370 - 11.000			
6:2FTS				8.900 - 220.000			

What levels of PFAS are acceptable in food contact materials?

Source: bioringpaper.com

California – banned intentionally added PFAS;
starting January 2023 > 100 ppm
Denmark – 20 ppm

Consumer Reports: 118 products from biggest fast food chains in US

37 – organic fluorine levels >20 ppm
22 – organic fluorine levels >100 ppm

½ at least one product > 100 ppm
Most – one or more products > 20 ppm

PFAS in Paper and Board FCM

Source: papertr.com

PFAS are not present in fresh paper fibers

However…

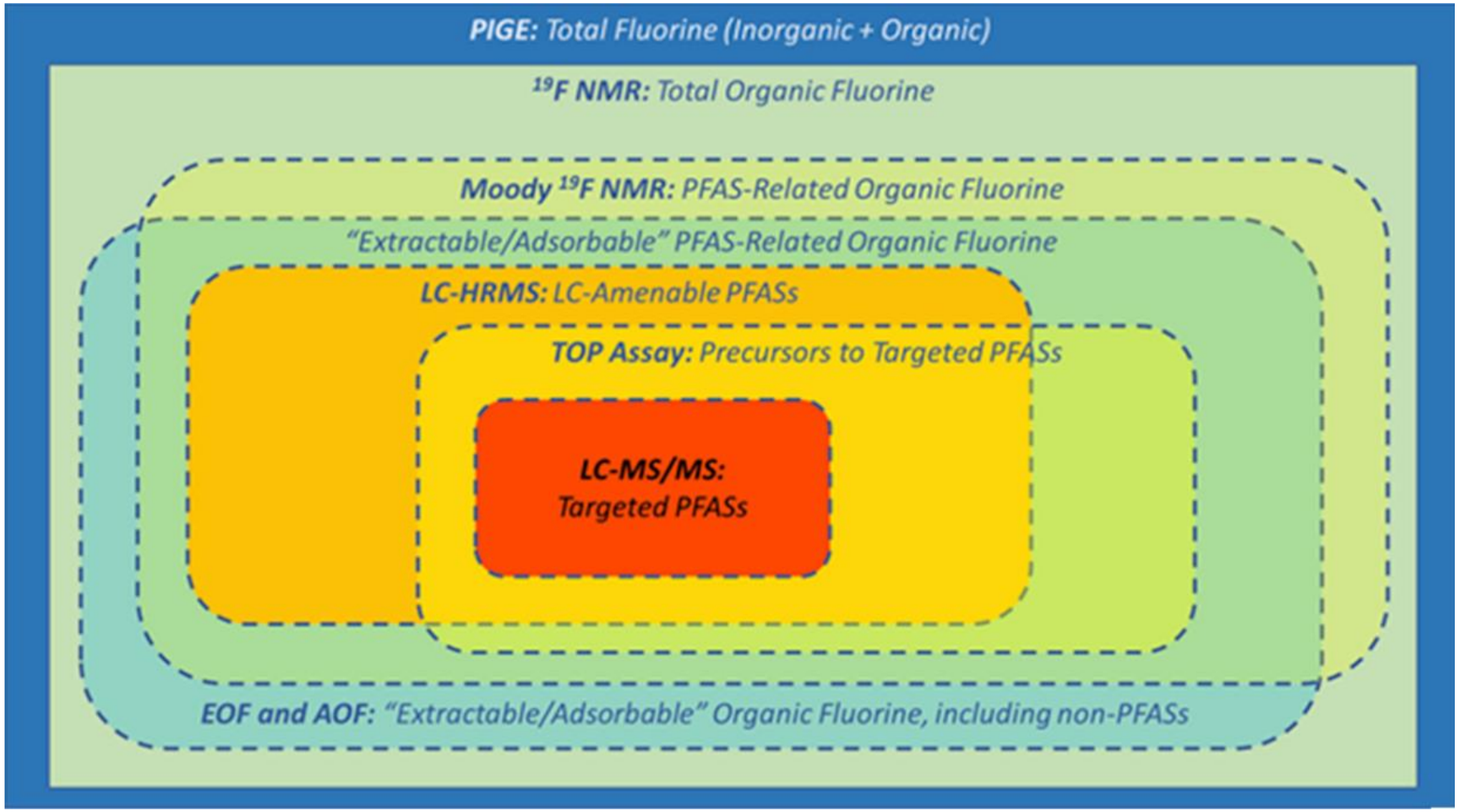
Source: Shutterstock

Source: dreamstime.com

Possible analytical challenges…

- Over 5000 different PFAS so far
- Precursors with known and unknown structures
- Polarity
- Ubiquitous presence in the environment – also in laboratory instrumentation
- Sampling issues:
  - ✓ Personal equipment (clothes treated with PFAS, fabric softeners, hand cremes…
  - ✓ Sampling containers – HDPE or PP
  - ✓ Lab equipment (PTFE tubing, filters, bottle head assembly, multisampler tubing parts…)

PFAS Analysis – an Overview



Source: McDonough, Guelfo et al. 2019 – Measuring Total PFASs in Water

