

Establishing the Updated US EPA 537.1 for PFAS Reliably in a Lab by Automated Sample Preparation with the Combination of XANA and D-EVA

Uwe Aulwurm, LCTech GmbH

August 2022



FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Which methods are applied actually



CHARACTERISTIC	EPA 537.1	EPA 533	EPA DRAFT 1633	DoD QSM / 537M	DIN 38407- 42	ISO 21675- 2019
MATRIX	Drinking Water	Drinking Water	Non-potable water, solids, biota	Non-potable water, solids, biota	Drinking water, ground water, surface water, treated wastewater	Drinking water, natural water, waste-water (< 2 g/L SPM)
COMPOUNDS	18	25	40	25	10	30
SPE - CARTRIDGE	SPE – SDVB	SPE – WAX	SPE – WAX, carbon clean-up	SPE – WAX, carbon clean-up	SPE – WAX	SPE – WAX
Automated SPE FREESTYLE	XANA-PFAS XANA TableTop	XANA-PFAS XANA TableTop	XANA-PFAS XANA TableTop SPE-PFAS (Dual)	XANA-PFAS XANA TableTop	XANA-PFAS	XANA-PFAS XANA TableTop
Concentration	D-EVA	D-EVA	D-EVA	D-EVA	D-EVA	D-EVA

FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Which methods are applied actually



	FREESTYLE SPE PFAS	FREESTYLE XANA PFAS TableTop	FREESTYLE XANA PFAS
Max. volume per sample	100 mL	250 mL (dedicated bottles required*)	4 L (10 L Upgrade possible)
Samples per sequence	27	30	24
Duration per sequence (depending on regulation and flow rates)	13 h (Dual-SPE for food matrices)	12 h (for US EPA 537.1)	9 h (for US EPA 537.1)
Samples at the same time	1	Up to 6	Up to 6
Location	On laboratory bench	On laboratory bench	On included table
Fumehood required	No		
PFAS compatibility	PE tubings, PTFE free syringe, PTFE free valves		
Solvent compatibility	Compatible with all solvents required		

*Thermo/Nalgene; P/N: 2104-0008

Sample Preparation Solutions by LCTech

Sample Preparation Solution for Water Samples

SOLUTIONS BY **LCTech**

Sampling

-
250 mL bottle

Clean-up with FREESTYLE XANA-PFAS System



SPE Material



Concentration with D-EVA

-
final volume-controlled



Analysis

Sample Preparation Solution for Food/Feed, Soil, Biota

Sampling

-
Homogenized sample

Extraction by PLE X-TRACTION



Clean-Up with FREESTYLE PFAS for SPE Cleanup (also Dual SPE)



SPE Material



Concentration with D-EVA

-
final volume-controlled



Analysis

Updated US EPA 537.1 - Summary of the Method

- Load 250 mL water sample + SUR onto SDVB SPE cartridge
- Load 2x 7.5 mL water (sample bottle rinsate) on cartridge and dry cartridge for 5 min with air/N₂
- Rinse sample bottle with MeOH (2x 4 mL), rinsate applied for elution
- Concentration to dryness
- Adjust to 1 mL volume with 96:4 % (vol/vol) methanol:water and IS
- Inject 10 µL into an LC-MS/MS equipped with a C18 column

