

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals that have been in use since the 1940s. These chemicals are attracting particular attention because they are very persistent in the environment and can build up in living organisms, risking adverse health impacts. The analysis of these compounds in drinking water is mainly based on EPA Method 537.1 which uses solid phase extraction (SPE) for sample enrichment and LC-MS/MS for analysis. Currently most testing laboratories are performing the sample extraction manually using a vacuum manifold, which is labor-intensive, time-consuming, and difficult to control flow rate. There is a high demand for automation of the SPE procedure.

The automation here is more challenging than in the case of other SPE methods, mainly because the EPA method uses more complex extraction steps and requires very low background levels. Many commonly used Teflon parts had to be replaced with other inert materials. Since July 2018, we have been working with testing laboratories from the United States and Australia to automate the sample extraction procedure for PFAS analysis. The work has resulted in a well-accepted solution that is fully automated, fast, clean, and robust. This application note shares the experience in instrumentation and transfer of a manual method to an automated system. Factors affecting recovery and background level are also discussed.

APPROACHES FOR OBTAINING CLEAN BACKGROUND

The minimum reporting level (MRL) of EPA method 537.1 for the 18 PFAS compounds is 0.53-6.3 ng/L⁽¹⁾. Interference from solvents, reagents, containers, and SPE instrument needs to be maintained below 1/3 of the MRL value. The EPA method emphasizes that care must be taken with automated SPE systems to ensure that PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the blanks.

The automation of SPE procedures is based on our SPE-03 8-channel SPE system. To meet the requirements on background, we carried out the following modifications:

- 1) Use polyethylene tubing for all solvent and sample lines
- 2) Replace all Teflon valve rotors
- 3) Optimize the flow path and remove dead zones during solvent cleaning

As shown in Fig. 1, the flow path of SPE-03 is based on two rotary valves. The channel selection valve uses a group of 3 ports to connect one syringe pump with one sample and one SPE cartridge. Each sample has an isolated flow path and a dedicated syringe pump. This design can effectively avoid cross contamination between samples within a batch and clean the entire flow path after each batch. Cleaning is also improved by minimizing tubing ID, length and the complexity of tubing connections

