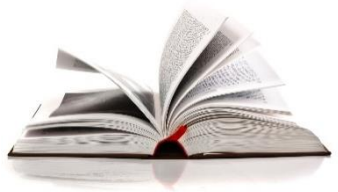
MACHEREY-NAGEL

The progress in the development of official methods for PFAS analysis using SPE and HPLC-MS/MS

NATIONAL ENVIRONMENTAL MONITORING CONFERENCE 2022

Dr. Achim Leitzke, 29 July 2022

Agenda

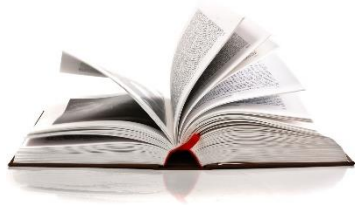


Introduction

Current solutions

Method Comparison

Summary



Introduction

Properties – Daily use – Distribution of PFAS in the environment-examples

- Health Concerns

Introduction

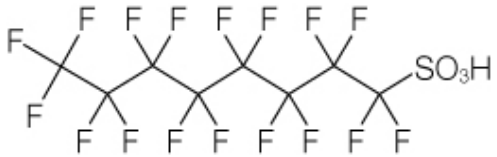
Properties and examples of PFAS

- ~ 4730 compounds known according to OECD
- All are nonnatural but man-made (used since the 1940s)
- Carbon chain: hydrogen is substituted by fluorine
- Structure: hydrophobic, lipophobic chain
  + hydrophilic „head“

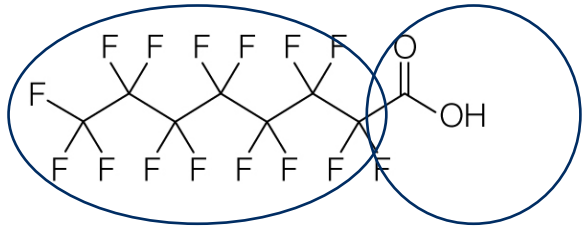
→ tensid-like → water-, dirt- and fat-repellent (non-sticky)

“Forever Chemicals”

Perfluorosulfonic acid



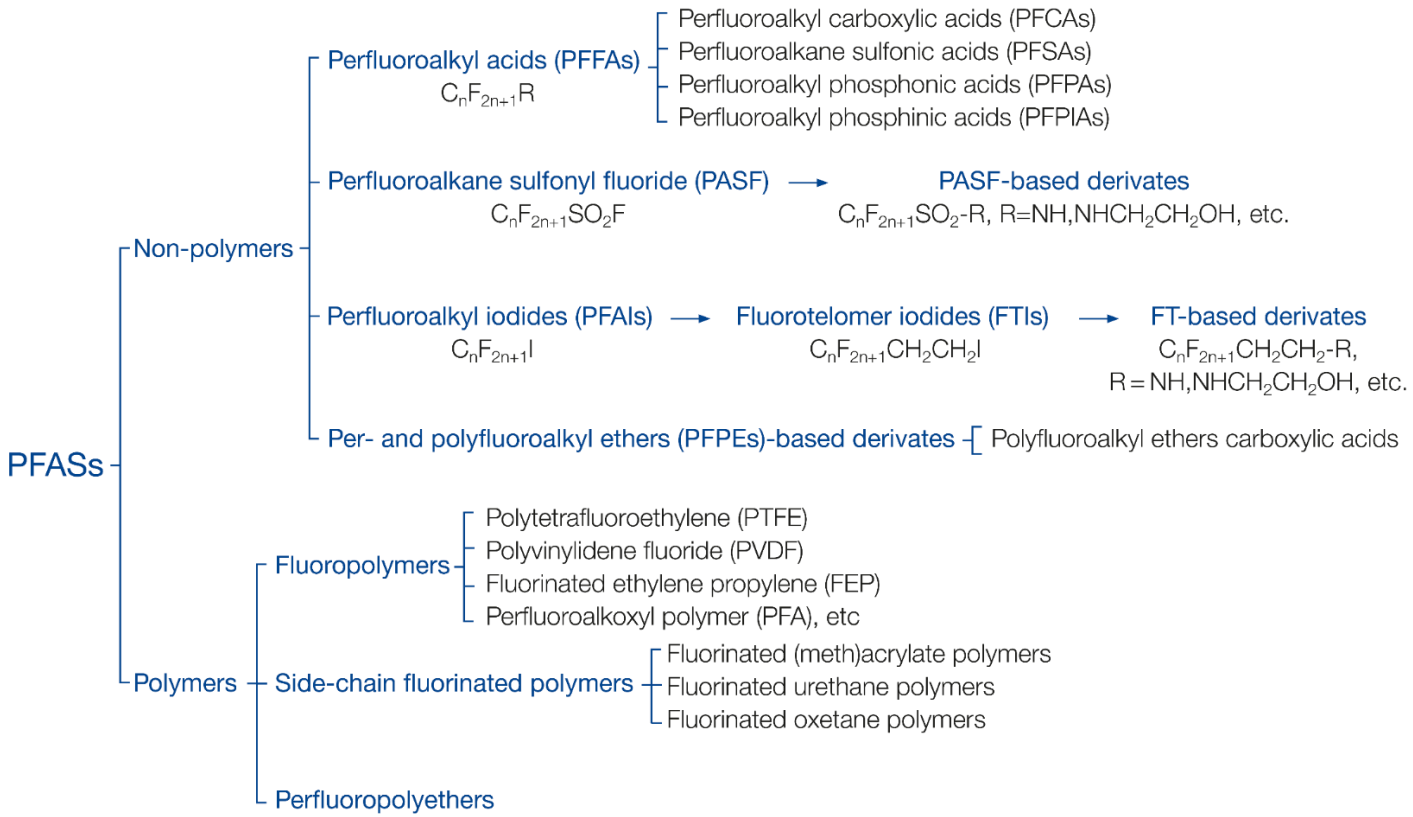
Perfluorooctanoic acid



hydrophobic hydrophilic

Introduction

Per- and polyfluoroalkyl substances (PFAS)