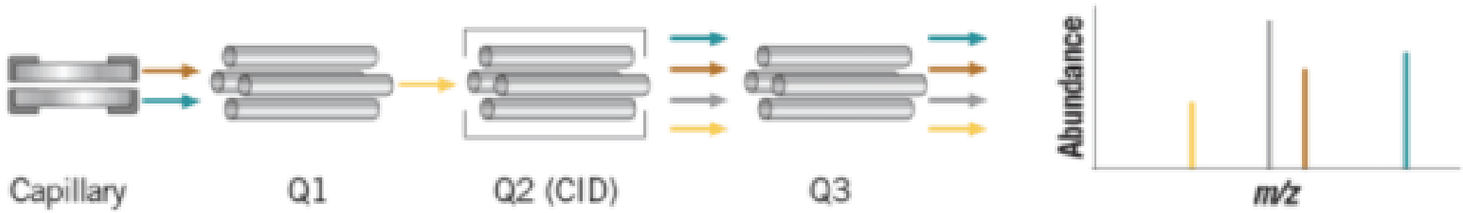
Analytical Approach

High-performance liquid chromatography coupled with triple quadrupole mass spectrometry – LC/MS-MS

Source: shimadzu.com

Separating power of LC & highly sensitive and selective mass analysis capability of triple quadrupole mass spectrometry

Targeted Analysis



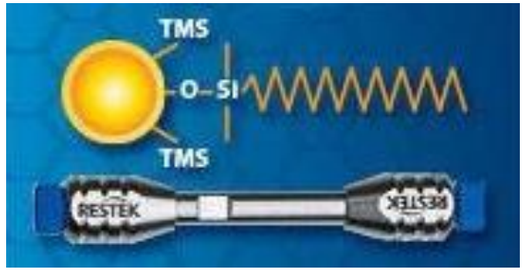
Compound	Acronim	Precursor ion	Product ion
1. Perfluoro-n-butanoic acid	PFBA	212.80	169.10
2. Perfluoro-n-pentanoic acid	PFPeA	262.80	219.10
3. Potassium perfluoro-1-butanesulfonate	L-PFBS	298.90	79.90
4. Sodium 1H.1H.2H.2H-perfluorohexane sulfonate	4:2FTS	326.90	306.90
			80.80
5. Perfluoro-n-hexanoic acid	PFHxA	312.90	268.95
6. Sodium perfluoro-1-pentanesulfonate	L-PFPeS	348.90	80.00
			98.95
7. Perfluoro-n-heptanoic acid	PFHpA	363.00	319.05
			169.10
8. Potassium perfluoro-1-hexanesulfonate	PFHxSK	398.90	80.05
			98.90
9. Sodium 1H.1H.2H.2H-perfluorooctane sulfonate	6:2FTS	426.90	407.10
			80.00
10. Perfluoro-n-octanoic acid	PFOA	413.00	369.10
			169.05
11. Sodium perfluoro-1-heptanesulfonate	L-PFHpS	449.00	80.00
			98.85
			169.15
12. Perfluoro-n-nonanoic acid	PFNA	463.00	419.00
			217.10

