

Laboratory considerations when analysing PFAS containing samples

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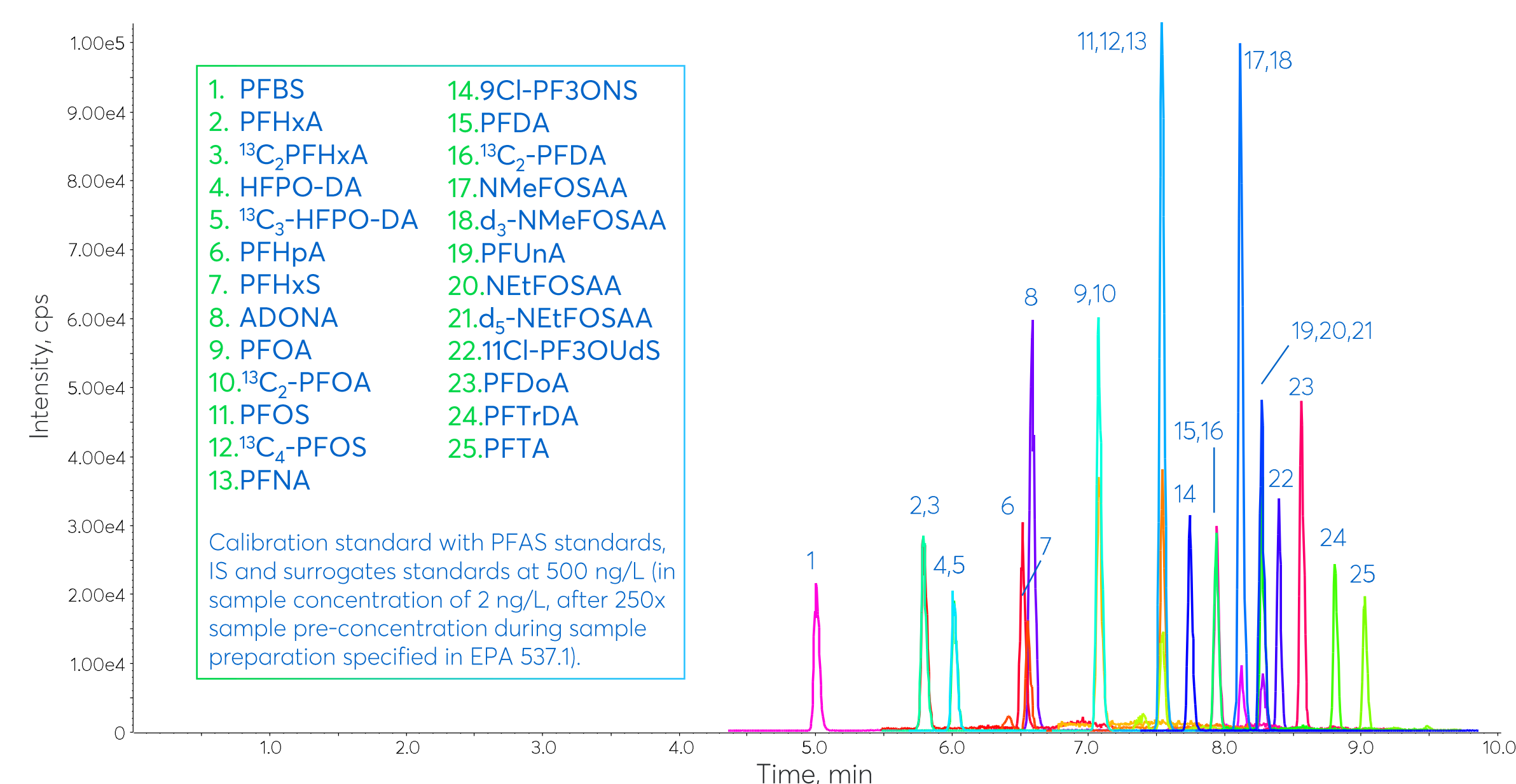
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1. Background

- Determination of PFAS by LC-MS in environmental matrices is very challenging for many reasons, including:
 - Low-level quantification required by regulatory authorities.
 - Diverse range of target compounds.
- Ubiquitous presence of PFAS containing materials within the natural/human environments means the potential for sample contamination is high.
- This includes the laboratory environment!
- It is therefore important to characterise potential sources of contamination within the laboratory.
- This work summarises experiences from within our laboratory when developing an LC-MS/MS method within a working "non-PFAS" laboratory for the analysis of PFAS according to EPA 537.1.