Introduction

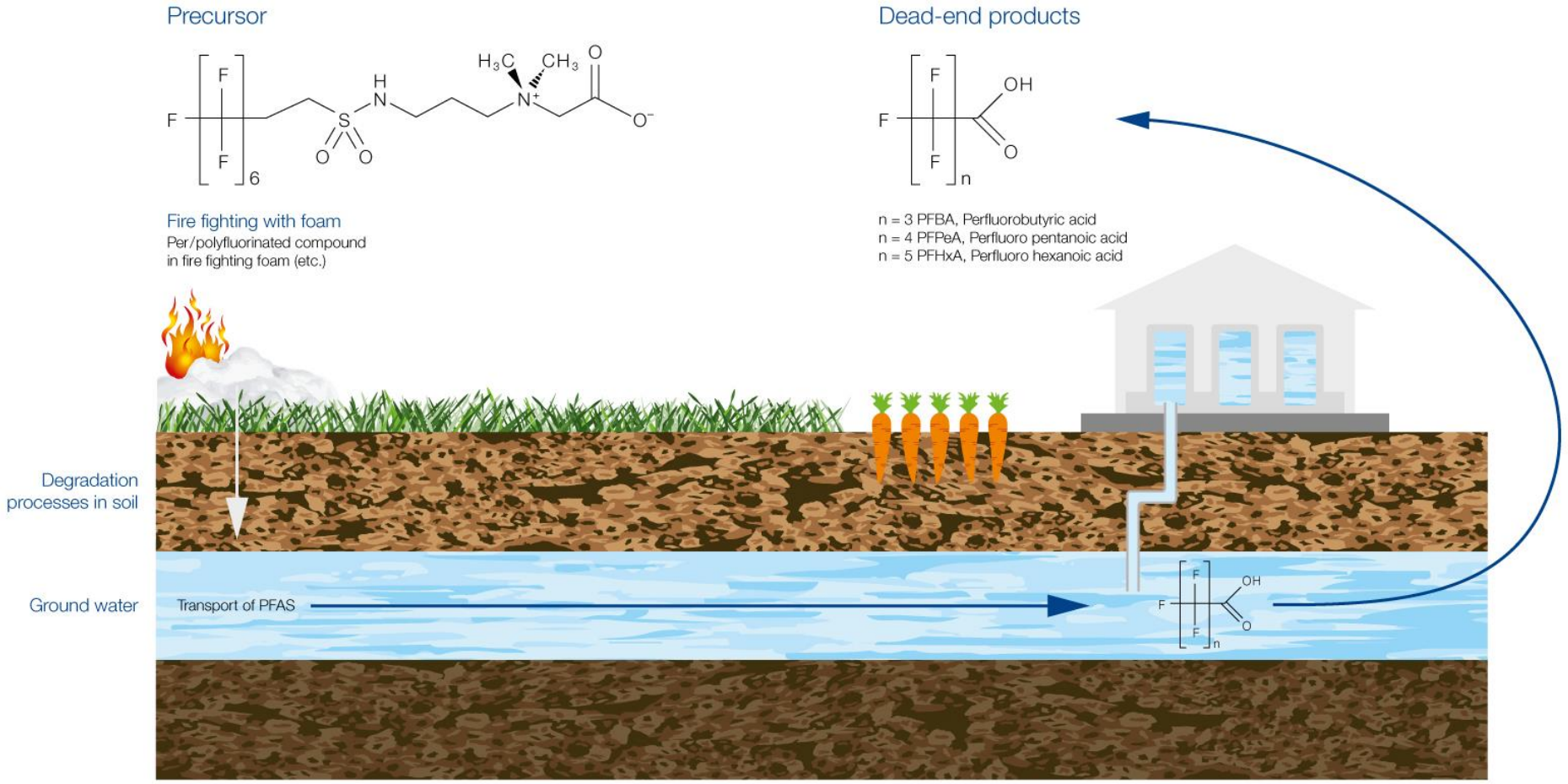
Appearance/daily use

- Fire-fighting foam
- Fiber coating
- Textile coating, e.g. seat covers, carpets, outdoor clothing
- Cookware
- Paper finishing
- Food packaging, e.g. pizza cartons, paper cups
- Building material, e.g. water resistant lacquer

Abundant in the (global) environment

Introduction

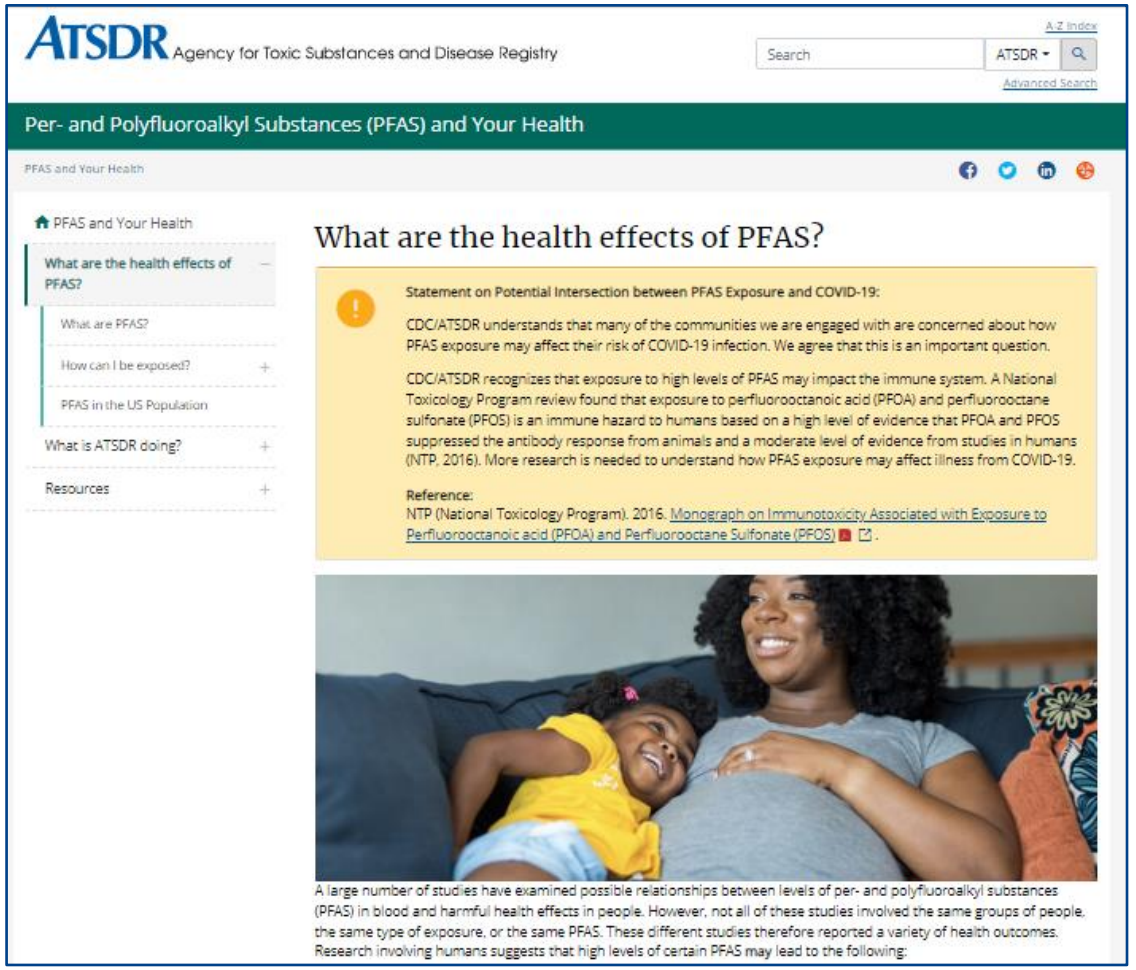
Distribution of PFAS in the environment-examples



Introduction

Health Concerns of PFAS

- Affects growth, learning, behavior
- Endocrine interference
- Increase cholesterol levels
- Affect the immune system
- Increase the risk of cancer
- Infertility



