TRAJAN

PFAS-Analysis in Environmental Matrices via Online SPE LC-MS/MS

Lilit Ispiryan, Workflow Development Specialist | Environmental Measurement Symposium | Garden Grove, CA | 5th August 2024

My background

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Workflow Development Specialist
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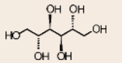
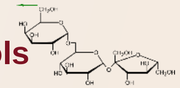
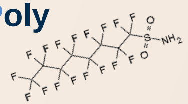
- MSc in Food Chemistry (2011-2016)
  - Technical University Dresden, Germany
- PhD in Food Science – Research and development of low FODMAP foods for IBS-patients (2017-2021)
  - University College Cork, Ireland
- Postdoctoral researcher – Research of plant-based proteins (2021-2022)
  - University College Cork, Ireland
- Since November 2022 – LC-MS Application specialist with Axel Semrau by Trajan

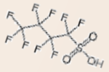


Fermentable
Oligosaccharides
Disaccharides
Monosaccharides
And
Polyols



Per- and Poly
Fluoro
Alkyl
Substances



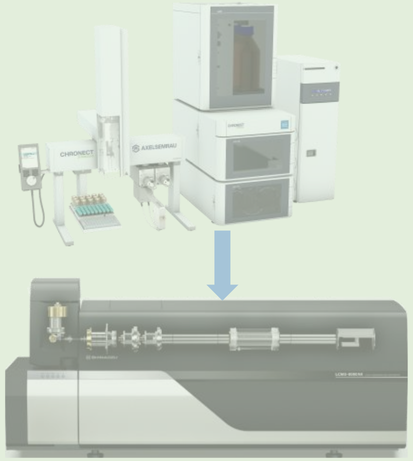


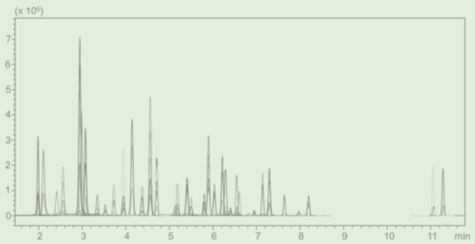
from one acronym to another ;)

Overview

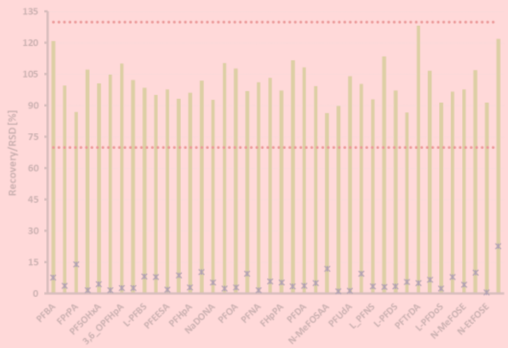
What do we do?

Development of PFAS analytics using CHRONECT Symbiosis





Potential of CHRONECT Symbiosis for efficient PFAS analysis in liquid and solid matrices



What do we do at Trajan site Axel Semrau?

We sense good chemistry! ☺

Develop complete “Turn-Key” solutions with a focus on automation and chromatography

- Axel Semrau founded in 1981
  Active in development, distribution and support for chromatography including sample preparation
- Since November 2021
  Part of the Trajan family
- Located in Sprockhövel, between Dortmund and Wuppertal
- ~60 employees: technical staff mostly chemists, electronic & IT engineers, software development, experienced direct sales

Focus on delivery of reliable routine analysis systems with special hardware and software development

Examples for complete solutions:
- Online LC-GC-FID analysis of MOSH/MOAH
- Fully automated workflow for MCPD analysis in oil and fat
- Online LC-GC-MS analysis of PAH in food and edible oils

In the pipeline

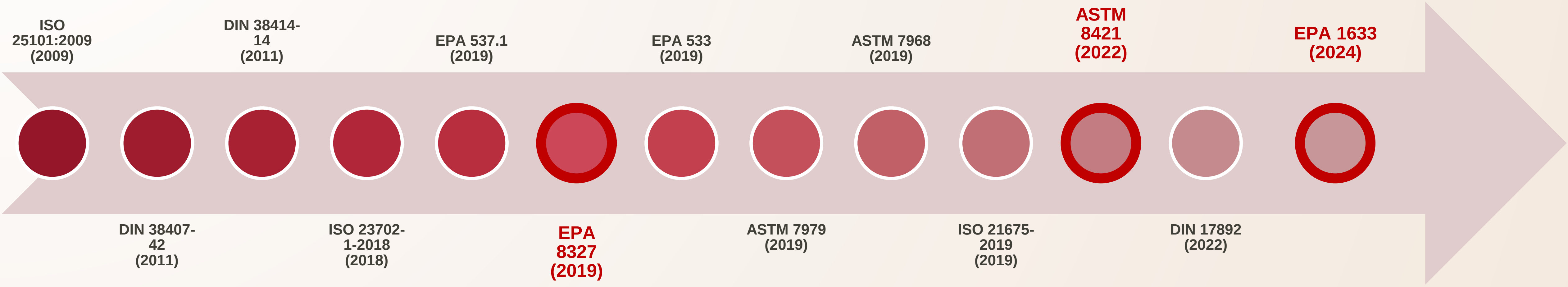
Currently in development:

Automation of PFAS Analysis in environmental matrices via online SPE LC-MS/MS in collaboration with US partners iChrom Solutions, Helmer Korb

iChrom SOLUTIONS
MAKING CONNECTIONS TO AUTOMATION

Overview official methods in US, EU, Germany

What is the basis of our method development?



US EPA 1633 is most recent method, has most extensive list of analytes, complex procedures for liquid & solid enviromental samples, that could benefit from automation and online SPE LC-MS/MS approach

A. For water: combined approach of co-solvation* & online SPE LC-MS/MS with 1633 compound list

B. For soil: simplification of 1633 method‘s complexity through automation-approach

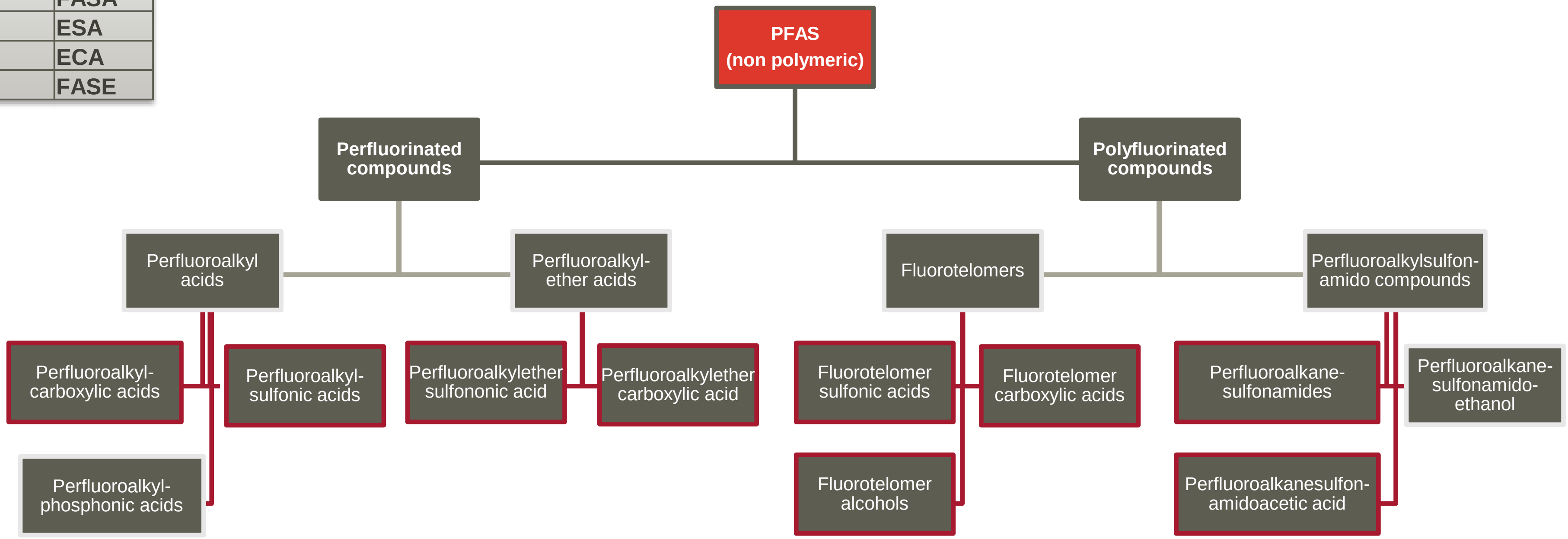
* co-solvation = dilution with 50 % MeOH to stabilise analytes, then typically direct LC-MS analysis

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

WELLINGTON LABORATORIES
Standards for Environmental Testing and Research

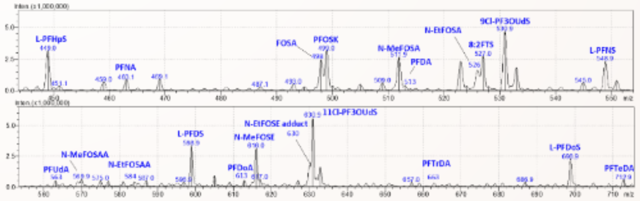
classes of PFAS	Perfluoroalykcarboxylic acids	CA
	Perfluoroalkanesulfonic acids	SA
	Fluorotelomer sulfonic acids	FTS
	Fluorotelomer carboxylic acids	FTC
	Perfluoroalkanesulfonamidoacetic acid	SAA
	Perfluoroalkanesulfonamides	FASA
	Perfluoroalkylether sulfononic acid	ESA
	Perfluoroalkylether carboxylic acid	ECA
	Perfluoroalkanesulfonamidoethanol	FASE

- 40 PFAS analytes from 9 different chemical classes
- Additional 31 isotopically labelled analogues



Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

Confirmation of all parent ions in full scans:



Selection of Analytes → Full Scan of individual mixtures → Tuning of analytes = MRM method → SPE – development

Labsolutions Realtime Analysis Feature: MRM Optimisation Assistant

MRM Optimisation

m/z fine tuning & voltage optimization for all precursor ions & product ions listed in EPA 1633

Optimization for Method

LCMS 8060NX conditions

MS mode: full scan
Ionisation: ESI negative ionization
Interface voltage: -1 kV
DL temp: 200 °C
Heat block: 200 °C
Interface: 200 °C
Nebu. gas: 3 L/min
Drying gas: 5 L/min
Heating gas: 15 L/min
Scan range: 200-800 m/z
Scan speed: 7500 u/sec

LC Nexera conditions

Injection volume: 10 µL
FIA: Flow Injection Analysis **AND** more difficult analytes: including gradient separation
Flow rate: 0.4 mL/min

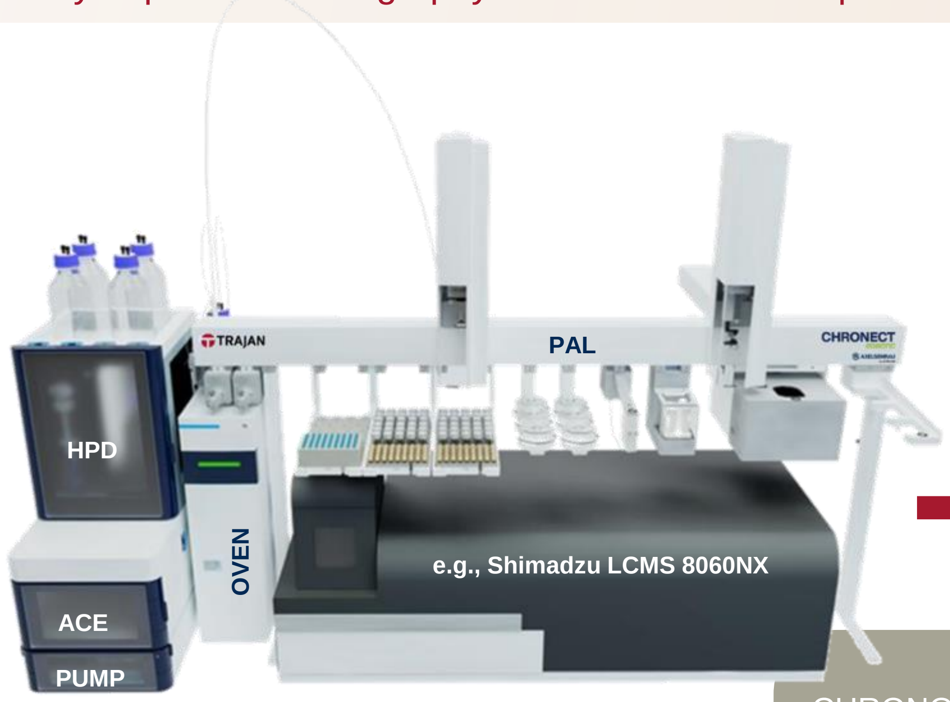
A = 2 mM NH_4OAc in 95:5 UPW:ACN
B = ACN

