Automated Extraction Method of PFAS From Difficult Environmental Matrices

Alicia D. Stell, Ph.D.

CEM Corporation

PFAS: Per- and Polyfluoroalkyl Substances









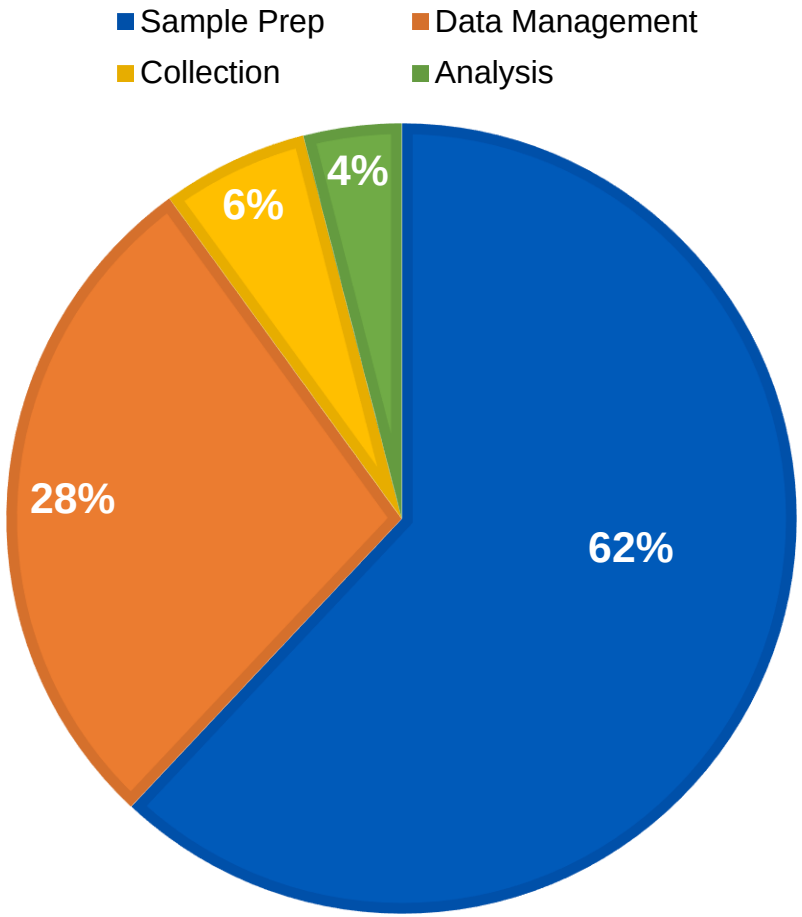

PFAS Regulated Methods

Matrix	Method
Drinking Water Surface Water Ground Water Waste Water	USEPA 537 USEPA 537.1 USEPA 533 USEPA 8327 ISO 21675.2019 ASTM 7979
Soil Solids/Sludge	USEPA 1633 (draft) ASTM 7968
Food	FDA

- Need for more methods addressing solid samples
- Solid samples require an extraction