Introduction

PFAS valuation in drinking water

US EPA

- Office of water (2022): PFBS 0.01 µg/L, HFPO-DA 2 µg/L
- Regions (2022): PFOA 0.060 µg/L, PFOS 0,040 µg/L, PFOS-K 0.040µg/l, PFNA 0.059 µg/L , PFBA 6.0 µg/L, PFHxS 0.39 µg/L, HFPO-DA 0.06 µg/L

European DIRECTIVE (EU) 2020/2184

- PFAS Total: 0.5 µg/L (totality of all per- and polyfluoroalkyl substances)
- SUM of PFAS: 0.1 µg/L (20 substances)

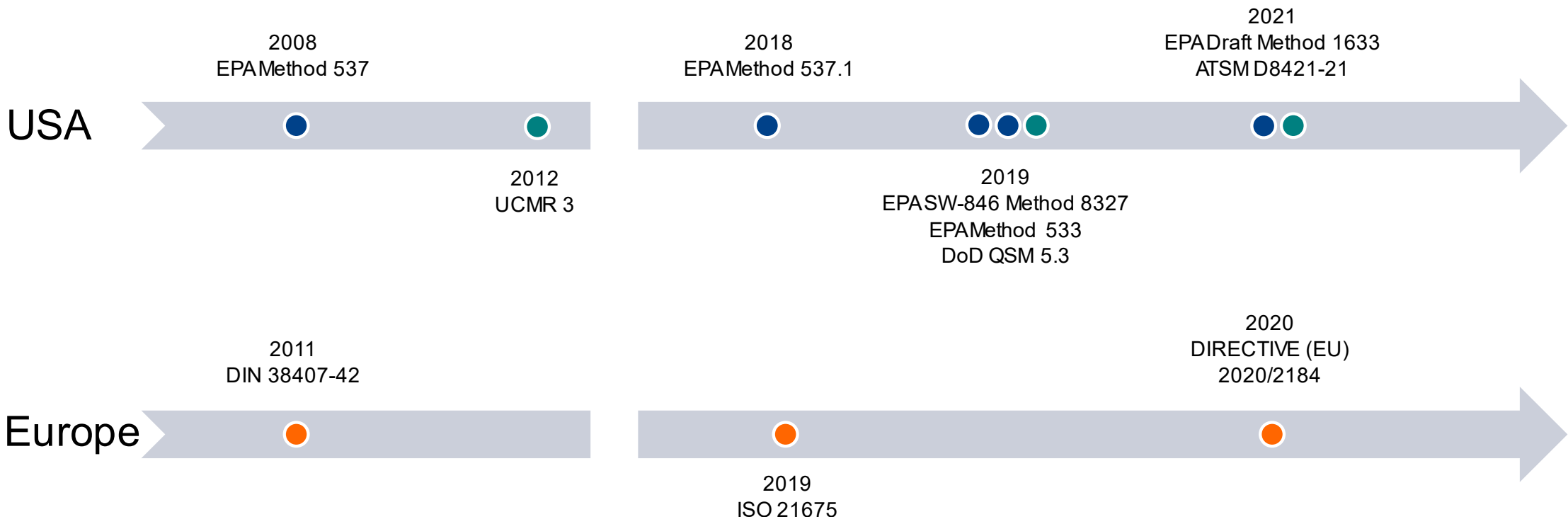
Sub-ppb detection limits required

Current solutions

Guidelines – Product solutions

Current solutions

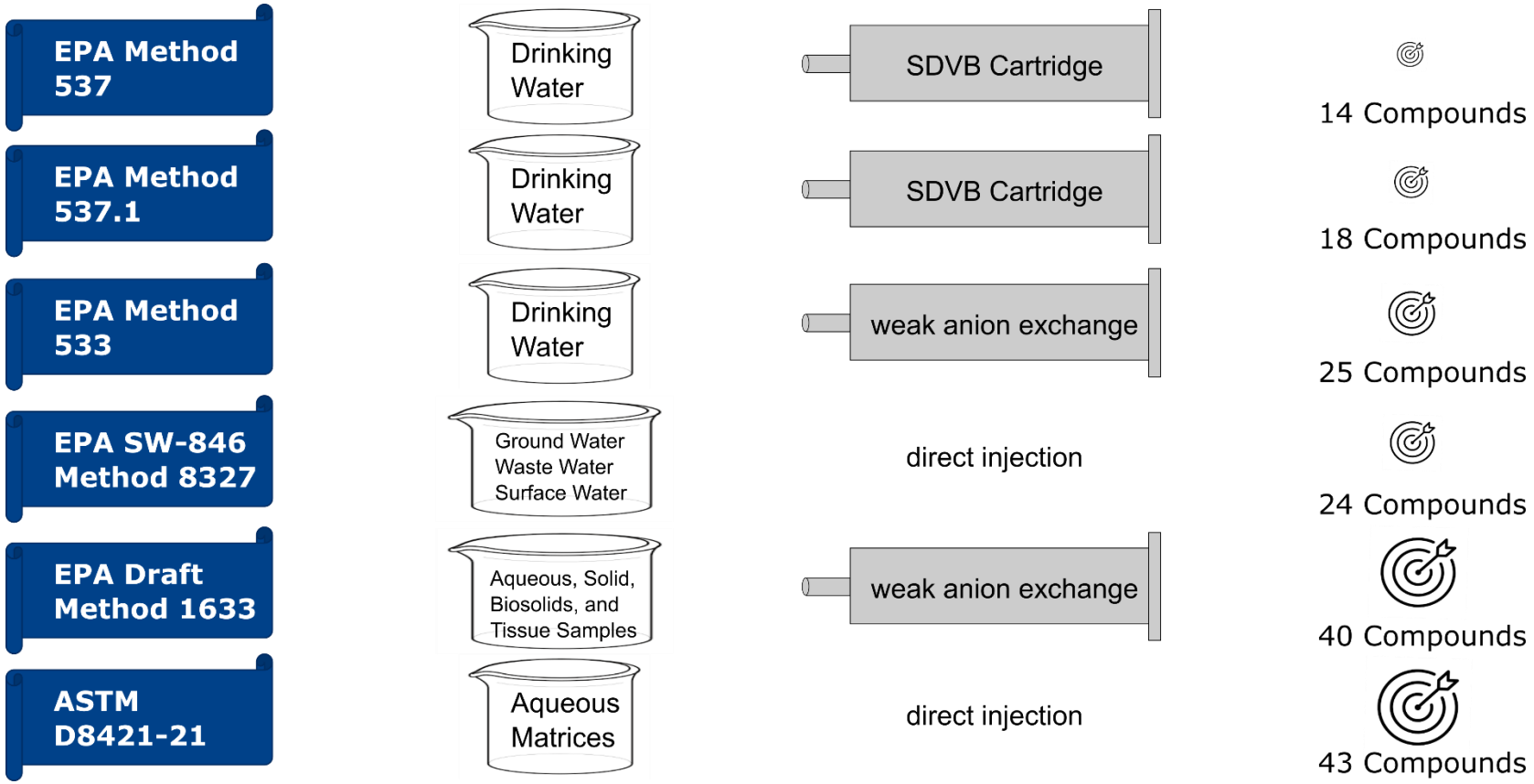
PFAS Guidelines – Landmarks



8 official methods have been adapted or developed in the last 4 years!

