APPBRIEF

Determination of PFAS in Drinking Water Using an Automated FREESTYLE XANA-PFAS System [1]

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Abstract

Water quality is of the utmost importance, and recently, the importance of analyzing water for emerging contaminants has been brought to light. Among the emerging compounds being determined are per- and polyfluorinated alkyl substances (PFAS), which have been found to be persistent environmental contaminants derived from various industries. For example, perfluorooctane sulfonate (PFOS) has been used in several different industries, including the semiconductor and photographic industries, in some firefighting foams, and in hydraulic fluids used in the aviation industry. Modern analytical labs are looking to automation to help increase sample throughput while ensuring the resulting data is of the highest quality. The following application brief shows the fully automated sample preparation of water samples for LC-MS/MS analysis by applying SPE with the FREESTYLE XANA-PFAS robotic system according to US EPA 537.1 [2]. The resulting extracts are introduced into an Agilent 6470 LC-MS/MS instrument for detection and quantification.

Keywords

Sample Preparation, LC-MS/MS, High Throughput Lab Automation, PFAS

Introduction

Per- and polyfluorinated alkyl substances (PFAS) products have been used for over 60 years. They enter the environment during manufacturing, use, and disposal. The analytical interest in these compounds has rapidly increased in the last few years. Research has revealed the high toxicity of PFAS compounds and, thus, the resulting need to regulate these substances. The current and upcoming regulations in the EU and US make it necessary to test drinking water for PFAS content. Different methods for PFAS determination in the EU and US exist. For example, ISO 21675, ISO 25101, DIN 38407-42, US EPA 537.1, and US EPA 533. All methods require solid phase extraction (SPE) prior to liquid chromatography-tandem mass spectrometry (LC-MS/MS). The European methods and US EPA 533 use SPE cartridges containing a weak anion exchanger, mixed-mode polymeric sorbent, whereas the US EPA 537.1 calls for a styrene-divinylbenzene polymer (SDVB).

By the application of fully automated parallel sample preparation, multiple samples can be processed at the same time [3]. Thus, high sample throughput with low demand for personnel resources is obtained.

The FREESTYLE XANA-PFAS robotic system is especially suited for PFAS determination because it contains no fluorine-containing plastics such as PTFE in the flow path, thus solving the significant issue of high blank values present in other systems. In this study, no measurable blank values were seen from the system.

Experimental

Materials.

The primary dilution standard containing mixed branched and linear perfluorinated compounds listed in the US EPA method 537.1 document were purchased from Wellington Laboratories (part number EPA-537PDSR1). The internal standards listed within the US EPA method 537.1 document were purchased from Wellington Laboratories (part number EPA-537IS). The surrogate standards listed within the US EPA method 537.1 document were purchased from Wellington Laboratories (part number EPA-537SS-R1).

Calibration curve samples were prepared by making the appropriate dilutions of the primary dilution standard in methanol containing 4% reagent water resulting in calibration standards having concentrations of 0.08, 0.20, 0.30, 0.40, 2.0, 4.0, and 20 ng/L.

Trizma® was purchased from Sigma (part number T-7193). 1.25 grams of Trizma® were added to polypropylene bottles to act as a preservative reagent. Two hundred-fifty (250) milliliters of water were added to each bottle, and the bottles were mixed well to dissolve. An appropriate volume of the primary dilution standards mix was added to create each replicate sample, resulting in 4 ng/L laboratory-fortified blank samples used for method evaluation. Ten (10) microliters of the surrogate standards mix were added to the laboratory-fortified blank samples. The samples were mixed before being processed using the automated solid phase extraction procedure. All other reagents and solvents used were reagent grade.

Instrumentation.

Figure 1: FREESTYLE XANA-PFAS robotic sampler used to automate EPA method 537.1.

All automated solid phase extractions were performed using an LCTech FREESTYLE XANA-PFAS robotic sampler, as shown in Figure 1. All analyses were performed using an Agilent 1290 Infinity II HPLC with an Agilent Zorbax RRHD, Eclipse Plus C18 column, (2.1 x 100 mm, 1.8 µm) analytical column, and Agilent InfinityLab PFC Delay Column. The HPLC system included the PFC-free HPLC conversion kit that minimizes PFAS background

from the LC system by substituting all critical parts of the LC system made from materials that contain organic fluorine compounds. The Agilent 6470 Triple Quadrupole Mass Spectrometer with Jet stream electrospray source was used for detection.