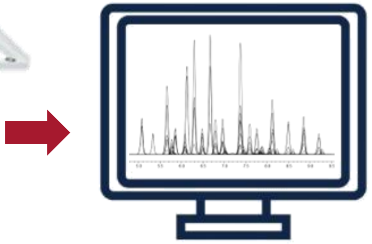
ID#	Acronym	Synonym	Name	Class	Cx	$[M-H]^-$	m/z precursor	m/z QI	m/z RI	m/z RI2
1	**MPFBA**		Perfluoro-n-($^{13}C_4$)butanoic acid	CA	C4	$[C_4F_7O_2]^-$	216.90	171.90	-	
2	**PFBA**		Perfluoro-n-butanoic acid	CA	C4	$[C_4F_7O_2]^-$	213.30	169.10	-	
3	**M3PFBA**		Perfluoro-n-(2,3,4-$^{13}C_3$)butanoic acid	CA	C4	$[C_4F_7O_2]^-$	216.00	171.95	-	
4	**PF4OPeA**	**PFMPA**	Perfluoro-4-oxapentanoic acid	ECA	C4	$[C_4F_7O_3]^-$	229.20	85.10	-	
5	**FPrPA**	**3:3 FTCA**	3-Perfluoropropyl propanoic acid	FTC	C6	$[C_6H_4F_7O_2]^-$	241.20	116.95	176.85	
6	**PFPeA**		Perfluoro-n-pentanoic acid	CA	C5	$[C_5F_9O_2]^-$	263.20	218.95	69.10	
7	**M5PFPeA**		Perfluoro-n-($^{13}C_5$)pentanoic acid	CA	C5	$[C_5F_9O_2]^-$	268.00	222.90	-	
8	**PF5OHxA**	**PFMBA**	Perfluoro-5-oxahexanoic acid	ECA	C5	$[C_5F_9O_3]^-$	279.20	85.00	-	
9	**M2-4:2FTS**		Sodium 1H, 1H, 2H, 2H-perfluoro-(1,2-$^{13}C_2$)hexanesulfonate	FTS	C6	$[C_6H_4F_9SO_3]^-$	329.10	81.00	308.90	
10	**4:2FTS**		Sodium 1H, 1H, 2H, 2H-perfluorohexanesulfonate	FTS	C6	$[C_6H_4F_9SO_3]^-$	327.10	306.90	81.00	
11	**3,6-OPFHpA**	**NFDHA**	Perfluoro-3,6-dioxaheptanoic acid	ECA	C5	$[C_5F_9O_4]^-$	200.9 (295‡)	85.00	85.00	
12	**M3PFBS**		Sodium perfluoro-1-(2,3,4-$^{13}C_3$)butanesulfonate	SA	C4	$[C_4F_9SO_3]^-$	302.10	80.00	99.00	
13	**L-PFBS**		Potassium perfluoro-1-butanesulfonate	SA	C4	$[C_4F_9SO_3]^-$	299.10	80.00	99.20	
14	**M5PFHxA**		Perfluoro-n-(1,2,3,4,6-$^{13}C_5$)hexanoic acid	CA	C6	$[C_6F_{11}O_2]^-$	318.00	272.90	120.10	
15	**MPFHxA**		Perfluoro-n-(1,2-$^{13}C_2$)hexanoic acid	CA	C6	$[C_6F_{11}O_2]^-$	315.20	270.10	119.10	
16	**PFHxA**		Perfluoro-n-hexanoic acid	CA	C6	$[C_6F_{11}O_2]^-$	313.20	268.75	119.10	
17	**M3HFPO-DA**		2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)($_{13}C_3$)propanoic acid	ECA	C5	$[C_5F_{11}O]^-$	287.00	169.00	185.00	
18	**HFPO-DA**	**GenX,**	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	ECA	C5	$[C_5F_{11}O]^-$	285.20	169.00	185.00	
19	**PFEESA**		Potassium perfluoro(2-ethoxyethane)sulfonate	ESA	C4	$[C_4F_9SO_4]^-$	315.00	134.90	69.05	82.90
20	**FPePA**	**5:3 FTCA**	3-Perfluoropentyl propanoic acid	FTC	C8	$[C_8H_4F_{11}O_2]^-$	341.00	236.90	256.95	216.90
21	**PFHpA**		Perfluoro-n-heptanoic acid	CA	C7	$[C_7F_{13}O_2]^-$	363.10	318.95	169.00	
22	**M4PFHpA**		Perfluoro-n-(1,2,3,4-$^{13}C_4$)heptanoic acid	CA	C7	$[C_7F_{13}O_2]^-$	367.00	321.90	-	
23	**L-PFPeS**		Sodium perfluoro-1-pentanesulfonate	SA	C5	$[C_5F_{11}SO_3]^-$	349.00	80.05	98.90	
24	**NaDONA**		Sodium dodecafluoro-3H-4,8-dioxanonanoate	ECA	C7	$[C_7HF_{11}O_4]^-$	376.80	85.05	251.05	
25	**M2-6:2FTS**		Sodium 1H, 1H, 2H, 2H-perfluor-(1,2-$^{13}C_2$)ooctanesulfonate	FTS	C8	$[C_8H_4F_{13}SO_3]^-$	429.10	81.10	409.00	
26	**6:2FTS**		Sodium 1H, 1H, 2H, 2H-perfluorooctanesulfonate	FTS	C8	$[C_8H_4F_{13}SO_3]^-$	427.00	406.95	81.00	
27	**MPFOA**		Perfluoro- n-(1,2,3,4-$^{13}C_4$)octanoic acid	CA	C8	$[C_8F_{15}O_2]^-$	417.00	372.00	-	
28	**M8PFOA**		Perfluoro- n-($^{13}C_8$)octanoic acid	CA	C8	$[C_8F_{15}O_2]^-$	421.00	375.90	-	
…										
71	**N-EtFOSA**		N-Ethylperfluoro-1-octanesulfonamide	FASA	C10	$[C_{10}H_5F_{17}NO_2S]^-$	526.00	218.95	119.05	168.90

Our Goal: automation of PFAS analytics using CHRONECT Symbiosis

Online SPE LC-MS/MS (automated Solid Phase Extraction followed by Liquid Chromatography and Tandem Mass Spectrometry)

- CHRONECT robotic PAL3: 160 cm Dual head PAL
  - automated sample preparation prior to online SPE LC-MS/MS and autosampler for direct and SPE injections
  - equipped with a variety of tools and modules, that are configured individually to meet the requirements of PFAS analysis: e.g., vortexer to resolubilize analytes prior to injection, PTFE tubing-free modules and tools; automated extraction of solid samples, etc.
- High-Pressure-Dispenser (HPD)
  - syringe pump connected to ACE and injection valve; delivers solvents and sample through cartridges, elutes the cartridge in peak focusing mode for PFAS analysis
  - equipped with WAX-online trap between HPD and injector for cartridge wash/condition/load
- Automated Cartridge Exchanger (ACE)
  - places cartridges in flow path and returns them into tray; 4 high-pressure valves set the flow path
  - Cartridges: Polymer WAX, ~3 mg sorbent material; 10x1 mm; housing material: PEEK
- SPH1299 Pump
  - can elute the cartridge depending on flow path setting: in peak focusing mode for PFAS analysis LC gradient merged with cartridge elution flow
  - PTFE eluent tubings + filters replaced PEEK tubings and stainless-steel frits, WAX-online trap instead 'classic' delay column
- Mistral – Column oven
  - PROTECOL C18 H125 150 mm x 2.1 mm analytical column
- Shimadzu LCMS 8060 NX





CHRONOS

- controls all robotic samplers & modules of different manufacturers
- intelligent, overlapping time schedules to improve throughput
- connects to most chromatography data systems

Our Goal: automation of PFAS analytics using CHRONECT Symbiosis

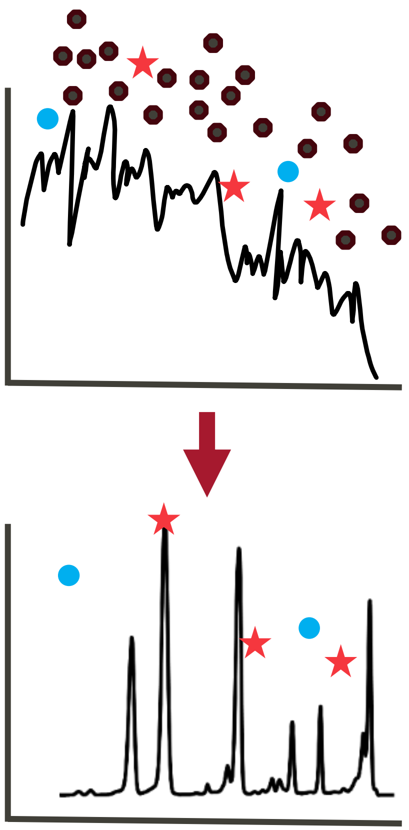
Online SPE LC-MS/MS: SPE (solid phase extraction) = sample preparation method

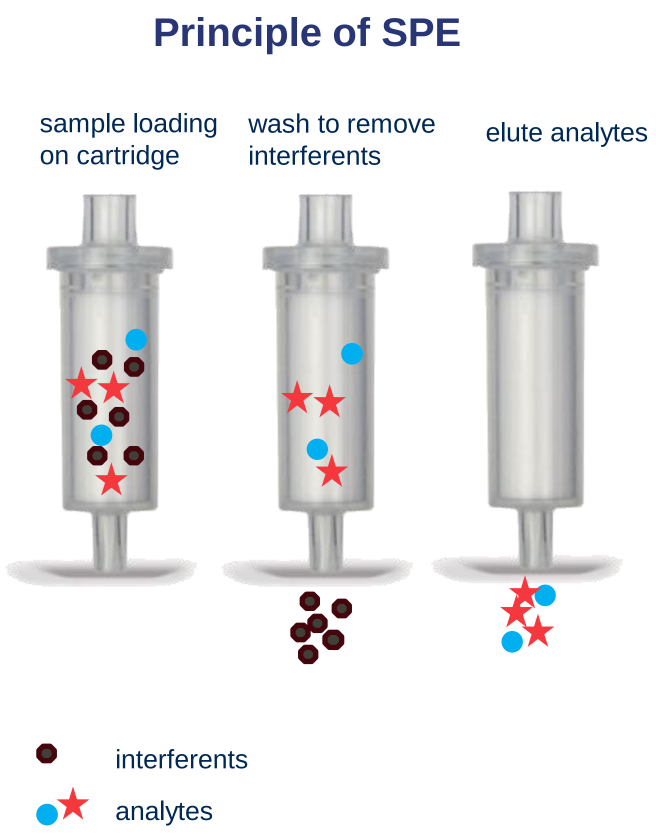
Why sample preparation

> Less interference in the detector
> Enhanced column life-time
> Enhance sensitivity
> Reduce matrix effects
> Reduce ion suppression
> Sample concentration

Sample preparation technologies

> Protein precipitation
> Liquid-Liquid Extraction
> **Solid Phase Extraction**



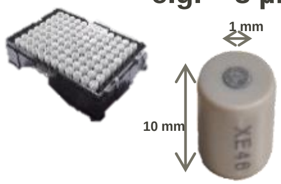


Our Goal: automation of PFAS analytics using CHRONECT Symbiosis

Online SPE LC-MS/MS (automated Solid Phase Extraction followed by Liquid Chromatography and Tandem Mass Spectrometry)

Benefits of online SPE LC-MS/MS

online SPE cartridge
e.g. ~ 8 µL volume



manual SPE cartridge
e.g. 6 mL volume

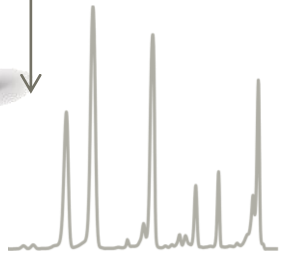
e.g. 10 cm

- reduced matrix interference
- more sensitivity & selectivity
- sample concentration
  - (high injection volumes & still good chromatography)
- longer system lifetime

analytical advantage of online SPE vs. direct injection

- less solvent & material usage
- less labor
- less human error
- lower costs

great economical & ecological advantage of online SPE vs. manual full size SPE



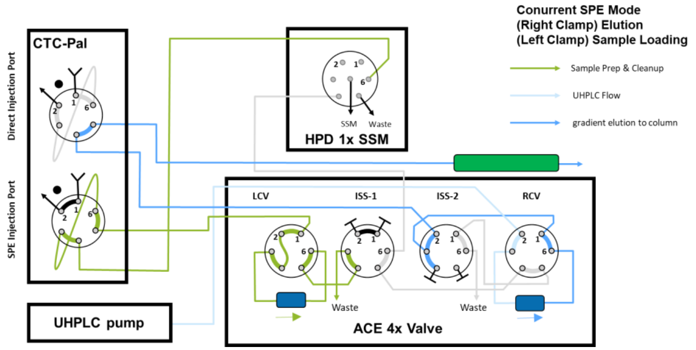
capacity of online cartridge may not be comparable to manual SPE: 3 mg sorbent vs. e.g. 300 mg

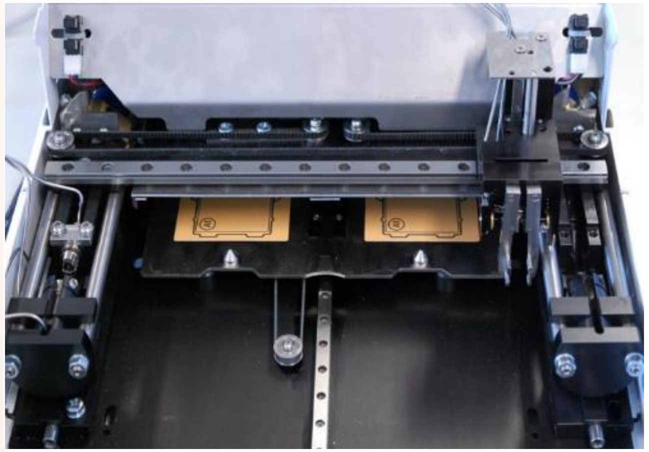
but: all analytes loaded on the cartridge are eluted directly onto column