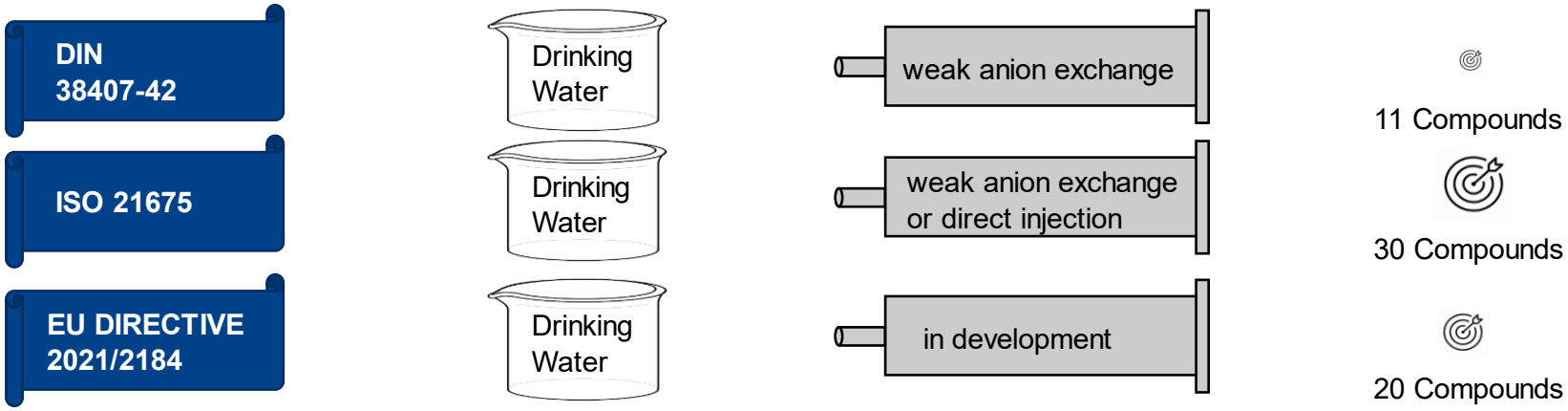
Current solutions

PFAS Guidelines – Method facts



Current solutions

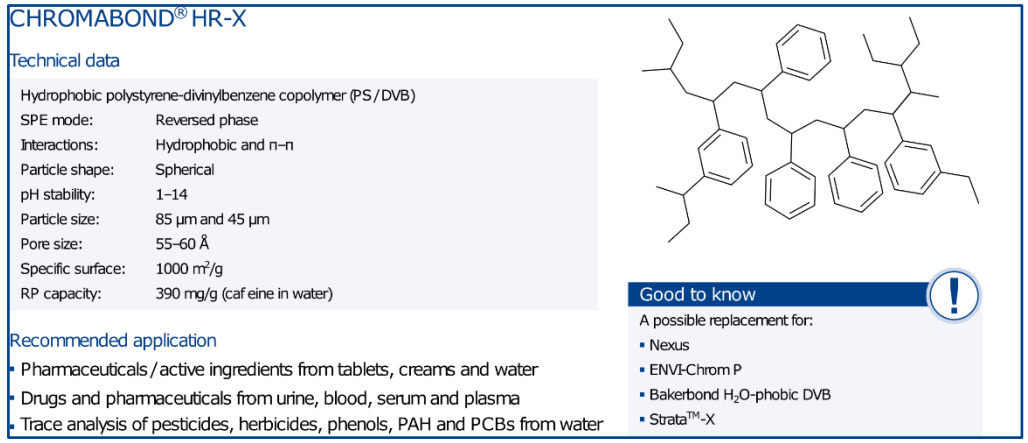
PFAS Guidelines – Method facts



Current solutions

Hydrophobic polystyrene-divenylbenzene copolymer – CHROMABOND® HR-X

- SDVB polymer
  - Specific surface 1000 m^2/g
  - RP capacity 390 mg/g
- required for good recovery and low detection limits
- Method is not sufficient for short-chain PFAS



CHROMABOND® HR-X

Technical data

Hydrophobic polystyrene-divinylbenzene copolymer (PS/DVB)	
SPE mode:	Reversed phase
Interactions:	Hydrophobic and π–π
Particle shape:	Spherical
pH stability:	1–14
Particle size:	85 µm and 45 µm
Pore size:	55–60 Å
Specific surface:	1000 m^2/g
RP capacity:	390 mg/g (caf eine in water)

Recommended application

- Pharmaceuticals / active ingredients from tablets, creams and water
- Drugs and pharmaceuticals from urine, blood, serum and plasma
- Trace analysis of pesticides, herbicides, phenols, PAH and PCBs from water

Good to know

A possible replacement for:

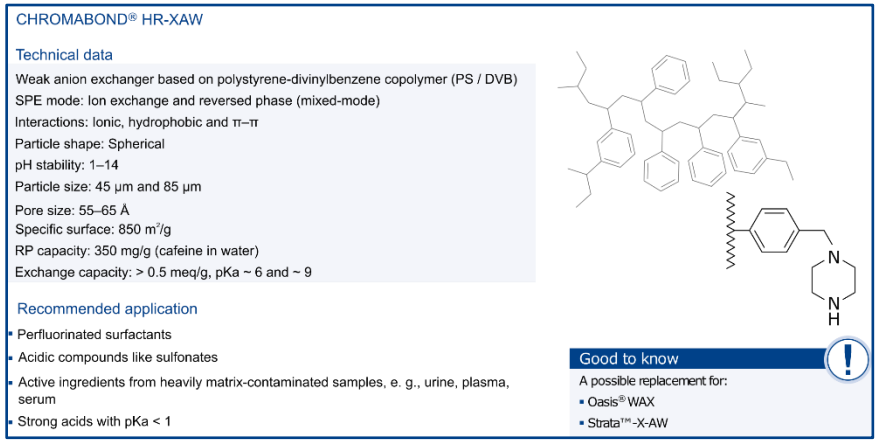
- Nexus
- ENVI-Chrom P
- Bakerbond H_2O-phobic DVB
- Strata™-X

Recommended for EPA Method 537, and EPA Method 537.1!

Current solutions

Weak anion exchanger – CHROMABOND® HR-XAW

- Weak anion exchanger (WAX)
  - mixed-mode polymeric sorbent
  - Particle size 45µm and 85 µm
  - pKa ~9
  - Exchange capacity > 0.5
- required for good recovery and low detection limits
- Methods are fully sufficient for short-chain PFAS!