Automated Solid Phase Extraction Procedure

1. User places the 250 mL water samples into the FREESTYLE XANA-PFAS sampler rack and corresponding 6 mL, 500 mg styrene divinylbenzene SPE cartridge (Agilent Bond Elut LMS) and 50 mL polypropylene centrifuge vials into their respective trays.
2. The FREESTYLE XANA-PFAS sampler conditions the SPE cartridge using 15 mL of methanol.
3. The FREESTYLE XANA-PFAS sampler conditions the SPE cartridge using 18 mL of reagent water.
4. The FREESTYLE XANA-PFAS sampler loads the entire water sample onto the SPE cartridge using a flow rate of 15 mL/min.
5. The FREESTYLE XANA-PFAS sampler rinses the empty sample bottle twice using 7.5 mL of reagent water each time loading the rinsate onto the SPE cartridge.
6. The FREESTYLE XANA-PFAS sampler dries the SPE cartridge for 5 minutes using nitrogen.
7. The FREESTYLE XANA-PFAS sampler elutes the SPE cartridge twice using 4 mL of methanol and collecting the eluate into a 50 mL polypropylene centrifuge tube.
8. The final extract is evaporated to dryness and then reconstituted using 1 mL of 96% methanol in water.
9. User adds 10 µL of the internal standard and mixes well before placing on the LC-MS/MS system.

LC Method Parameters

Pump: Gradient (800 bar)

Flow rate = 0.4 mL/min

Mobile Phase: A – 5 mM Ammonium Acetate in Water

B – Methanol

Run time: 18 min

Injection volume: 2.0 µL

Column Temperature: 30 °C

Mass Spectrometer Parameters:

Operation: Electrospray negative mode

Gas Temperature: 300 °C

Gas Flow (N2): 9 L/min

Nebulizer pressure: 45 psi

Sheath Gas Flow (N2): 10 L/min

Sheath Gas Temperature: 260 °C

Capillary voltage: 3500 V

Nozzle voltage: 500 V

Delta EMV: 0 V

The mass spectrometer acquisition parameters are shown in Table 1 with qualifier ions.

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Compound Name	Precursor (m/z)	Product (m/z)		Fragmentor (V)		CE (V)	
PFTeDA	712.9	668.5	169	100	60	12	0
PFTrDA	663	618.7	169	101	101	8	15
11Cl-PF3OUdS	631	451	85	70	70	38	30
PFDoA	613	568.9	268.7	79	100	12	7
Et-FOSAA-D5	589	419		115		15	
Et-FOSAA	584	525.9	419	115	115	15	15
*Me-FOSAA-D3	573	418.9		115		19	
Me-FOSAA	570	482.9	418.9	115	115	15	12
PFUnA	563	519	218.7	83	100	8	15
9Cl-PF3ONS	531	351	351/83	100	98	28	20/30
PFDA-13C2	514.9	469.9		91		8	
PFDA	513	468.6	218.7	91	100	8	8
*PFOS-13C4	502.9	80		110		46	
PFOS	498.9	99	80	100	100	46	46
PFNA	462.9	418.9	169	76	76	8	17
*PFOA-13C2	415	370		79		8	
PFOA	412.9	368.9	169	79	79	8	17
PFHxS	398.9	99	80	80	110	42	45
ADONA	377	251	84.9	95	95	1	38
PFHpA	362.9	319	169	82	82	1	17
PFHxA 13C2	314.9	269.9		70		4	
PFHxA	313	268.6	119	70	70	4	22
PFBS	298.9	98.9	80	110	110	30	42
HFPO-DA-13C3	287	169		100		1	
HFPO-DA	285	185	169	100	100	12	1

* Internal Standard

Table 1: Mass spectrometer acquisition parameters.