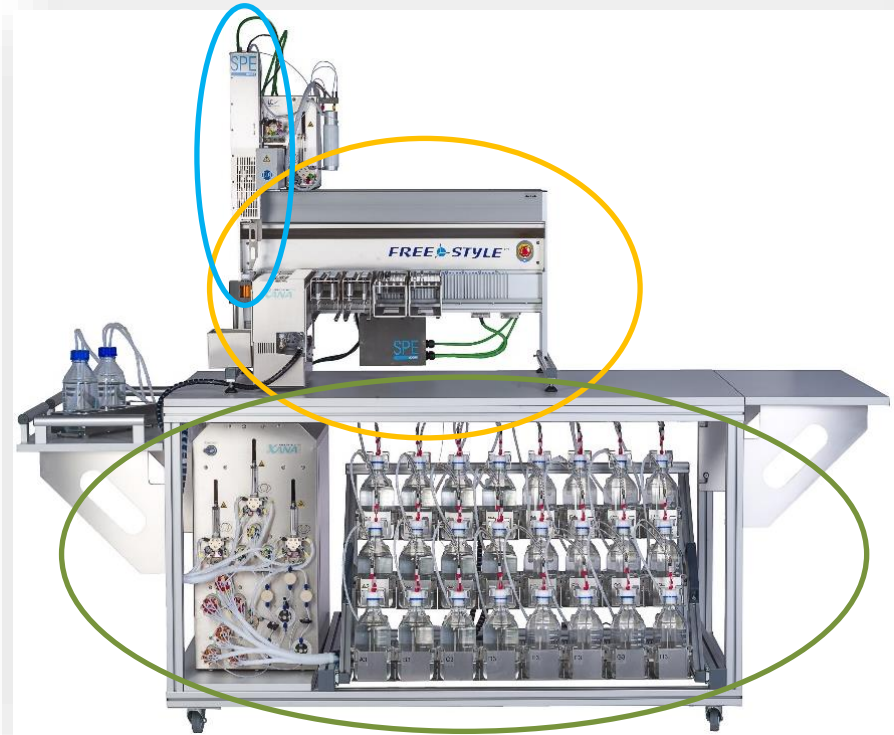
FREESTYLE and D-EVA for Automated Sample prep in PFAS Analysis

Automated SPE as Introduced on NEMC 2020

SOLUTIONS BY **LC** Tech

- FREESTYLE SPE PFAS or
 - FREESTYLE SPE XANA PFAS
- FREESTYLE-SPE-XANA**

- Minimized fluoroplastic components
- No PFAS background
- Robust 24/7 automation



FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

The Guarantor of a Robust Throughput

Non-stop policy – a unique error handling

The screenshot shows the SPE Planner software interface. The main window displays a sequence of steps for sample preparation. The steps are: Conditioning, Emptying, Load, Washing, Drying, and Eluting. The current step is 'Washing', which is highlighted in yellow. The 'Washing' step details include: Volume: 4 ml, Repeats: 2 x, Total: 12 ml, Suction Speed: 5 ml/min, Dispensing Speed: 10 ml/min, Waiting time after dosage: 10 sec, and Waiting time after step: 5 sec. The 'Calculated time' for this step is 5.7 min. The 'SPE Steps' section shows a total of 6 steps with a total time of 24.6 min. The 'Input Vials' table shows 3 vials, and the 'Result vials' table shows 3 vials. The 'Pressure limit for syringe pump' field is set to 110 digits. A blue arrow points from the 'Pressure Monitoring' text to this field.

Step No.	Owner	Count	Type	Basic type	ID
3	Load	1	Type1/20	LAD	603

Step No.	Owner	Count	Type	Basic type
3	Conditioning	1	Type1/20	LAD

Pressure Monitoring

Once this monitoring alerts a blocked cartridge, this one will be taken out of the sequence (noted in report) and the rest of the sequence processed

FREESTYLE and D-EVA for Automated Sample prep in PFAS Analysis

Highlight for Throughput- External Working Station

SOLUTIONS BY



- PE transfer tube system acc. to material chapter of the method
- Pumps pump 3 samples in parallel with flow rates of 1 - 30 mL/min.
- Conditioning, washing, rinsing and drying of 3 columns in parallel with up to 8 solvents for conditioning, rinsing and washing
- Detection of empty bottles, positions that are not used aren't processed!



FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Highlight for Throughput

SOLUTIONS BY **LC** Tech

Parallel loading and overlapping process on Working Station on FREESTYLE platform:

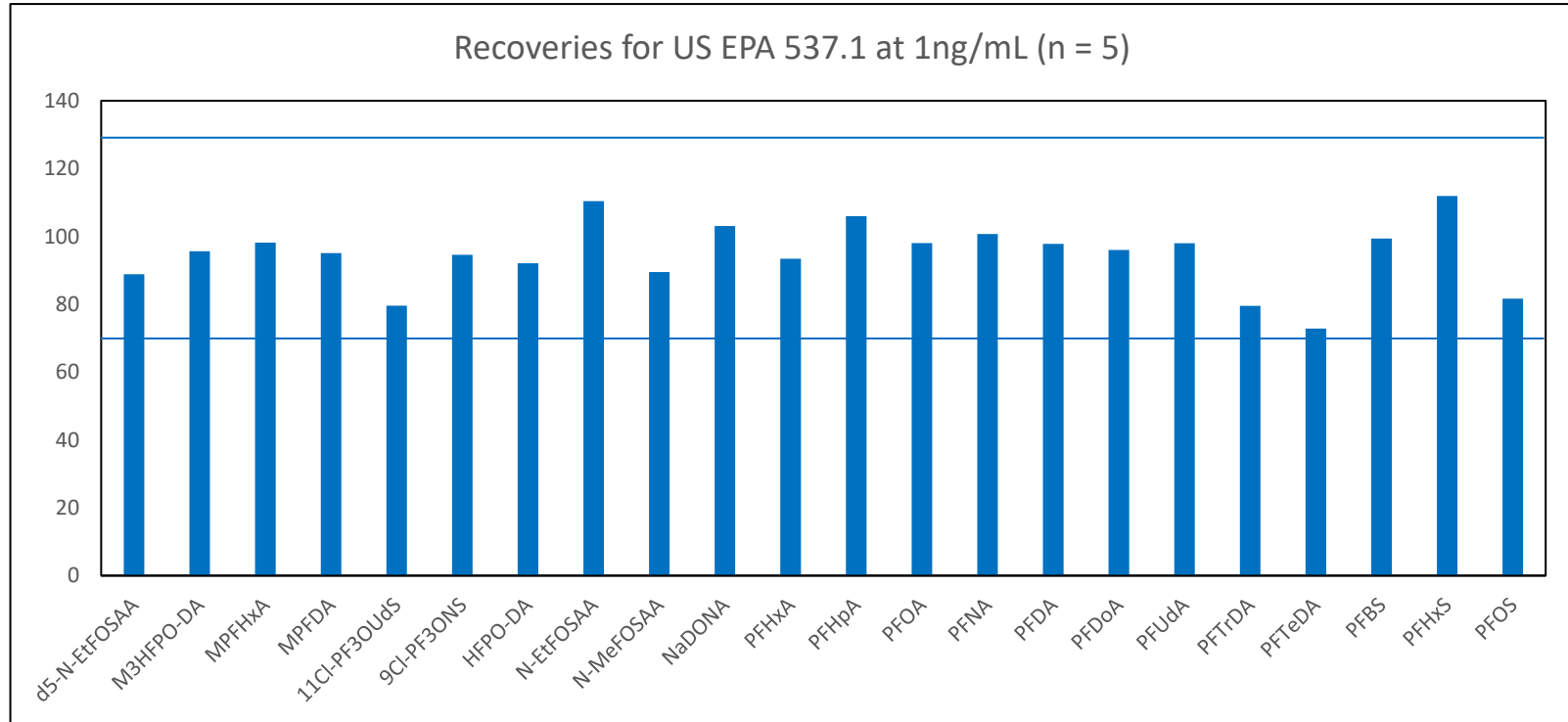
- Processes 2 x 3 samples in parallel
- Tightens 6 columns pressure-tight
 - Loads 3 columns in parallel
 - Dries 3 columns in parallel
- With central discharge



FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Automated SPE Applied Acc. to US EPA 537.1