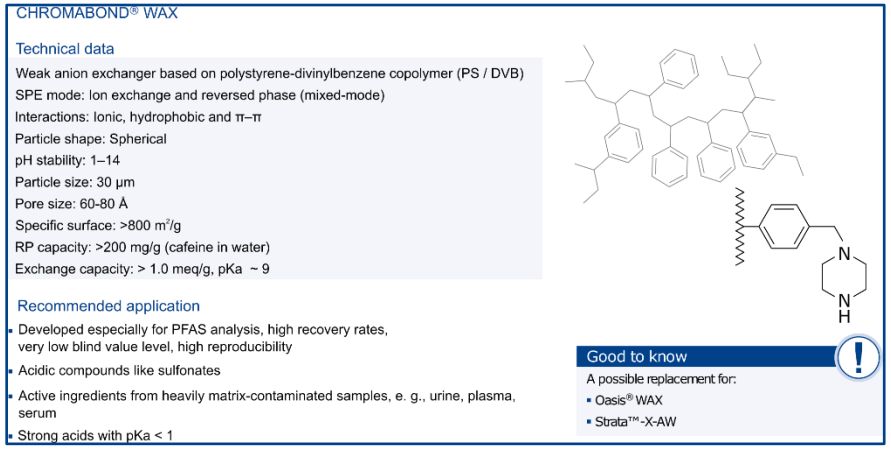


Data show that this works for EPA Method 533!

Current solutions

Weak anion exchanger – CHROMABOND® WAX

- Weak anion exchanger (WAX)
  - mixed-mode polymeric sorbent
  - Particle size 30 µm
  - pKa ~9
  - Exchange capacity > 1.0
  - Very low blind value Levels
- Good recovery rates PFOA (101.8 ± 8%), PFOS (92.7 ± 10.1%)
- Suitable for a wide range of PFAS


CHROMABOND® WAX

Technical data

Weak anion exchanger based on polystyrene-divinylbenzene copolymer (PS / DVB)
SPE mode: Ion exchange and reversed phase (mixed-mode)
Interactions: Ionic, hydrophobic and π–π
Particle shape: Spherical
pH stability: 1–14
Particle size: 30 µm
Pore size: 60-80 Å
Specific surface: >800 m^2/g
RP capacity: >200 mg/g (cafeine in water)
Exchange capacity: > 1.0 meq/g, pKa ~ 9

Recommended application

- Developed especially for PFAS analysis, high recovery rates, very low blind value level, high reproducibility
- Acidic compounds like sulfonates
- Active ingredients from heavily matrix-contaminated samples, e. g., urine, plasma, serum
- Strong acids with pKa < 1

Good to know

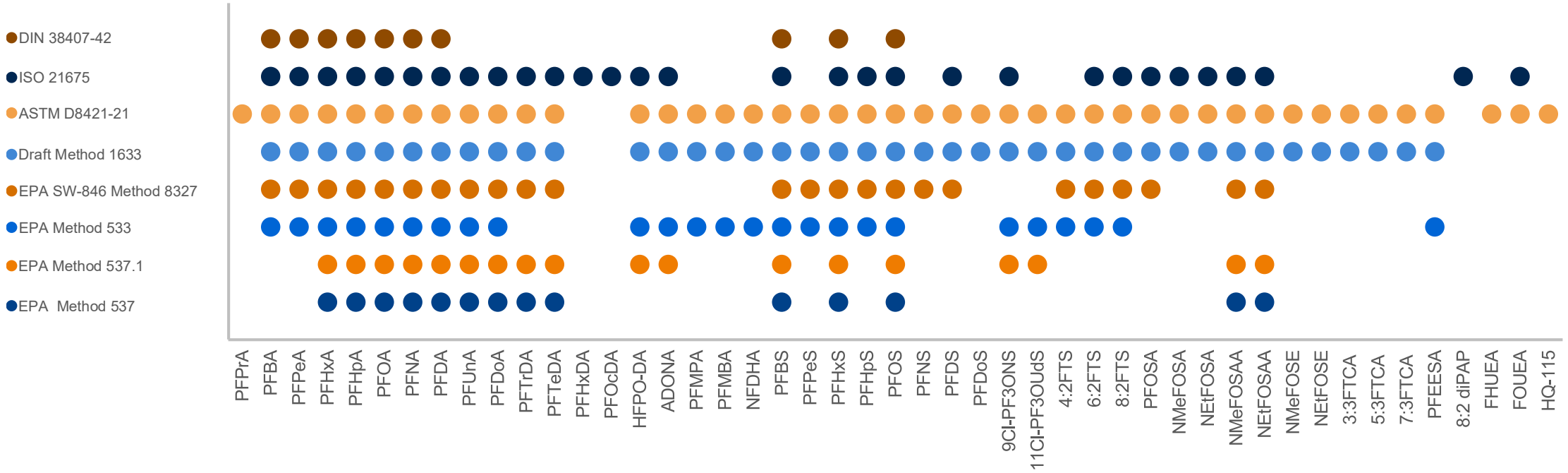
A possible replacement for:
- Oasis® WAX
- Strata™ -X-AW

Fulfills EPA Method 533, EPA Draft Method 1633!

Method comparison

Method comparison

Scope of analytes



Method comparison

Method differences

	EPA Method 537/537.1	EPA Method 533
SPE Column	SDVB SPE cartridges	weak anion exchange, mixed-mode polymeric sorbent, approximately 33 µm, pKa ~8
Conditioning	two steps (methanol, water)	three steps (methanol, aqueous phosphate buffer, water)
Elution	one step (methanol)	one step (NH_3 in methanol)

Method comparison

Method differences

	EPA Draft 1633	ISO 21675
Sample preparation	Setting a neutral pH value for sample	Setting a acidic pH value for sample
SPE Column	solid-phase extraction cartridges, pKa ~8	copolymer cartridges
Elution	one step (NH_3 in methanol)	two steps (methanol, NH_3 in methanol)
Eluent exchange	No eluent exchange (neutralization and additional clean-up with GCB)	Evaporation to a final volume of e.g. 1 ml, redissolve in methanol/water

Method comparison

Method differences

- Direct injection: Only for simple matrices and higher MRL´s

	EPA SW-846 Method 8327	ASTM D8421-21	ISO 21675
Sample preparation	No acid addition	Addition of acetic acid	No acid addition
Sample filtration	GxF, 0.2µm pore-size GHP	Polypropylene, 0.2 µm pore-size or equivalent	nylon or GxF, 1 µm to 10 µm pore-size

Method comparison

LC-MS/MS Analysis (EPA Method 533)

HPLC conditions	
DELAY Column	EC 50/2 NUCLEODUR® PFAS Delay (REF 760673.20)
Column	EC 100/2 NUCLEODUR® PFAS, 3 µm (REF 760666.20)
Eluent A	5 mM ammonium acetate in water
Eluent B	5 mM ammonium acetate in methanol
Gradient	Hold 40 % B for 1 min, in 8 min from 40 % B to 95 % B, hold 95 % B in 0.1 min to 40% B, hold 40 % B for 2.9 min
Flow rate	0.3 mL/min
Temperature	40 °C
Injection volume	1 µL