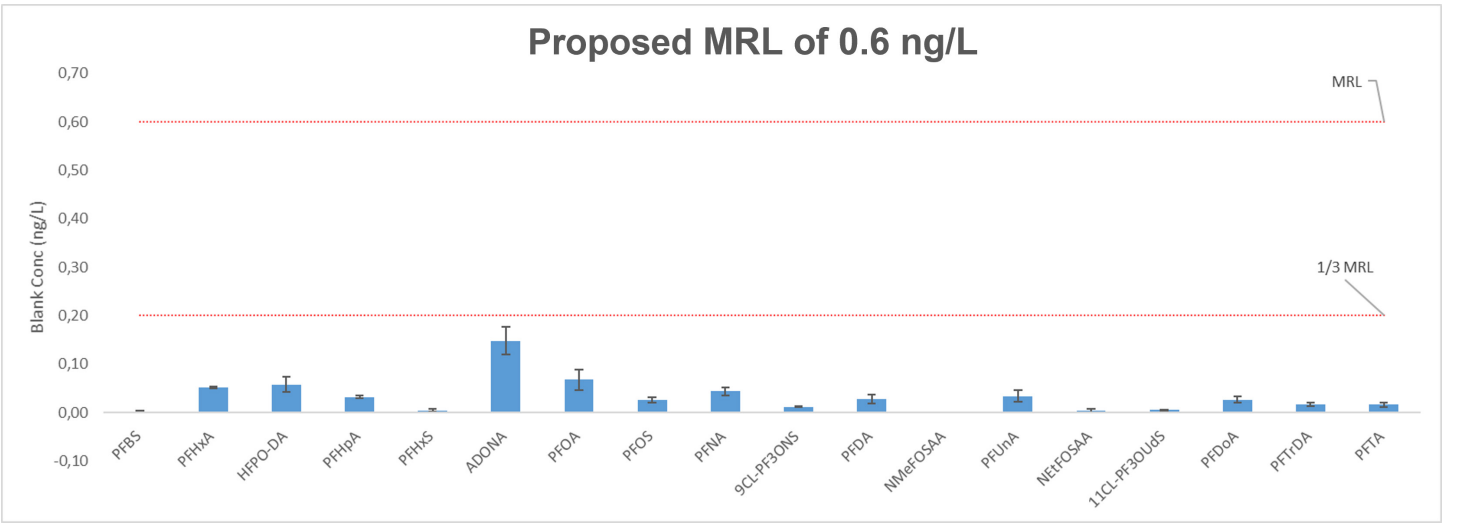

Figure 2: Demonstration of Low Background of FREESTYLE XANA-PFAS robotic sampler.