SOLUTIONS BY



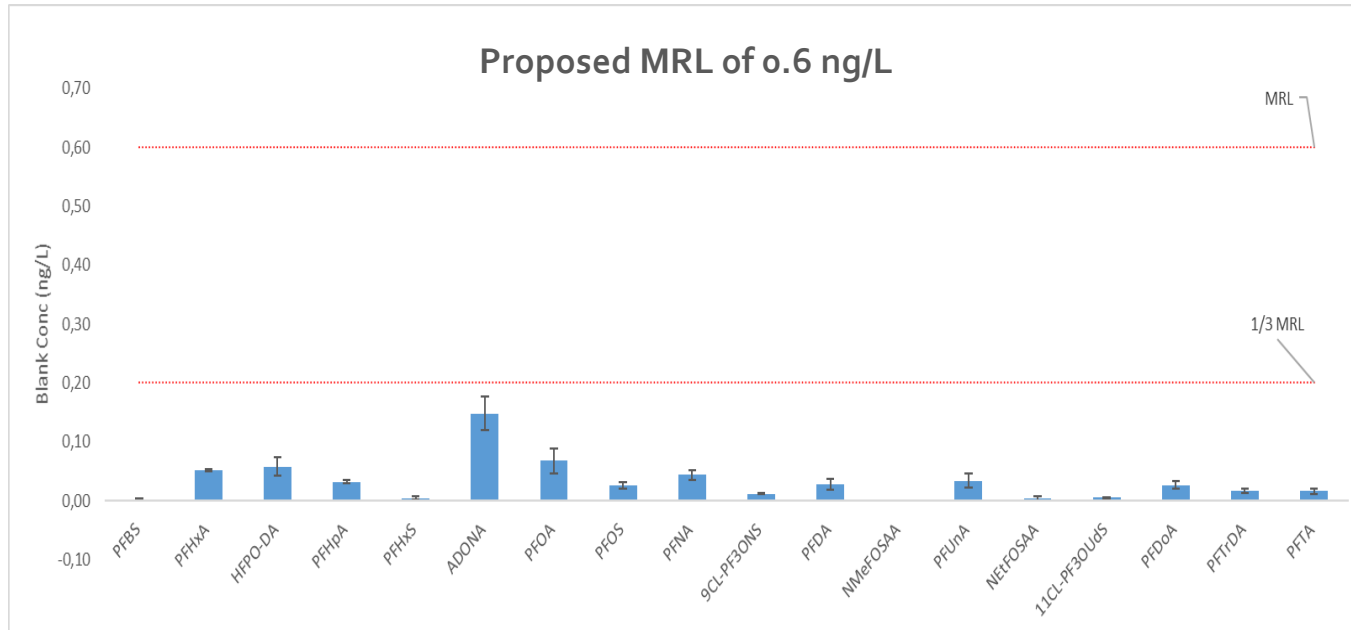
FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Automated SPE Applied Acc. to US EPA 537.1



Demonstration of low background:

All analytes are below 1/3 of lowest standard; Proposed MRL of 0.6 ng/L



Apparent background derives from the solvents, which was proven in additional experiments

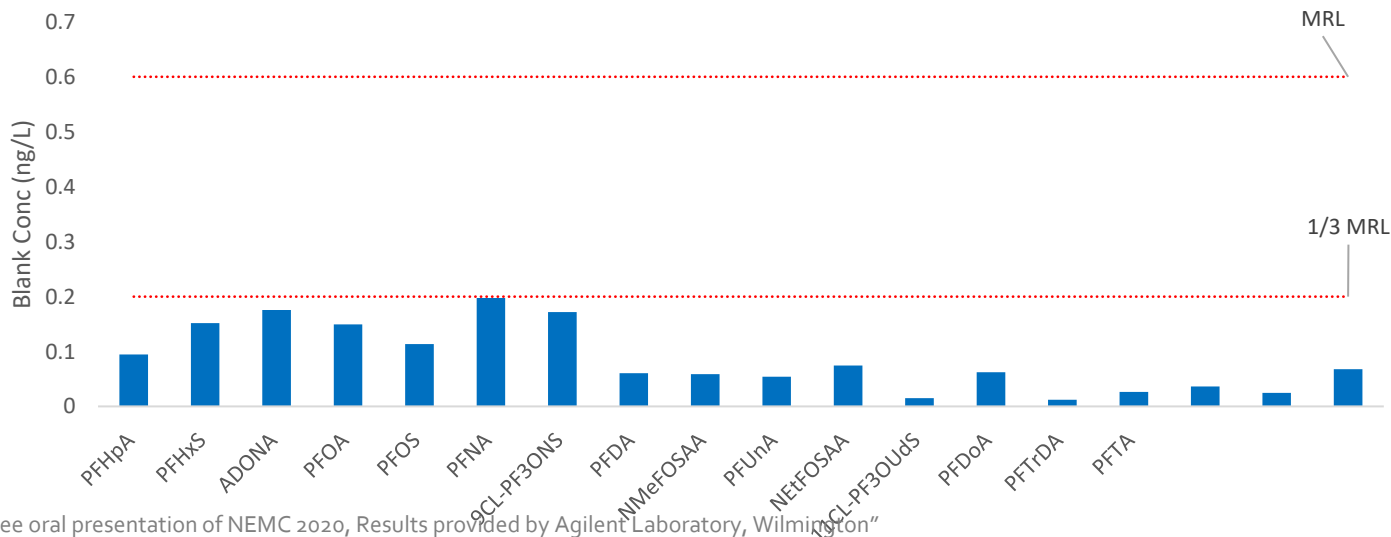
US EPA 537.1 does not allow subtraction of blind values