Compound	Acronim	Precursor ion	Product ion
13. Potassium perfluorooctanesulfonate	PFOSK	498.90	79.95
			98.90
14. Sodium 1H.1H.2H.2H-perfluorodecane sulfonate	8:2FTS	526.90	506.90
			81.05
15. Perfluoro-n-decanoic acid	PFDA	513.10	469.05
16. Sodium perfluoro-1-nonanesulfonate	L-PFNS	548.90	80.00
			98.90
17. N-Methyl-Perfluoroctanesulfonamido acetic acid	N-MeFOSAA	570.00	419.10
			512.00
			219.10
18. N-Ethyl-Perfluoroctanesulfonamido acetic acid	N-EtFOSAA	584.00	419.05
			526.00
			482.95
19. Perfluoro-1-octanesulfonamide	FOSA	498.00	78.00
20. Perfluoro-n-undecanoic acid	PFUdA	562.80	518.90
			269.00
21. Sodium perfluoro-1-decanesulfonate	L-PFDS	598.90	80.00
			99.00
22. Perfluoro-n-dodecanoic acid	PFDoA	612.90	568.75
23. Perfluoro-n-tridecanoic acid	PFTrDA	662.90	618.95
24. Perfluoro-n-tetradecanoic acid	PFTeDA	713.00	669.00
			168.85
			268.95

LC and MS System Parameters

LC System and Parameters	
LC System:	Shimadzu LCMS-8050
Analytical Column:	Restek Raptor C18 2.7µm 50 x 2.1 mm
Delay Column:	Restek PFAS Delay Column 5 µm x 50 mm x 2.1 mm
Column temperature:	40°C
Injection:	5 µl
Mobile phase	A: 5 mM ammonium acetate
	B: MeOH
Flow rate:	0.4 ml/min
Run time:	10 min