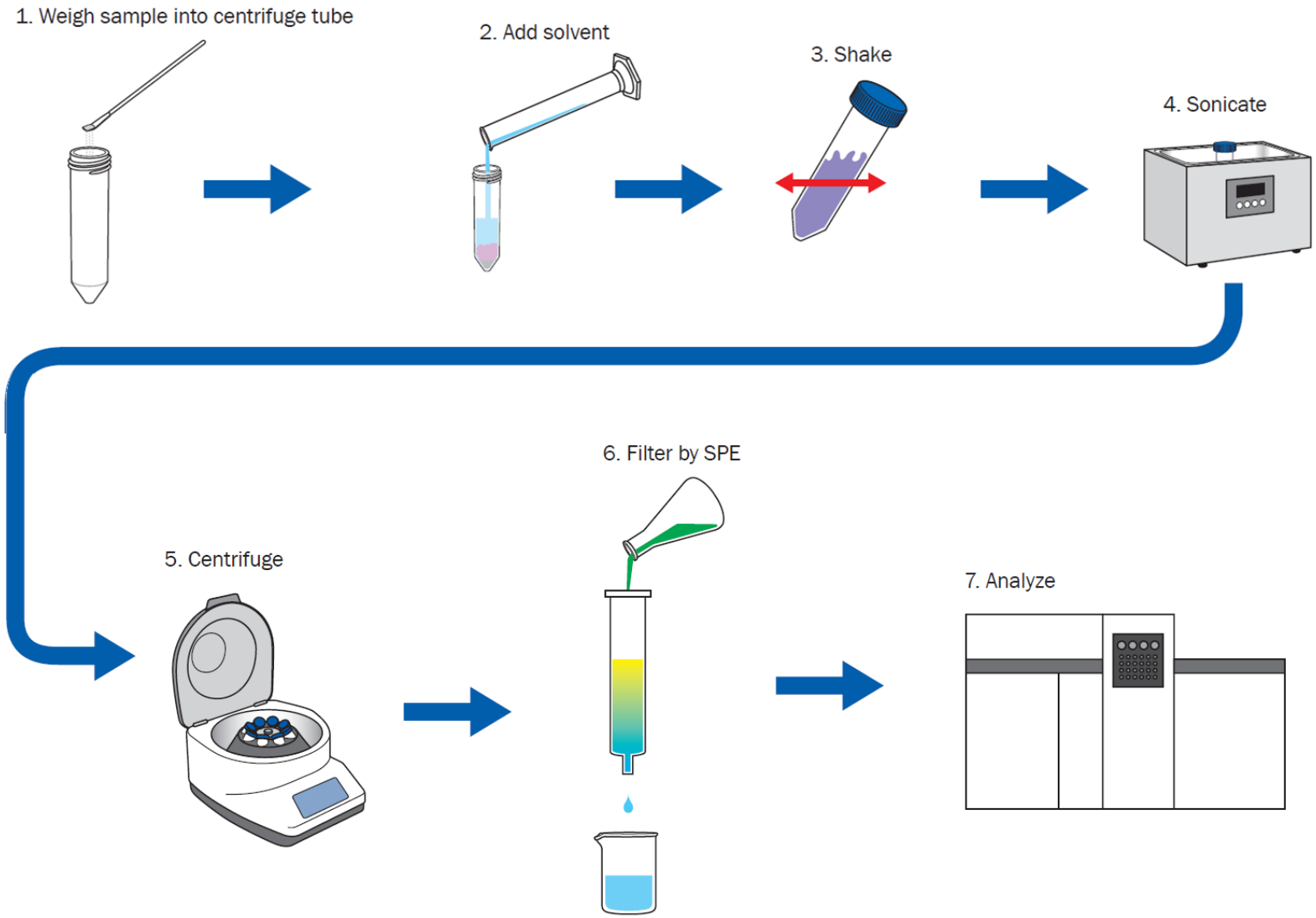
Sample Preparation is the Bottleneck

Time Spent on Typical Analysis

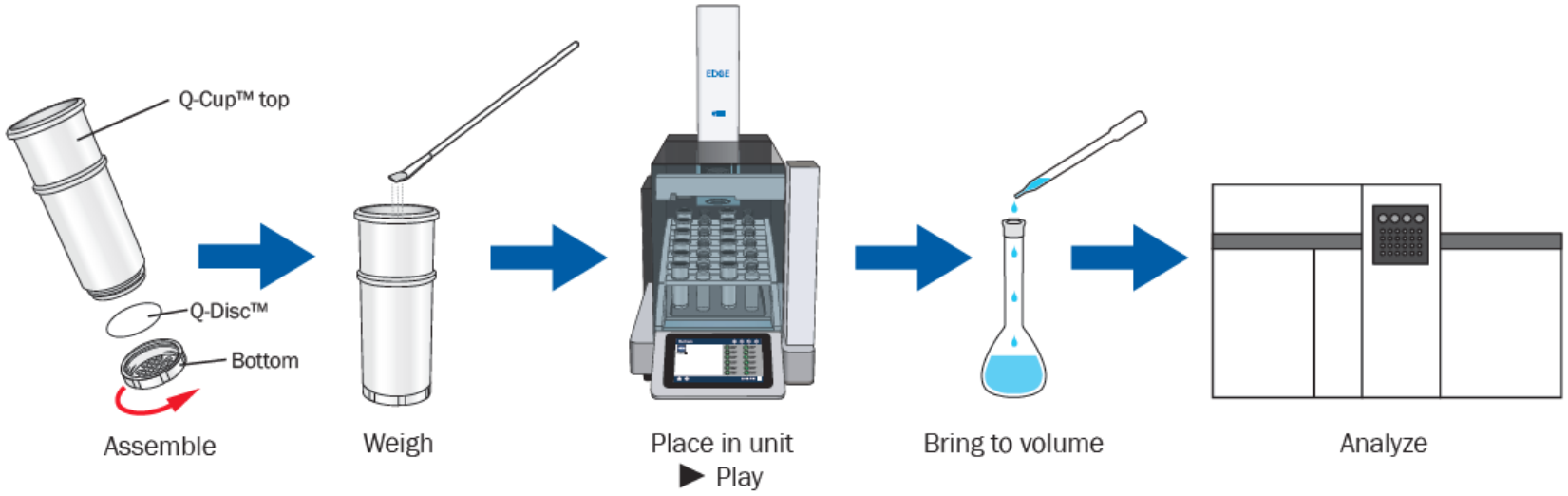


R.E. Majors, LC/GC Magazine

Typical PFAS Extraction from Soil

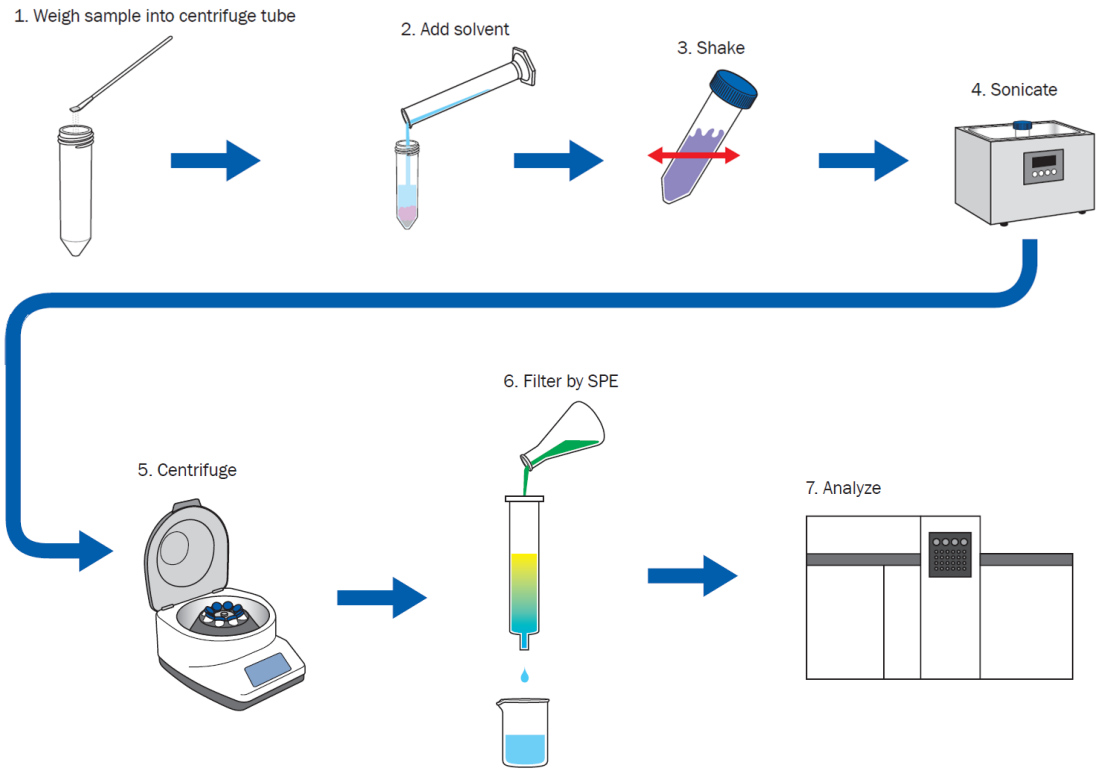


EDGE Extraction

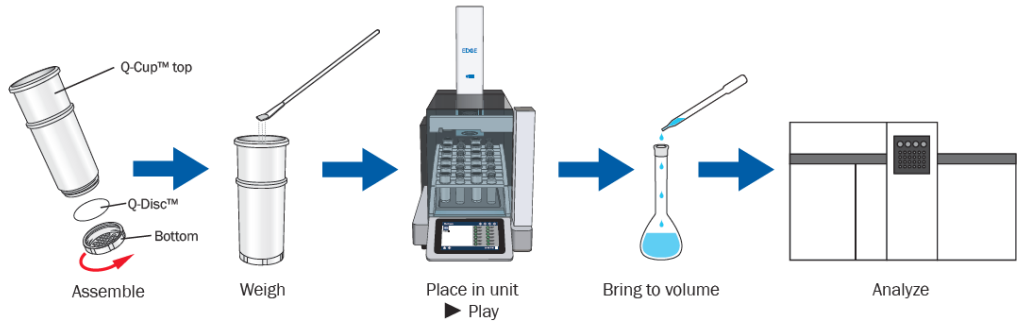


Standard versus EDGE Extraction

Standard



EDGE



EDGE Advantages

- Automation
- In-cell Cleanup
- Simple
- Multi-matrix Multi-residue Method
- PFAS free

PFAS Free Instrumentation

- PEEK and Polypropylene Tubing
- Side Enclosure
- Centrifuge Tube Collection