*see oral presentation of NEMC 2020, Results provided by Agilent Laboratory, Wilmington"

Additional Info Demonstration of Low Background

Despite the fact that all values are according to requirement, check for the cause of contamination by evaporating all solvents offline.

Evaporation Experiment of the sum of all solvents in the protocol without FREESTYLE involved

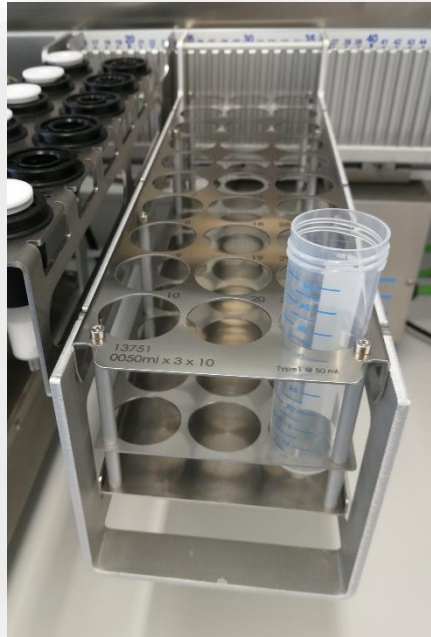


*see oral presentation of NEMC 2020, Results provided by Agilent Laboratory, Wilmington

Homework After Last Talk – No Cross-Contamination

- Customer results acc. to ISO 21675:2019 which covers 30 PFAS analytes
- Reporting Limit: $\geq 0,2$ ng/L
- Blank value for highly contaminated samples e.g. 4500 ng/L
 - Cross-contamination $\sim 0,2$ %
 - Applicable for drinking water analysis
- Duration for 24 samples with additional rinsing ~ 8 h

Homework After Last Talk - Evaporation



- Collected eluate in Falcon tubes
- Common systems that use final volume detection by light barrier have glass vessels involved – PFAS adhere to these
- Therefore only cost and time consuming N_2 blow-down used

„The next step is where we need automation as well....“

FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Please meet our D-EVA

SOLUTIONS BY



FREESTYLE and D-EVA for Automated Sample prep in PFAS Analysis

The Solution

SOLUTIONS BY 

Vacuum Centrifugation „Powered by LCTech“

- D-EVA consists of:
 - Centrifuge with special software and default settings
 - Cryotrap
 - Rotor
 - Special LCTech sensor
- Rotors for 15 mL and 50 mL Falcon™ Tubes available



FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

The Solution

SOLUTIONS BY 

- Challenges remaining:
 - Evaporation stop at defined low final volume needed for PFAS analysis
 - Avoid overheating at end of evaporation
- ➔ **Special LCTech sensor and software** developed for automatic STOP
- ➔ Energy supply via light, no overheating at end of process