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

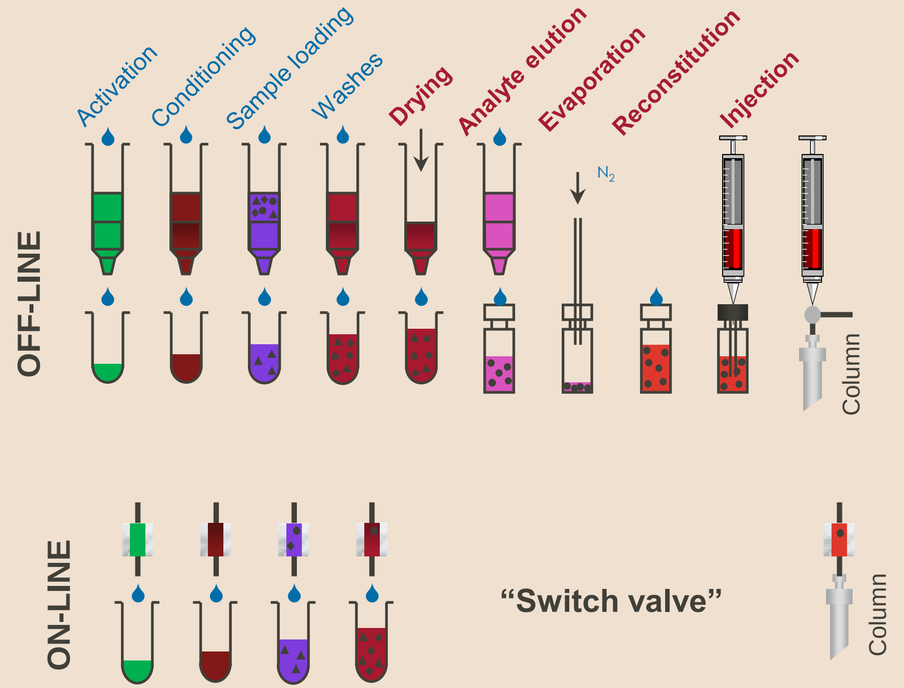
Selection of Analytes → Full Scan of individual mixtures → Tuning of analytes = MRM method → **SPE – development**

CHRONECT Symbiosis PFAS Workstation





Principle of online SPE



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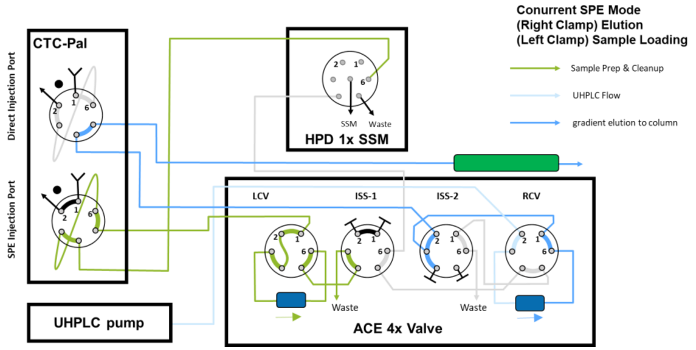
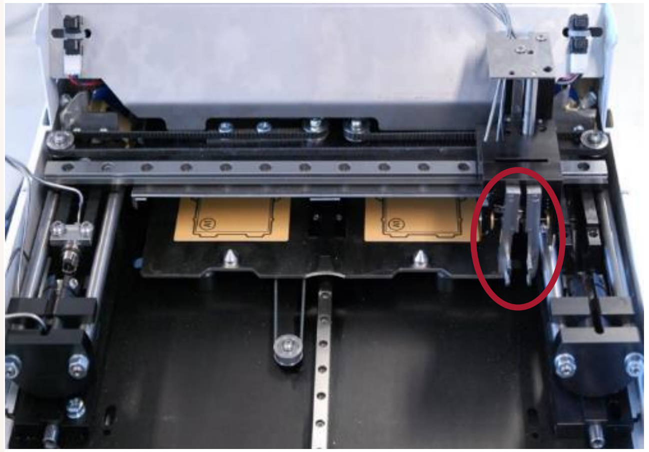
CHRONECT Symbiosis PFAS Workstation



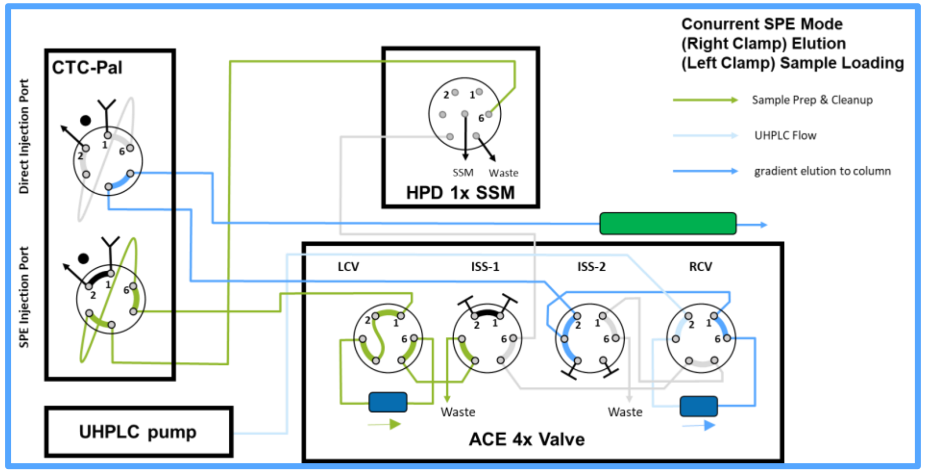


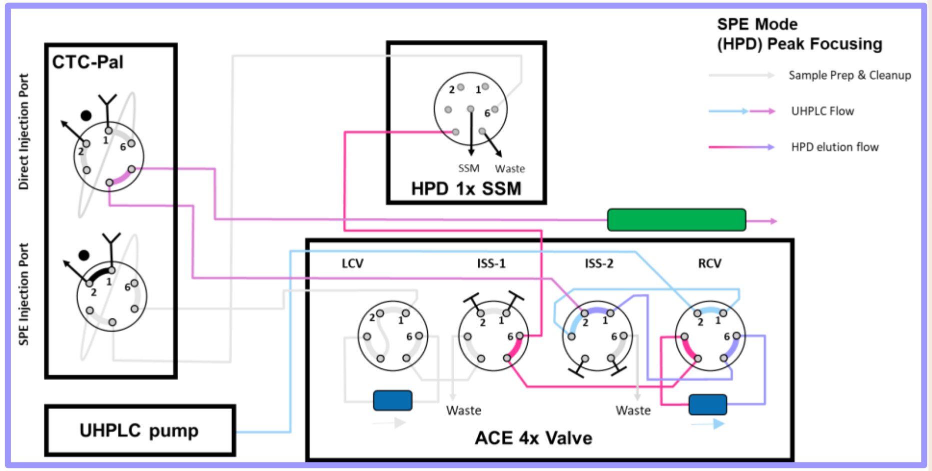
Principle of online SPE

- valve on HPD, 4 valves on ACE and PAL-injection valves set the flow path
- sample is loaded into loop in PAL injector
- gripper places cartridge into left clamp
- solvents for cleaning, conditioning and equilibration are pushed through cartridge into waste via port 6 of the HPD
- SPE injection valve switches into inject-position and sample is pushed through onto cartridge via HPD port 6
- elution of cartridge in right clamp
  - with LC gradient (standard flow path SPE)
  - with HPD **or** additional pump, merging LC flow towards column

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

CHRONECT Symbiosis PFAS Workstation



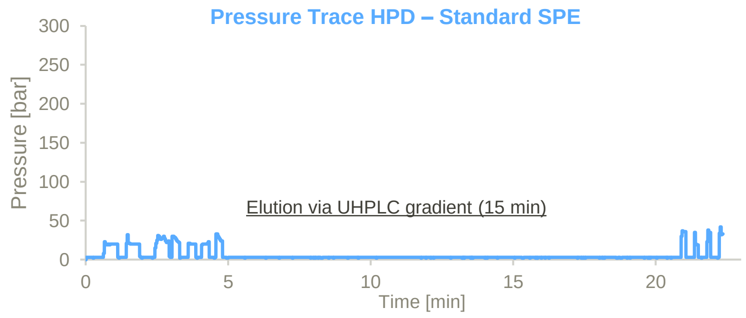


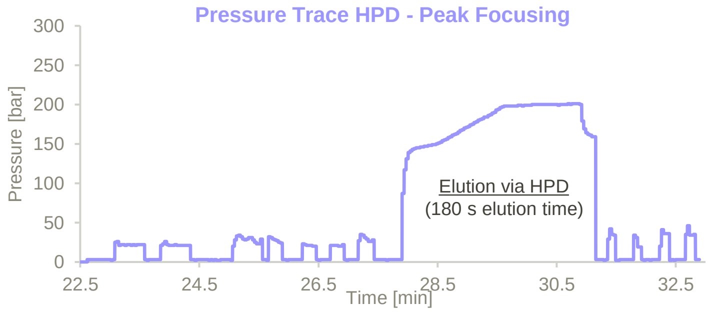
Standard flow path SPE
elution of the cartridge with LC gradient

- **mobile phase must be strong enough to elute the cartridge**

Peak Focusing SPE
elution of the cartridge **with HPD or 2nd pump**,
merged in ISS-2 valve with LC flow

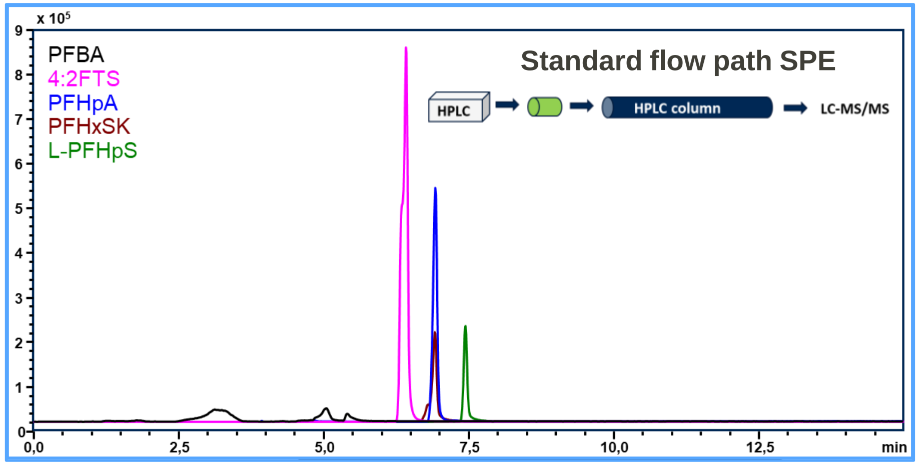
- **when system pressure below 300 bar elution with HPD, otherwise additional pump**

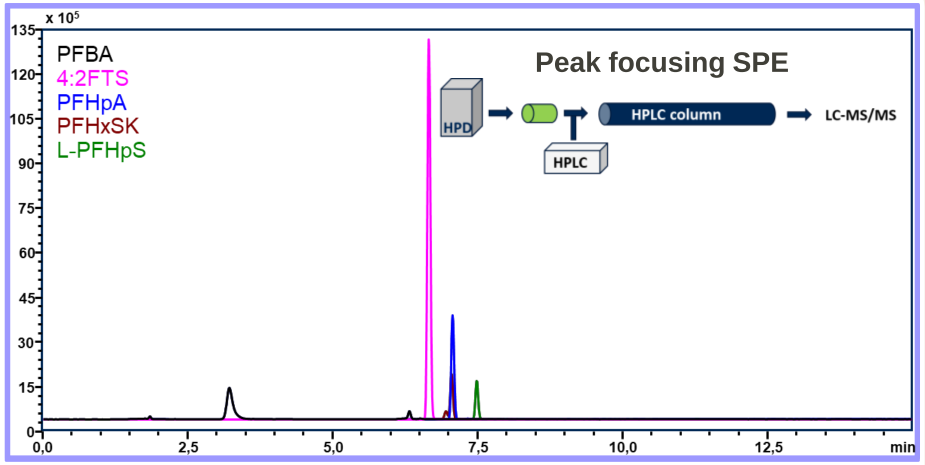




Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

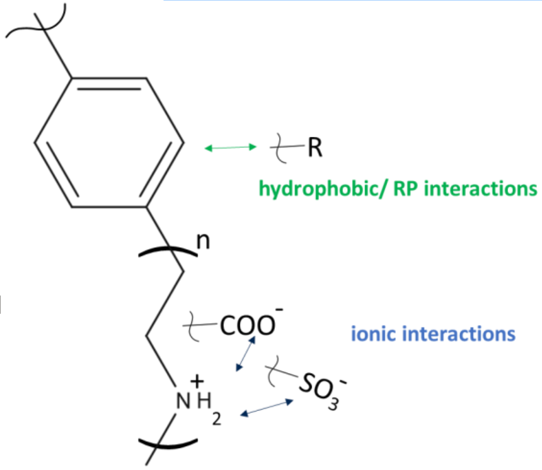
CHRONECT Symbiosis PFAS Workstation





Cartridge:
WAX = weak anion exchanger

- mixed mode for strong acids
- protonated at low to neutral pH
- elution with basic methanol deprotonates amine group and releases analytes



- charged, most acidic PFAS are best retained on WAX material through ionic interactions
- **only eluted at high pH with MeOH**

