Manual Extraction of PFAS in Drinking Water in Compliance with ISO 21675

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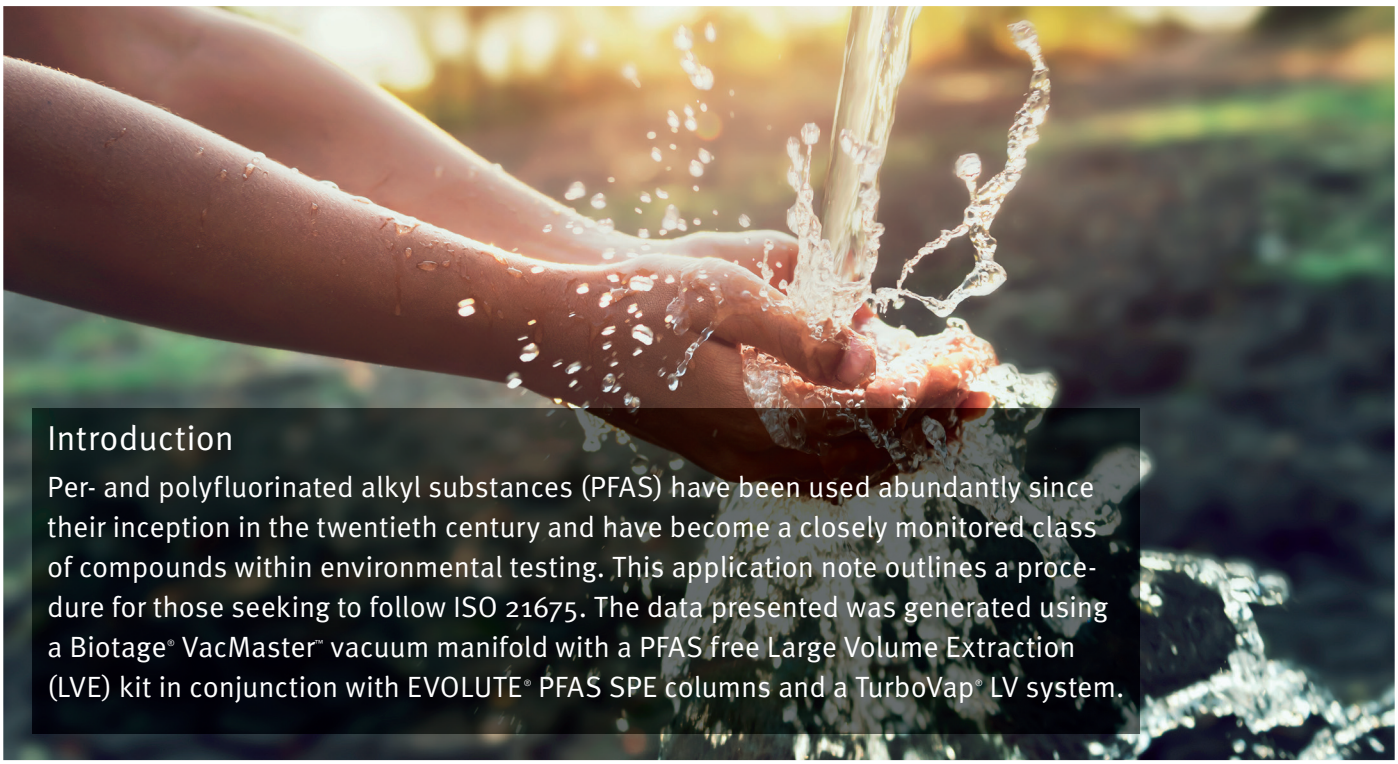

Introduction

Per- and polyfluorinated alkyl substances (PFAS) have been used abundantly since their inception in the twentieth century and have become a closely monitored class of compounds within environmental testing. This application note outlines a procedure for those seeking to follow ISO 21675. The data presented was generated using a Biotage® VacMaster™ vacuum manifold with a PFAS free Large Volume Extraction (LVE) kit in conjunction with EVOLUTE® PFAS SPE columns and a TurboVap® LV system.

Equipment and Materials Used

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- Biotage® VacMaster™ 20 Sample Processing Station With 15 mm Rack, p/n 121-2015ML, fitted with polypropylene (PFAS free) stopcocks (p/n 121-0009-PP)
- Biotage® VacMaster™ LVE Kit (PFAS) for 1, 3, 6 mL SPE Columns (p/n 121-2190)
- EVOLUTE® PFAS 500 mg/6 mL SPE Columns, p/n 614-0050-CP
- EVOLUTE® PFAS 150 mg/6 mL SPE Columns, p/n 614-0015-CP
- TurboVap® LV Automated Solvent Evaporation System, p/n 415000
- TurboVap® LV Multi Rack (48 Positions, 10–20 mm Tubes), p/n 414964

Wellington Laboratories

- ISO 21675:2019 Labelled Stock Solution, 1.2 mL, p/n ISO 21675-LSS
- ISO 21675:2019 Native Stock Solution, 1.2 mL, p/n ISO 21675-NSS

Ordering Information

Part Number	Description	Qty
121-2015ML	Biotage® VacMaster™ 20 Sample Processing Station With 15 mm Rack	1
121-2190	Biotage® VacMaster™ LVE Kit (PFAS) for 1, 3, 6 mL SPE Columns	1
121-0009-PP	Polypropylene (PFAS) Stopcocks	10
614-0050-CP	EVOLUTE® PFAS 500 mg/6 mL columns	30
614-0015-CP	EVOLUTE® PFAS 150 mg/6 mL columns	30
415000	TurboVap® LV Automated Solvent Evaporation System	1
414964	TurboVap® LV Multi Rack (48 Positions, 10–20 mm Tubes)	1

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Analytes

Table 1. Listing of Target Analytes and Internal Standards.

