Supplemental Information for:

Evaluation of iodide chemical ionization mass spectrometry for gas and aerosol-phase per- and polyfluoroalkyl substances (PFAS) analysis

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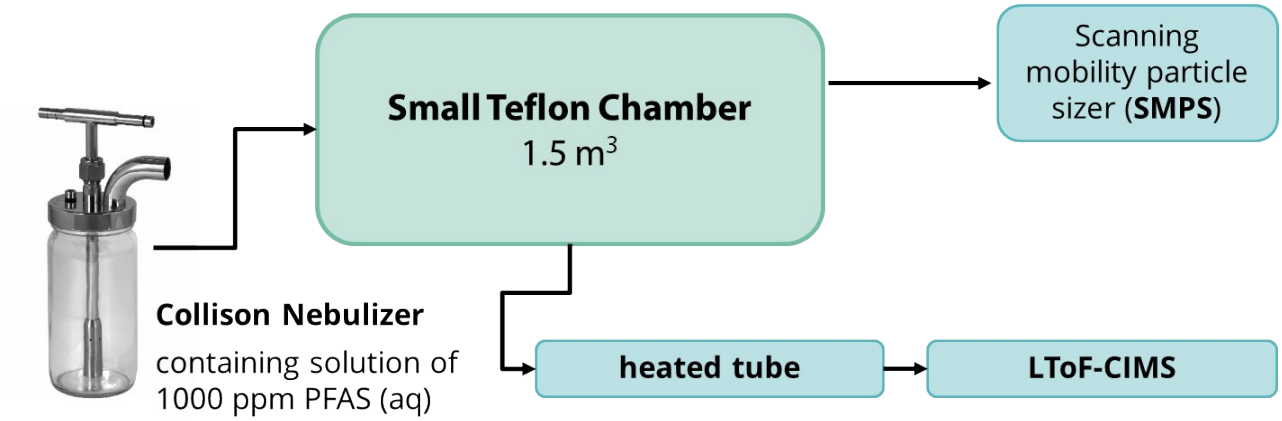
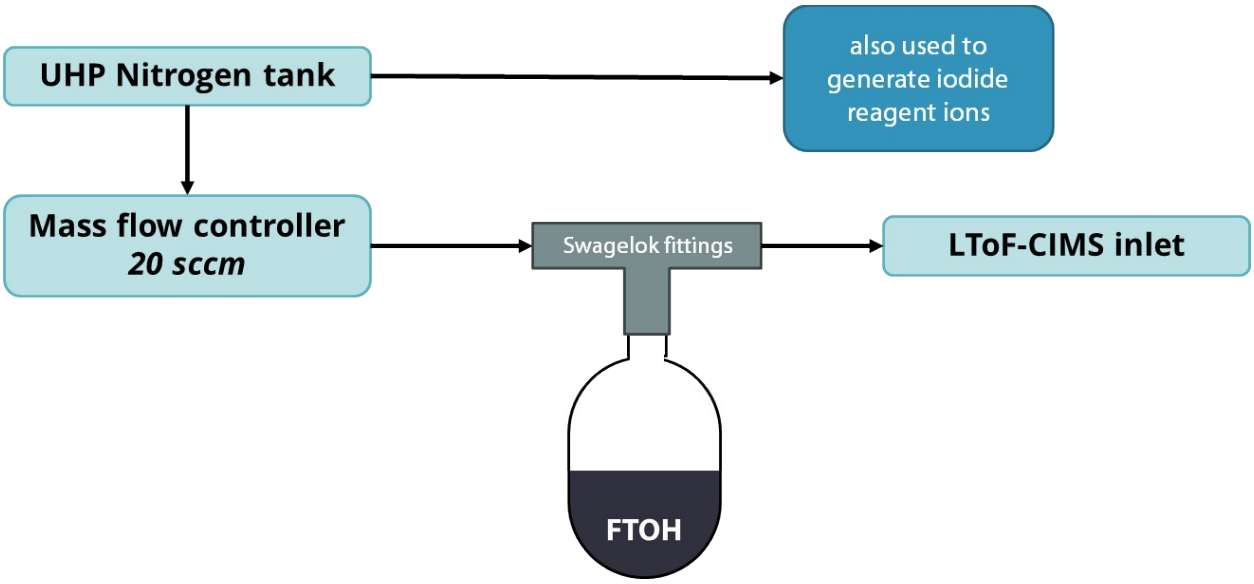
Supplemental Information



