A New On-line SPE LC-HRMS Method for Simultaneous Analysis of Selected Emerging Contaminants in Surface Waters

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Supplementary Infromation

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Table S1. PFAS analytes and isotopically labelled standards, abbreviations, target ions and retention time (RT).

PFAS analyte	Abbreviation	*m/z* target ion	RT, min	Internal standard
Perfluoro-3-methoxypropanoic acid	PFMPA	228.97411	1.69	M5PFPeA
Perfluoropentanoic acid	PFPeA	262.97601	2.15	M5PFPeA
Perfluoropentanoic acid-$^{13}C_5$	M5PFPeA	267.99278	2.15	
Perfluorobutane sulfonic acid	L-PFBS	298.94299	2.34	M3PFBS
Perfluorobutane sulfonic acid,$^{13}C_3$	M3PFBS	301.95306	2.34	
Perfluoro-4-methoxybutanoic acid	PFMBA	278.97092	2.40	M3PFBS
Perfluoro (2-ethoxyethane) sulfonic acid	PFEESA	314.93791	2.68	M3PFBS
4:2 fluorotelomer sulfonate	4:2FTS	326.97429	2.92	M2-4:2FTS
4:2 fluorotelomer sulfonate, $^{13}C_2$	M2-4:2FTS	328.98100	2.92	
Perfluorohexanoic acid	PFHxA	312.97281	3.01	M5PFHxA
Perfluorohexanoic acid-$^{13}C_5$	M5PFHxA	317.98959	3.01	
Perfluoropentane sulfonic acid	L-PFPeS	348.93980	3.17	M5PFHxA
Perfluoroheptanoic acid	PFHpA	362.96962	3.90	M4PFHpA
Perfluoroheptanoic acid, $^{13}C_4$	M4PFHpA	366.98304	3.90	
Perfluorohexane sulfonic acid	L-PFHxS	398.93660	3.99	M3PFHxS
Perfluorohexane sulfonic acid, $^{13}C_3$	M3PFHxS	401.94667	3.99	
Sodium dodecafluoro-3H-4, 8-dioxanonanoate	NaDONA	376.96887	4.00	M3PFHxS
6:2 fluorotelomer sulfonate	6:2FTS	426.96790	4.64	M2-6:2-FTS
6:2 fluorotelomer sulfonate, $^{13}C_2$	M2-6:2FTS	428.97461	4.64	
Perflurooctanoic acid	PFOA	412.96643	4.69	M8PFOA
Perflurooctanoic acid, $^{13}C_8$	M8PFOA	420.99326	4.69	
Perfluroheptane sulfonic acid	PFHpS	448.93341	4.79	M8PFOA
Perfluorononanoic acid	PFNA	462.96323	5.38	M9PFNA
Perfluorononanoic acid, $^{13}C_9$	M9PFNA	471.99343	5.38	
Perfluorooctane sulfonic acid	L-PFOS	498.93022	5.41	M8PFOS
Perfluorooctane sulfonic acid, $^{13}C_8$	M8PFOS	506.95706	5.41	
Perfluoro(2-((6-chlorohexyl)oxy)ethanesulfonic acid)	9 Cl-PF3ONS	530.89558	5.76	M2-8:2-FTS
8:2 fluorotelomer sulfonate	8:2FTS	526.96152	5.97	M2-8:2-FTS
8:2 fluorotelomer sulfonate, $^{13}C_2$	M2-8:2-FTS	528.96823	5.97	
Perfluorodecanoic acid	PFDA	512.96004	5.98	M6PFDA
Perfluorodecanoic acid, $^{13}C_6$	M6PFDA	518.98017	5.98	
Perfluoroundecanoic acid	PFUDA	562.95684	6.51	M7PFUdA
Perfluoroundecanoic acid, $^{13}C_7$	M7PFUdA	569.98033	6.51	
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11 Cl-PF3OUdS	630.88919	6.76	M7PFUdA
Perfluorododecanoic acid	PFDoA	612.95365	6.97	MPFDoA
Perfluorododecanoic acid, $^{13}C_2$	MPFDoA	614.96036	6.97	

Table S2. Pharmaceuticals, pesticide, bisphenol analytes and internal standards, target ions and retention time (RT) using Negative (-) and Positive (+) Electrospray Ionisation (ESI) in Selected Ion Monitoring (SIM).