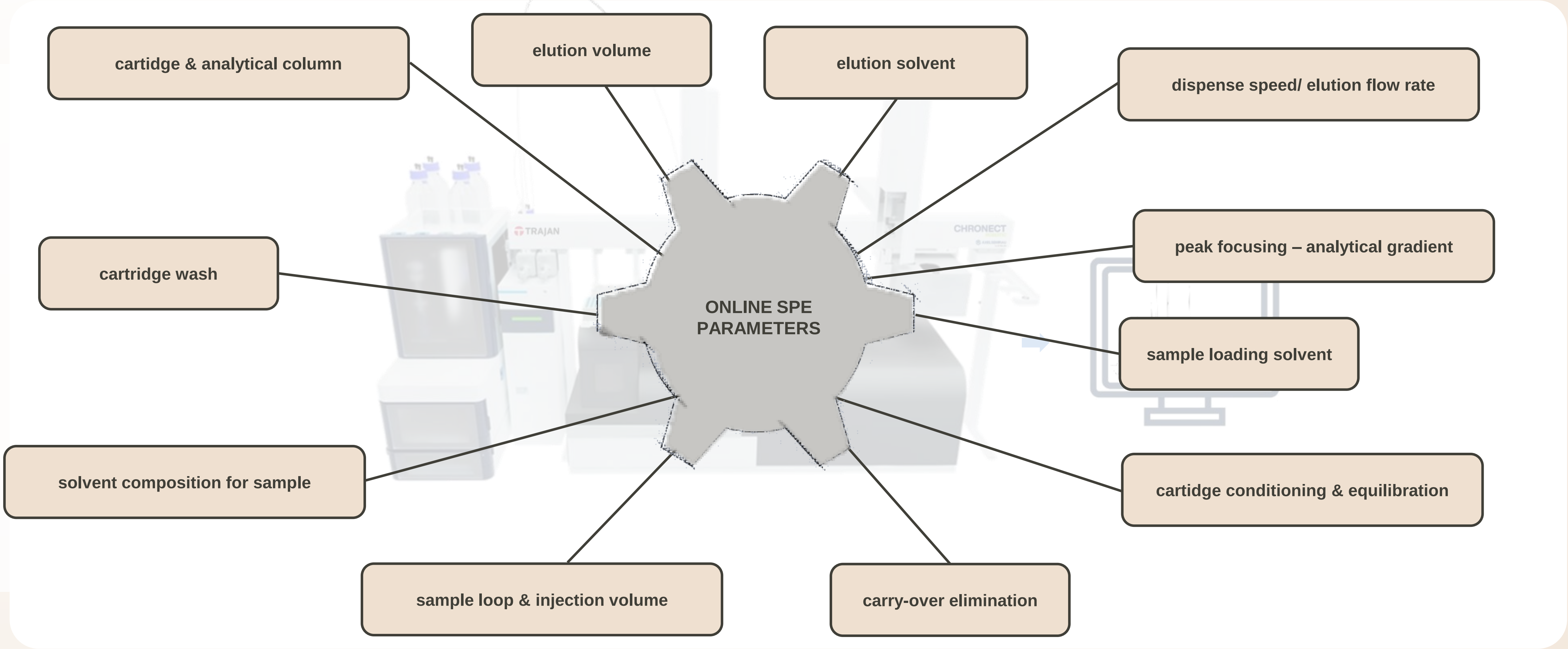
- uncharged PFAS are retained through hydrophobic interactions, but easily eluted with MeOH

Analytical columns for PFAS:
RP C18-phases

- different SPE and analytical column chemistries
- strong basic mobile phase rarely compatible with C18 column
- PFAS have broad range of polarities → via peak focusing all PFAS eluted off cartridge, „accumulated“ at column start, separated through gradient
- peak focusing is resulting in sharper peaks & less tailing

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

WATER ANALYTICS - online SPE method development

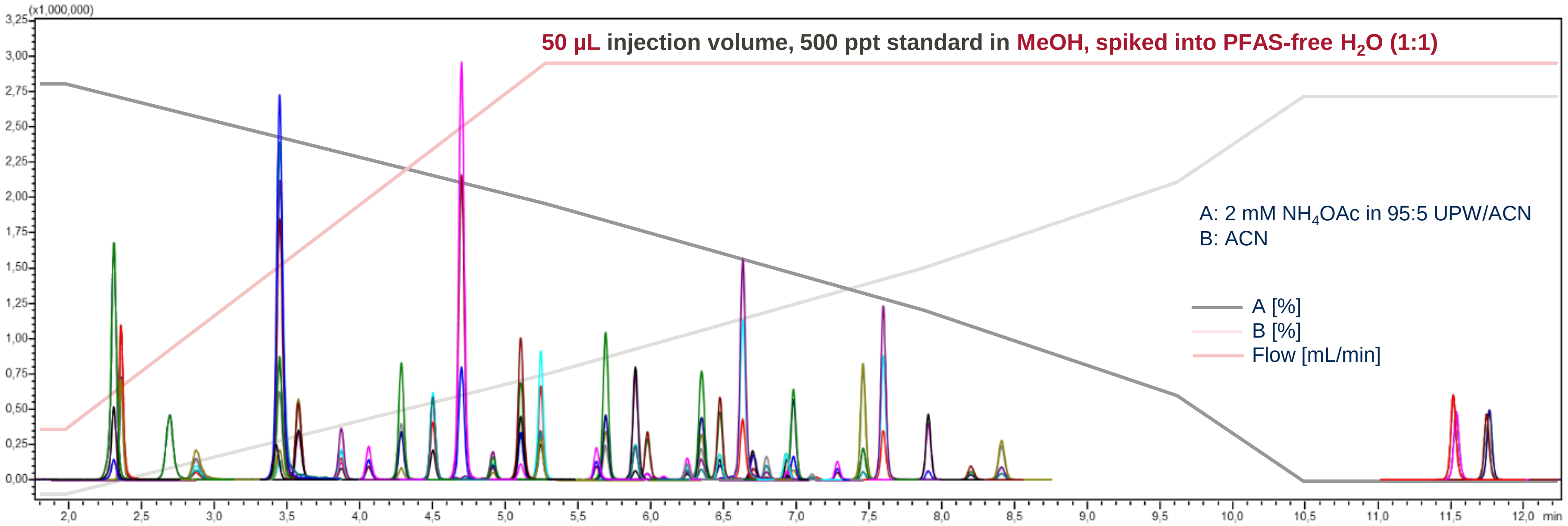


Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

WATER ANALYTICS - online SPE method development

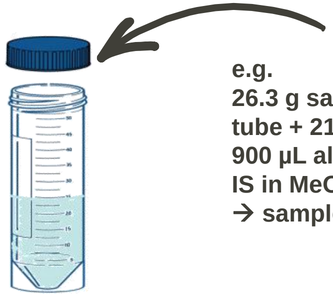
Optimised SPE method

1. Cartridge conditioning	• 2 % NH_3 (NH_4OH) in MeOH • 1:1 0.1 M FA:MeOH, then MeOH • 0.3 M FA
2. Sample loading	• Overfill injection in loop (50 µL) • Loading on cartridge with UPW
3. Cartridge wash	• Rinse solution: 1:1 0.1 M FA:MeOH
4. Elution	• 8 min via HPD with 2 % NH_3 in MeOH (800 µL mixing in with gradient)
5. Cartridge wash	• MeOH, UPW, 2 % NH_3 in MeOH



„Dilute & shoot“ approach combined with online SPE LC-MS/MS

- sampling of water sample in pre-weighed PP container, addition of MeOH to entire sample to reach 50 % MeOH content, stabilizing and resolubilizing potential surface-adsorbed analytes



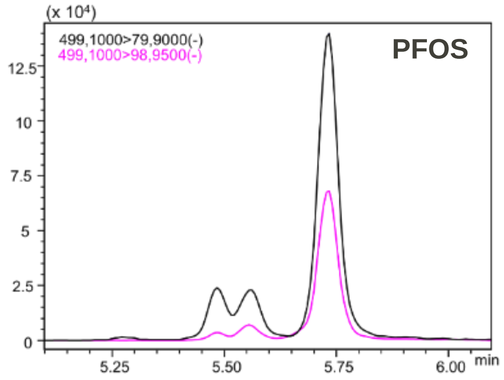
e.g.
26.3 g sample in pre-weighed PP tube + 21 mL MeOH
900 µL aliquot in LC vial + 100 µL IS in MeOH
→ sample contains 50 % MeOH

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

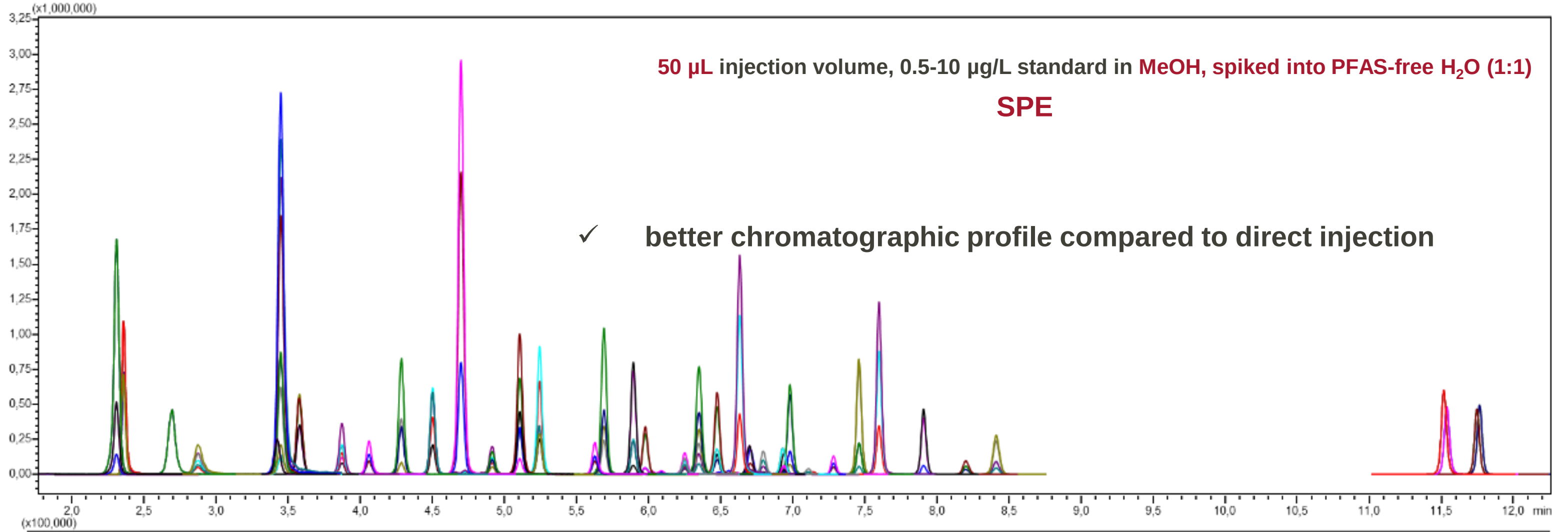
WATER ANALYTICS - online SPE method development

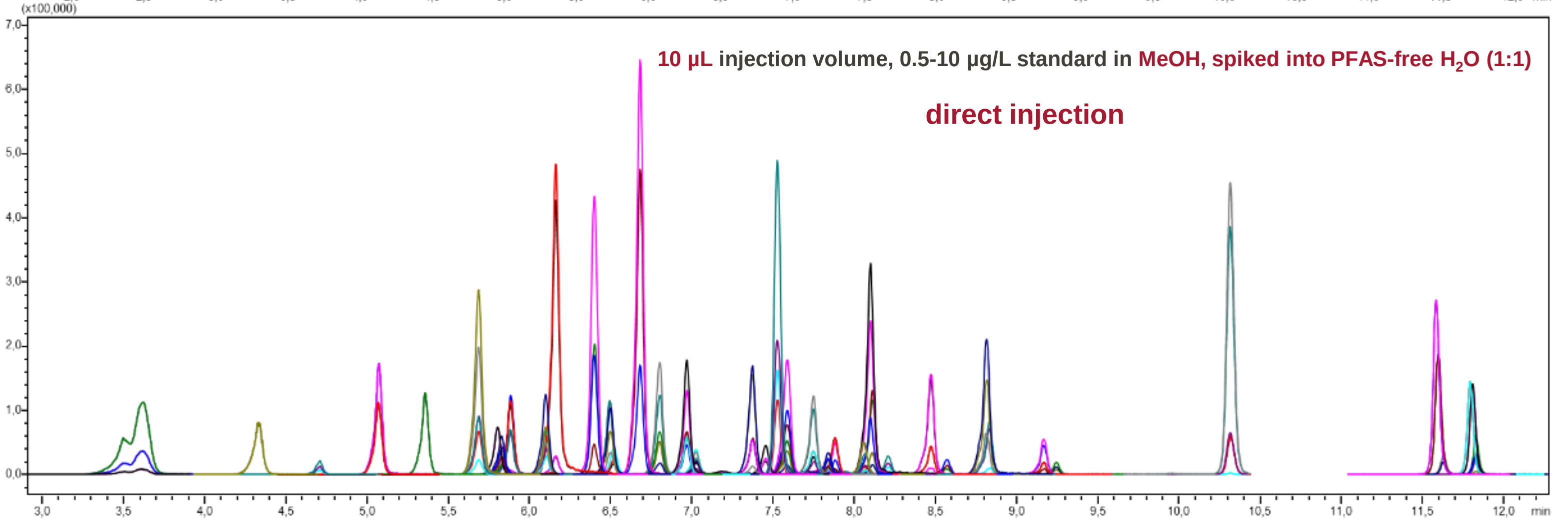
Optimised SPE method

1. Cartridge conditioning	• 2 % NH_3 (NH_4OH) in MeOH • 1:1 0.1 M FA:MeOH, then MeOH • 0.3 M FA
2. Sample loading	• Overfill injection in loop (50 µL) • Loading on cartridge with UPW
3. Cartridge wash	• Rinse solution: 1:1 0.1 M FA:MeOH
4. Elution	• 8 min via HPD with 2 % NH_3 in MeOH (800 µL mixing in with gradient)
5. Cartridge wash	• MeOH, UPW, 2 % NH_3 in MeOH