- Nitrogen Option
- PFAS free consumables

EDGE Sample Prep

EDGE Sample Prep

Layered in Q-Cup (sample holder)

Q-Disc	S1 (C9+G1+C9)

- C9 = 40 µm porosity Cellulose G1 = 2.7 µm porosity Glass Fiber

EDGE Sample Prep

Layered in Q-Cup (sample holder)

Salts	6 g: Sodium Sulfate 1.75 g: Sodium Chloride (Sewer Sludge Only)
Q-Disc	S1 (C9+G1+C9)

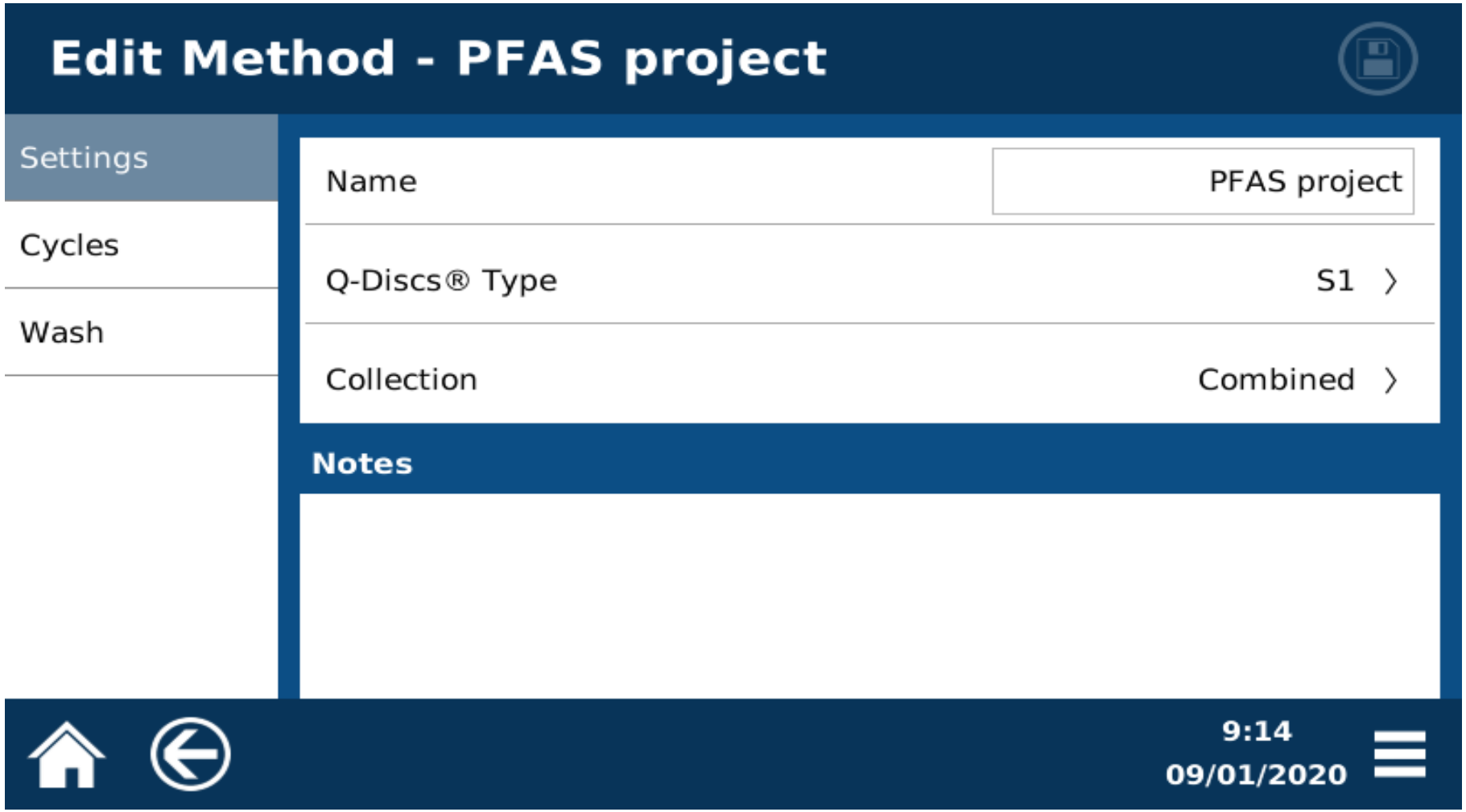
EDGE Sample Prep

Layered in Q-Cup (sample holder)	
Sample	5 g: Soil or Sewer Sludge
Salts	6 g: Sodium Sulfate 1.75 g: Sodium Chloride (Sewer Sludge Only)
Q-Disc	S1 (C9+G1+C9)