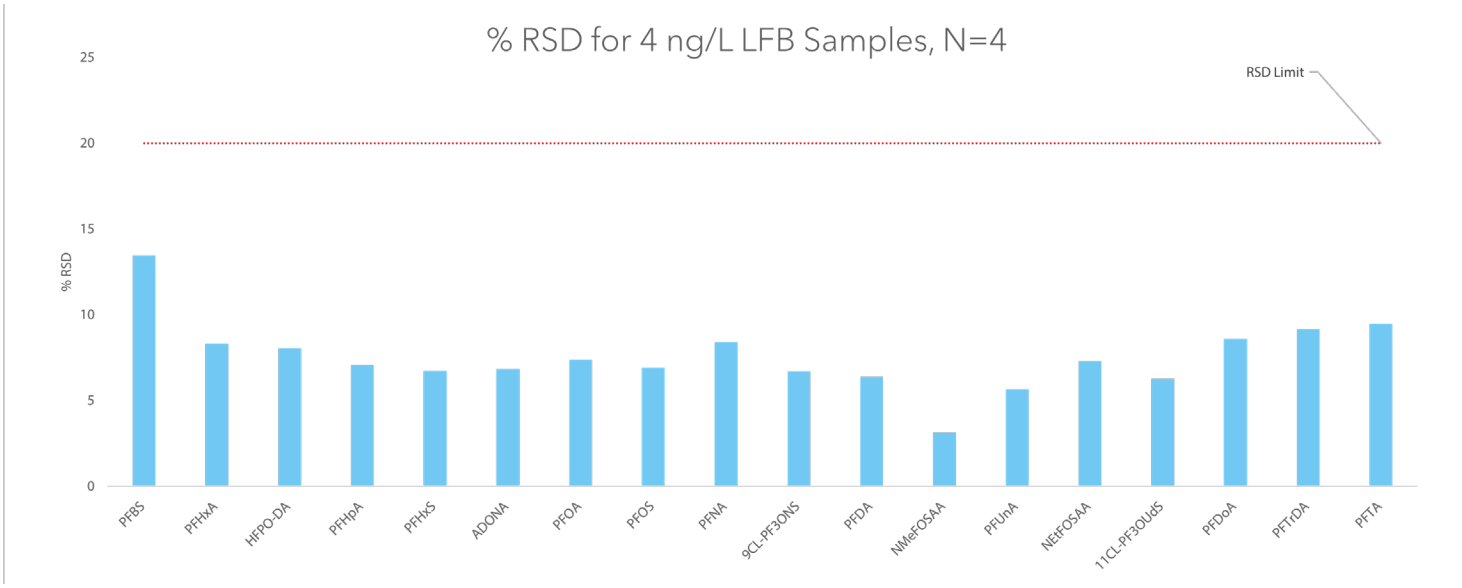

Figure 3: Results of Initial Demonstration of Precision (IDP).

Figure 2 shows the low background obtained after the automated extraction of blank water samples. Responses observed at the retention times of all PFAS compounds were shown to be below 1/3 of the response of the proposed MRL of 0.6 ng/L.

Calibration curve samples were analyzed using five replicates of each concentration level. As shown in Figure 3, the % recoveries for all target and surrogate PFAS compounds from all calibration curve samples were found to be within 70% to 130%, which meets the acceptance criteria laid out within the EPA method 537.1.

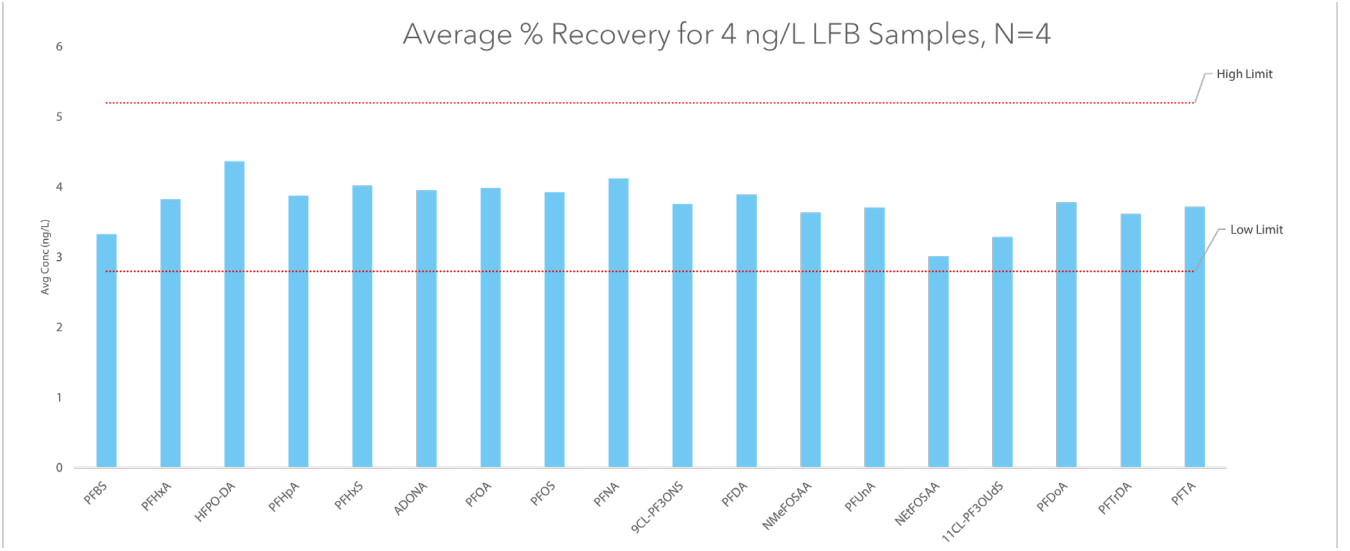

Figure 4: Results of Initial Demonstration of Accuracy (IDA).