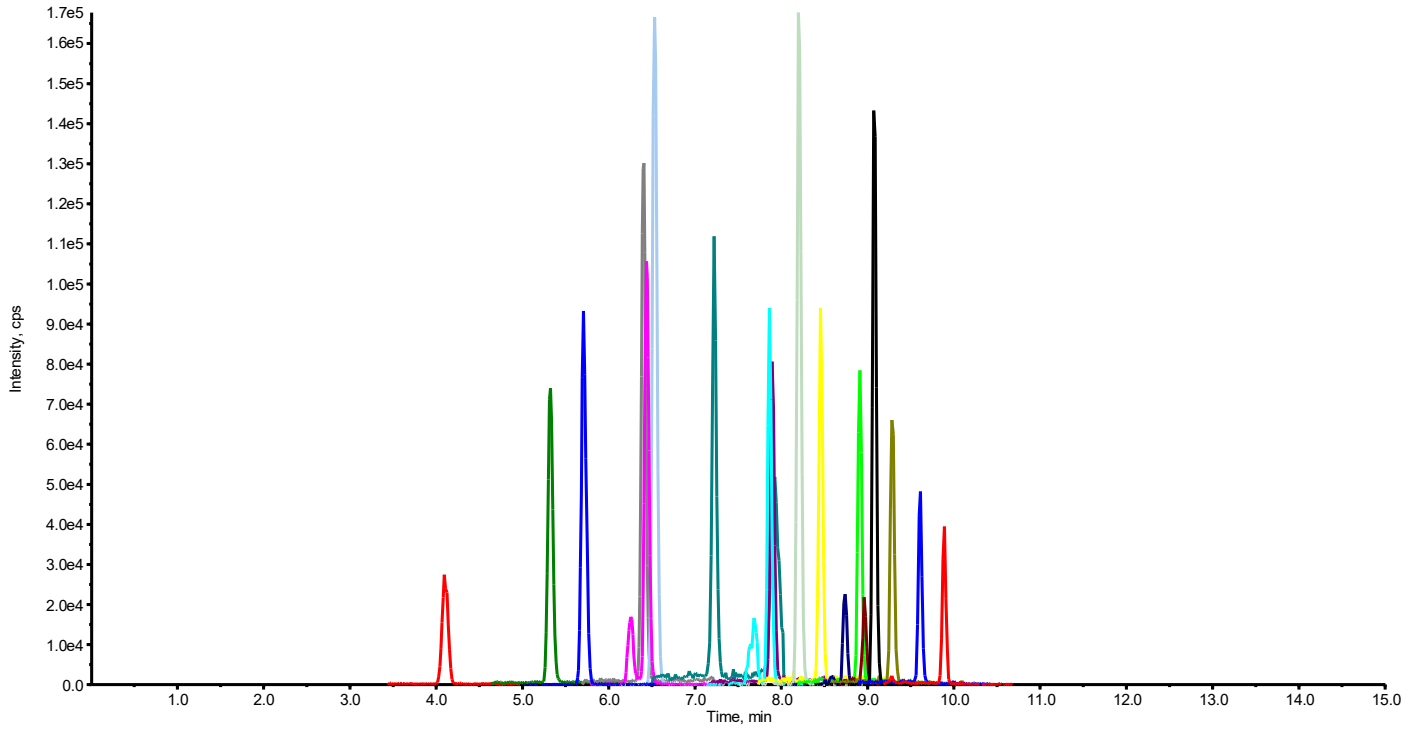
Method comparison

LC-MS/MS Analysis (EPA Method 533)

MS conditions (API 5500 SCIEX)	
Acquisition mode	SRM
Interface	ESI
Polarity	negative
Curtain Gas	30
Collision Gas	medium
Ionspray Voltage	-4500 V
Temperature	400 C
Ion Source Gas 1	50
Ion Source Gas 2	60
Detection Window	60 sec

Method comparison

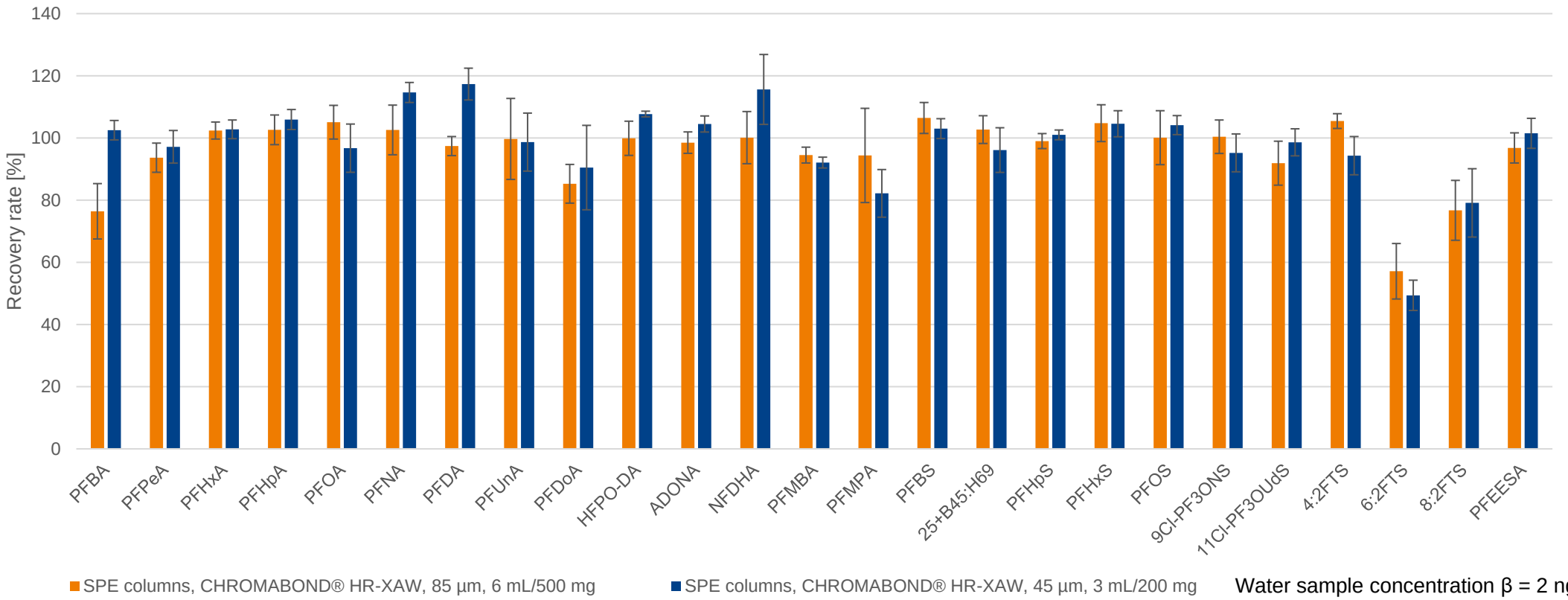
LC-MS/MS Analysis (EPA Method 533)



https://www.mn-net.com/media/pdf/21/26/5a/ApplicationNote-02-2021-PFAS-EPA533.pdf