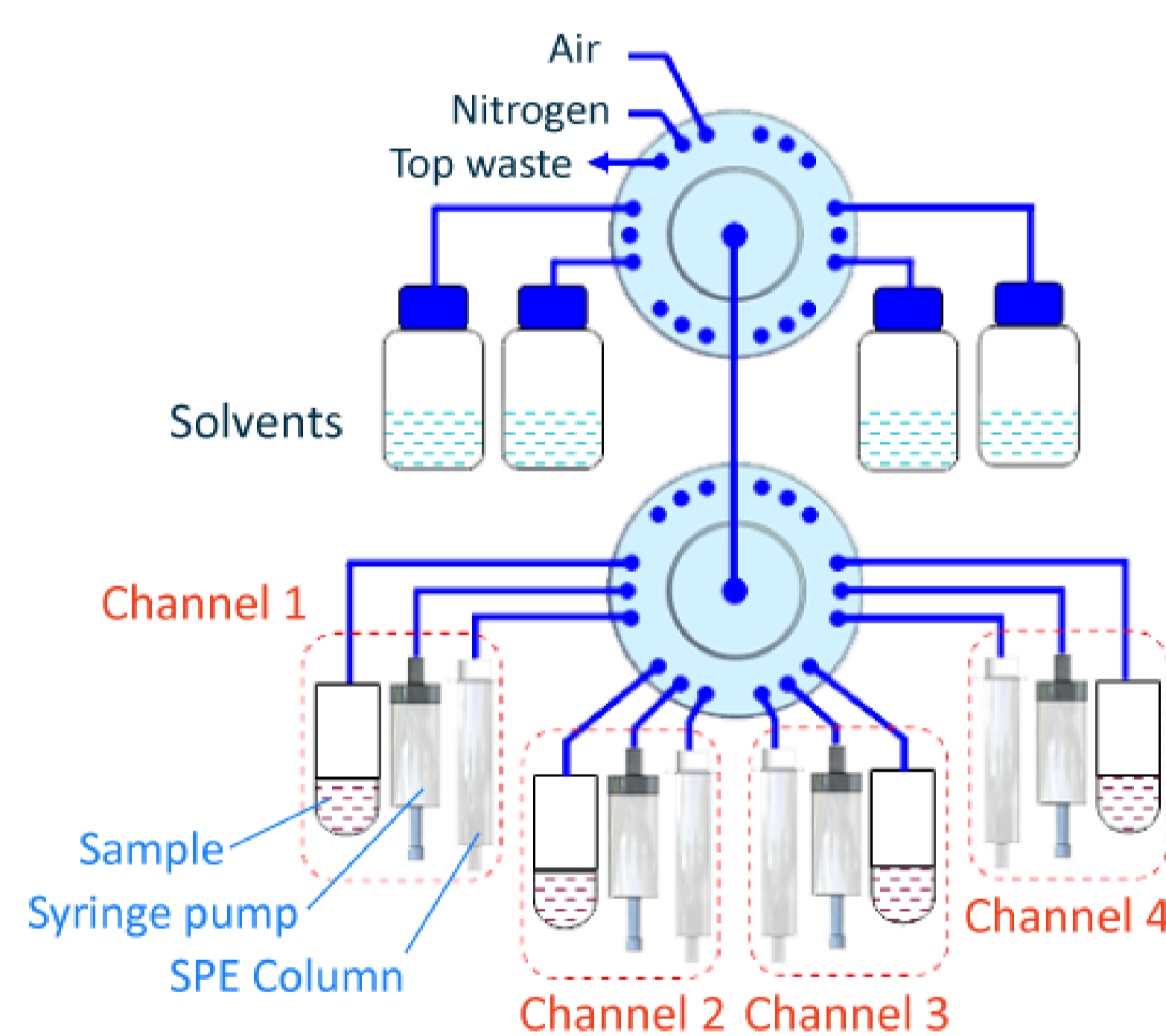


Fig 1. Flow path of SPE-03 based on two valves. (Showing 4 of 8 Channels)

- 4) Devise a closed sample loading system to avoid contamination from the environment.



Fig 2. SPE-03 with closed sample loading set up and shortened sample tubing.

- 5) Design an effective and efficient cleaning method to be run between batches

The cleaning procedures after each batch takes less than 10 minutes. This includes setup and running the cleaning method. All parts in contact with samples are thoroughly cleaned with about 10mL of methanol per channel. Cleaning protocol can be easily modified as necessary.

Initial Demonstration of Low System Background

Below are the background levels [ppt] obtained from a customer performing EPA Method 537.1. LRBs were extracted simultaneously on all 8 positions of the SPE-03 system. For 2ppt MRL, background levels must be <0.667 ppt. All compounds were well below this requirement.

Compound	Pos 1	Pos 2	Pos 3	Pos 4	Pos 5	Pos 6	Pos 7	Pos 8
PFBS	ND	ND	ND	ND	ND	ND	ND	ND
PFHxA	ND	ND	ND	ND	ND	ND	ND	ND
HFPO-DA (GenX)	ND	ND	ND	ND	ND	ND	ND	ND
PFHpA	ND	ND	ND	ND	ND	ND	ND	ND
PFHxS	ND	ND	ND	ND	ND	ND	ND	ND
ADONA	ND	ND	ND	ND	ND	ND	ND	ND
PFOA	0.060	0.036	0.052	0.007	0.076	0.072	0.012	0.006
PFOS	ND	ND	ND	ND	ND	ND	ND	ND
PFNA	ND	ND	ND	ND	ND	ND	ND	ND
9Cl-PF3ONS	ND	ND	ND	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND	ND	ND	ND
NMeFOSAA	ND	ND	ND	ND	ND	ND	ND	ND
PFUnA	ND	ND	ND	ND	ND	ND	ND	ND
NEtFOSAA	ND	ND	ND	ND	ND	ND	ND	ND
11Cl-PF3OUdSND	ND	ND	ND	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND	ND	ND	ND
PFTDA	ND	ND	ND	ND	ND	ND	ND	ND
PFTA	ND	ND	ND	ND	ND	ND	ND	ND

MODIFICATIONS TO ACHIEVE FULL AUTOMATION

The SPE procedure for PFAS analysis involves the rinsing of sample bottles after sample loading to wash down adsorbed analytes. The MOD-004 sample bottle racks and spray adapters are designed to mount the sample bottles upside down and allow a strong jet of solvent to spray upward. The top, bottom and the inner walls of the bottles can be effectively washed and the rinsate passed through the SPE cartridges.