Analytes	***m/z* target ion**	**RT, min**	**Internal standard**	**Ionisation Mode**
Propamocarb	189.15975	1.18	Propamocarb-D_7	positive
Tepraloxydim	342.14666	2.56	Atrazine-D_5	positive
Carboxin	236.07398	3.02	Atrazine-D_5	positive
Atrazine	216.10105	3.47	Atrazine-D_5	positive
DEET	192.13829	3.62	Atrazine-D_5	positive
Propachlor	296.02396	3.66	Atrazine-D_5	positive
Diclofenac	212.08367	3.72	Atrazine-D_5	positive
Ibuprofen	205.12340	3.96	Reserpine	negative
Paracetamol	152.07061	4.31	Atrazine-D_5	positive
Terbuthylazine	230.11670	4.55	Atrazine-D_5	positive
Dimethomorph	388.13101	4.85	Atrazine-D_5	positive
Malathion	331.04334	4.97	Atrazine-D_5	positive
Prometryn	242.14339	5.27	Atrazine-D_5	positive
Acetochlor	270.12553	5.46	Atrazine-D_5	positive
Metolachlor	284.14118	5.22	Atrazine-D_5	positive
Phoxim	299.06138	6.44	Atrazine-D_5	positive
Prosulfocarb	252.14166	7.02	Atrazine-D_5	positive
Ethion	384.99489	7.68	Atrazine-D_5	positive
Bisphenol S	249.02270	1.81	Reserpine	negative
Bisphenol B	241.12340	4.51	Reserpine	negative
Atrazine D_5	221.13243	3.47		positive
Propamocarb D_7	196.20369	1.18		positive
Reserpine	607.26610	6.45		negative
Reserpine	609.28066	6.43		positive

Table S3. On-line SPE, UHPLC and MS conditions for ECs analysis (adapted from Kourtchev *et al.,*[1])

	On-line SPE. conditions			**UPLC conditions**		
Mobile phase	A: 0.1% Formic acid in water			A: 2 mM ammonium acetate in water/methanol, 90/10 (v/v))		
	B: Methanol			B: Methanol		
Gradient method	Time, min	%B	Flow, mL min^{-1}	Time, min	%B	Flow, mL min^{-1}
	0 5 5.1 6.5 6.6 9 9.1	0 0 100 100 0 0 0	1 1 3 3 3 3 0.5	0 1 1.1 9 12 18 18.1 22	0 0 33.3 88.9 98.9 98.9 0 0	0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3
Column temperature (°C)	25			35		
Injection volume, mL	1					
On-line SPE Pump status						
Time, min		**Loading pump status**		**Eluting pump status**		
0 1 19.1		To SPE column To waste To SPE column		Direct to analytical column To SPE & onto analytical columns Direct to analytical column		
MS conditions						
ESI parameters				**SIM parameters**		
Spray voltage (kV)		3.5		**dd-MS2**		Confirmation
Sheath gas flow rate		40		**Resolution**		70,000
Capillary temp. (⁰C)		325		**Isolation window**		1 m/z
Aux gas flow rate		10		**AGC target**		5e4
Aux gas heater temp (⁰C)		300		**Maximum IT.**		Auto
Sweep gas flow rate		0		**Loop count**		1
				MSX count		10