Method comparison

Recovery rates EPA 533

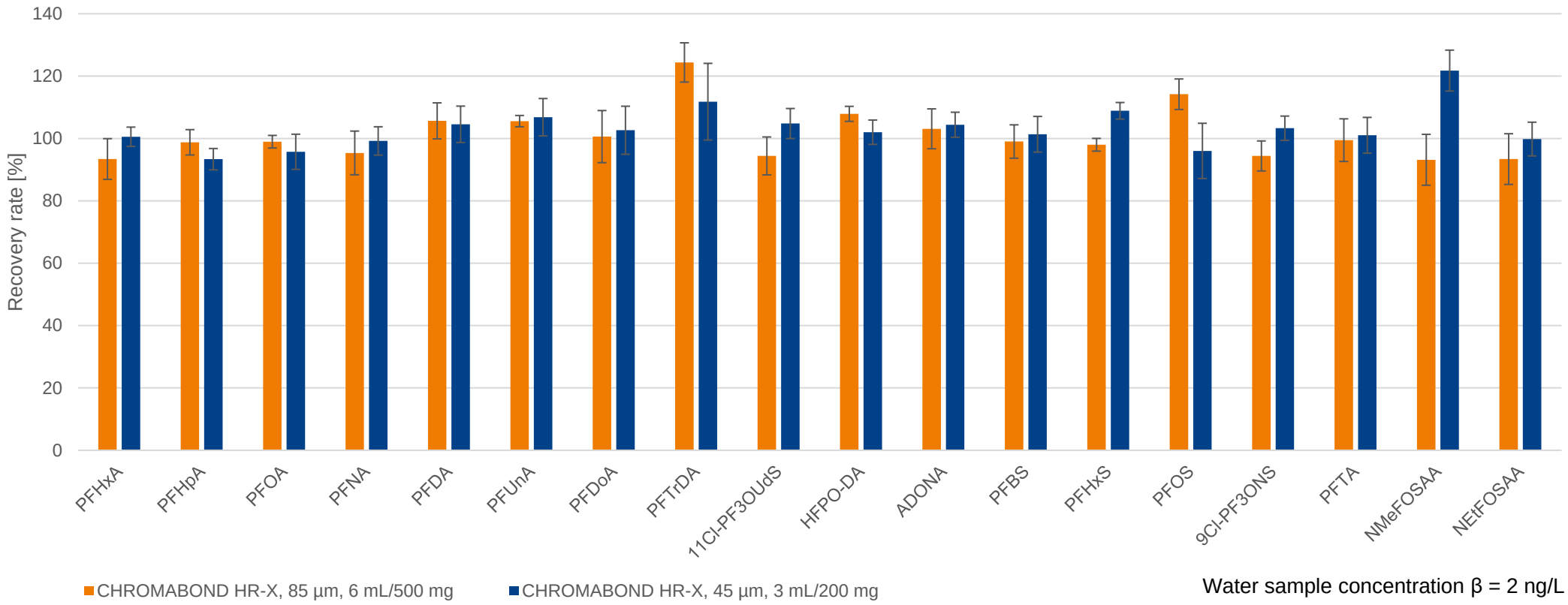


Water sample concentration β = 2 ng/L

https://www.mn-net.com/media/pdf/21/26/5a/ApplicationNote-02-2021-PFAS-EPA533.pdf

Method comparison

Recovery rates EPA 537.1

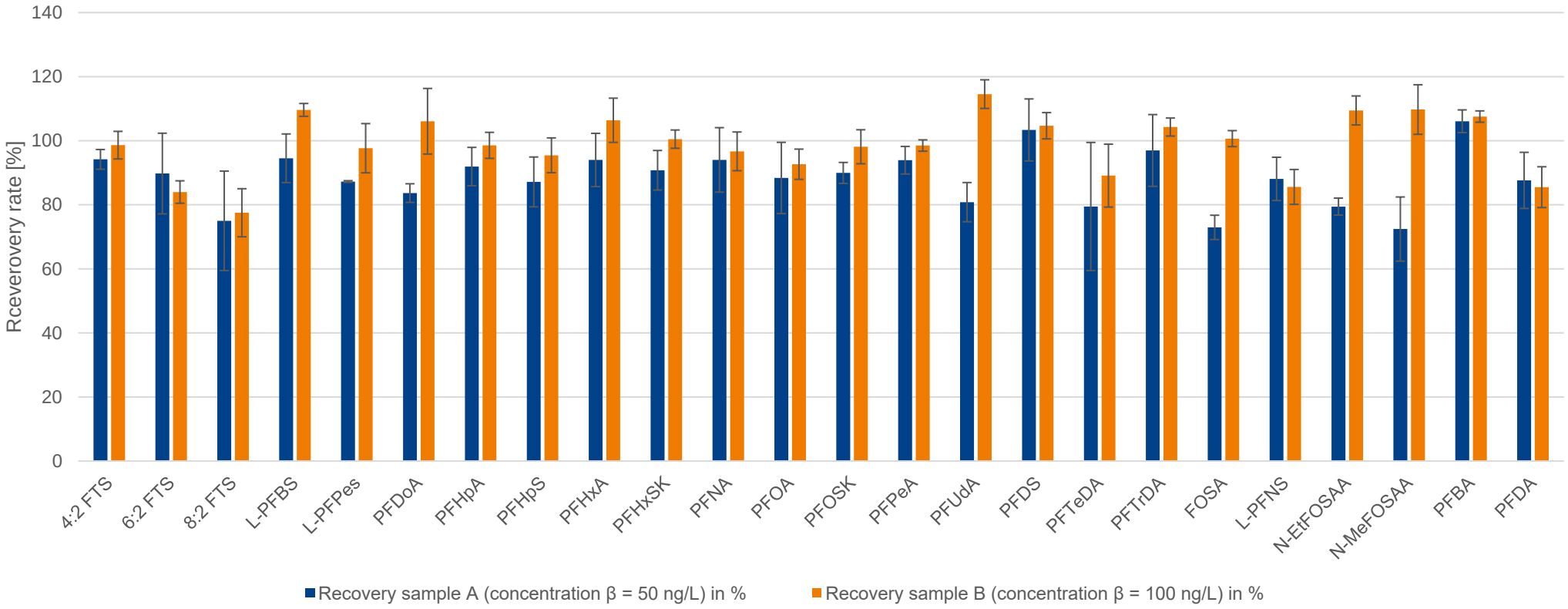


Water sample concentration β = 2 ng/L

https://www.mn-net.com/media/pdf/c0/db/6e/ApplicationNote-01-2021-PFAS-EPA537_1.pdf