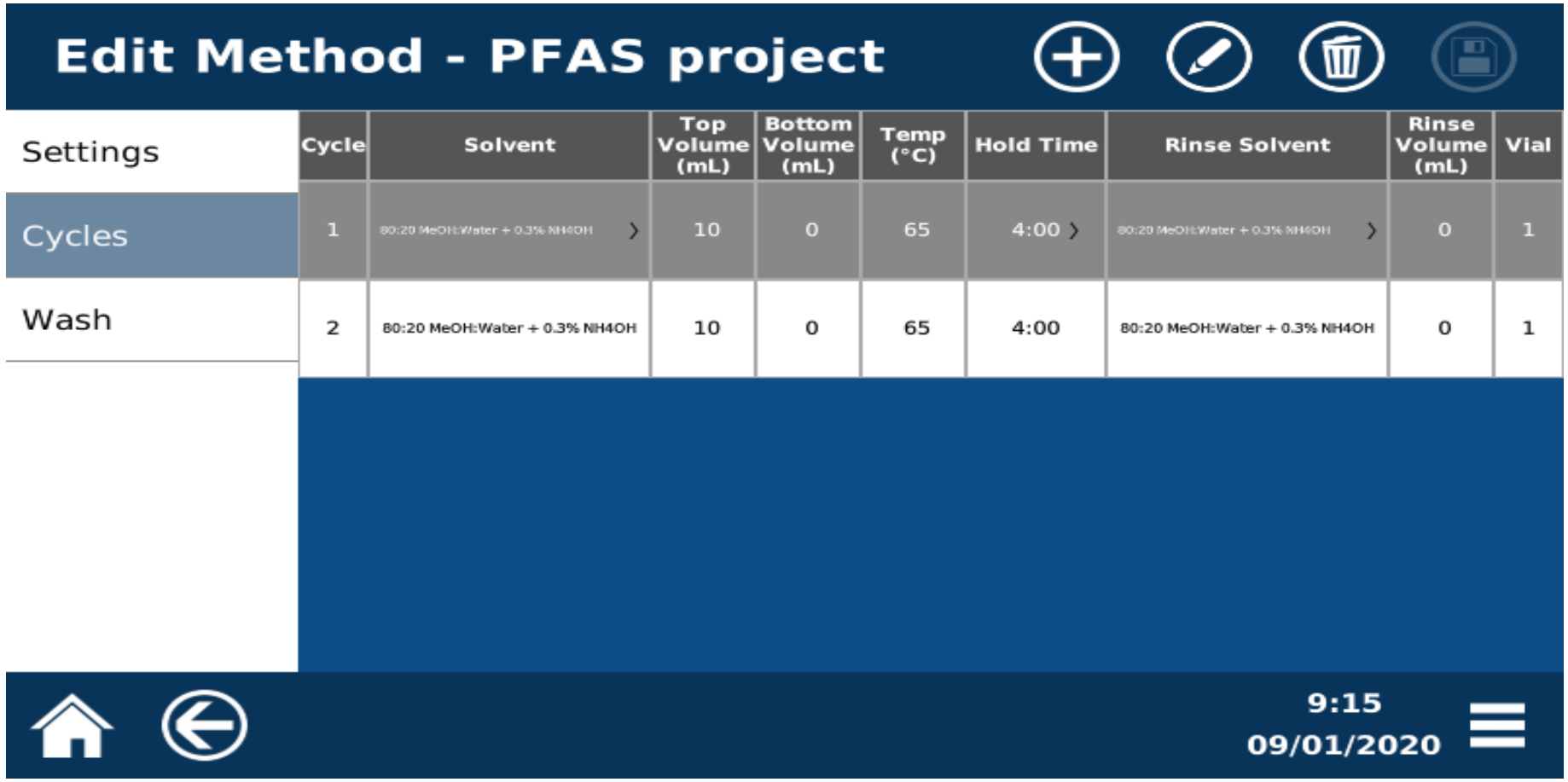
EDGE Sample Prep

Layered in Q-Cup (sample holder)	
Spike	Wellington Laboratories: PFAC30PAR and MPFAC-24ES Soil: 2 ng/g and 200 ng/g Sewer Sludge: 76.6 ng/g
Sample	5 g: Soil or Sewer Sludge
Salts	6 g: Sodium Sulfate 1.75 g: Sodium Chloride (Sewer Sludge Only)
Q-Disc	S1 (C9+G1+C9)