SI Figure S1. Schematic of heated tube setup. Aerosol is generated via a Collison nebulizer and injected into a Teflon chamber. Aerosol is sampled from the chamber through a tube wrapped in heating tape, where it is vaporized. The resulting vapors are measured via LtoF-CIMS.



SI Figure S2. Schematic of diffusion tube setup. Diffusion tube is a glass bulb that in this case, contains 1 mL of pure FTOH. A controlled flow of UHP nitrogen is pushed through the headspace of the tube to generate gaseous FTOH molecules, which then enter the LToF-CIMS inlet, where they are subsequently ionized and detected.

SI Table S1. Initial voltage settings used for the LToF-CIMS in this study. These voltages were optimized to maximum detection of the PFAS-iodide cluster across all PFAS studied.

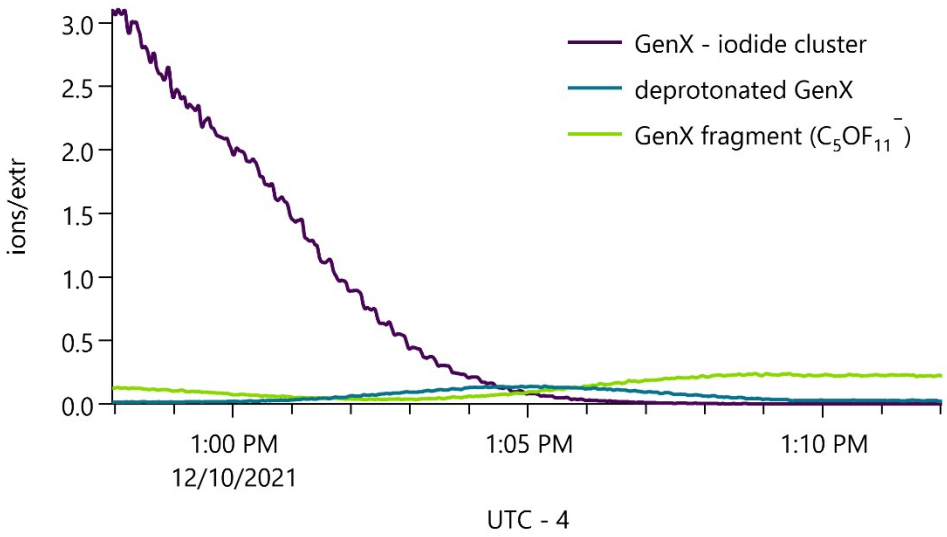
Component	Module Code	Voltage (V)
IMR	124	0.05
Nozzle	56	0.05
SSQ EP	57	0.1
SSQ Front	49	0.2
SSQ Back	50	-0.3
Lens Skimmer	53	-0.19
Skimmer	28	4

SI Table S2. The contents of this table, in .txt form, were used for ToF Power Supply (TPS) scripting to conduct voltage ion declustering scans. The first column represents seconds, the second column represents the RC code for the component, the third column (A) means the values in the fourth column are absolute voltages (as opposed to relative) and the fourth column are the voltages the component is to be set to. Our voltage declustering scans had a duration of 690 seconds, but for brevity's sake, only the first 60 seconds are shown here.