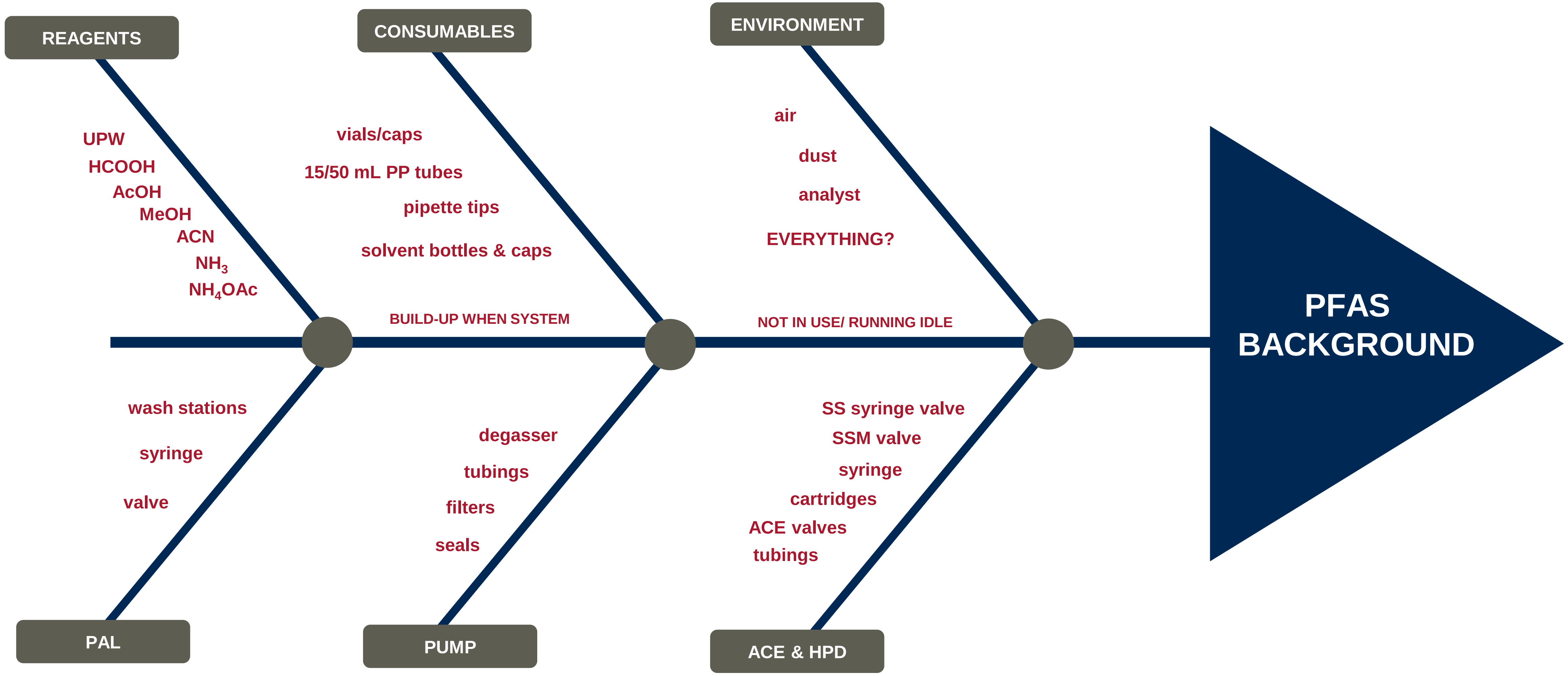
✓ **baseline separation of branched isomers**





Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

WATER ANALYTICS - online SPE method development



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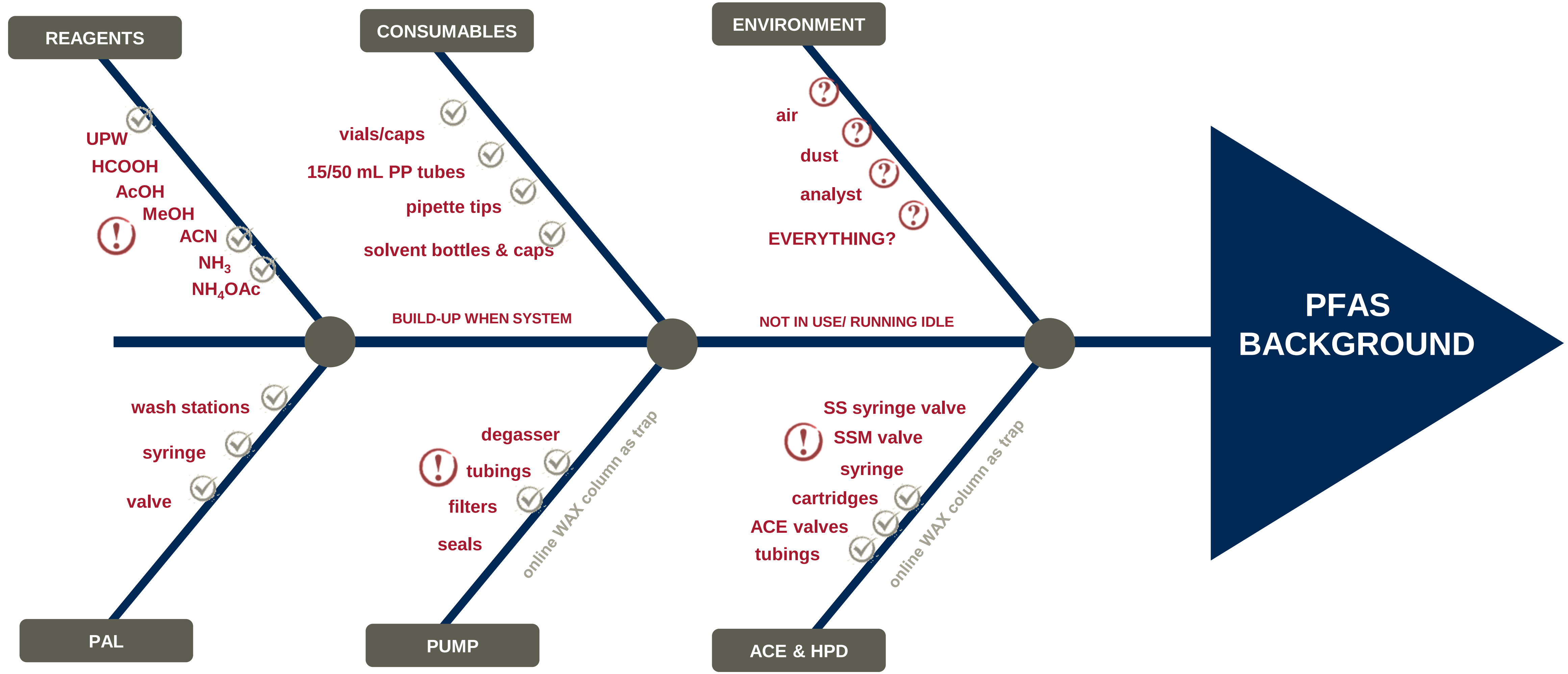

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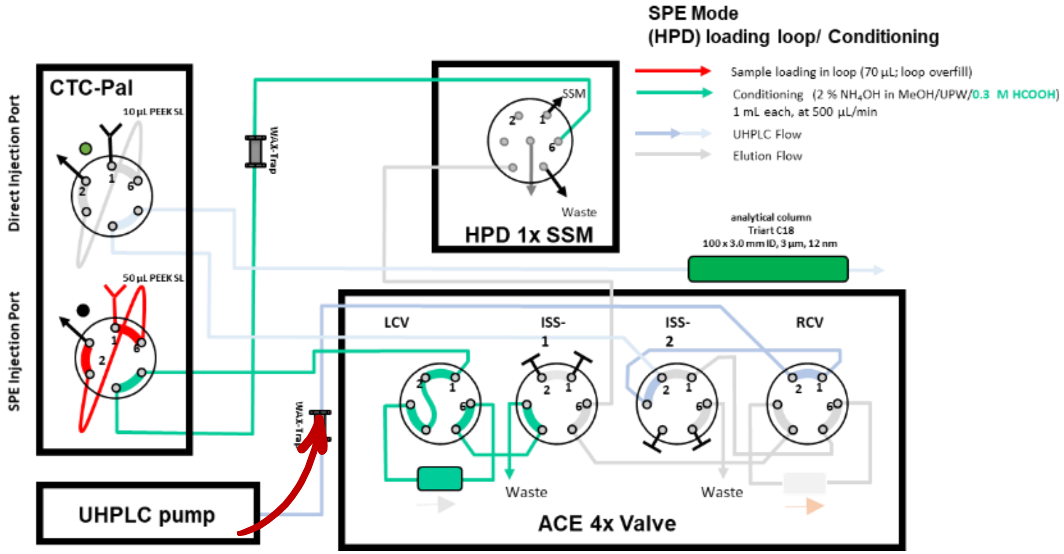