FREESTYLE and D-EVA for Automated Sample prep in PFAS Analysis

Racks with Falcon™ Tubes

SOLUTIONS BY **LC** Tech



Rack for parallel processing of 10 x 50 mL Falcon™ Tubes

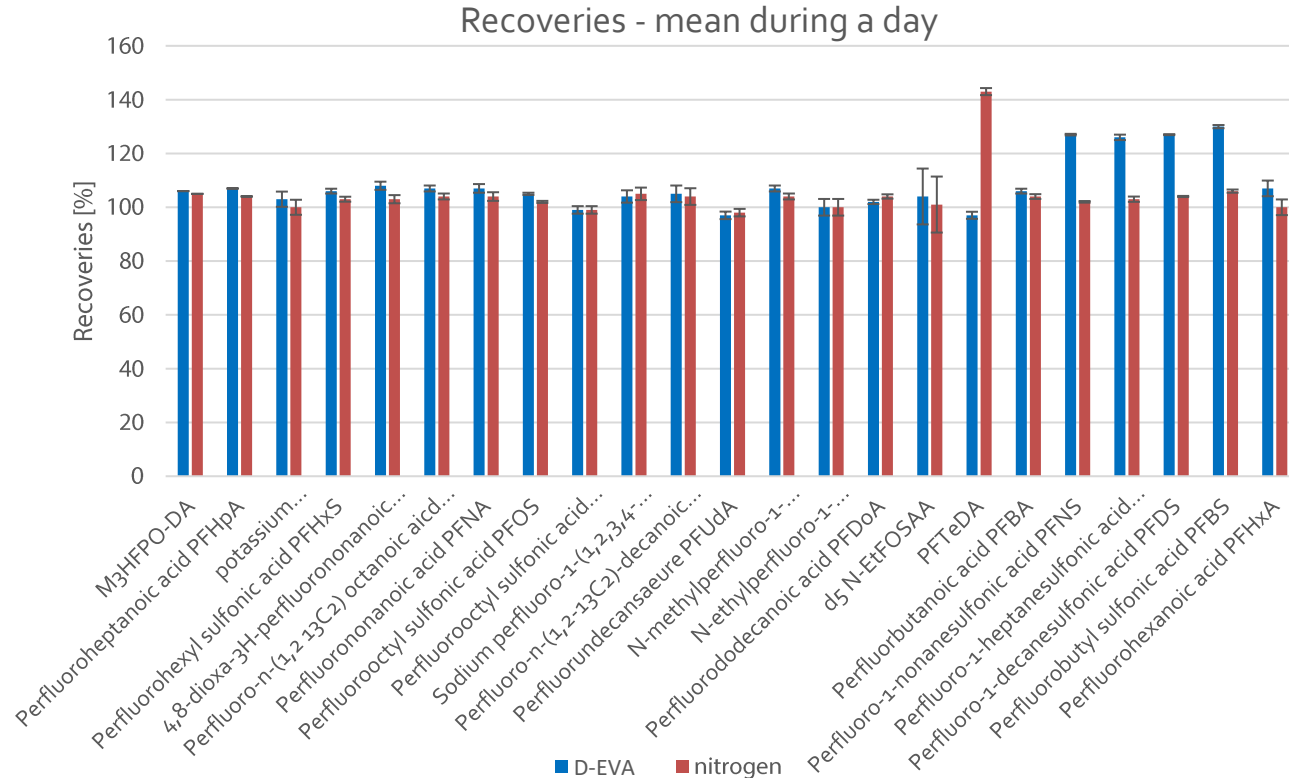


Rack for parallel processing of 23 x 15 mL Falcon™ Tubes

FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

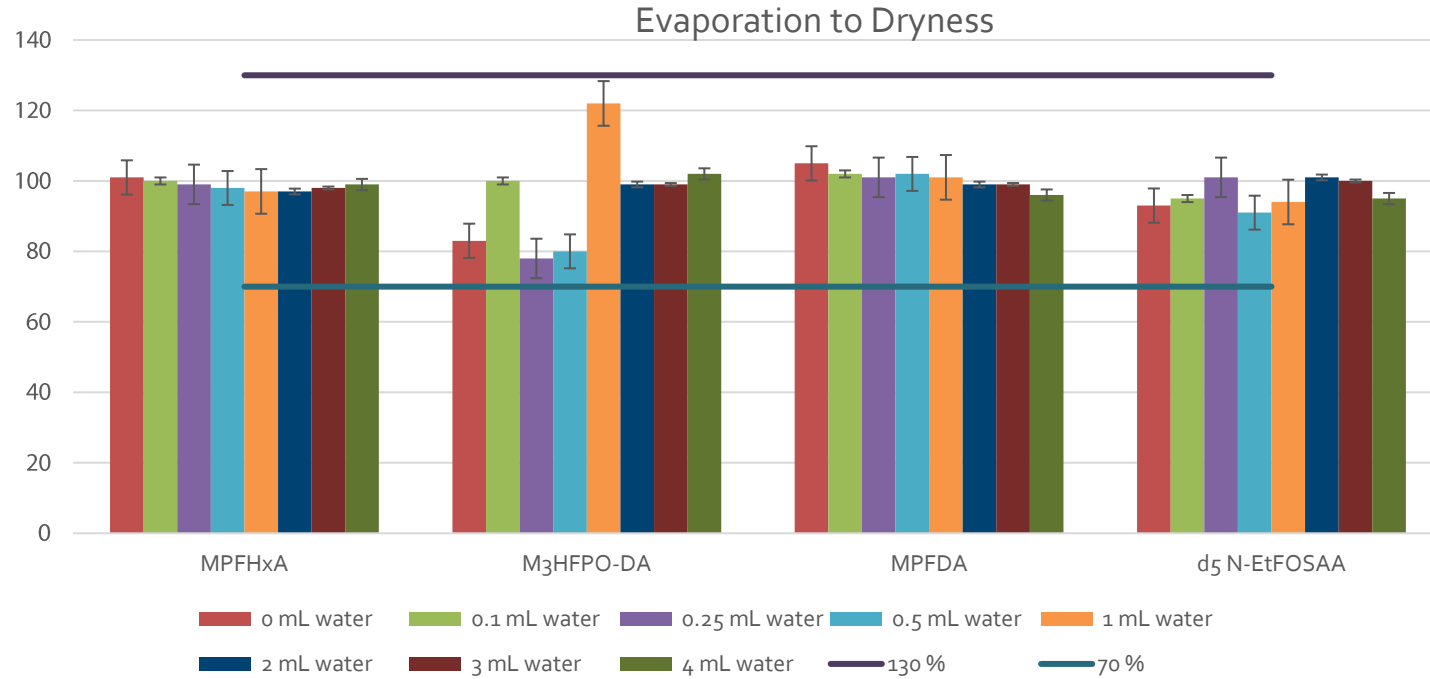
Results – Recoveries

SOLUTIONS BY
LC Tech



FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Results – Recoveries with Residual Water



Robustness against residual water in sample, with program "short" to dryness

Cross-contamination Check SUR

n = 12	Rec. [%]	c [ng/mL]
$^{13}\text{C}_2$ -PFHxA	96.8	0.002
$^{13}\text{C}_3$ -HFPO-DA	78.2	0.000
$^{13}\text{C}_2$ -PFDA	97.7	0.018
d ₅ -NEtFOSAA	96.3	0.156

D-EVA - The Evaporation Solution for US EPA 537.1

- Significantly faster than N₂ blow-down
- Parallel processing of up to 23 samples
- Direct transfer into HPLC vial insert
- No cross-contamination
- Tolerant against residual water
- No cleaning steps during entire process
- No fume hood required

FREESTYLE and D-EVA for Automated Sample Prep in PFAS Analysis

