

Supporting Information

Biomonitoring of Perfluorinated Compounds in a Drop of Blood

Pan Mao and Daojing Wang*

Newomics Inc., Emeryville, California, United States

*Correspondence should be addressed to:

Daojing Wang, Ph.D.

Newomics Inc.

5980 Horton Street, Suite 525

Emeryville, CA 94608

Phone: 510-879-7576

Email: wang@newomics.com

Summary: The supporting information contains a total of 5 pages (S-1 to S-5) including two figures (Figure S1 and Figure S2) and two tables (Table S1 and Table S2).

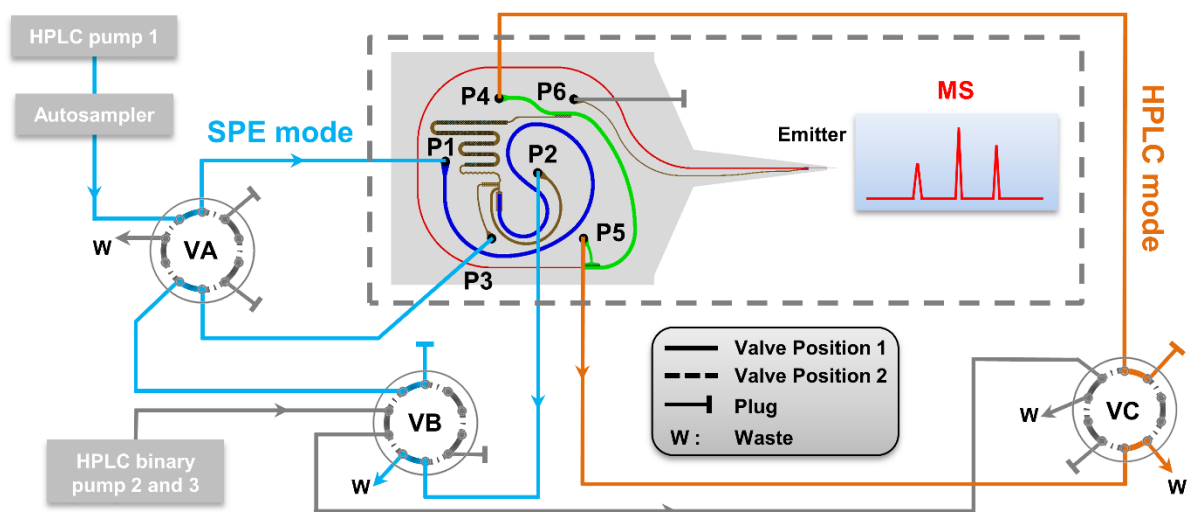


Figure S1. Operation of the SPE-LC-MS chip. System configuration and fluidic connection with external valves and pumps for chip operation. VA, VB, and VC are 2-position switching valves. Positions shown are those during SPE sample loading. P1-P6 are inlet/outlet ports.