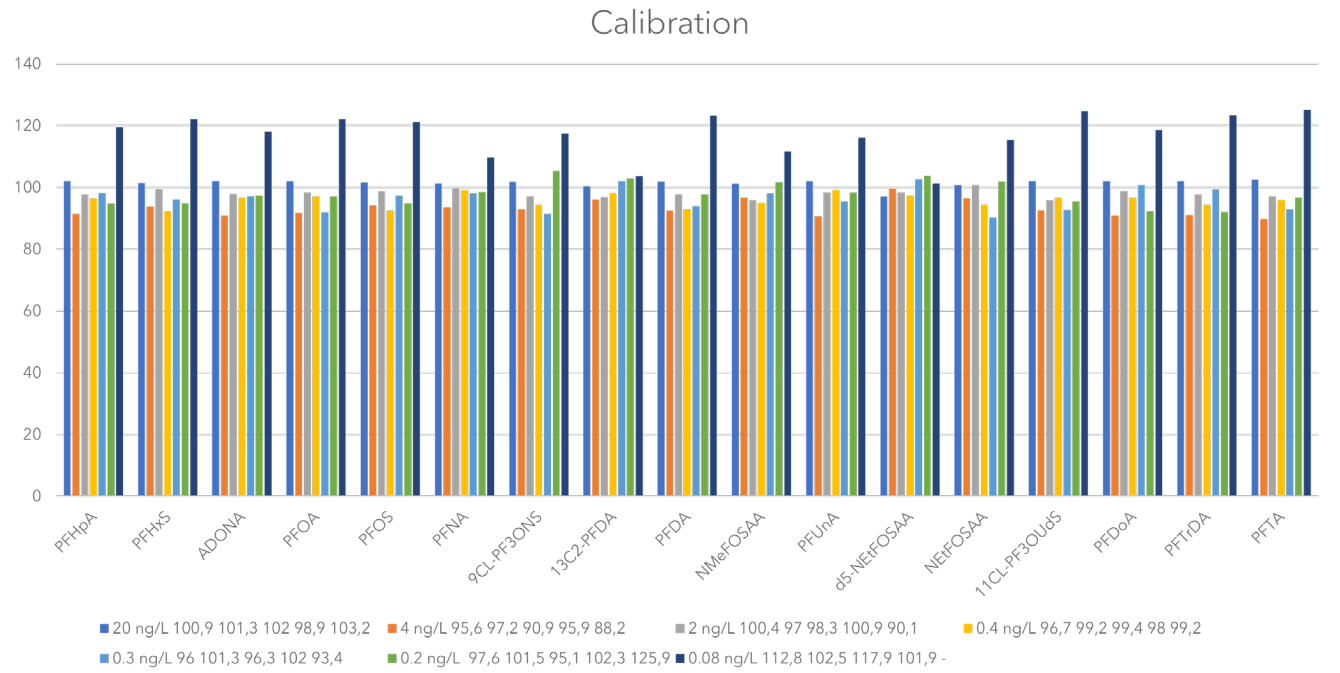

Figure 5: Calibration Curve Results.

The precision of the automated method was evaluated for all PFAS compounds using four replicate extracted laboratory-fortified blank samples having PFAS compound concentrations of 4 ng/L. Figure 4 shows that the precision for all PFAS compounds determined was found to be within the acceptance limit stated in EPA method 537.1 of being less than 20% RSD. To meet the acceptance criteria for the initial demonstration of accuracy (IDA) of EPA method 537.1, the average recovery of the replicate values of the laboratory-fortified blank samples used to establish precision must fall within ±30% of the actual value.

Figure 5 shows that the % recoveries for all PFAS compounds were found to meet this acceptance criteria.

Separate work [4] has demonstrated that the D-EVA vacuum centrifuge evaporator shown in Figure 6 can be used to successfully evaporate EPA method 537.1 extracts after processing using the FREESTYLE XANA-PFAS robotic sampler. The D-EVA evaporator allows up to 22 of the 50 mL centrifuge vials used to capture the eluant during the automated solid phase extraction to be evaporated to dryness. An integrated sensor allows the evaporator to stop once the extracts have been completely evaporated.

The evaporator uses infrared lamps to keep the samples at the desired temperature during evaporation. Once complete, these lamps are immediately shut off to ensure evaporated extracts are not overheated, leading to losses. As shown in Figure 7, the mean intra-day recoveries from twelve replicates of laboratory-fortified blank samples containing the EPA method 537.1 PFAS compounds were found to be within the acceptance criteria of 70% to 130%.

Figure 6: D-EVA Vacuum Centrifugation Evaporator used for Automated Evaporation of PFAS Extracts.