Gradient:	Time (min)	%B
	0	20
	8	95
	8.01	20
	10	20



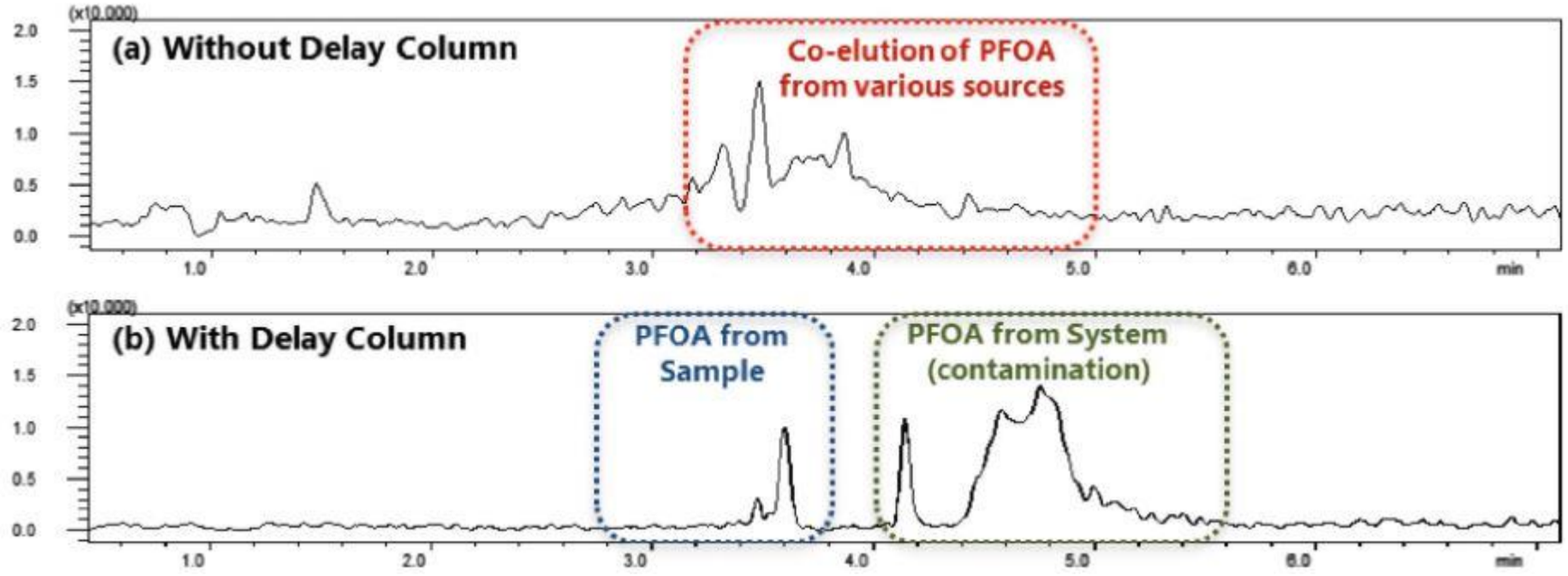
Analytical column

Delay column

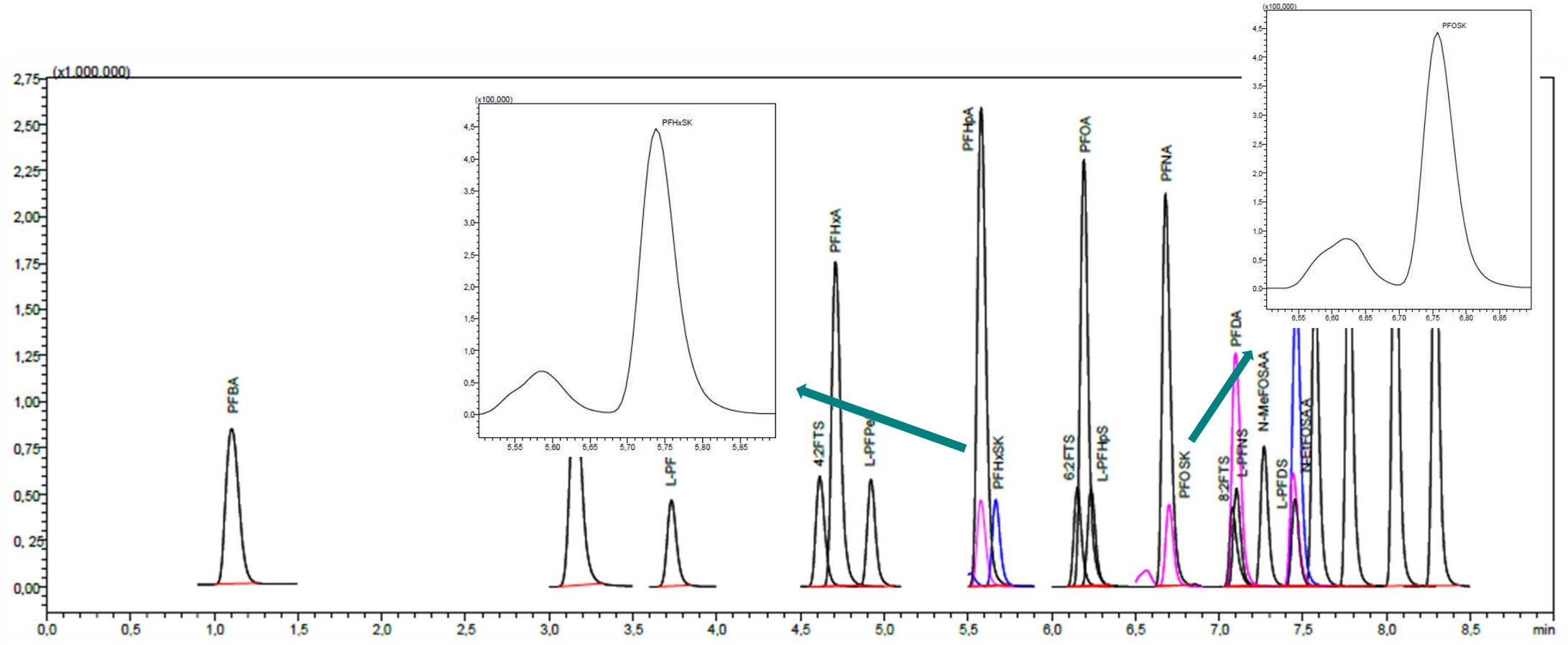
MS Acquisition Parameters	
MS Instrument:	Schimadzu LCMS-8050
Interface:	ESI
Interface Temperature:	300°C
Desolvation Line Temperature:	100°C
Heat Block Temperature:	200°C
Heating Gas Flow:	10 l/min
Drying Gas Flow:	10 l/min
Nebulizing Gas Flow:	2 l/min
Interface Voltage	-0.5 kV