Low recoveries of some analytes call for soaking the SPE cartridge with solvents for 1-2 minutes⁽¹⁾. The SPE-03 provides two options for this process: 1) To use a wait command after each solvent elution and 2) to use a very slow flow rate. The syringe pump can deliver fluids down to 0.5 mL/min.

With these two modifications, SPE-03 is able to perform full automation for the SPE procedures in PFAS analysis. After pressing the start button, the instrument will go through all the SPE steps automatically.

OPTIMIZATION OF SPE PARAMETERS

Although the method does not allow changing the extraction steps, the flow rate can still be adjusted. The SPE cartridge conditioning requires a slower flow rate so that the polymer-based sorbent is well soaked. 5mL/min was found to be suitable for this step. For sample loading, we validated recovery at flow rate of 15 mL/min, which is the highest allowed by EPA Method 537.1. This reduces sample loading time. However, when the cartridge is clogged or has high resistance, the pump may not be able to push the sample through the SPE cartridge as quickly. In the case of SPE-03, a blockage detection and management feature can monitor the resistance and automatically reduce flow rate when the SPE cartridge resistance is too high. The flow rate for fraction collection using 2 x 4 mL methanol rinse is set at 5 mL/min to allow time for solvent and analyte interaction. Under these conditions, the processing time for eight 250-mL samples is 75 minutes.

Below are the IDC and MRL data from a customer performing EPA Method 537.1.

IDC - 4 x 50ppt LFBs

Requirements: Mean < ±30%, RSD < 20%

Compound	%Recovery	%RSD
PFBS	84	5.16
PFHxA	93	7.81
HFPO-DA (GenX)	95	6.59
PFHpA	104	8.71
PFHxS	99	1.81
ADONA	101	4.92
PFOA	104	5.60
PFOS	95	3.98
PFNA	105	4.73
9Cl-PF3ONS	96	1.88
PFDA	96	8.48
NMeFOSAA	101	3.93
PFUnA	96	6.78
NEtFOSAA	101	1.26
11Cl-PF3OUdS	86	1.84
PFDoA	87	4.83
PFTDA	89	7.81
PFTA	85	10.11

MRL - 7 x 2ppt LFBs

Requirements: Mean ± HR_{PIR} < ±50%

Compound	%Recovery	%RSD
PFBS	100	5.69
PFHxA	101	4.77
HFPO-DA (GenX)	97	5.14
PFHpA	111	5.02
PFHxS	104	3.79
ADONA	101	5.92
PFOA	112	8.08
PFOS	102	2.24
PFNA	105	7.59
9Cl-PF3ONS	96	2.95
PFDA	96	8.52
NMeFOSAA	98	5.56
PFUnA	100	5.47
NEtFOSAA	103	4.21
11Cl-PF3OUdS	95	6.38
PFDoA	95	12.66
PFTDA	95	11.45
PFTA	92	5.99