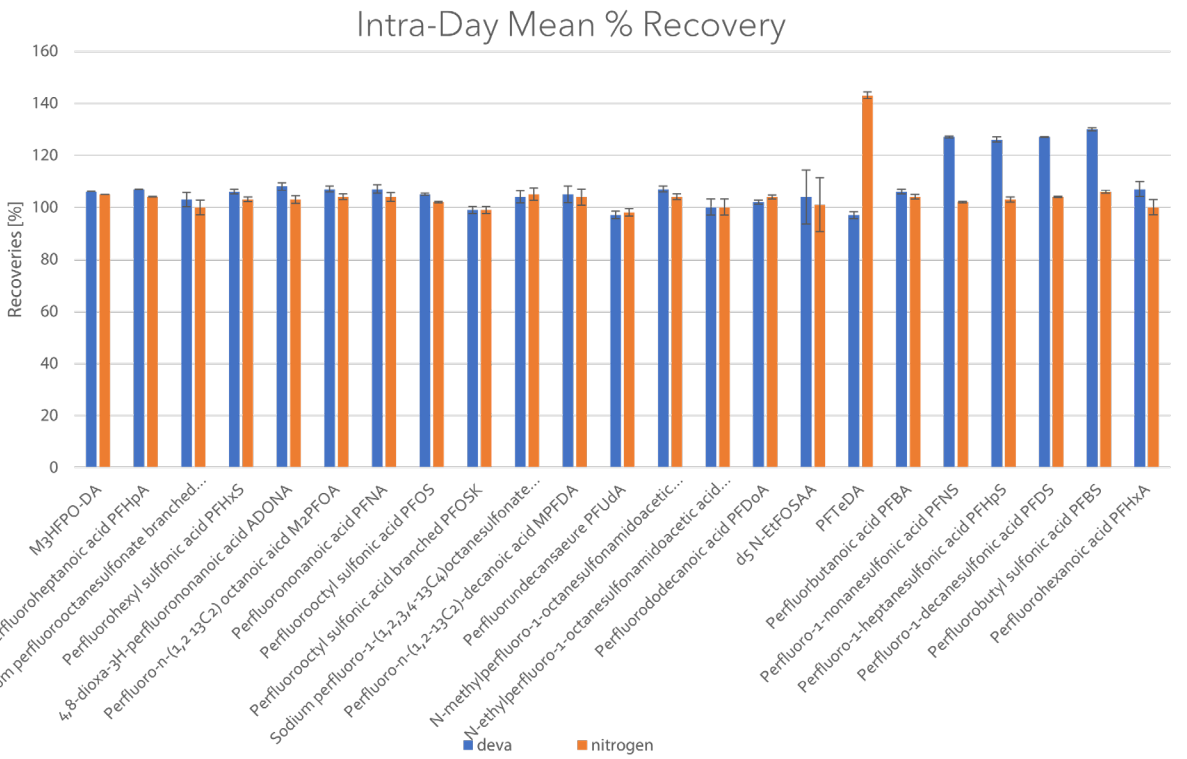

Figure 7: Mean %Recoveries of PFAS compounds of EPA method 537.1 after evaporation using D-EVA.

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Conclusions

As a result of this study, we were able to show the following:

- All PFAS compounds found within EPA method 537.1 can be successfully extracted from water samples using an automated large-volume solid phase extraction method and determined using the Agilent 6470 Triple Quadrupole Mass Spectrometer.
- This method was readily automated using the FREESTYLE XANA-PFAS sampler.
- The background obtained using the FREESTYLE XANA-PFAS sampler was shown to be below 1/3 of the response of the proposed MRL of 0.6 ng/L.
- Linear calibration curves were achieved for all PFAS compounds, with % recoveries found to be within 70% to 130% for all calibration levels meeting the EPA method 537.1 acceptance criteria.
- The automated method proved to be accurate and precise. The % recovery of laboratory-fortified blank samples fell within ±30% of the actual value and precision for all PFAS compounds determined was found to be less than 20% RSD, which meets the acceptance criteria of EPA method 537.1.

References

1. Based on the talk "Automated Sample Preparation for PFAS following the updated US EPA 537.1 with FREESTYLE XANA PFAS", LCTech, 2020.
2. United States Environmental Protection Agency, Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/ Tandem Mass Spectrometry, https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL, accessed July 2022.
3. LCTech Application Note No. AN0033, Determination of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Water with FREESTYLE XANA and LC-MS/MS, 2022.
4. LCTech Application Note No. AN0045, D-EVA – Automated EVAporation of PFAS compliant to US-EPA 537.1, 2021.

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