2. Methodology

- A chromatographic method based on EPA 537.1 was developed and used to assess potential contamination sources.
- Pipette tips, centrifuge tubes & 4 mL polypropylene bottles were verified to be PFAS free by extraction with 1 mL MeOH.
- Autosampler vials and caps were tested by addition of 300 µL MeOH.
- Laboratory consumable and tubing samples were weighed into 10 mL centrifuge tubes, 1990 µL MeOH & 10 µL IS solution added.
- All samples were vortex mixed for 30 minutes.



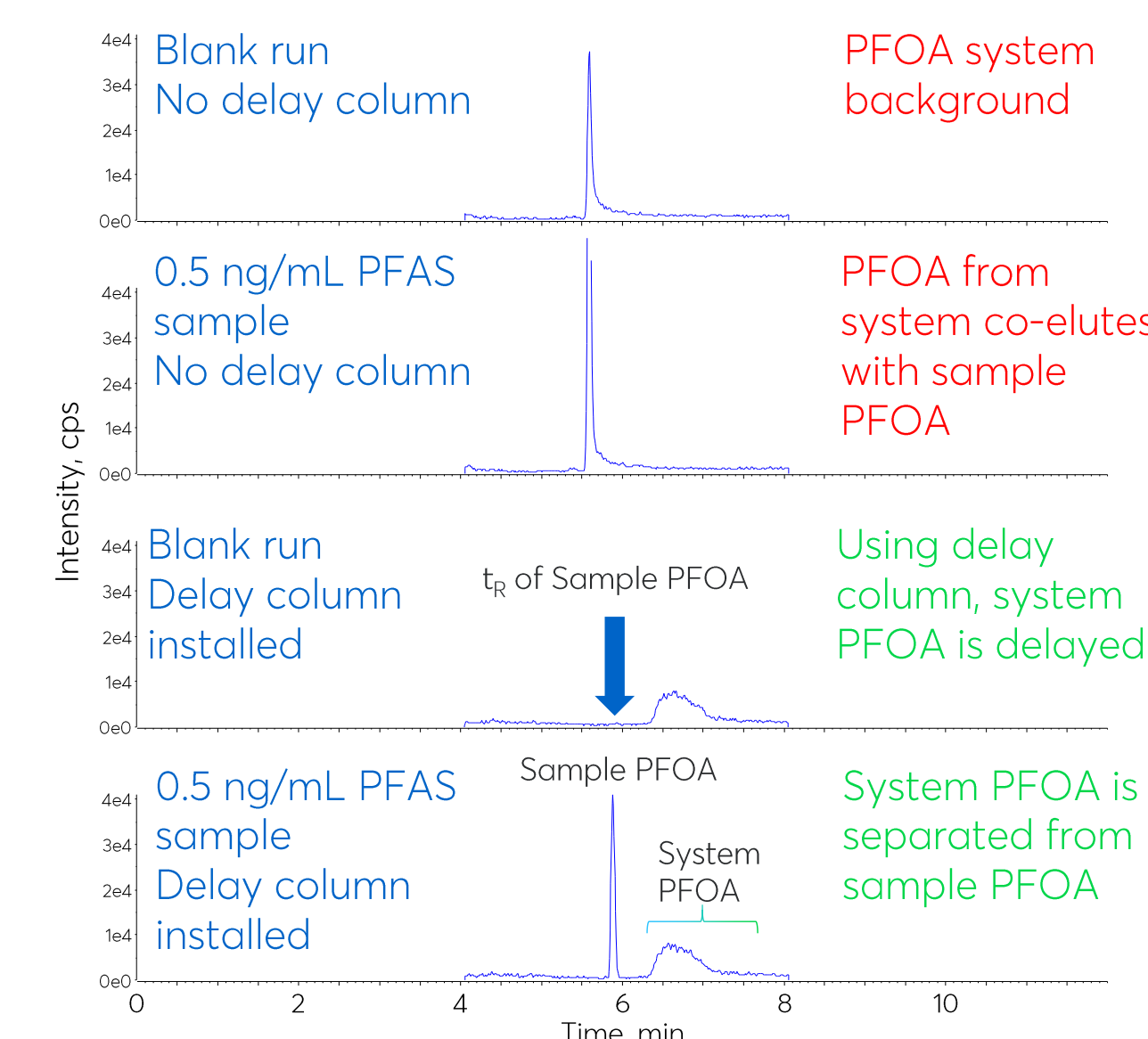
Column: Avantor® ACE® Excel® 3 C18, 100 x 2.1 mm
 Delay Column: Avantor® ACE® PFAS Delay Column, 50 x 2.1 mm
 Mobile Phases: A: 5 mM ammonium acetate in H₂O
 B: MeOH
 Flow Rate: 0.4 mL/min
 Temperature: 40 °C
 Injection volume: 1 µL
 Detection: Sciex QTRAP® 6500+ LC-MS/MS system.
 Ionisation mode: ESI, negative mode; Source temperature: 450 °C;
 Curtain gas: 30 psig; Ionspray™ source voltage: -4500 V;
 Ion source gas: 60 psig