EDGE Method

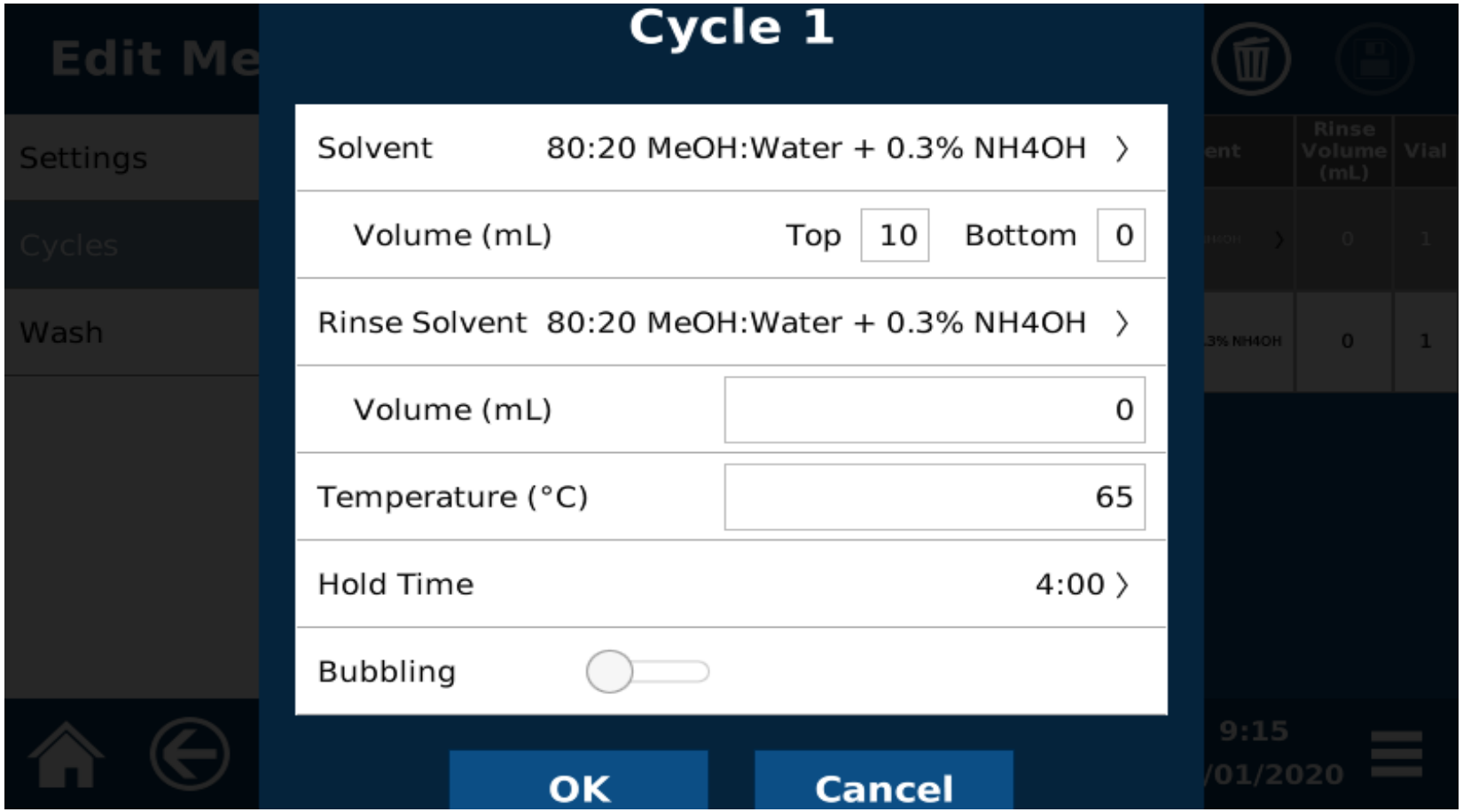

Edit Method - PFAS project
Settings
Cycles
Wash
Name
PFAS project
Q-Discs® Type
S1
Collection
Combined
Notes
9:14
09/01/2020

EDGE Method



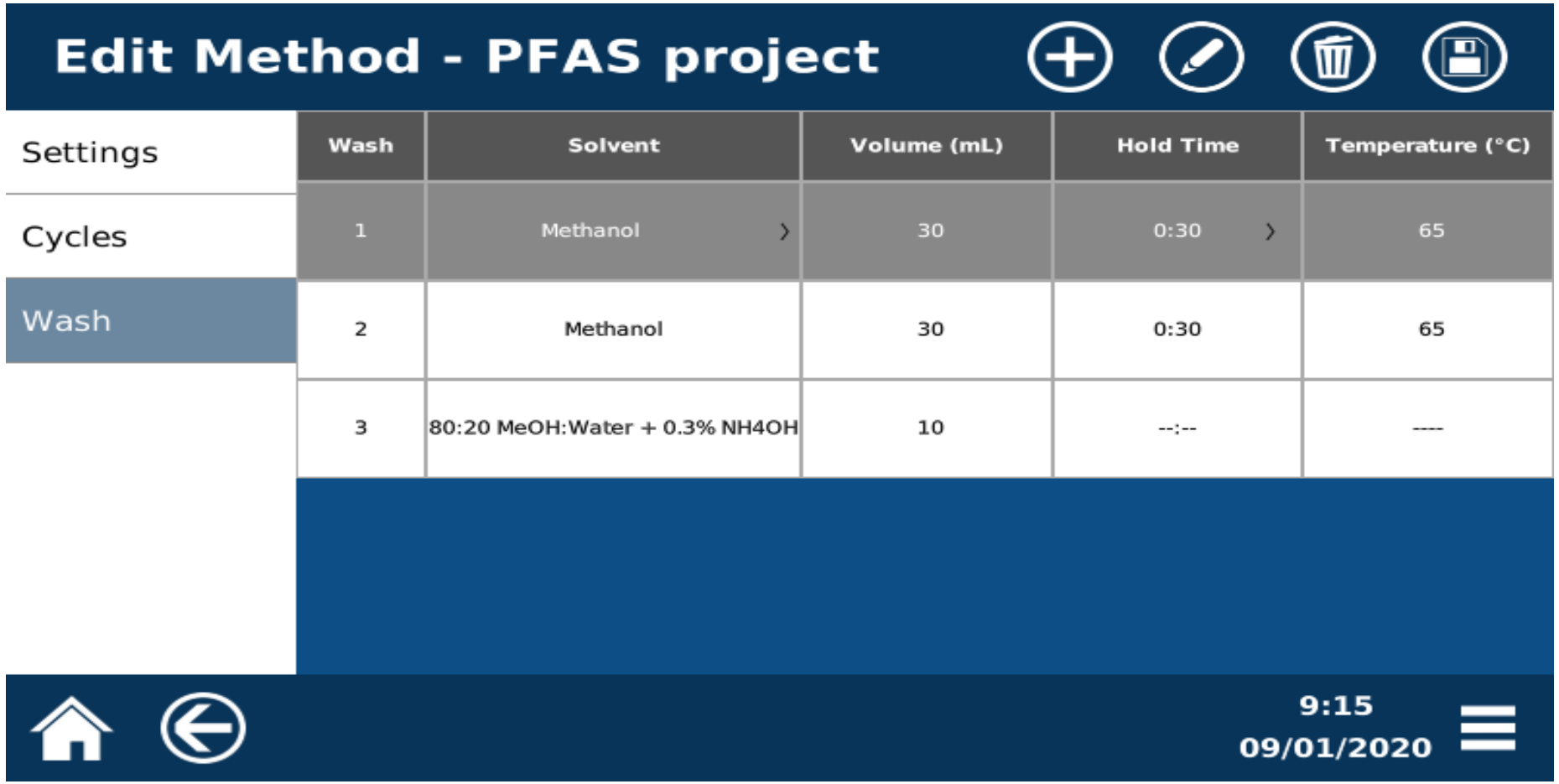
- For sewer sludge: added 2min of bubbling, increased top volume to 20 mL, increased hold time to 5 min

EDGE Method



- For sewer sludge: added 2min of bubbling, increased top volume to 20 mL, increased hold time to 5 min