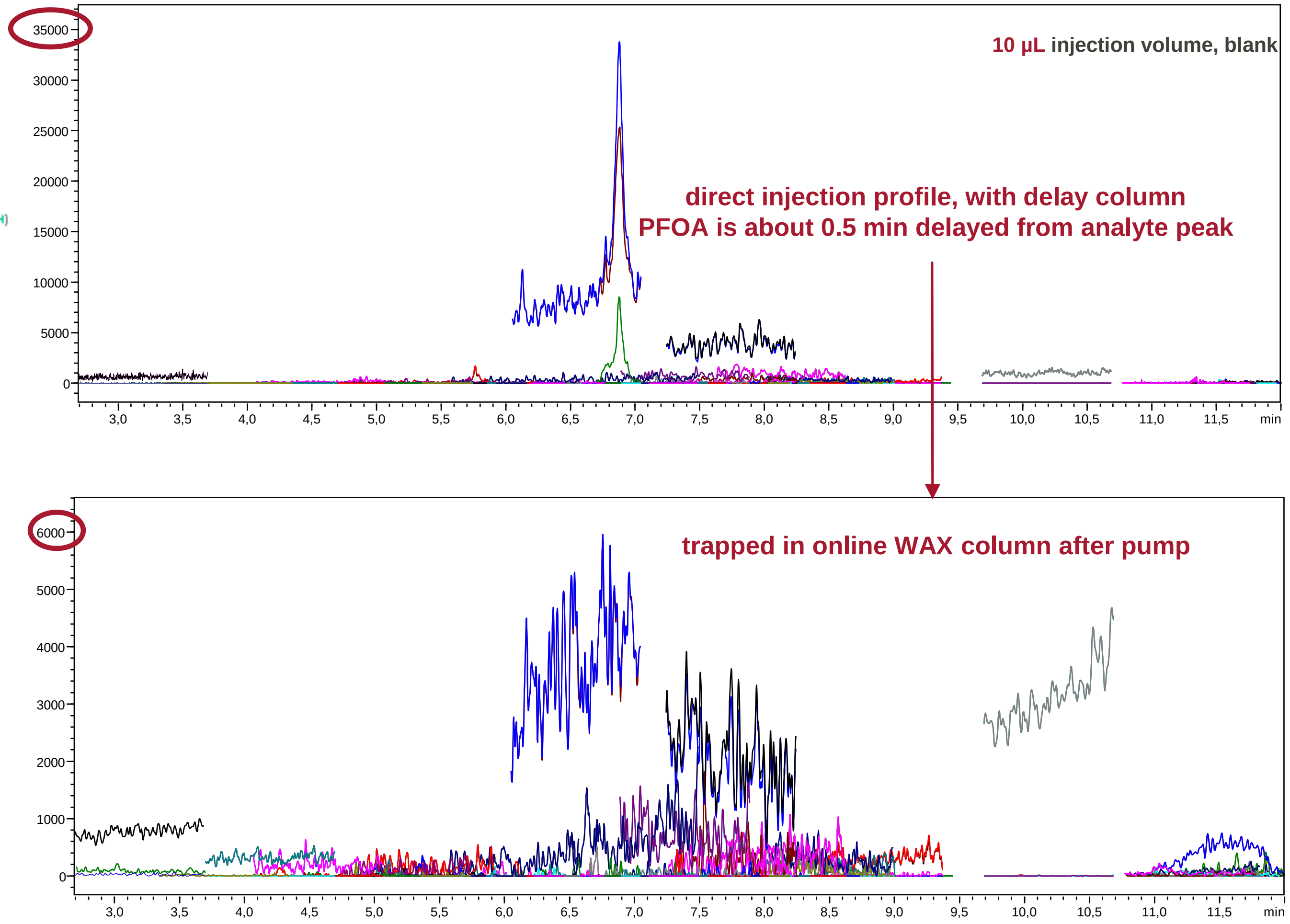

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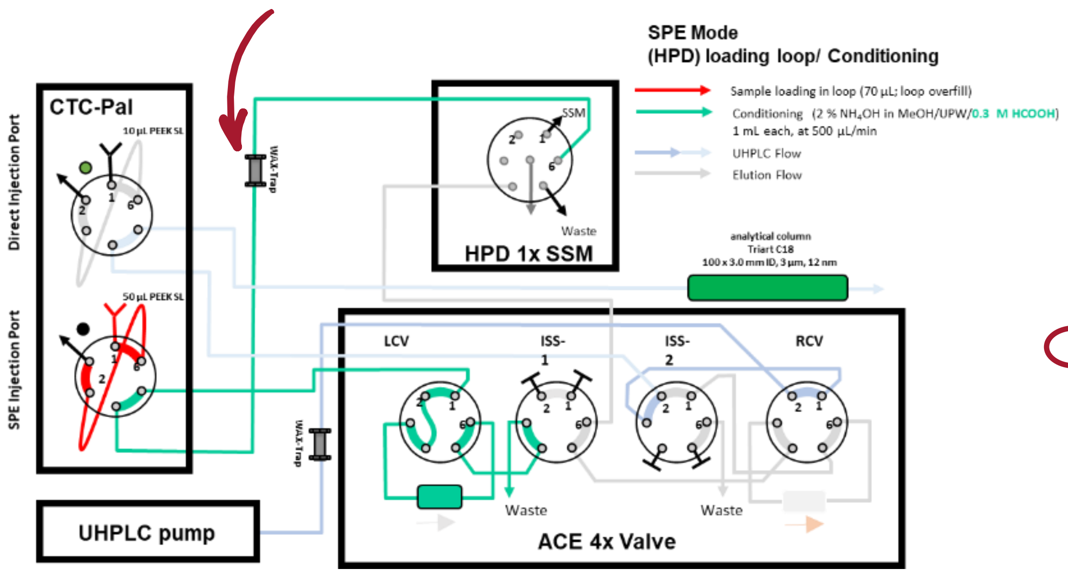
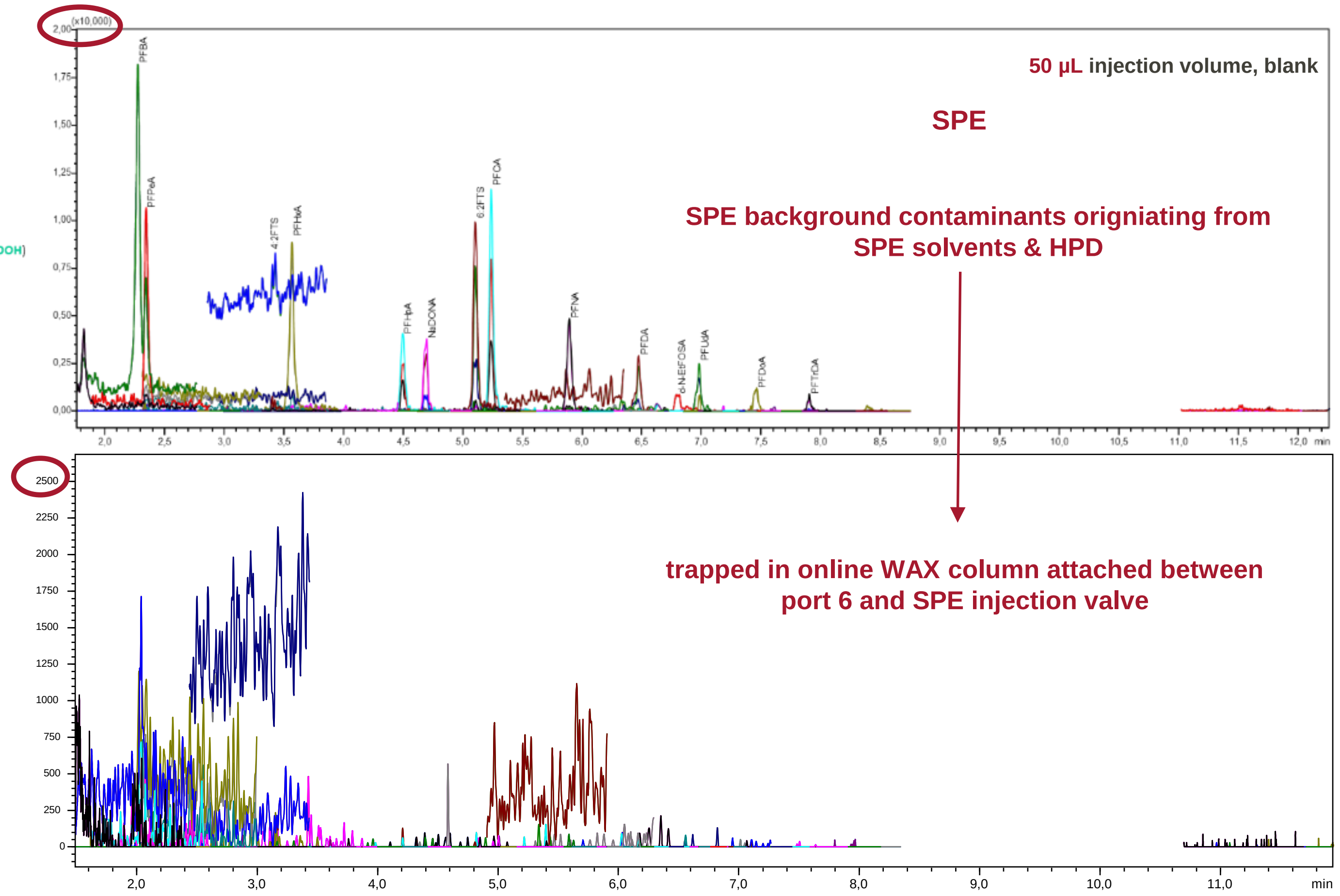




Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

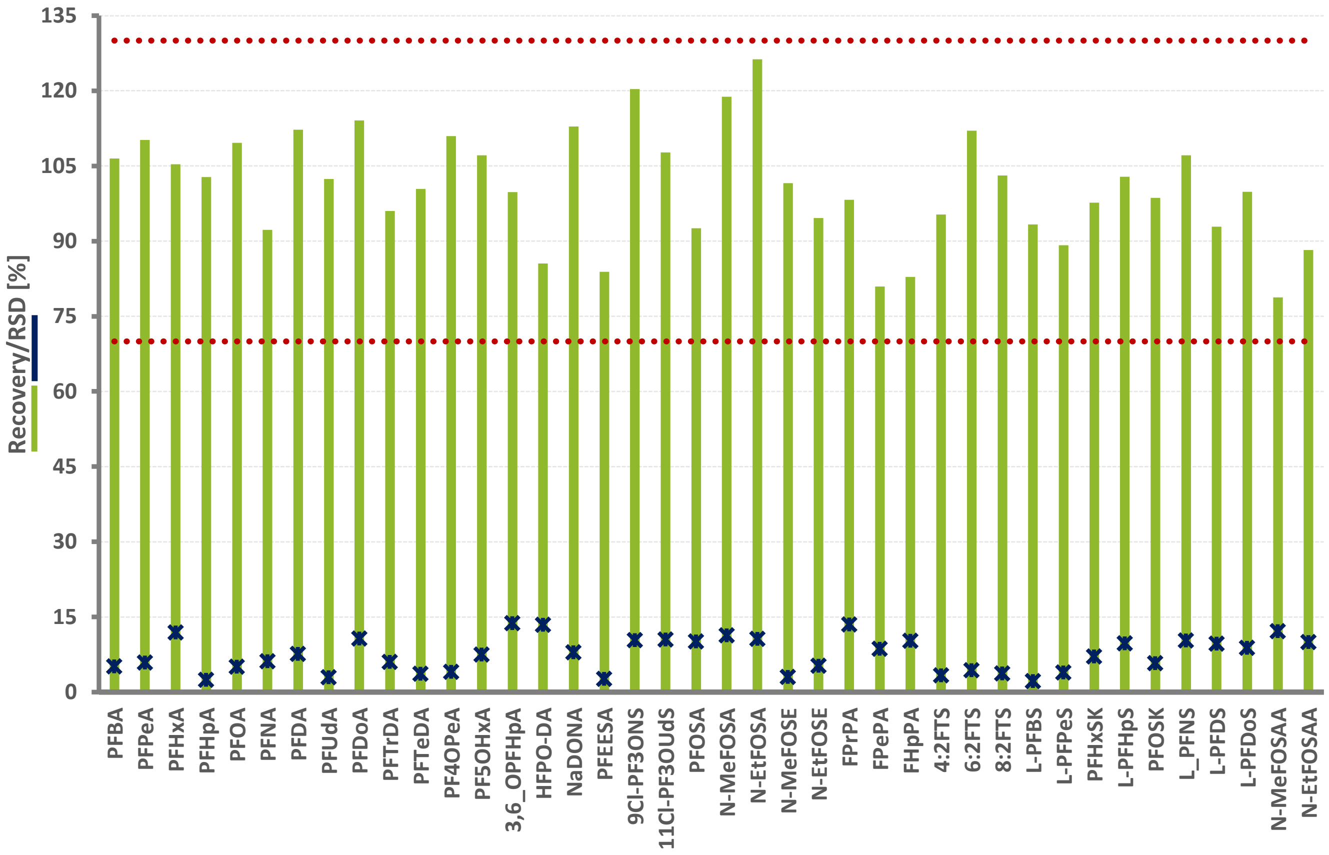
Selection of Analytes → Full Scan of individual mixtures → Tuning of analytes = MRM method → **SPE – method validation**

First MDL study demonstrates powerful potential of CHRONECT Symbiosis Workstation PFAS

9 spiking replicates, prepared and measured on 3 different days, at levels 5-100 ng/L depending on compound

- **<1 to < 5 ng/L MDLs of all CA, SA, FTS, ECA**
- **7 compounds, uncharged PFAS or weaker acidity (FASA & FTC) are subject to further optimization with MDLs >10 ng/L**
- **good recoveries for all compounds, 80-126 %**
- **7-9 replicates of low analyte spike extractions prepared on 3 days: ~8 % RSD**
- **PFAS contamination-free tailored system**
- **participation in proficiency test & round robin for**

Recoveries and RSD at low spiking levels, n=9



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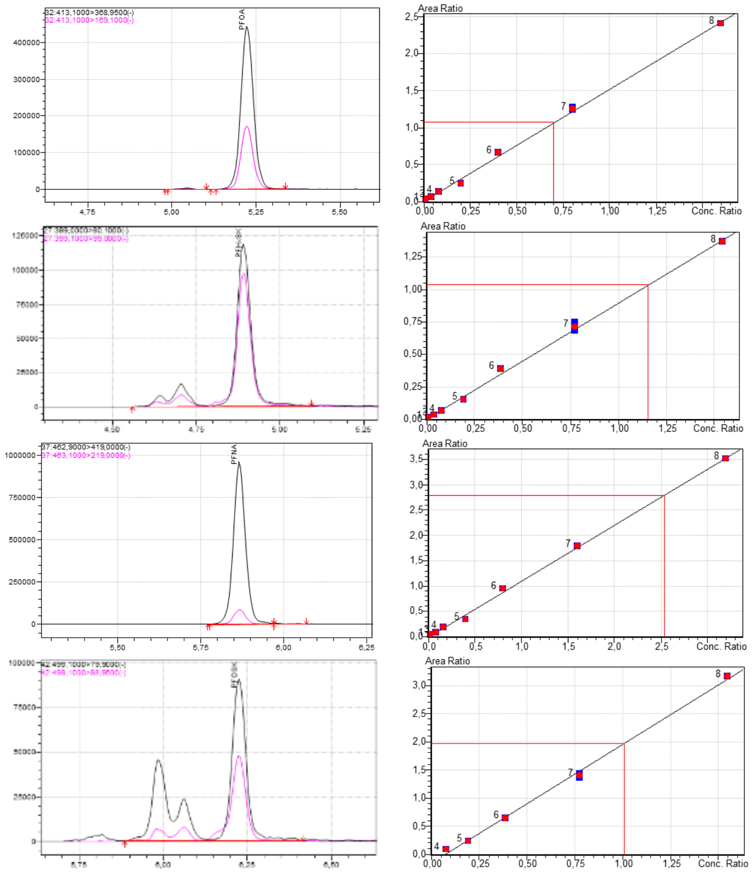
- **participation in proficiency test & round robin for drinking water and ground water samples**

Proficiency test sample:
drinking water with 4 EU regulated PFAS all within limits

PFOS (sum of linear and branched isomers)	1.145 ± 0.059 ppb
PFHxS (sum of linear and branched isomers)	1.360 ± 0.022 ppb
PFNA	1.584 ± 0.026 ppb
PFOA	0.898 ± 0.020 ppb

PFAS concentrations presented as average of triplicate analysis ± standard deviation



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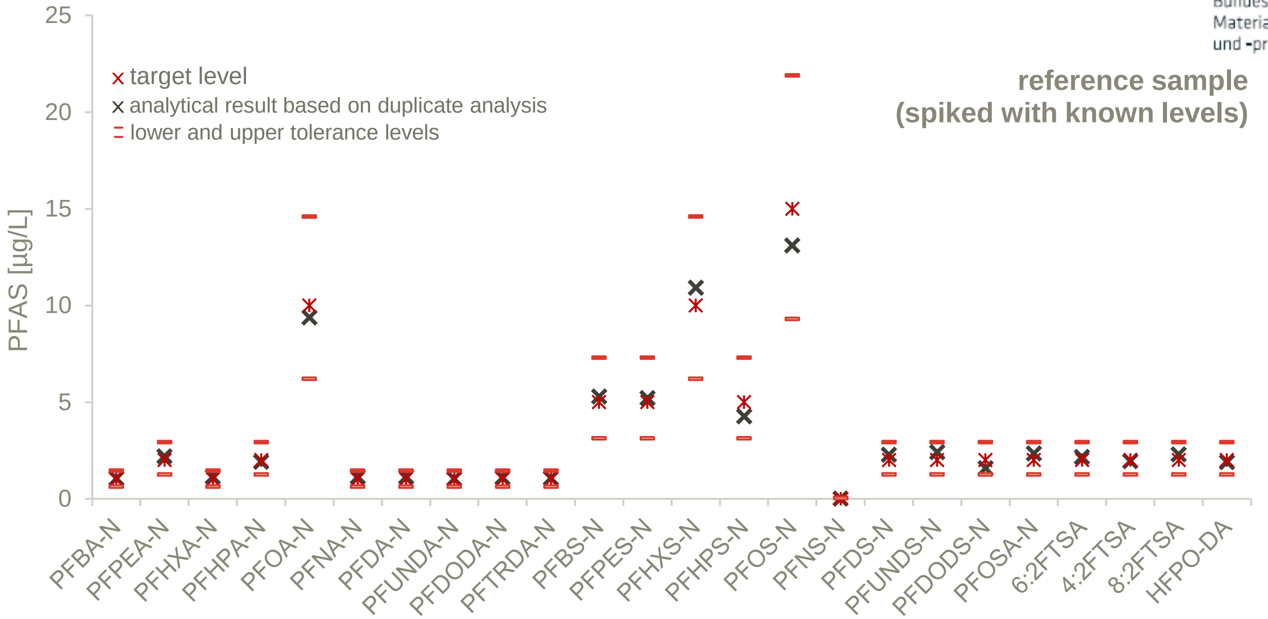
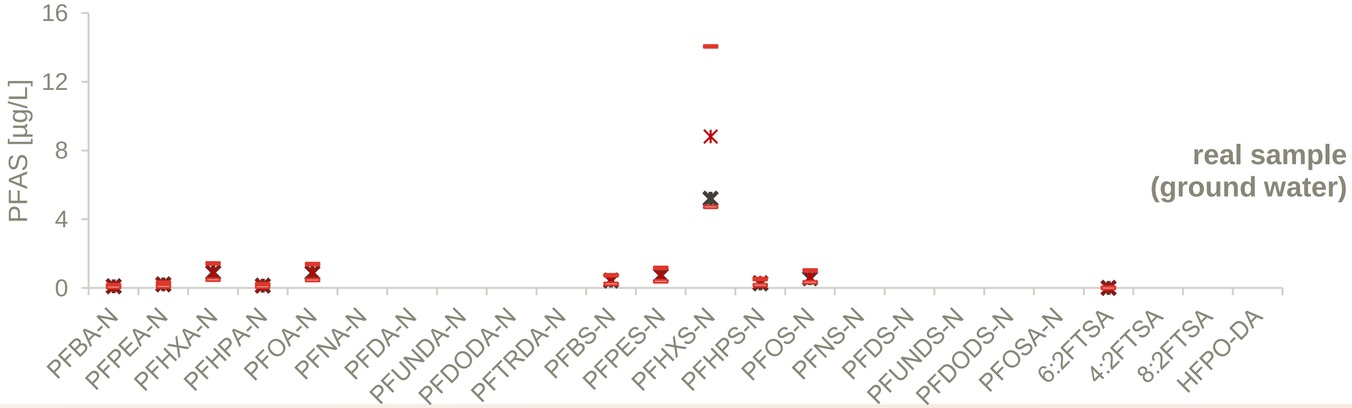
- participation in proficiency test & **round robin** for drinking water and **ground water samples**