Streamlining the process:



	FREESTYLE SPE PFAS	FREESTYLE XANA PFAS TableTop	FREESTYLE XANA PFAS
Max. volume per sample	100 mL	250 mL (dedicated bottles required*)	4 L (10 L Upgrade possible)
Samples per sequence	27	30	24
Samples at the same time	1	Up to 6	Up to 6
Location	On laboratory bench	On laboratory bench	On included table
Fumehood required	No		
PFAS compatibility	PE tubings, PTFE free syringe, PTFE free valves		
Solvent compatibility	Compatible with all solvents required		
Duration per SPE sequence (for usual US EPA 537.1 flow rates)	13 h (Dual-SPE for food matrices)	12 h	9 h
D-EVA for 10/23 Samples	33/ 77 mins	33/ 77 mins	33/ 77 mins

*Thermo/Nalgene; P/N: 2104-0008

Cliffhanger for Next NEMC Session

Sample Preparation Solution for Water Samples

SOLUTIONS BY **LC** Tech



Sample preparation Solution for Food/Feed, Soil, Biota



* Demonstration for Soil, Biota, ... Solids

** Columns for US EPA 537.1, 533, 1633

Thank you for Your Attention!



Questions? Visit us at booth #9 and #10



LCTech GmbH
Daimlerstraße 4
info@LCTech.de
84419 Obertaufkirchen, Germany