Sorry for the delay….

- PTFE tubing is common in mobile phase lines
- PFAS delay column is installed between the mixer and injector
- Not an analytical column
- Prevents PFAS upstream of the injector from coeluting



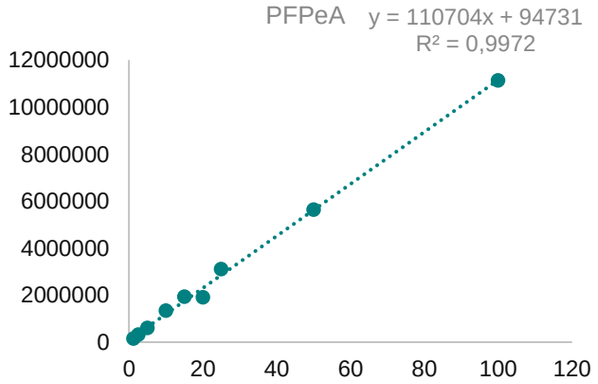
LC Separation

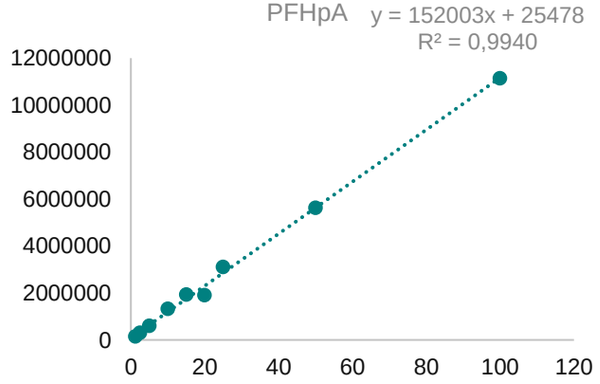


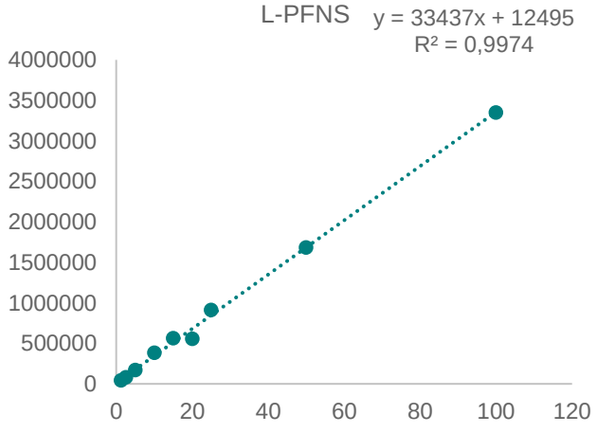
Linearity and Reproducibility

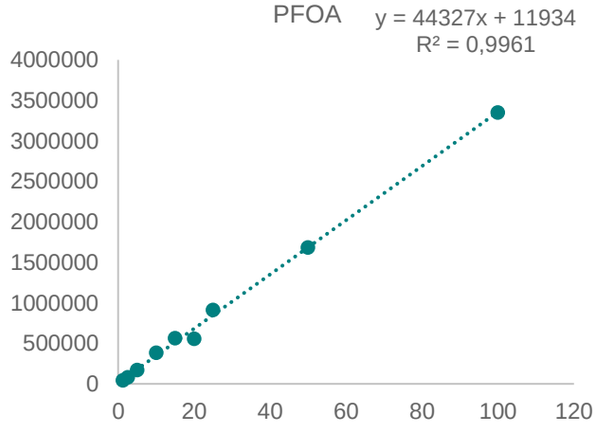
High range linearity: 9 calibration points: 1.25 – 100 pg/µl
Low range linearity: 10 calibration points: 20 – 0.01 pg/µl