Target Analyte	Acronym	CAS
Perfluoro-n-butanesulfonic acid	PFBS	375-73-5
Perfluoro-n-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-n-heptanesulfonic acid	PFHpS	375-92-8
Perfluoro-n-octanesulfonic acid	PFOS	1763-23-1
Perfluoro-n-decanesulfonic acid	PFDS	335-77-3
Perfluorooctanesulfonamide	FOSA	754-91-6
N-methyl perfluoroctanesulfonamide	N-MeFOSA	31506-32-8
N-ethyl perfluorooctanesulfonamide	N-EtFOSA	4151-50-2
N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6
6:2 Fluorotelomer sulfonic acid	6:2 FTSA	27619-97-2
8:2 Fluorotelomer sulfonic acid	8:2 FTSA	39108-34-4
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	73606-19-6
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUnDA	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoDA	307-55-1
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid	PFOcDA	16517-11-6
8:2 Fluorotelomer unsaturated carboxylic acid	8:2 FTUCA	70887-84-2
8:2 Polyfluoroalkyl phosphate diester	8:2 diPAP	678-41-1
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
4,8-Dioxa-3H-perfluorononanoic acid	DONA	919005-14-4

Target Analyte	Acronym	CAS
Internal Standard		
Sodium perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	$^{13}C_3$-PFBS	
Sodium perfluoro-1-[1,2,3-$^{13}C_3$]hexanesulfonate	$^{13}C_3$-PFHxS	
Sodium perfluoro-1-[1,2,3-$^{18}O_2$]hexanesulfonate	$^{18}O_2$-PFHxS	
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	$^{13}C_4$-PFOS	
Sodium perfluoro-1-[1,2,3,4-$^{13}C_8$]octanesulfonate	$^{13}C_8$-PFOS	
Perfluoro-1-[$^{13}C_8$]octanesulfonamide	$^{13}C_8$-FOSA	
N-methyl-d3-perfluoro-1-octanesulfonamide	d_3-N-MeFOSA	
N-ethyl-d5-perfluoro-1-octanesulfonamide	d_5-N-EtFOSA	
N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid	d_3-N-MeFOSAA	
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid	d_5-N-EtFOSAA	
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-octane sulfonate	$^{13}C_2$-6:2 FTSA	
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-decane sulfonate	$^{13}C_2$-8:2 FTSA	
Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	$^{13}C_4$-PFBA	
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]pentanoic acid	$^{13}C_5$-PFPeA	
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2$-PFHxA	
Perfluoro-n-[1,2-$^{13}C_5$]hexanoic acid	$^{13}C_5$-PFHxA	
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	$^{13}C_4$-PFHpA	
Perfluoro-[1,2-$^{13}C_4$]octanoic acid	$^{13}C_4$-PFOA	
Perfluoro-[1,2-$^{13}C_8$]octanoic acid	$^{13}C_8$-PFOA	
Perfluoro-n-[$^{13}C_5$]nonanoic acid	$^{13}C_5$-PFNA	
Perfluoro-n-[$^{13}C_9$]nonanoic acid	$^{13}C_9$-PFNA	
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2$-PFDA	
Perfluoro-n-[1,2-$^{13}C_6$]decanoic acid	$^{13}C_6$-PFDA	
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_2$]undecanoic acid	$^{13}C_2$-PFUnDA	
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	$^{13}C_7$-PFUnDA	
Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2$-PFDoDA	
Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid	$^{13}C_2$-PFTeDA	
Perfluoro-n-[1,2-$^{13}C_2$]hexadecanoic acid	$^{13}C_2$-PFHxDA	
2H-Perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid	$^{13}C_2$-8:2 FTUCA	
Sodium bis(1H,1H,2H,2H-[1,2-$^{13}C_2$]perfluorodecyl)-phosphate	$^{13}C_4$-8:2 diPAP	
Tetrafluoro-2-heptafluoropropoxy-$^{13}C_3$-propanoic acid	$^{13}C_3$-HFPO-DA	

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Solution Preparation

Ammonia/Methanol Solution

1. Add 400 µL of NH_4OH for every 100 mL of methanol to a clean beaker.
2. Agitate to homogenize.
3. Prepare new solution daily.

Acetate Buffer

1. Measure out 499.5 mL of reagent water in a clean beaker.
2. Add 0.193 g of NH_4Ac.
3. Sonicate the solution for 5 minutes until the salt is fully dissolved.
4. Add 570 µL of glacial acetic acid.
5. Agitate to homogenize the solution.