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Analytes	Accuracy, %RE	Precision, %RSD	Accuracy, %RE	Precision, %RSD.	Accuracy, %RE	Precision , %RSD	Accuracy, %RE	Precision, %RSD
PFAS	**0.25 pg mL^{-1}**		**0.6 pg mL^{-1}**		**3.5 pg mL^{-1}**		**7.5 pg mL^{-1}**	
PFMPA	12.0	0	-7.0	10.7	1.1	4.8	-14.9	5.9
PFPeA	-10.7	4.9	-3.9	1.5	-3.1	0.4	2.6	0.5
L-PFBS	2.3	6.6	-15.6	13.2	2.6	3.7	-5.3	4.4
PFMBA	10.1	16.4	-16.5	16.3	-4.7	11.8	-16.4	10.4
PFEESA	15.7	6.4	-8.0	5.5	1.7	3.3	-6.2	5.2
4:2 FTS	7.1	18.5	-7.6	1.7	1.7	4.8	-5.6	5.4
PFHxA	-17.1	16.2	-14.8	7.6	1.7	8.8	-5.9	4.6
L-PFPeS	-2.5	2.6	-8.1	2.1	2.2	7.1	-4.6	3.0
PFHpA	16.9	19.4	-5.1	4.0	1.9	8.4	-5.8	5.4
PFHxS	-11.5	9.3	-5.7	5.3	-1.6	4.4	-4.6	6.2
NaDONA	9.5	2.0	-8.7	2.2	0.3	5.4	-6.9	4.0
6:2 FTS	-1.1	12.1	-10.1	3.2	0.0	6.1	-6.5	4.3
PFOA	14.8	12.4	-12.2	2.8	3.1	7.3	-5.2	5.0
L-PFHpS	5.2	6.8	-7.3	1.9	4.6	6.3	-3.3	4.9
PFNA	17.1	7.0	-8.5	1.4	2.4	5.2	-6.3	5.2
PFOS	15.5	7.3	-12.2	1.9	-1.0	4.9	-6.8	4.3
9Cl-PF3ONS	-10.9	4.7	-8.5	2.5	4.6	3.3	-5.0	5.9
8:2 FTS	10.2	20.7	-4.7	2.2	0.1	3.9	-5.2	3.8
PFDA	5.0	14.9	-10.4	4.7	3.9	4.6	-2.7	4.1
PFUdA	11.1	13.1	-11.8	5.6	1.6	4.8	-6.0	4.2
11Cl-PF3OUdS	5.2	13.8	-8.4	6.7	6.7	14.7	-7.7	15.3
PFDoA	17.9	13.8	-12.8	5.6	-3.8	4.6	-7.5	4.8
Pesticides	**1.5 pg mL^{-1}**		**6 pg mL^{-1}**		**20 pg mL^{-1}**		**70 pg mL^{-1}**	
Propamocarb	>20	>20	15.4	4.4	-0.07	4.6	-0.9	6.2
Tepraloxydim	7.5	10.4	5.9	8.7	8.9	14.8	-1.9	4.9
Carboxin	18.5	10.2	15.1	19.5	-2.8	5.4	-0.2	5.1
Atrazine	20.3	10.8	14.3	6.8	1.1	5.7	1.1	5.5
DEET	2.6	9.3	11.2	9.3	-4.8	5.1	1.5	6.0
Propachlor	-6.6	10.8	12.9	5.4	0.2	5.4	1.0	5.9

Terbuthylazine	16.7	9.9	9.1	5.8	-0.4	6.0	2.9	5.1
Dimethomorph	13.1	10.7	12.5	4.9	2.0	4.7	2.4	5.0
Malathion	20.0	12.3	14.4	5.7	2.0	5.1	4.1	5.6
Prometryn	>20	12.6	12.4	5.5	0.6	6.1	2.6	5.0
acetochlor	>20	>20	16.1	10.2	2.7	7.7	7.0	5.5
Metolachlor	>20	9.6	14.5	5.7	2.0	6.1	1.5	6.3
Prosulfocarb	19.8	12.7	11.8	5.3	-0.1	6.2	0.4	6.8
Ethion	1.2	>20	16.7	10.7	6.9	7.4	4.1	5.5
Phoxim	-9.8	18.1	12.4	7.4	8.01	7.5	4.7	7.1
Pharmaceuticals								
Diclofenac	>20	>20	-3.7	4.9	5.6	4.5	-0.5	5.3
Paracetamol	18.5	>20	9.3	9.1	-4.4	5.2	-8.4	9.4
Ibuprofen	-7.4	>20	6.7	12.8	19.6	10.3	-15.4	6.8
Bisphenols		**15 pg mL^{-1}**		**35 pg mL^{-1}**		**120 pg mL^{-1}**	**160 pg mL^{-1}**	
Bisphenol S	18.1	-12.7	12.0	-11.4	2.5	-5.5	6.9	-12.6
Bisphenol B	>20	14.4	11.5	-2.0	1.2	-9.0	0.4	-0.8

Reference

1 I. Kourtchev, S. Hellebust, E. Hefferman, J. Wenger, S. Towers, E. Diapouli, and K. Eleftheriadis, *Sci. Total Environ.,* 2022, DOI: 10.1016/j.scitotenv.2022.1554

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