Time (mins)	% B
0	5
0.1	20
8.5	95
10.5	95
10.6	5

Full method details: Avantor® ACE® Application Note #7820 (<https://av.cmd2.vwr.com/pub/apl/chrom/main?key=C-13278>).

3. Mobile phase background

- PFHxA, PFHpA, PFOA, PFOS, PFNA & PFDA detected in system blanks.
- Similar profile observed in solvent line tubing extract.
- Use of PFAS delay column resolves potential quantification issues.



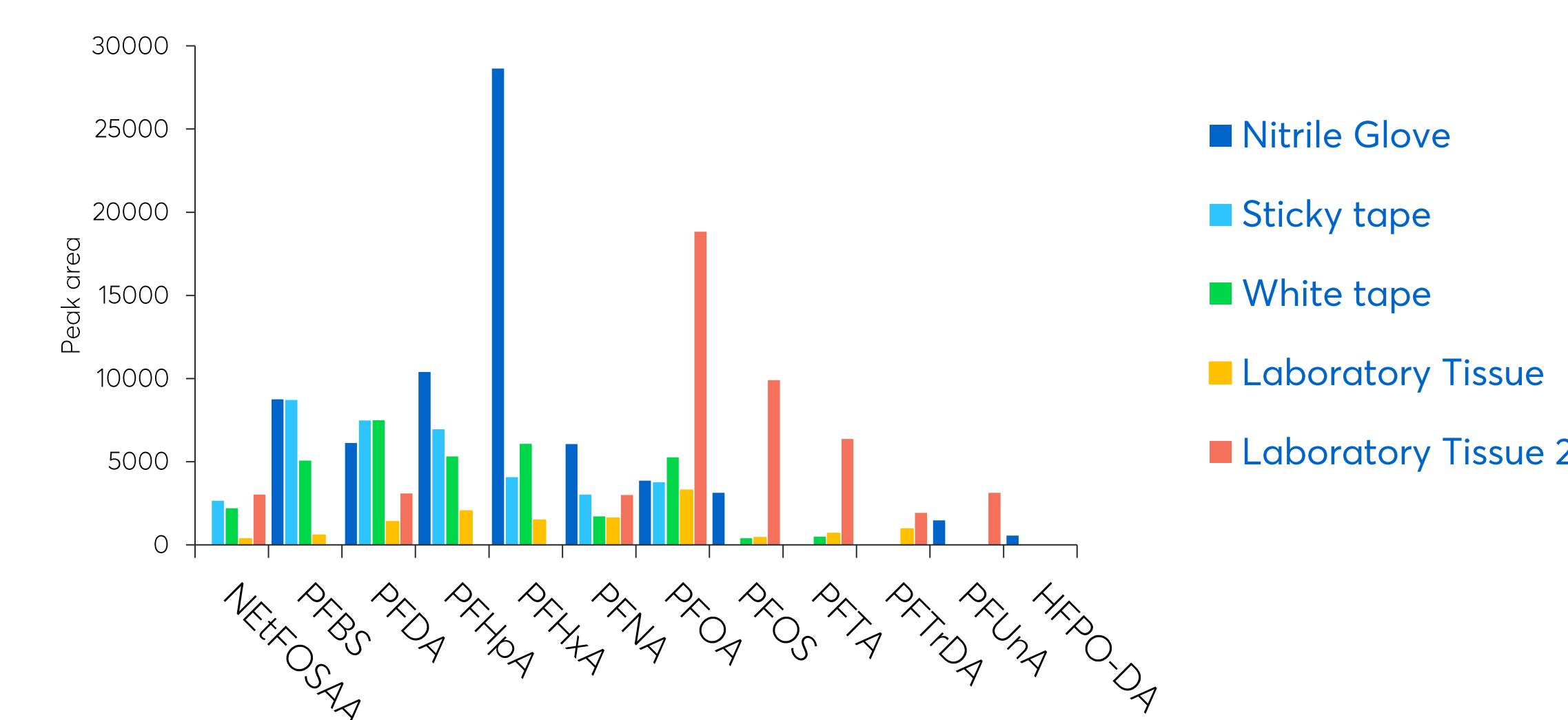
- Use of delay column mandatory
- Exchange solvent lines with PEEK

4. Consumable testing for extractable PFAS

- Vials & caps recommended for PFAS analysis were screened.
- ADONA was observed from one manufacturer and determined to originate from polyimide/silicone cap.

	Blank run	1	2	3	1	3
Vial Manufacturer	N/A					
Vial material	N/A	PP	PP	PP	PP	PP
Cap Manufacturer	N/A	1	2	3	3	1
Septum material	N/A	PP	PP	PI/Si	PI/Si	PP
ADONA	×	×	×	✓	✓	×
Other PFAS (18 cpds)	×	×	×	×	×	×

- A variety of common laboratory consumables were also qualitatively screened.
- Detectable PFAS were extracted from a number of these.
- Assessment of potential sources can be used to refine workflows to reduce risk.



- Regular testing of LC-MS consumables recommended.
- Screening of laboratory consumables to optimise workflows recommended.

5. Sample blowdown

- Sample preparation step (spe extraction into 8 mL MeOH, N₂ blowdown and reconstitution to 1 mL) was anticipated to be a potential source of contamination.
- During testing, samples were found to become contaminated with PFHxA during the blowdown step.
- Simplification of the blowdown apparatus to a single glass or PP pipette tip and use of an activated carbon trap didn't resolve the issue.
- PFHxA believed to originate from nylon gas lines used to connect site air compressor and nitrogen generator to blowdown apparatus.
- Use of N₂ cylinder with polypropylene tubing resolved this issue.