MAXIMIZING THE USE OF LAB RESOURCES AND SAMPLE THROUGHPUT

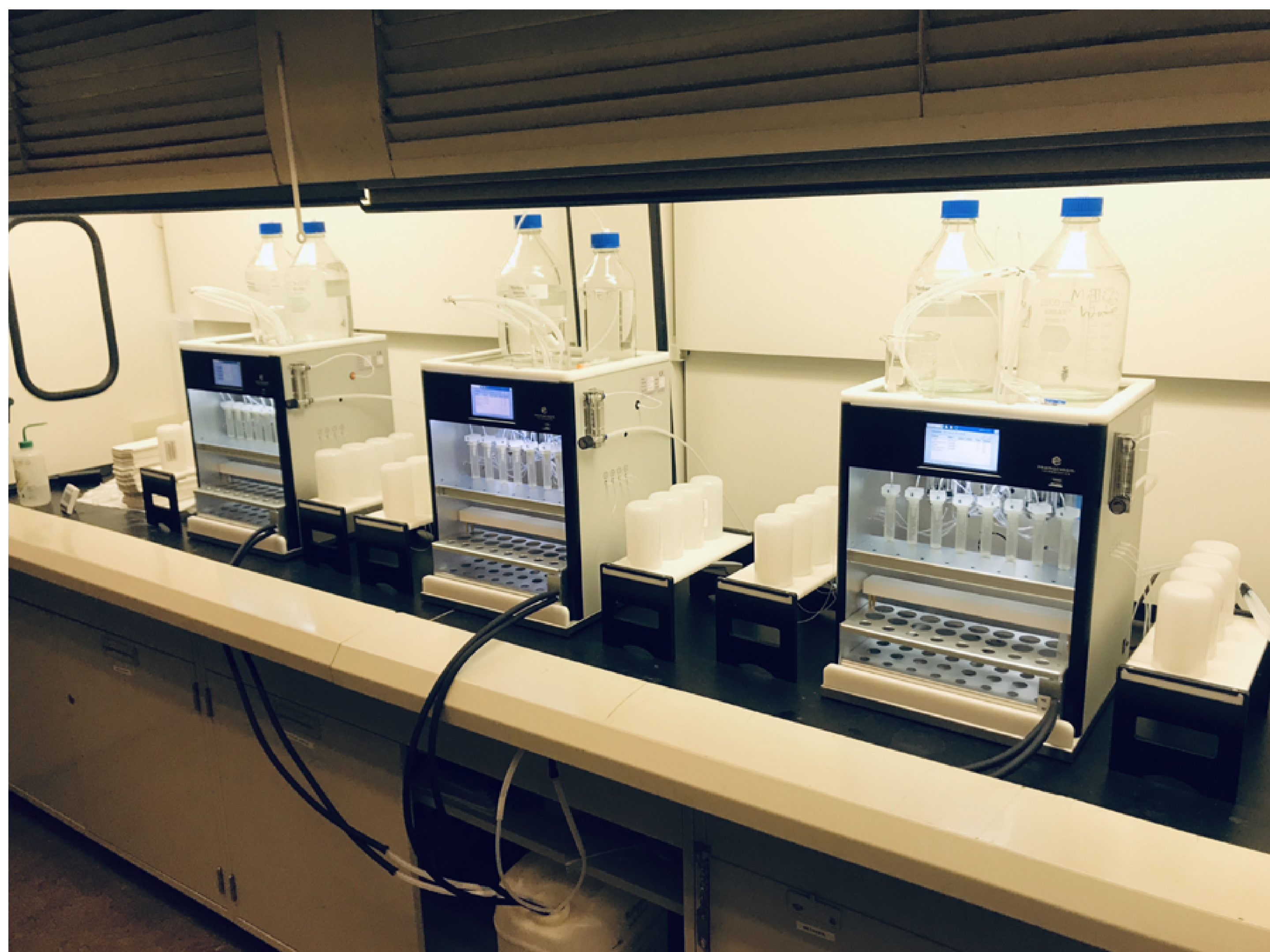
The LC-MS/MS analysis for one sample takes 30-40 minutes, depending on LC columns and the gradient profile. This is equivalent to 36 to 48 runs every 24 hours. After taking into account the runs for calibration and QC, the processing capacity for field samples is around 20 per day.

To make full use of the LC-MS/MS instrument, a similar number of field samples should be extracted during working hours. One SPE-03 unit can extract 20 field samples and 4 quality control samples in 3 batches. This takes the instrument 4.5 to 5 hours, including system cleaning. When the extraction of the final batch is complete, there is still sufficient time to finish the evaporation of the collected fractions. By overlapping the LC-MS/MS analysis and sample extraction, up to 20 field samples can be analyzed per day using just one SPE-03 system.

Manual labor is also greatly reduced when the automated SPE system is looking after the extraction. One chemist is sufficient to look after the routine sample preparation work.

CONCLUSION

The SPE-03 system is a highly efficient system capable of processing 8 samples in parallel. It can fully automate PFAS extraction following EPA Method 537.1 while exceeding background and recovery requirements. Other PFAS methods performed by the system include EPA Method 533, modified EPA Method 537.1, DoD QSM 5.3 and similar methods outside of North America. The SPE-03 was used in September 2019 during the multi-lab validation for EPA Method 533.



References

1. U.S. EPA. Method 537.1, Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Version 1.0, November 2018