	High concentration range		Low concentration range	
Compound	Linearity (R^2)	RSD%	Linearity (R^2)	RSD%
PFBA	0.9984	0.94	0.9921	1.39
PFPeA	0.9982	1.96	0.9916	2.00
L-PFBS	0.9990	1.15	0.9857	2.70
4:2FTS	0.9950	1.09	0.9916	3.89
PFHxA	0.9966	1.09	0.9931	4.71
L-PFPeS	0.9991	0.98	0.9860	5.26
PFHpA	0.9956	1.00	0.9940	2.93
PFHxSK	0.9991	1.03	0.9821	5.43
6:2FTS	0.9944	1.19	0.9956	3.30
PFOA	0.9883	1.00	0.9961	2.05
L-PFHpS	0.9988	1.33	0.9850	3.75
PFNA	0.9857	0.91	0.9970	2.24
PFOSK	0.9991	1.04	0.9861	6.20
8:2FTS	0.9767	1.78	0.9980	5.10
PFDA	0.9749	1.03	0.9870	3.95
L-PFNS	0.9988	3.35	0.9974	3.37
N-MeFOSAA	0.9993	2.31	0.9852	10.21
N-EtFOSAA	0.9904	3.06	0.9840	2.90
FOSA	0.9992	0.84	0.9945	4.95
PFUdA	0.9782	1.78	0.9976	5.09
L-PFDS	0.9984	1.73	0.9870	3.40
PFDoA	0.9972	1.82	0.9891	5.54
PFTrDA	0.9981	4.78	0.9833	9.52