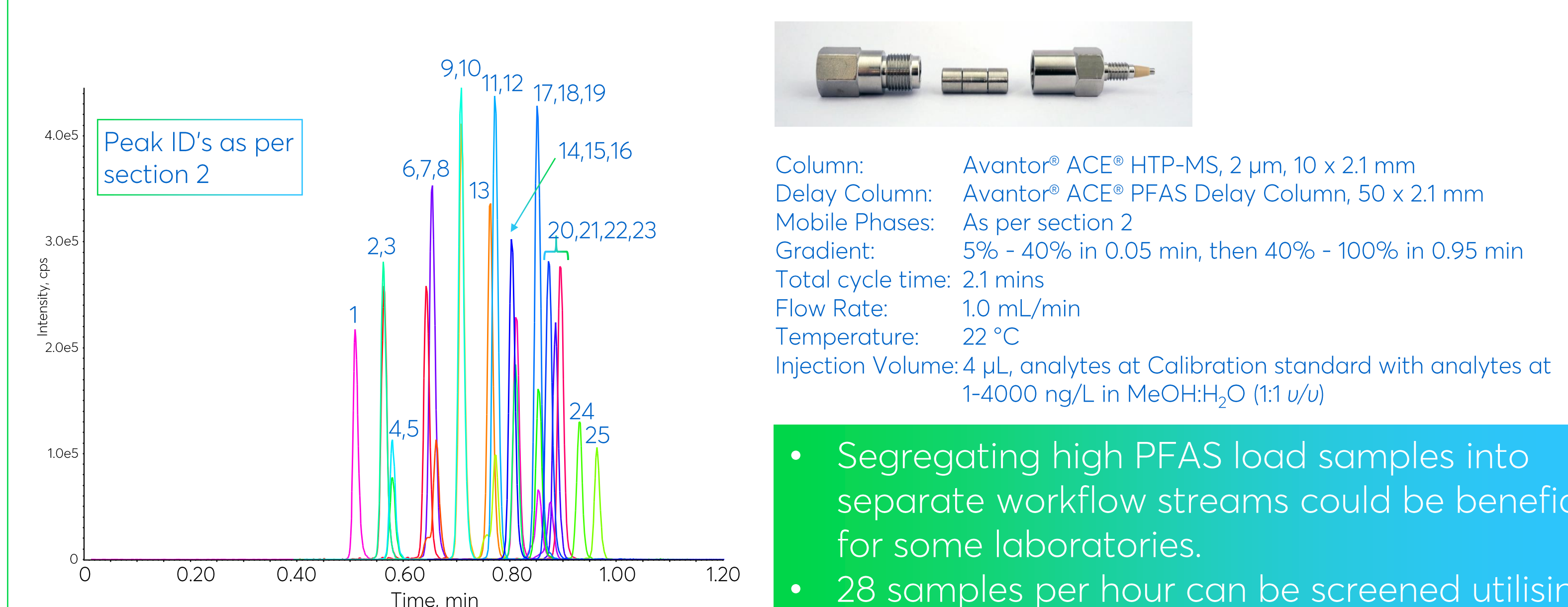
Extractable PFAS content of gas line materials

	Nylon	Polyurethane	PTFE (source 1)	PTFE (source 2)
PFHxA	1.53 ng/g	0.05 ng/g	-	-
ADONA	-	0.02 ng/g	2.03 ng/g	-
PFNA	0.05 ng/g	-	-	-
HFPO-DA	-	-	0.09 ng/g	-
PFTTrDA	-	0.05 ng/g	-	-

- Nitrogen blowdown apparatus can potentially be a significant source of sample contamination

6. Rapid sample pre-screening

- High PFAS load samples could potentially cross-contaminate other samples during parallel/subsequent processing.
- Pre-screening samples to identify and segregate high PFAS load samples could mitigate this risk, but is time consuming.
- A novel pre-screening method using a 10 mm column is under development to provide a rapid solution for pre-screening aliquots of water samples.



- Segregating high PFAS load samples into separate workflow streams could be beneficial for some laboratories.
- 28 samples per hour can be screened utilising a short 10 mm column.

7. Conclusions

- Several potential sources of PFAS contamination were identified.
- Use of Delay column & PFAS grade solvents resolved issues related to LC system background.
- Screening of LC, general laboratory consumables and laboratory equipment highly recommended to identify potential sources and eliminate from analytical workflows.
- A rapid sample pre-screening methodology is under development.