Working Spiking Solution

1. Dilute 100 µL of the native stock solution with 900 µL of methanol to achieve a 10 ppt solution.

Summary of SPE method

SPE Column Format

EVOLUTE® PFAS 500 mg/6 mL or EVOLUTE® PFAS 150 mg/6 mL

Sample Pre-Treatment

Adjust the pH of each sample to 3 using glacial acetic acid. Add targets and internal standards.

Conditioning

Condition each column with 0.1 % NH_4OH in methanol (10 mL) followed by methanol (10 mL).

Equilibration

Equilibrate each column with reagent water (10 mL).

Sample Loading

Load sample at a flow rate of 5 mL/min.

Wash

Rinse the sample container with acetate buffer solution (10 mL) and load onto the column. Repeat using reagent water (10 mL).

Dry

Dry the column for 5 minutes at a flow rate of 5 mL/min.

Elution

Rinse the sample container with methanol (5 mL) and use to elute the analytes from the column at a flow rate of 2 mL/min. Repeat using 0.1 % NH_4OH in methanol (5 mL).

Post Extraction

Concentrate the extract to a volume of 1 mL and analyze.

Sample Preparation Procedure

1. Clean all parts of the Biotage® VacMaster™ system per the procedure given in Appendix A.
2. Set up and fill new sample containers with of water; 250–500 mL are typical for this method.
3. Add glacial acetic acid to each of the sample containers to reduce the pH to 3 (approximately 100 µL for 250 mL sample volumes and 200 µL for 500 mL sample volumes).
4. Verify the pH of the sample is 3 using pH paper. To reduce the possibility of contamination, a duplicate volume was collected and adjusted to the appropriate pH and the same volume of acid was added to the sample container.
5. Prepare for the determination of the initial sample volume by either marking the level of the sample on the container or by weighing the sample container.
6. Add 20 µL of the undiluted Labeled Stock Solution to each of the sample containers. If desired, fortify a sample using target analytes: the addition of 125 µL or 37.5 µL of the native stock solution will yield either 50 ppt or 15 ppt concentrations respectively, while the addition of 50 µL of the working spiking solution will yield a 2 ppt concentration. If the mixes used were different than the ones outlined in this note, adjust the concentration or spiking amounts as needed.
7. Load the desired EVOLUTE® PFAS columns onto the Biotage® VacMaster™. Seal any unused positions using VacMaster™ Port Sealing Plugs (p/n 121-0005)
8. Rinse each column with 10 mL of 0.1 % NH_4OH in methanol and apply vacuum at 10 mL/min to pull it to waste. Do not allow the sorbent to go dry.
9. Rinse each column with 10 mL of methanol and apply vacuum at 10 mL/min to pull it to waste. Do not allow the sorbent to go dry.
10. Rinse each column with 10 mL of reagent water and apply vacuum at 10 mL/min to send it to waste. Do not allow the water level to drop below the top of the packing.
11. Using the Biotage® VacMaster™ LVE Kit, place one end of the cleaned tubing into the bottom of each of the sample containers, and secure in position using the clips provided.
12. Load the samples onto the columns using a flow rate of 5 mL/min.
13. Once the sample has been fully loaded, rinse the sample containers using 10 mL of acetate buffer solution, swirl to ensure the full rinsing of the container, and load the aliquot onto the column at a rate of 5 mL/min.
14. Rinse the sample containers using 10 mL of reagent water, swirl to ensure the full rinsing of the container, and load the aliquot onto the column at a rate of 5 mL/min.
15. Dry the column for 5 minutes at a rate of 5 mL/min.
16. Load 15 mL centrifuge tubes into the rack corresponding to each of the column positions and load into the Biotage® VacMaster™.
17. Rinse each sample container using 5 mL of methanol and swirl to ensure the full rinsing of the container. Load the aliquot through the appropriate column and collect at a dropwise rate.
18. Rinse each sample container using 5 mL of 0.1% NH_4OH in methanol and swirl to ensure the full rinsing of the container. Load the aliquot through the appropriate column and collect at a dropwise rate.
19. Determine the initial sample volume by either using a graduated cylinder and filling the sample container to the original mark or by taking an additional weight of the container.
20. Transfer the centrifuge tubes to the TurboVap® LV system and concentrate the samples to just under 1 mL using nitrogen according to the parameters in Table 2.
21. Bring the final extract to 1 mL and transfer to an autosampler vial.
22. Load the extract onto a calibrated LC-MS/MS system and process using the conditions given in the below sections.

Table 2. TurboVap® LV Concentration Protocol.

Bath Temp:	60 °C
Evaporation Mode	Method (Ramp Gradient)
Manifold Setup	48 positions
Rack Row Height	120 mm*
Step 1:	1.5 L/min for 20 min
Step 2:	3.0 L/min for 15 min
Step 3:	3.5 L/min for 45 min

*The nozzle position was adjusted such that it was as far to the right as possible to give the user a clear view of the vortex within the tube.