EDGE Method



- For sewer sludge: increased wash 3 volume to 40 mL

Minimal Post work

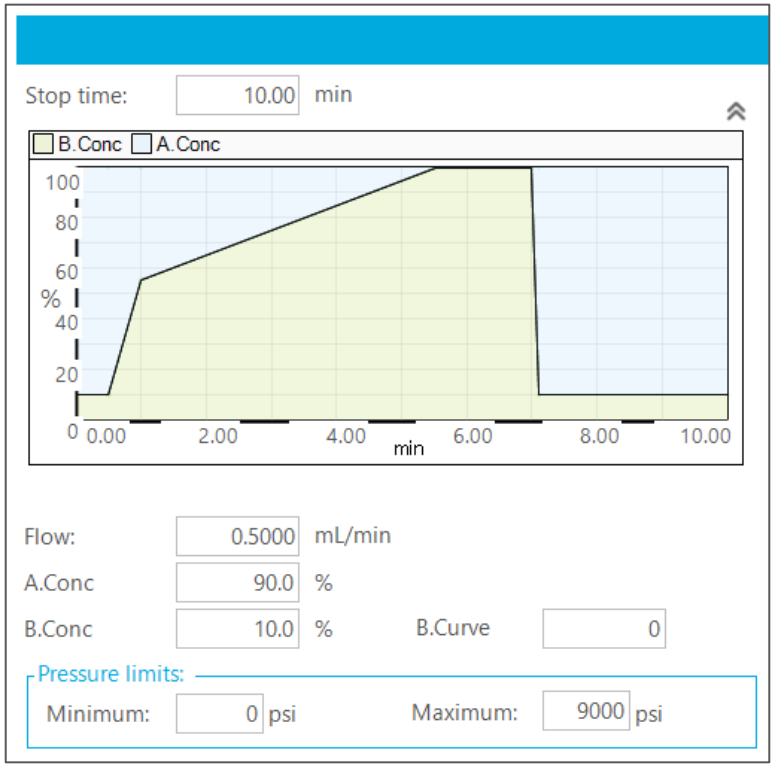
Dilute to known volume
20mL

Neutralize
20 µL Formic Acid

- For sewer sludge: diluted with methanol 1:10

Instrument Conditions (Soil)

Acquisition Parameters	
HPLC System	ExionLC™ HPLC System
MS/MS System	SCIEX 5500+ QTRAP
Ion Source	Turbo V™
Injection Volume	1 µL
Analytical Column	Phenomenex. Gemini C18 3 µm, 3 x 100 mm
Delay Column	Phenomenex. Gemini C18 5 µm, 3 x 50 mm
LC Flow Rate	500 µL/min
Mobile Phases	Water & MeOH (both with 10 mM ammonium acetate)
Source & MS Parameters	TEM = 600 C GS1= 60, GS2 = 60 ISV = -4500 CUR = 35, CAD = 8

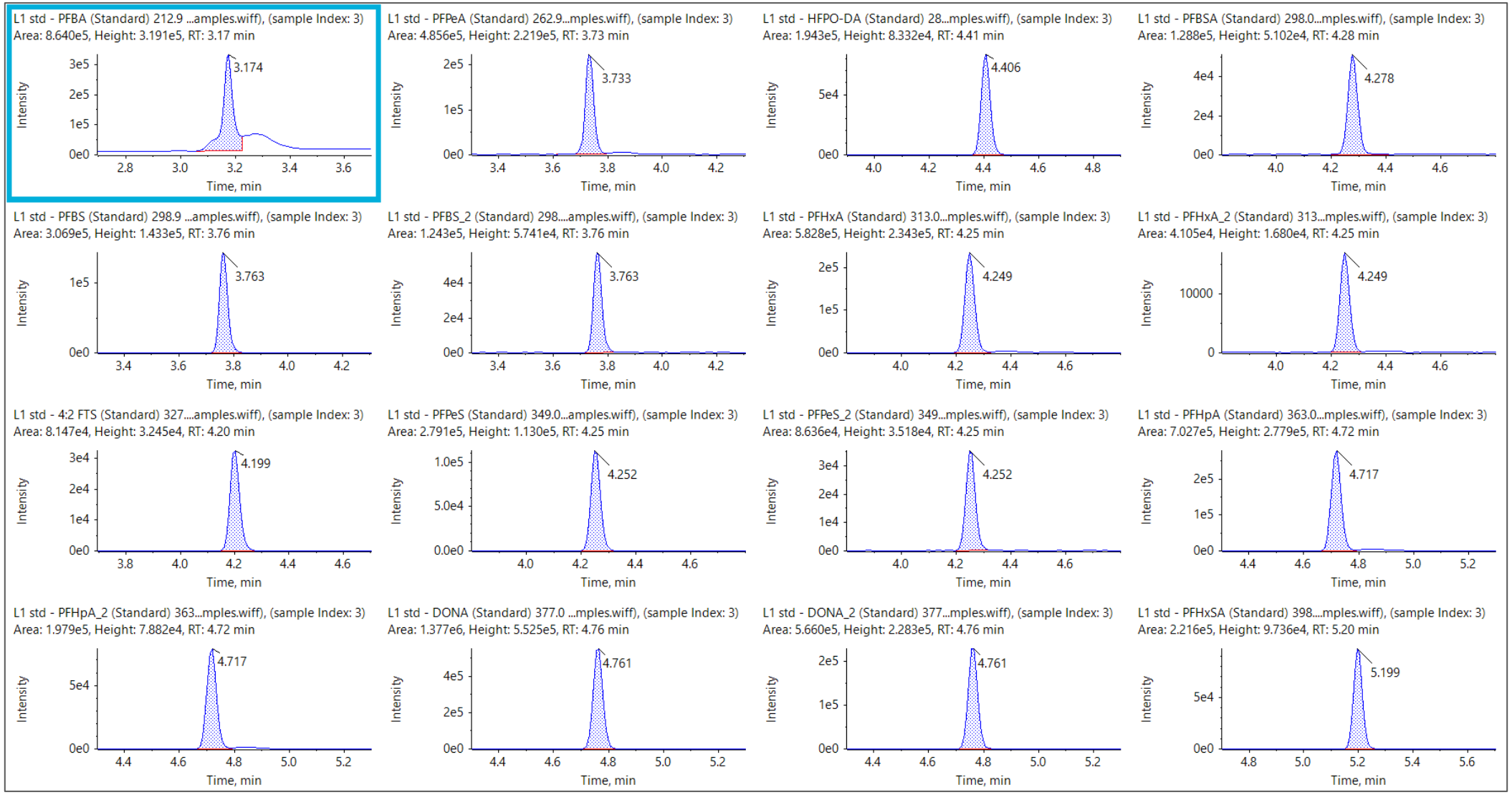


Flow program

Flow program | Simple

	Time	Flow	A.Con	B.Con	B.Curve
1		0.5000	90.0	10.0	0
2	0.50	0.5000	90.0	10.0	0
3	1.00	0.5000	45.0	55.0	0
4	5.50	0.5000	1.0	99.0	0
5	7.00	0.5000	1.0	99.0	0
6	7.10	0.5000	90.0	10.0	0
7	10.00	0.5000	90.0	10.0	0