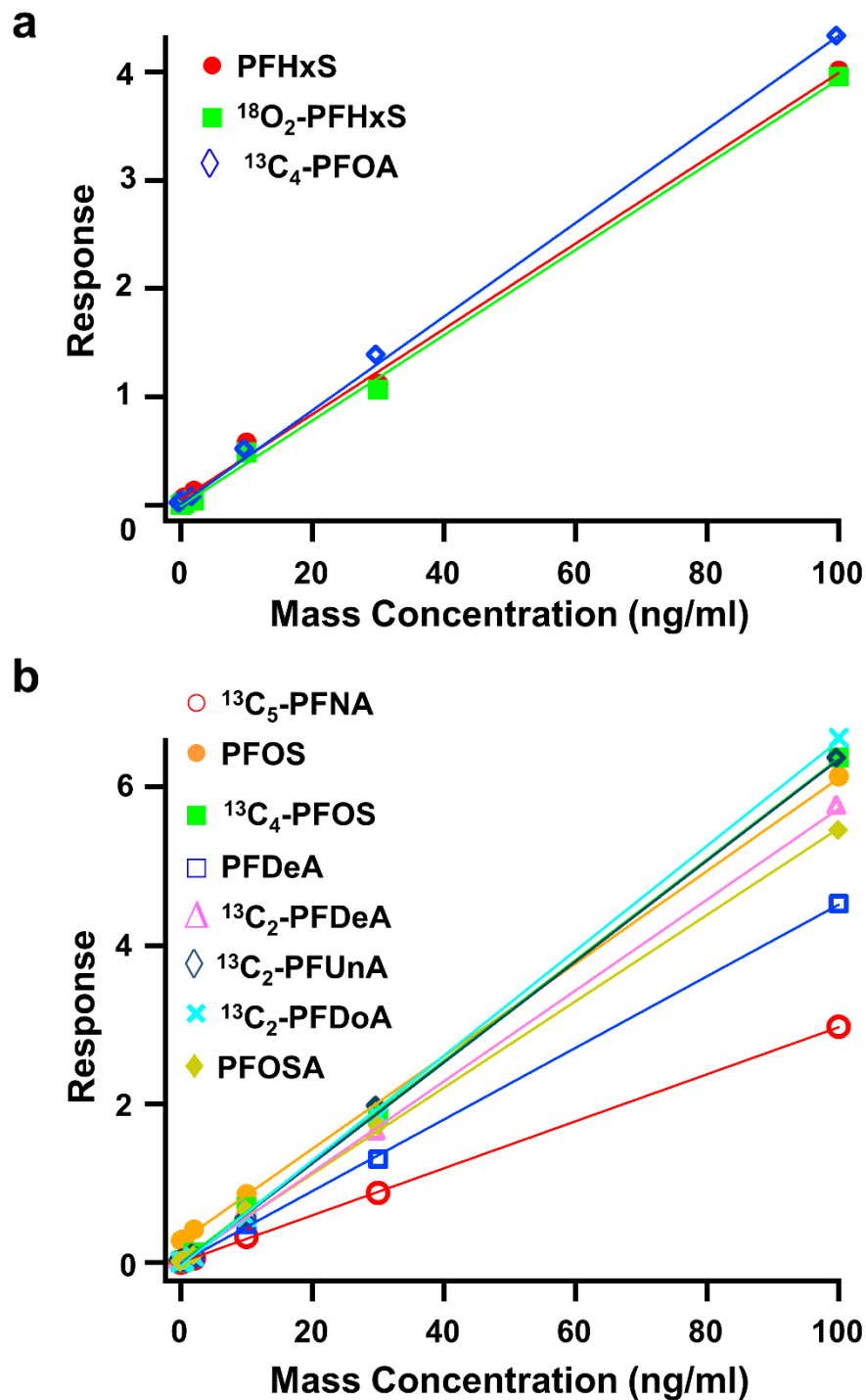


Figure S2. The calibration curves for PFC compounds. The response was obtained by calculating the ratios of peak areas between analytes and the internal standards over the concentration ranges of 0 - 100 ng/ml. (a) Response of PFHxS, $^{18}\text{O}_2$ -PFHxS, and $^{13}\text{C}_4$ -PFOA using $^{13}\text{C}_8$ -PFOA as the internal standard. (b) Response of $^{13}\text{C}_5$ -PFNA, PFOS, $^{13}\text{C}_4$ -PFOS, PFDeA, $^{13}\text{C}_2$ -PFDeA, $^{13}\text{C}_2$ -PFUnA, $^{13}\text{C}_2$ -PFDoA, and PFOSA using $^{13}\text{C}_8$ -PFOS as the internal standard.

Table S1. The workflow for on-chip and online SPE-LC-MS analysis

Steps	Method	Fluidic and Valve Control				
		P1	P2	P3	P4	P5
1	Condition SPE column (20 μ l LC Solvent B, 10 μ l/min)	Pump1 VA-1	Waste VB-1	Plug VA-1	Plug VC-1	Waste VC-1
2	Equilibrate SPE column (20 μ l LC Solvent A, 10 μ l/min)	Pump1 VA-1	Waste VB-1	Plug VA-1	Plug VC-1	Waste VC-1
3	Load 4 μ l sample onto SPE column	Pump1 VA-1	Waste VB-1	Plug VA-1	Plug VC-1	Waste VC-1
4	Wash SPE column (20 μ l LC Solvent A, 10 μ l/min)	Pump1 VA-1	Waste VB-1	Plug VA-1	Plug VC-1	Waste VC-1
5	Elute SPE column and enrich eluents on trap column (20 μ l LC Solvent B, 1 μ l/min, mixed with LC Solvent A at 20 μ l/min)	Pump1 VA-1	Plug VB-2	Pump2 VA-1,VB-2	Plug VC-1	Waste VC-1
6	Run HPLC gradient elution and acquire LC-MS/MS data	Plug VA-2	Plug VB-2	Plug VA-2,VB-2	Pump3 VC-2	Plug VC-2

Table S2. List of PFCs used in this study with their molecular and product ions in negative ESI-MS, along with collision energy, cone voltage, and linear range

Target Analytes	Molecular Weight	Observed Precursor Ion (m/z)	Observed Product Ion (m/z)	Collision Energy (eV)	Cone Voltage (V)	Linear Range (ng/ml)	R ² Value
PFHpA* [#]	364.063	362.962	318.962	10	25	0.05-100	N/A
PFHxS ^{&}	422.097	398.938	98.988	10	25	0.05-100	0.9976
¹⁸ O ₂ ⁻ PFHxS ^{&}	420.097	402.945	102.945	10	25	0.05-100	0.9982
PFOA* [#]	414.071	412.963	368.961	10	25	0.05-100	N/A
¹³ C ₄ -PFOA [#]	418.040	416.973	371.975	10	25	0.05-100	0.9998
PFNA* [#]	464.078	462.978	418.970	10	25	0.05-100	N/A
¹³ C ₅ -PFNA [#]	469.040	467.995	422.990	10	25	0.05-100	0.9998
PFOS ^{&}	522.113	498.950	98.988	10	25	0.05-100	0.9996
¹³ C ₄ -PFOS ^{&}	526.082	502.954	98.988	10	25	0.05-100	0.9998
PFDeA [#]	514.086	512.972	468.980	10	25	0.05-100	0.9997
¹³ C ₂ ⁻ PFDeA [#]	516.071	514.980	469.979	10	25	0.05-100	0.9996
¹³ C ₂ ⁻ PFUnA [#]	566.079	564.990	519.990	10	25	0.05-100	0.9995
¹³ C ₂ ⁻ PFDoA [#]	616.087	615.000	570.000	10	25	0.05-100	0.9994
PFOSA ^{&}	499.146	497.953	77.978	10	25	0.05-100	0.9993
Internal Standards							
¹³ C ₈ -PFOA [#]	422.010	420.987	375.987	10	25		
¹³ C ₈ -PFOS ^{&}	530.052	506.974	98.988	10	25		

* Those compounds had strong background signals in our HPLC system.

[#] Perfluoroalkylcarboxylic acids were quantified using their product ions.

[&] Perfluoroalkylsulfonates and perfluorooctanesulfonamides were quantified using their precursor ions.