Time (s)	Module Code	Type	Voltage Set (V)
0	28	A	4
0	124	A	0.05
0	56	A	0.05
0	57	A	0.1
0	49	A	0.2
0	50	A	-0.3
0	53	A	-0.19
15	28	A	3.5
15	124	A	-0.45
15	56	A	-0.45
15	57	A	-0.4
15	49	A	-0.3
15	50	A	-0.8
15	53	A	-0.69
30	28	A	3
30	124	A	-0.95
30	56	A	-0.95
30	57	A	-0.9
30	49	A	-0.8
30	50	A	-1.3
30	53	A	-1.19
45	28	A	2.5
45	124	A	-1.45
45	56	A	-1.45
45	57	A	-1.4
45	49	A	-1.3
45	50	A	-1.8
45	53	A	-1.69
60	28	A	2
60	124	A	-1.95
60	56	A	-1.95
60	57	A	-1.9
60	49	A	-1.8
60	50	A	-2.3
60	53	A	-2.19

SI Table S3. FIGAERO program. The table below describes the steps of each desorption cycle. Prior to the cycle, the actuator was moved to the XCH mode to expose the filter, allowing for a solution of PFAS to be deposited onto it.

time (min)	filter setpoint (°C)	heating block setpoint (°C)	actuator position	desorption gas flow (sccm)
0	0	0	COL	0
1	280	330	DES	2000
6	280	330	DES	2000
11	280	330	DES	2000
22	--	--	DES	100
24	--	--	XCH	100
25	25	25	XCH	100



SI Figure S3. Example of voltage scanning data for GenX showing GenX - iodide cluster, deprotonated GenX, and fragment. GenX undergoes fragmentation, but to a minimal degree under "typical" dV conditions (the leftmost portion of the graph). The fragment yields about 10% of the signal of the GenX-iodide cluster. An iodide adduct of the protonated version of the fragment was not detected.

SI Table S4. Summary of analytes and pertinent information on their detection.

Abbreviation	Dominant species?	Class	Technique Used	Formula	Exact mass
PFBA$^-$		PFCA	Heated tube	$C_4F_7O_2^-$	212.98
PFBA/I$^-$	X			$C_4HF_7O_2I^-$	340.89
PFHxA$^-$				$C_6F_{11}O_2^-$	312.97
PFHxA/I$^-$	X			$C_6HF_{11}O_2I^-$	440.88
PFOA$^-$				$C_8F_{15}O_2^-$	412.97
PFOA/I$^-$	X			$C_8HF_{15}O_2I^-$	540.88
GenX$^-$				$C_6F_{11}O_3^-$	328.97
GenX/I$^-$	X			$C_6HF_{11}O_3I^-$	456.88
PFBS$^-$	X	PFSA	FIGAERO	$C_4F_9O_3S^-$	298.94
PFBS/I$^-$				$C_4HF_9O_3SI^-$	426.85
PFOS$^-$	X			$C_8F_{17}O_3S^-$	498.93
PFOS/I$^-$				$C_8F_{17}O_3SI^-$	625.83
6:2 diPAP$^-$	X	diPAP	FIGAERO	$C_{16}H_8F_{26}O_4P^-$	788.97
6:2 diPAP/I$^-$				$C_{16}H_9F_{26}O_4PI^-$	916.89
8:2 diPAP$^-$	X			$C_{20}H_8F_{34}O_4P^-$	988.96
8:2 diPAP/I$^-$				$C_{20}H_9F_{34}O_4PI^-$	1116.87
4:2 FTOH$^-$		FTOH	Diffusion tube	$C_6H_4F_9O^-$	263.01
4:2 FTOH/I$^-$	X			$C_6H_5F_9OI^-$	390.92
6:2 FTOH$^-$				$C_8H_4F_{13}O^-$	363.01
6:2 FTOH/I$^-$	X			$C_8H_5F_{13}OI^-$	490.92
8:2 FTOH$^-$				$C_{10}H_4F_{17}O^-$	463.00
8:2 FTOH/I$^-$	X			$C_{10}H_5F_{17}OI^-$	590.91
iodide	N/A	reagent and background ions	N/A	I^-	126.90
iodide/water				IH_2O^-	144.92
triiodide				I_3^-	380.71
nitric acid/iodide				$IHNO_3^-$	189.90