Example Chromatogram – 2 ng/mL standard



Soil Data: High Spike 200 ng/g

PFAS	% Recovery	% RSD (n=3)
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	91	9.7
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)	90	11
1H,1H,2H,2H-perfluorohexane sulfonic acid (4:2 FTS)	101	5.8
N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA)	95	12
N-methylperfluoro-1-octanesulfonamidoacetic acid (MeFOSAA)	87	12
perfluoro-1-butanesulfonic acid (PFBS)	97	13
perfluoro-1-decanesulfonic acid (PFDS)	91	14
perfluoro-1-heptanesulfonic acid (PFHpS)	96	12
perfluoro-1-nonanesulfonic acid (PFNS)	91	16
perfluoro-1-octanesulfonamide (PFOSA)	85	20
perfluoro-1-pentanesulfonic acid (PFPeS)	88	11
perfluorohexanesulfonic acid (PFHxS)	97	11

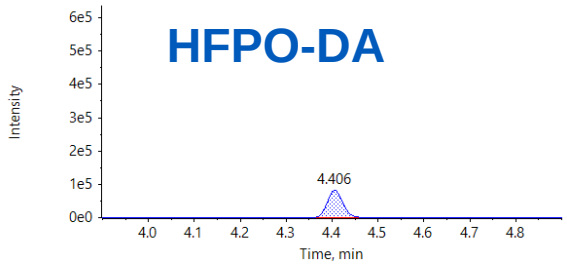
Soil Data: High Spike 200 ng/g

PFAS	% Recovery	RSD (n=3)
perfluoro-n-butanoic acid (PFBA)	87	12
perfluoro-n-decanoic acid (PFDA)	89	15
perfluoro-n-dodecanoic acid (PFDoA)	87	10
perfluoro-n-heptanoic acid (PFHpA)	86	10
perfluoro-n-hexanoic acid (PFHxA)	88	11
perfluoro-n-nonanoic acid (PFNA)	88	10
perfluoro-n-octanoic acid (PFOA)	91	10
perfluoro-n-pentanoic acid (PFPeA)	86	9.5
perfluoro-n-tetradecanoic acid (PFTeDA)	91	11
perfluoro-n-tridecanoic acid (PFTrDA)	87	11
perfluoro-n-uoecanoic acid (PFUdA)	87	12
perfluorooctanesulfonic acid (PFOS)	98	8.9

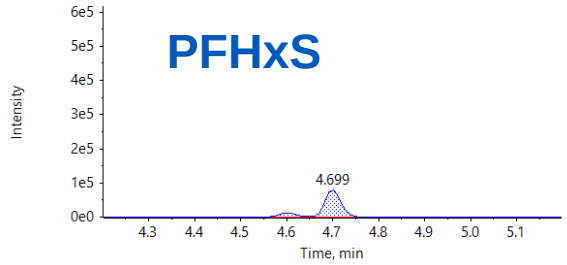
No Carryover – Sample Immediately After High Spike

2 ng/mL std

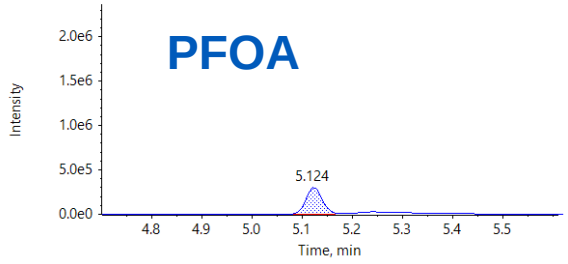
L1 std - HFPO-DA (Standard) 285.0 / 169.0...-04-CEM samples.wiff), (sample Index: 3)
Area: 1.943e5, Height: 8.332e4, RT: 4.41 min



L1 std - PFHxS (Standard) 399.0 / 80.0 - (...4-04-CEM samples.wiff), (sample Index: 3)
Area: 2.304e5, Height: 7.853e4, RT: 4.70 min

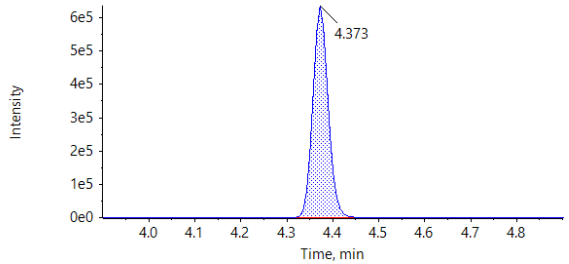


L1 std - PFOA (Standard) 413.0 / 369.0 - (...4-04-CEM samples.wiff), (sample Index: 3)
Area: 6.766e5, Height: 3.003e5, RT: 5.12 min

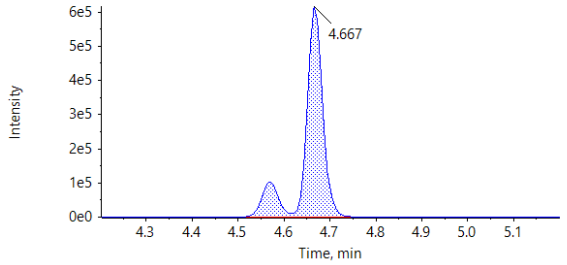


High Spike

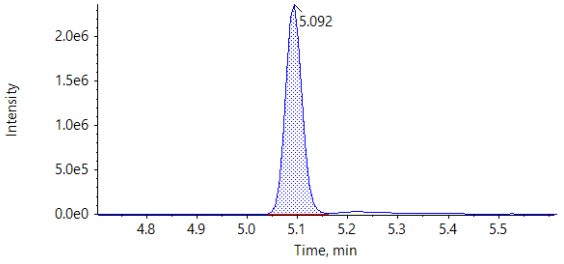
Sample 12 - HFPO-DA (Quality Control) 28...4-CEM samples.wiff), (sample Index: 20)
Area: 1.466e6, Height: 6.350e5, RT: 4.37 min