Method comparison

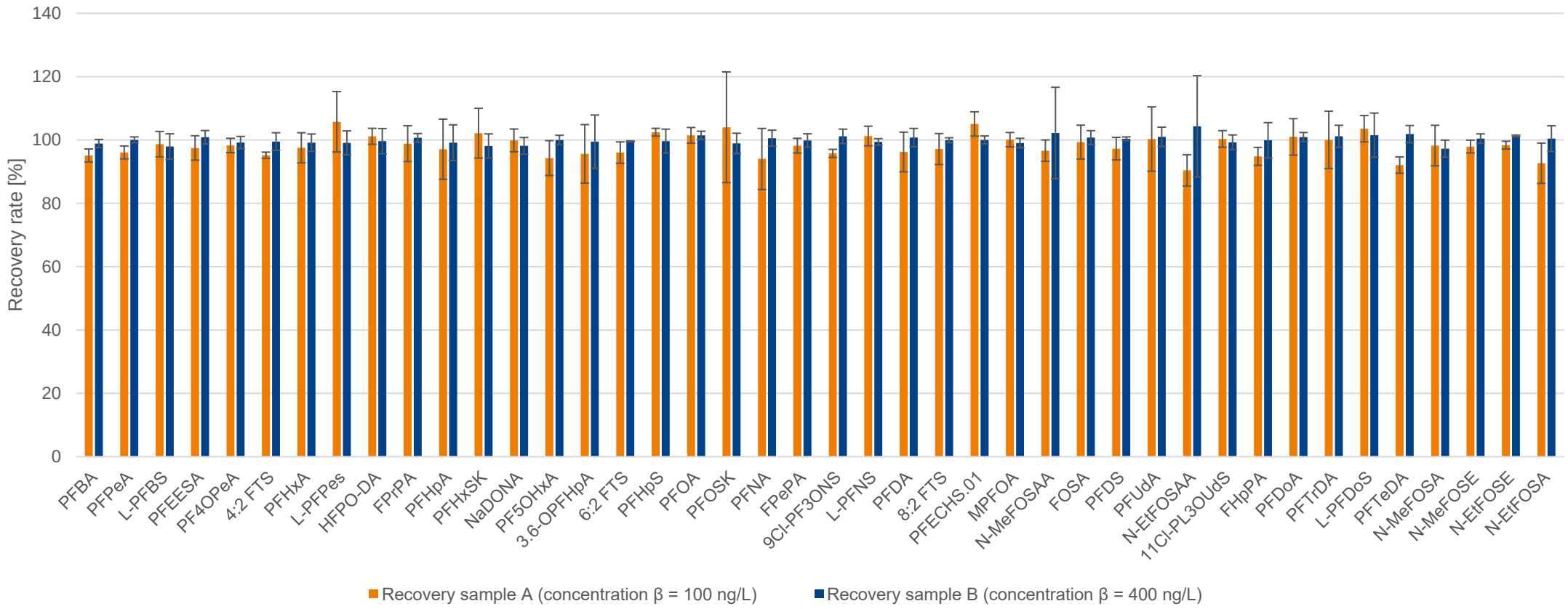
Recovery rates EPA SW-846 Method 8327 (Direct injection)



https://www.mn-net.com/media/pdf/29/d7/f8/AN-05-2021-PFAS-EPA8327.pdf

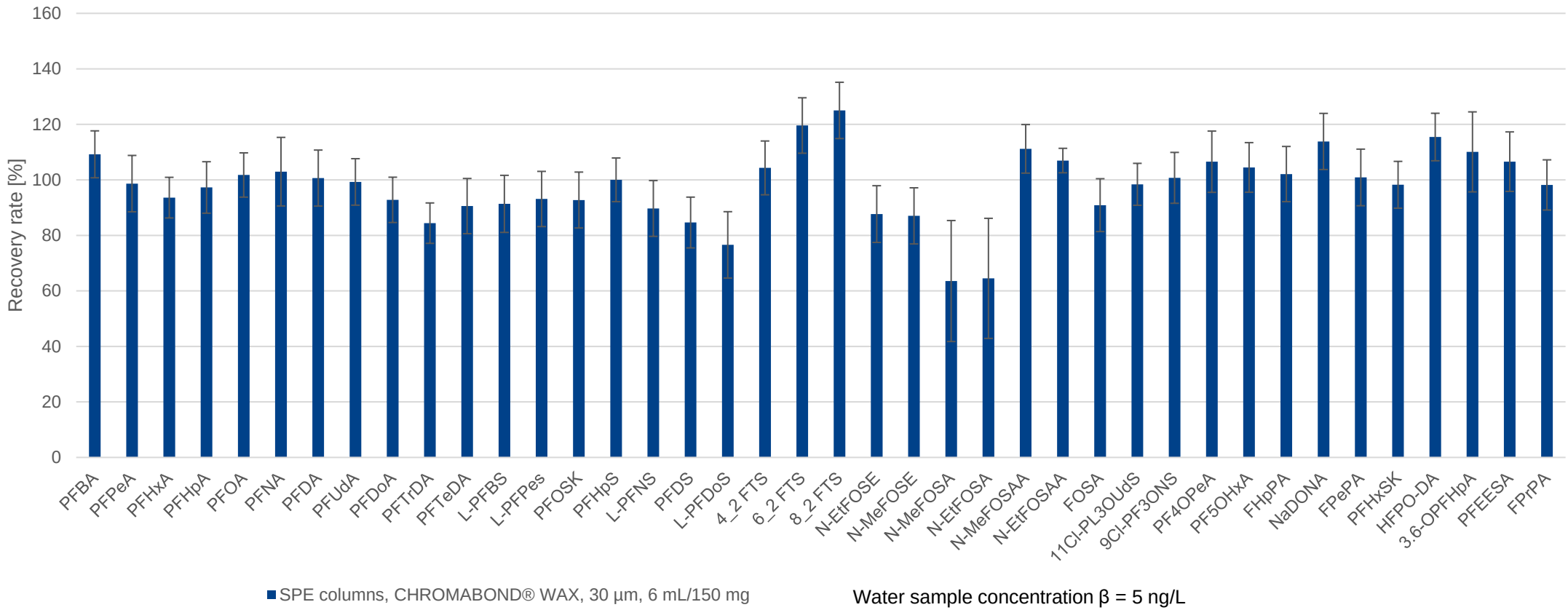
Method comparison

Recovery rates ASTM D8421-21 (Direct injection)



Method comparison

Recovery rates EPA Draft Method 1633



Water sample concentration β = 5 ng/L

Method comparison

Recovery rates

- For most PFAS: **80 – 100 %**
- Recovery rate and reproducibility decrease with length of PFAS-chain
- All presented products are very suitable for PFAS analysis

Method comparison

The development of PFAS analysis leads to several analytical challenges !

- Laboratory costs increase with higher requirements (lower MRL, MS-Sensitivity, PFAS standards, surrogates …)
- Sample handling gets more complicated (adsorption effects, PFAS different chemical properties, low blind value Levels …)
- Are such complex methods necessary for water monitoring?
  - Short chain PFAS have the highest impact on human health
  - Long chain PFAS make analysis costy

Summary

Summary

Scope of PFAS analyts for monitoring is expanding day by day!

- Many powerful methods have been developed in recent years
- Each Method shows strength and weaknesses
- Products for PFAS analysis get more and more optimized and specialized
- PFAS analysis is nothing for beginners

MACHEREY-NAGEL

„Forever chemicals“ will keep us busy!

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