BAM Bundesanstalt für Materialforschung und -prüfung

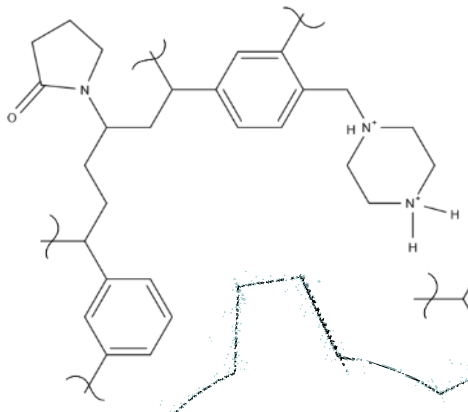
Round robin with groundwater, 24 analytes

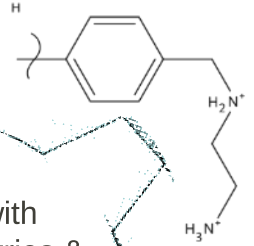




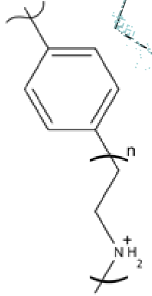
Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

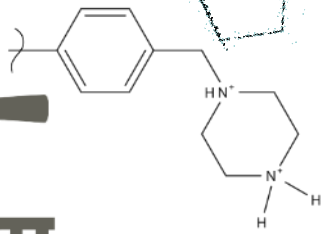
What we currently work on and what's planned?





WAX sorbents with different chemistries & ionic and RP exchange capacities: improve retention of uncharged and lower acidity PFAS





continue investigation on method's potential for soil analysis: studies on real soil samples

further optimize chromatography to improve TDCA separation and remove later eluters' gap

potential of 2D SPE? preceding SPE in luer lock cartridge format for Robotic PAL3 can be automated prior to Symbiosis online SPE

can we reach the low target LOQs in the EU of up to 0.001 µg/kg?

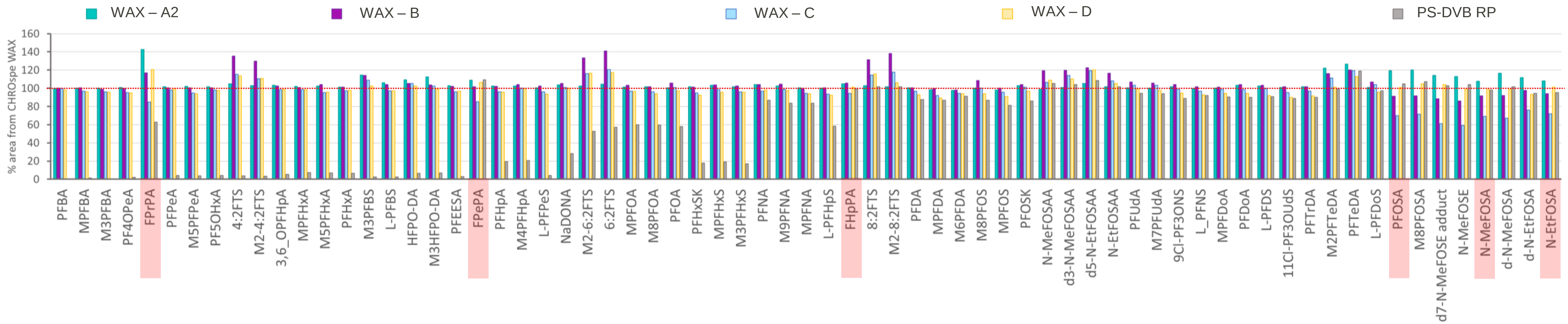
explore use of CHRONECT symbiosis for analysis of PFAS in different food matrices (PFAS tailored QuEChERS extraction)

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

Screening of alternative SPE sorbent material

	previous material					impossible to fill the small particle size	
SPE Phase	WAX - A	WAX - A2	WAX - B	WAX - C	WAX - D	WAX- E	PS-DVB RP
Particle Size	25-35 µm	5-20 µm (av. by volume 17 µm)	30 µm	30 µm or 45/85 µm	33 µm	5 µm	15- 20 µm
Pore Diameter	80 Å	80 Å	80 Å	60-80 Å or 55-65 Å	n.a.	n.a.	100 Å
Shape	irregular	spherical	n.a.	shperical	n.a.	n.a.	irregular
pKa of basic modification	n.a.	n.a.	6 & 9	6 & 9 (5.3 & 9.7 piperazin)	7.5 & 10.7 (enthylendiamin pubchem)	7.5 & 10.7 (enthylendiamin pubchem)	none
Content	2.8 mg (10 x 1 mm format	3.04 mg (10 x 1 mm format)	2.32 mg	1.87 mg	2.11 mg	2.11 mg	2.37 mg
mechanism of retention	ionic, π-π, hydrophobic	ionic, π-π, hydrophobic	ionic, π-π, hydrophobic	ionic, π-π, hydrophobic	ionic, π-π, hydrophobic	ionic, π-π, hydrophobic	π-π, hydrophobic; no ionic retention!
exchange capacity	n.a.	n.a.	0.6 meq/g	>0.8 meq/g or >0.5 meq/g	n.a.	n.a.	n.a.

- **red line = previous material; bars represent % analyte-area of alternative SPE sorbent material from larger particle size DVB phase with polyimino modifications**



- **same material with smaller particle size shows better retention for all weak performers: uncharged FOSA-compounds & weakest acidic telomer CA**

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

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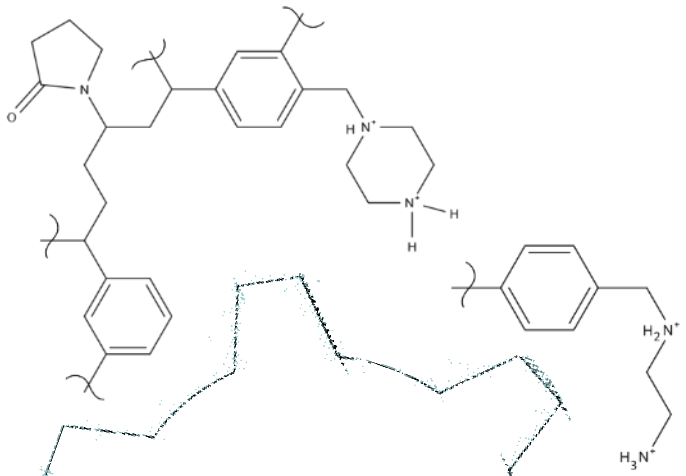
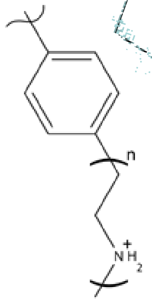
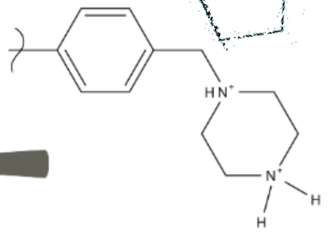
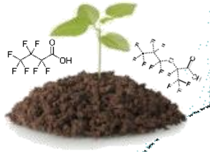






MDL studies for solid & liquid environmental studies with new cartridge material



automated extractions of soil combined with online SPE LC-MS/MS

2 g soil sample + EIS

3 x extraction of pellet with 0.3 % NH_4OH in MeOH (4 mL; 6 mL; 2 mL)

transfer supernatant in vial containing envicarb

neutralise supernatant with FA

800 µL sample + 733 µL UPW in LC vial to reach 50 % MeOH/aq.

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Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

PFAS analysis in soil and other solid matrices

Selection of Analytes → Full Scan of individual mixtures → Tuning of analytes = MRM method → SPE – method development → **Analysis of solid samples**

CHRONECT robotic PAL 3 equipped with:

- Tools:
  - left arm: LCMS-tool equipped with transparent PEEK sample loop
  - right arm: customized tool with luer lock adapter for liquid transfer & filtration
- Modules:
  - fast wash + LCMS tool wash pump (4 wash solutions)
  - solvent station with UPW & 10 % FA
  - 2 x vortex mixers with 6 x 10 mL, 2 x 20 mL, 2 x 2 mL slots
  - decapper
  - cooling peltier sack
  - centrifuge with 6 x 10 mL slots
  - 2 x tray holders for samples, empty & dSPE vials, needles, filters

method outline 1633

time & resource intensive manual process

1. weigh 5 g soil
2. EIS addition
3. 3 x extraction of pellet with 0.3 % NH_4OH in MeOH (6 mL; 10 mL; 5 mL)
4. dSPE with EnviCarb
5. water addition if needed
6. concentrate under N_2 flow
7. dilute with water and neutralise with FA / NH_4OH
8. manual SPE
9. filter → LC-MS/MS

automated workflow

manual:

1. weigh 2 g soil

fully automated:

2. EIS addition
3. 3 x extraction of pellet with 0.3 % NH_4OH in MeOH (4 mL; 6 mL; 2 mL)
4. dSPE with EnviCarb
5. ~~water addition if needed~~
6. ~~concentrate under N_2 flow~~
7. neutralise with FA, filter, dilute with water
8. ~~manual SPE~~
9. online SPE LC-MS/MS

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

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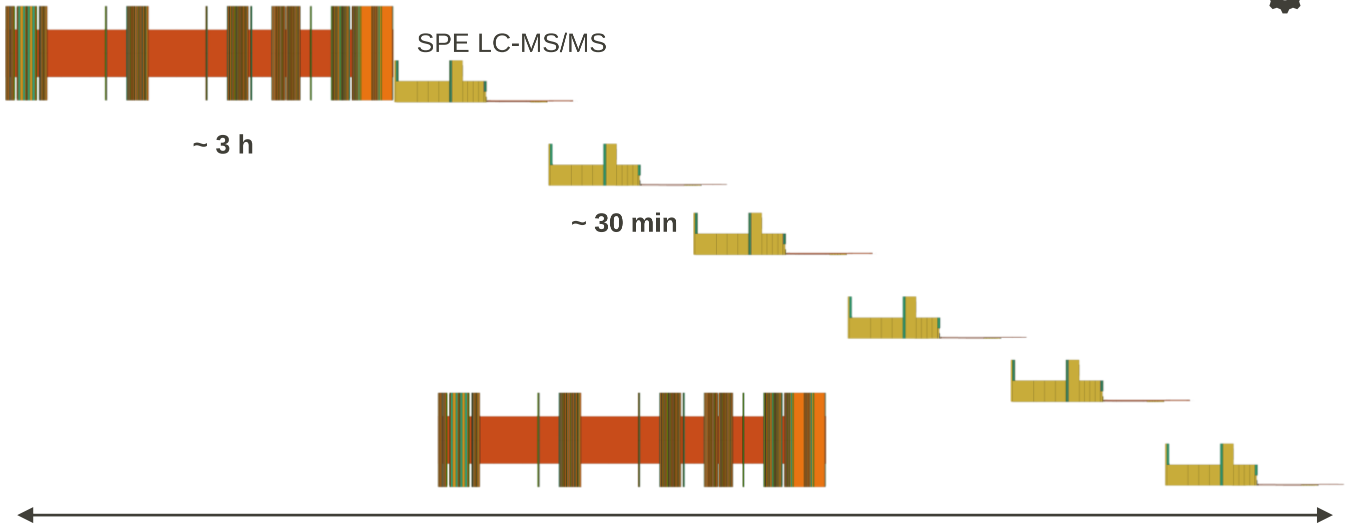
CHRONOS – calculates overlapping time schedules maximizing sample throughput

extraction of soil samples
(incl. solid liquid extraction & dSPE)



~ 5.5 h from weighed sample to analytical result for 6 samples
analyst's required action: start method & evaluate data

Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

PFAS analysis in soil and other solid matrices

Selection of Analytes → Full Scan of individual mixtures → Tuning of analytes = MRM method → SPE – method development → **Analysis of solid samples**

Automated extraction of solid samples using CHRONECT PAL3 with SPE LC-MS/MS

- initial trials using spiked Ottawa sand show potential of CHRONECT Symbiosis to greatly simplify the EPA 1633 soil method:
  - ✓ **no solvent exchange needed**: neutralization of basic MeOH extract → dilution with PFAS-free water to reach **50 % aqueous composition → online SPE LC-MS/MS**
- **close to 100 % recoveries** for all compounds; spiking levels between **0.1-0.2 ng/g (0.5-2.3 ng/g for 9 compounds)** using same 50 % MeOH/H_2O calibration curve as for water analysis

