

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 need 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 poster shares the experience in instrumentation and transfer of a manual method to an automated system. Factors affecting the 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. The interference from solvents, reagents, containers, and SPE instrument needs to be maintained below 1/3 of the MRL value. Interference can come from contaminants of similar properties and also from the analytes that are present in many common laboratory supplies and SPE devices. 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 blank test.

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 lines
- 2) Replace all Teflon moving parts with UHMWPE or PEEK parts
This includes syringe pump plungers and 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

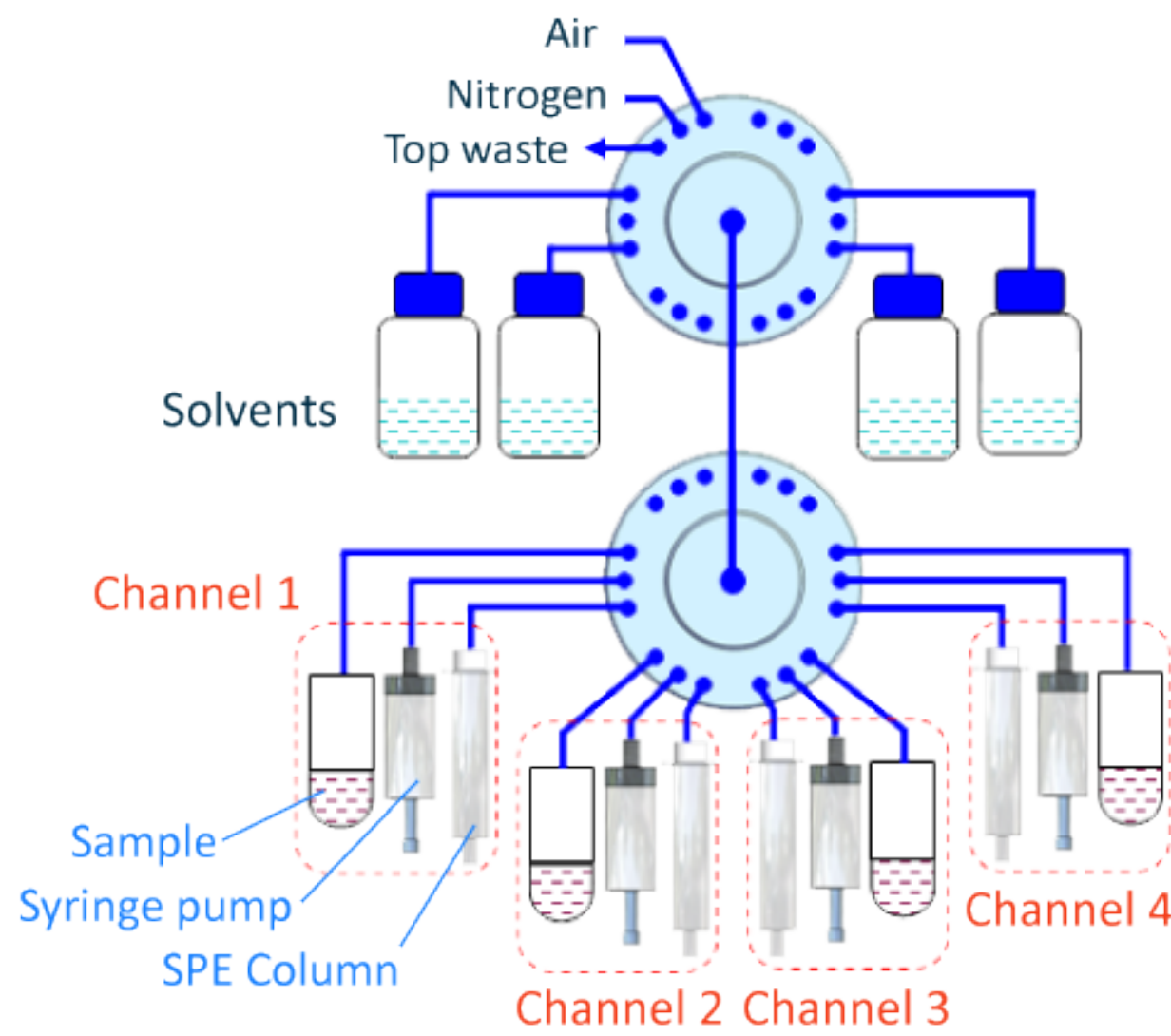


Fig 1. Flow path of SPE-03 based on two valves.

- 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 5-minute cleaning method. All parts in contact with samples are thoroughly cleaned with only 10mL of methanol per channel

With the above mentioned modifications, system background was well under the tightest limits for all our installations.

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. 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 results we obtained during one of our installations for 1 batch of 2 blanks, 3 x 1ppt spikes and 3 x 100ppt spikes. MRL was 1ppt, all blanks came out well below 0.1ppt.

Compound	Blank1	Blank2	Lspk1	Lspk2	Lspk3	Hspk1	Hspk2	Hspk3
PFBS	----	----	84.65	82.34	77.64	87.31	91.03	93.5
PFHxA	----	----	98.24	100.27	91.86	92.37	94.82	100.07
HFPO-DA	----	----	95.51	96.71	87.68	92.73	94.86	100.5
PFHpA	----	----	103.7	107	99.09	100.67	101.61	108.91
PFHxS	----	----	92.02	83.23	78.46	99.14	102.16	107.89
ADONA	----	----	98.35	98.24	98.71	100.4	101.52	108.49
PFOA	----	----	104.99	96.47	96.33	100.56	99.73	106.4
PFNA	----	----	83.1	95.73	93.58	100.28	100.48	106.8
PFOS	----	----	82.06	83.33	88.51	95.81	99.68	104.33
9CI-PF3ONS	----	----	81.25	81.59	79.59	93.32	98.12	101.58
PFDA	----	----	94.15	92.36	91.73	97.46	98.99	105.01
N-MeFOSAA	----	----	81.9	88.92	87.57	96.44	96.96	104.18
N-EtFOSAA	----	----	90.63	85.73	71.39	95.59	92.92	101.45
PFUnA	----	----	87.79	92.24	95.06	94.83	97.72	102.05
11CI-PF3OUds	----	----	81.13	79.36	77.53	92.29	97.14	100.47
PFDoA	----	----	86.37	90.73	94.01	94.63	97.61	104.22
PFTriA	----	----	88.35	93.14	91.94	94.64	97.74	105.38
PFTreA	----	----	92.08	101.13	92.38	92.62	96.45	101.31

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.