Sample 12 - PFHxS (Quality Control) 399.0...04-CEM samples.wiff), (sample Index: 20)
Area: 1.688e6, Height: 6.155e5, RT: 4.67 min

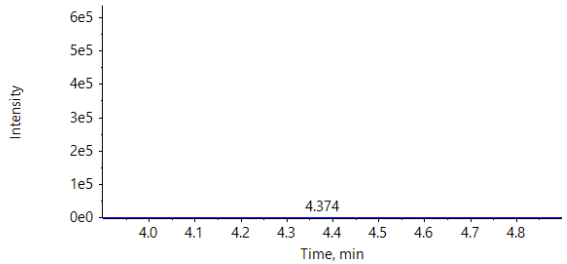


Sample 12 - PFOA (Quality Control) 413.0 ...04-CEM samples.wiff), (sample Index: 20)
Area: 5.445e6, Height: 2.360e6, RT: 5.09 min

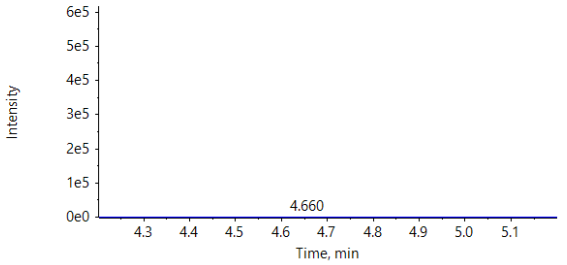


Blank

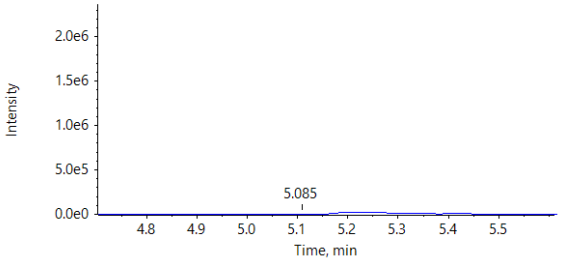
Sample 13 - HFPO-DA (Unknown) 285.0 / 1...4-CEM samples.wiff), (sample Index: 21)
Area: 7.439e2, Height: 2.750e2, RT: 4.37 min



Sample 13 - PFHxS (Unknown) 399.0 / 80.0...4-CEM samples.wiff), (sample Index: 21)
Area: 1.267e3, Height: 3.684e2, RT: 4.66 min



Sample 13 - PFOA (Unknown) 413.0 / 369.0...4-CEM samples.wiff), (sample Index: 21)
Area: 4.427e3, Height: 1.716e3, RT: 5.09 min



ERA Soil CRM Data

PFAS	% Recovery	RSD (n=2)
PFBA	88	13
DONA	96	18
4:2 FTS	106	15
HFPO-DA	86	13
PFDoA	92	7.5
PFHpS	99	19
PFHxS	108	20
PFOSA	95	24
PFOS	105	15
PFUnA	98	16

Instrument Conditions (Sewer Sludge)

Acquisition Parameters	
HPLC System	ACQUITY UPLC I Class PLUS Waters PFAS Kit
MS/MS System	Xevo TQ-XS
Injection Volume	10 µL
Analytical Column	ACQUITY BEH C18 2.1mm x 100mm, 1.7 µm
LC Flow Rate	0.3 mL /min
Mobile Phases	Water & MeOH (both with 2 mM ammonium acetate)
Source & MS Parameters	Ion mod ESI- Capillary Voltage 0.5 kV Desolvation Temperature 350 °C Desolvation Flow 900 L/hr Cone Flow 150 L/hr

UPLC Gradient		
Time (min)	**%A**	**%B**
0	95	5
1	75	25
6	50	50
13	15	85
14	5	95
17	5	95
18	95	5
22	95	5

Sewer Sludge Data

PFAS	% Recovery	% RSD (n=3)
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	114	5.1
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)	115	6.5
1H,1H,2H,2H-perfluorohexane sulfonic acid (4:2 FTS)	115	3.9
N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA)	110	4.3
N-methylperfluoro-1-octanesulfonamidoacetic acid (MeFOSAA)	108	4.0
perfluoro-1-butanesulfonic acid (PFBS)	120	2.1
perfluoro-1-decanesulfonic acid (PFDS)	110	7.1
perfluoro-1-heptanesulfonic acid (PFHpS)	116	5.8
perfluoro-1-nonanesulfonic acid (PFNS)	113	8.0
perfluoro-1-octanesulfonamide (PFOSA)	115	5.8
perfluoro-1-pentanesulfonic acid (PFPeS)	120	1.7
perfluorohexanesulfonic acid (PFHxS)	120	3.1

- Spikes compared to post-spiked samples

Sewer Sludge Data

PFAS	% Recovery	RSD (n=3)
perfluoro-n-butanoic acid (PFBA)	121	1.9
perfluoro-n-decanoic acid (PFDA)	112	9.2
perfluoro-n-dodecanoic acid (PFDoA)	110	8.8
perfluoro-n-heptanoic acid (PFHpA)	119	3.6
perfluoro-n-hexanoic acid (PFHxA)	116	2.4
perfluoro-n-nonanoic acid (PFNA)	114	7.9
perfluoro-n-octanoic acid (PFOA)	116	5.1
perfluoro-n-pentanoic acid (PFPeA)	117	2.7
perfluoro-n-tetradecanoic acid (PFTeDA)	106	7.3
perfluoro-n-tridecanoic acid (PFTrDA)	107	11
perfluoro-n-uoecanoic acid (PFUdA)	115	5.1
perfluorooctanesulfonic acid (PFOS)	111	9.6

- Spikes compared to post-spiked samples

Conclusions

- EDGE instrumentation is PFAS free
- No contamination from sample preparation or consumables
- Good recoveries and RSD values for high spiked and CRM soil and sewer sludge samples
- No carryover from high spike sample
- EDGE is a rapid, simple, and efficient technology for the extraction of PFAS from difficult matrices

Acknowledgements

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Benedict Liu
Applications Scientist

- Thank you to SCIEX for performing the soil analysis
- Thank you to Waters for performing the sewer sludge analysis

Questions

Organic.Support@cem.com