2 g sand + 1 mL UPW + EIS & natives

↓

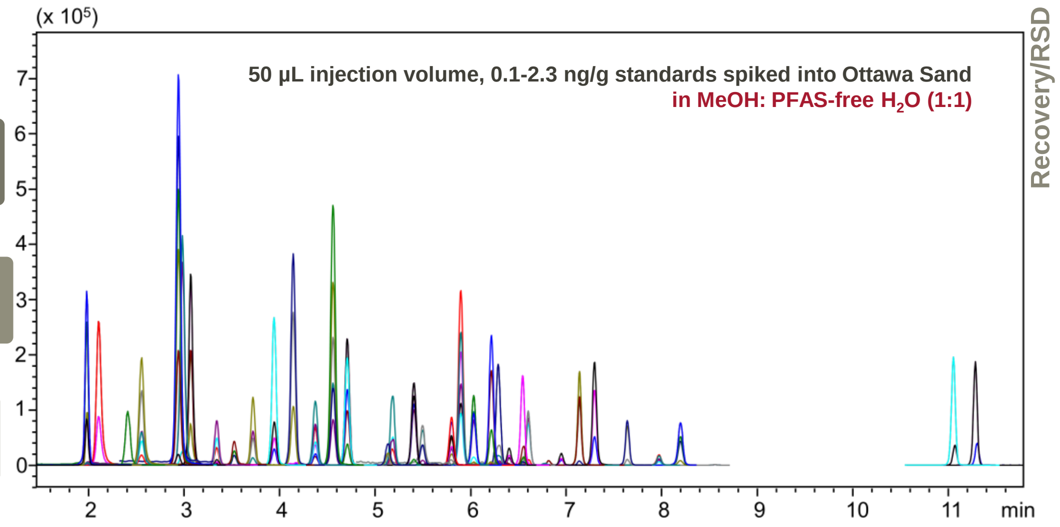
3 x extr. of pellet with 0.3 % NH_4OH in MeOH (4 mL; 6 mL; 2 mL)

↓

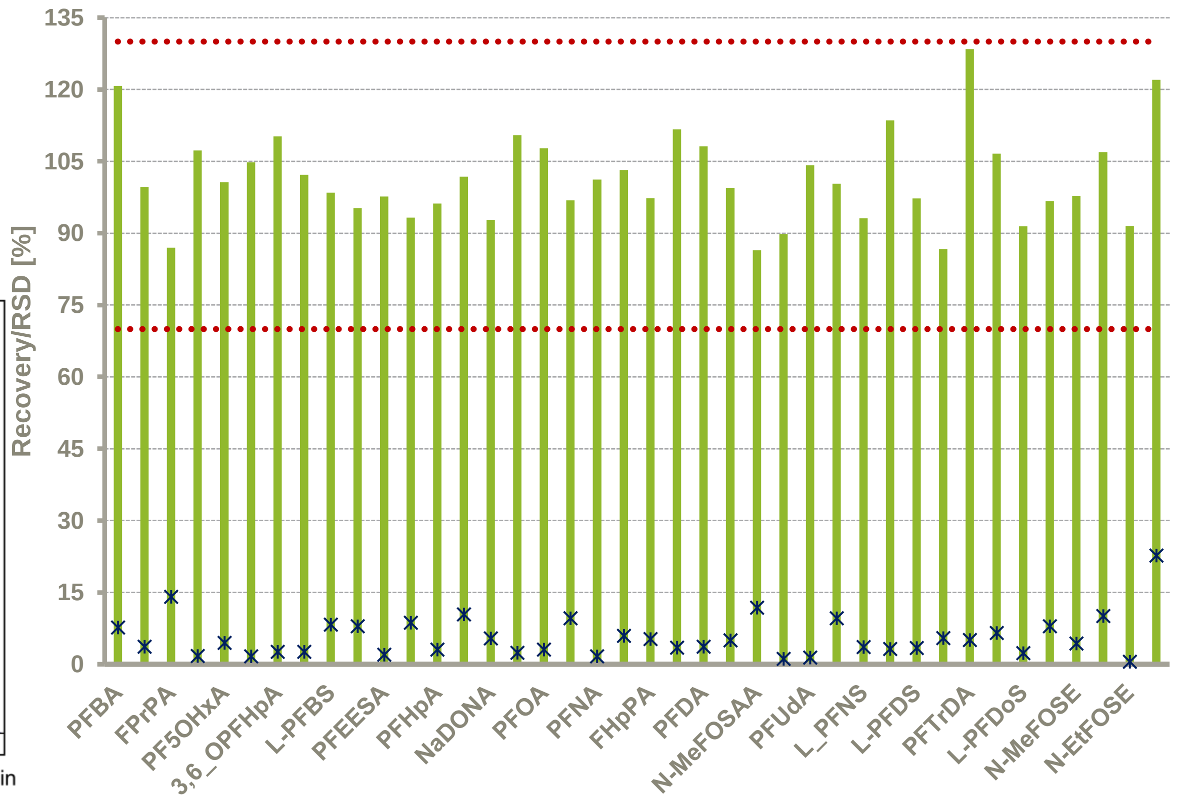
neutralise supernatant with FA

↓

800 µL sample 727 µL UPW in LC vial to reach 50 % MeOH/aq.

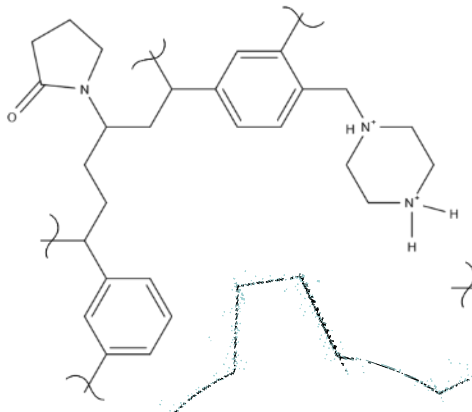


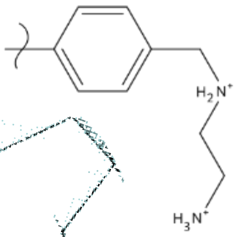
Recoveries and RSD at mid-level spiking (n=3)

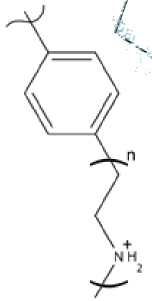


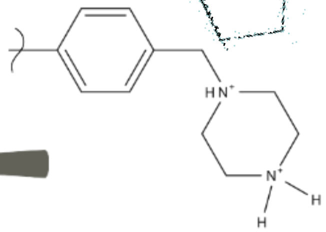
Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

What we currently work on and what's planned?

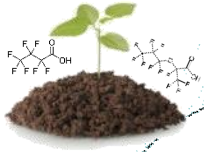








MDL studies for solid & liquid environmental studies with new cartridge material



validation of automated extractions + online SPE LC-MS/MS of soil (CRM, MDL study)

2 g soil sample + EIS

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neutralise supernatant with FA

800 µL sample + 733 µL UPW in LC vial to reach 50 % MeOH/aq.

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PFAS analysis in soil and other solid matrices

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✓ participation in round robin for the analysis of soil & eluates

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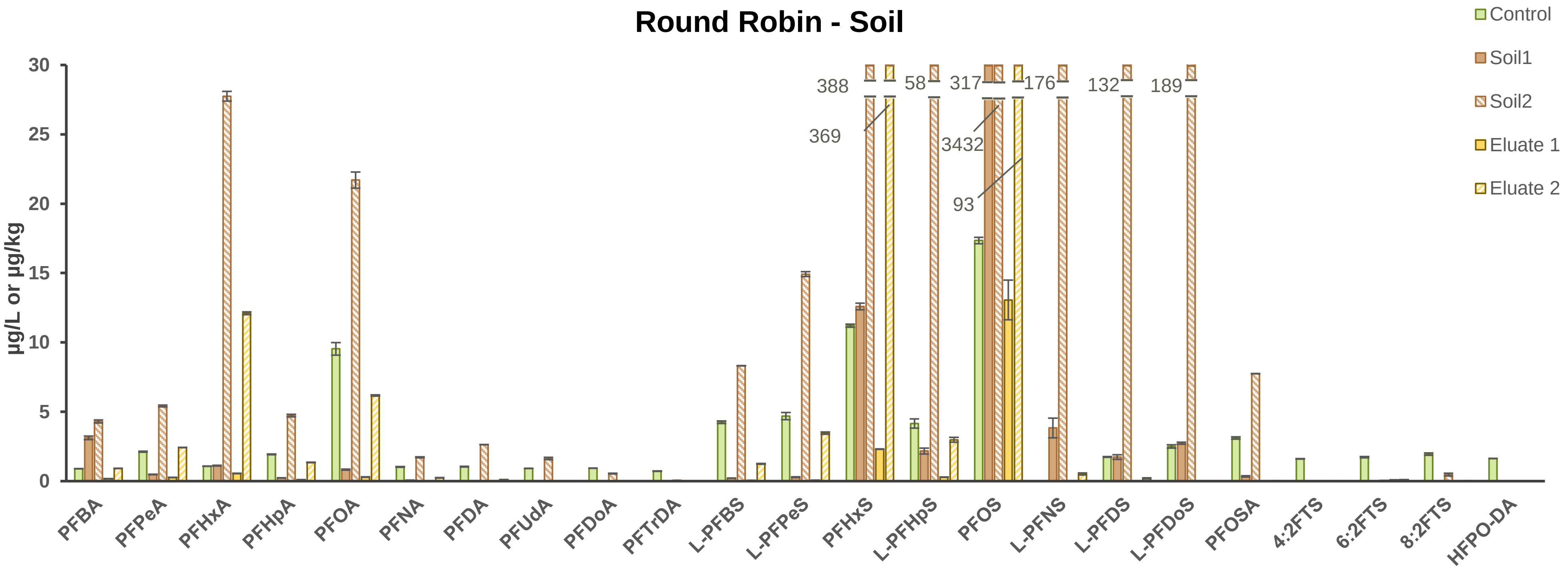
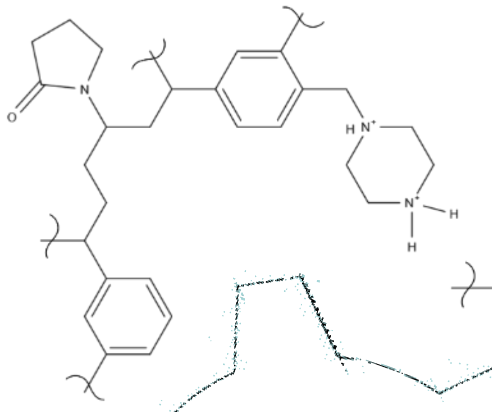
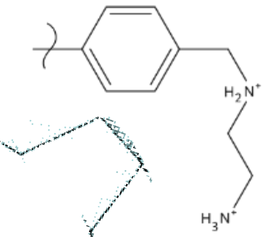


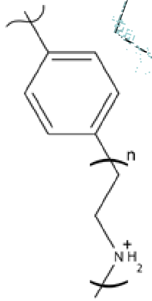
evaluation pending

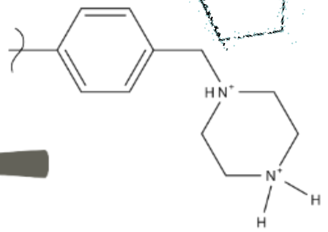
Automation of PFAS analytics using CHRONECT Symbiosis – based on EPA 1633

What we currently work on and what's planned?









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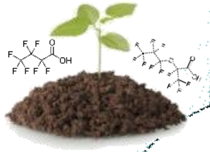

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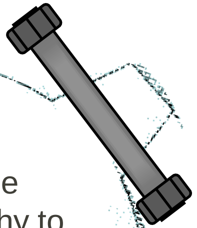

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SETAC

SETAC NORTH AMERICA 45TH ANNUAL MEETING

20-24 OCTOBER 2024 ★ FORT WORTH, TEXAS

4 | Challenges in PFAS Analyses and Detection

Description & Chairs

Lilit Ispiryan , Helmer Korb

Per- and polyfluoroalkyl substances (PFAS) have garnered significant attention due to their persistence, bioaccumulation, and potential health risks. This session aims to bring together experts from diverse fields to discuss the multifaceted challenges associated with PFAS analyses ultimately aiming to advance our understanding of PFAS contributing to effective environmental and health management.

We will delve into the complexities of analyzing PFAS in various matrices, explore state-of-the-art and novel techniques for sample preparation and detection, and address the evolving landscape of analytes and detection limits. Key topics will comprise for instance matrix diversity: PFAS occur in a wide range of matrices, including water, soil, biological matrices or food. We invite experts to will share their experiences in handling these diverse sample types and the unique challenges they pose. In this context efficient sample preparation is crucial for accurate PFAS analysis. Presenters will discuss extraction methods, such as solid-phase extraction (SPE), and matrix-specific considerations. Especially time- and resource efficient automated techniques supporting more accurate and sustainable lab-practices are increasingly in demand. From liquid chromatography-mass spectrometry (LC-MS) to high-resolution mass spectrometry (HRMS), the most appropriate and precise PFAS detection techniques will be discussed, while addressing challenges related to selectivity, sensitivity, and interference.

Furthermore, the list of routinely analyzed compounds from the PFAS family continues to expand. New compounds are discovered or known compounds are added due to their recently recognized significance. The challenges of keeping up with this ever-growing list of analytes should be addressed. As importantly, regulatory requirements demand lower detection limits. Speakers are invited to share strategies for achieving ever-decreasing detection levels while maintaining analytical accuracy and robustness.

Keywords:

PFAS, Water Quality, Soil,

THANK YOU…

…for your attention!

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iChrom SOLUTIONS
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Questions ?

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