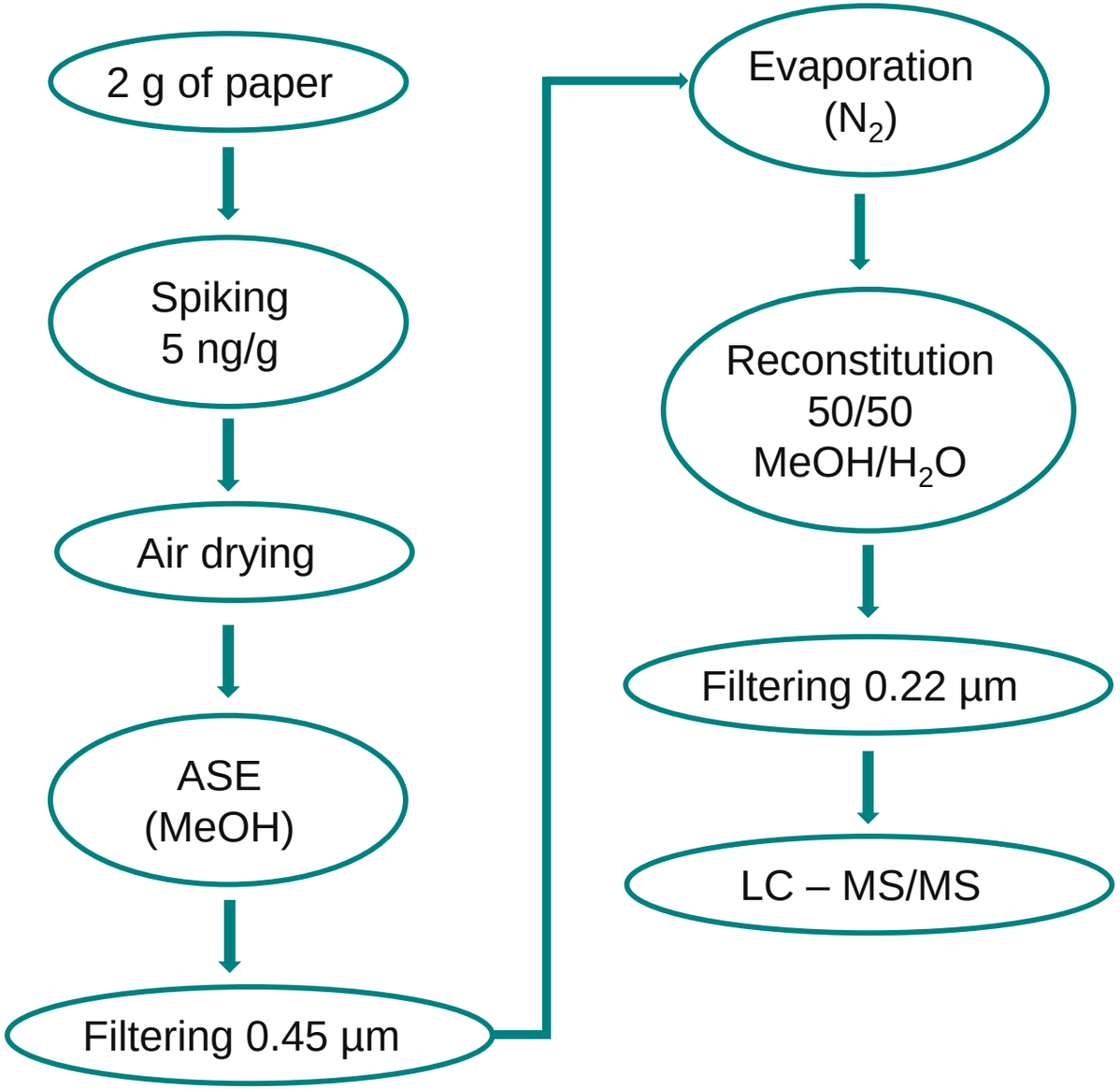






Extraction Experiments

Paper sample:
recycled paper 70 g/m^2 (no PFAS)



Extraction – linearity and recovery

- Spiking the sample with PFAS mixture:
  100, 50, 20, 10, 5, 2.5, 1, 0.5 and 0.1 ng/g
- Extraction: ASE with MeOH
- Average linearity: **0.9705**
- Average recovery: **88.7%**

What is next?

- ✓ Optimization of the method (extraction, linearity, recovery…)
- ✓ LOQ and LOD
- ✓ Analysis of real samples (paper straws, paper cups, fast food packaging…)

Compound	Linearity (R^2)	Recovery (%)
PFPeA	0.9933	84.6
L-PFBS	0.9933	91.4
4-2FTS	0.9877	89.2
PFHxA	0.9933	89.3
L-PFPeS	0.9932	89.3
PFHpA	0.9932	86.3
PFHxSK	0.9934	90.3
6:2FTS	0.9880	85.3
PFOA	0.9929	87.8
L-PFHpS	0.9929	89.7
PFOSK	0.9922	90.4
8:2FTS	0.9828	85.3
PFDA	0.9898	89.0
L-PFNS	0.9901	88.9
N-MeFOSAA	0.9900	86.7
N-EtFOSAA	0.9818	88.9
FOSA	0.9889	93.2
PFUdA	0.9853	89.4
L-PFDS	0.9868	90.5
PFDoA	0.9710	89.4
PFTrDA	0.9050	90.4
PFTeDA	0.6665	89.6

Conclusions

- ✓ Despite their benefits, PFAS pose a risk worth measuring
- ✓ Method for specifically identifying and quantifying PFAS in food packaging
- ✓ Shimadzu LCMS-8050 reliably measures PFAS up to 0.01 pg/µl
- ✓ Suitable for high-throughput multi-component analysis
- ✓ Integral part of a simple and efficient method for monitoring and quantification of PFAS

Acknowledgements

Institute of Analytical
Chemistry and Food Chemistry

Prof. Erich Leitner

Thank you for your attention

Presenter:

Milica Jovanovic MSc
Technical University of Graz
Institute for Analytical Chemistry and Food Chemistry
8010 Graz/Austria
Tel: 0316 873-32517
Email: milica.jovanovic@tugraz.at