Feasibility of Closing the PFAS Mass Balance: Exploring the Potential of Liquid Sampling Atmospheric Pressure Glow Discharge (LS-APGD) with Orbitrap Mass Spectrometry for neutral PFAS

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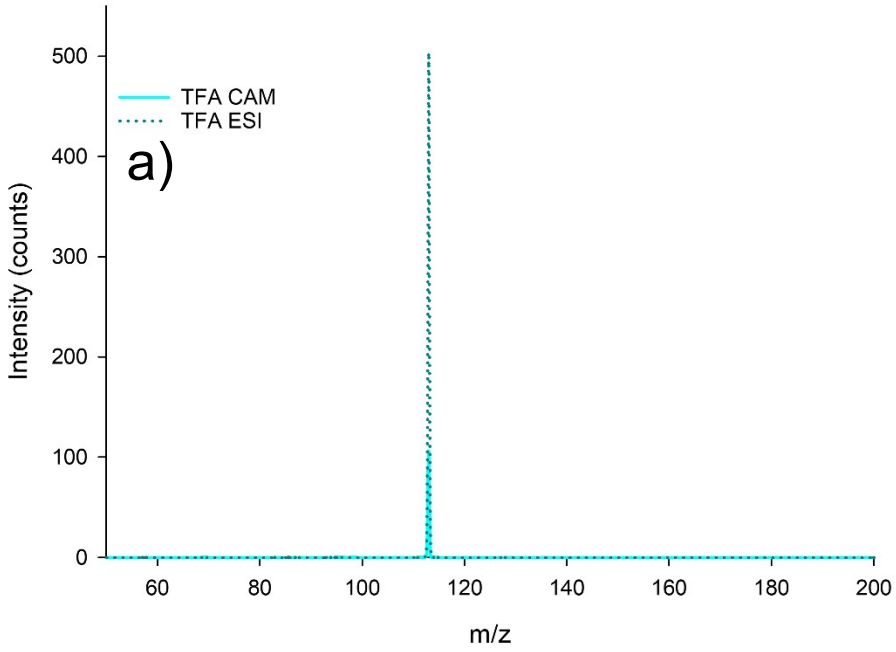
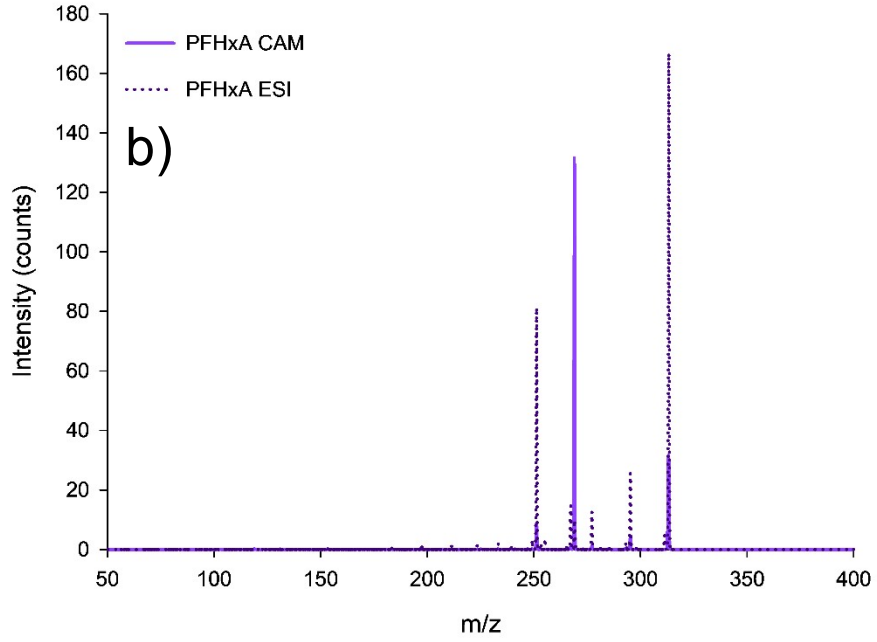
Keywords: fluorocarbons, perfluoroalkanes, electrospray, FTOH, PFCA, PFSA, orbitrap

Supporting information

Table 1: Mass error on the different PFAS fragments.

Compound	Major Fragment	Theoretical m/z	Observed m/z
TFA	$[M-H]^-$	112.9850	112.98636
TFA	$[M-COOH]^-$	68.9952	68.99656
PFBA	$[M-H]^-$	212.97863	212.9799
PFBA	$[M-COOH]^-$	168.9888	168.9900
PFHxA	$[M-H]^-$	312.97223	312.97244
PFHxA	$[M-COOH]^-$	268.9824	268.98309
PFDA	$[M-H]^-$ -	512.95943	512.96039
PFDA	$[M-COOH]^-$	468.9696	468.97031
PFHxS	$[M-H]^-$	398.936016	398.9368
PFHxS	$[SO_3]^-$	79.956816	79.95811
PFHxS	$[SO_3F]^-$	98.955216	98.95653


TFA CAM
TFA ESI
a)
Intensity (counts)
m/z
0
100
200
300
400
500
60
80
100
120
140
160
180
200


PFHxA CAM
PFHxA ESI
b)
Intensity (counts)
m/z
0
20
40
60
80
100
120
140
160
180
50
100
150
200
250
300
350
400

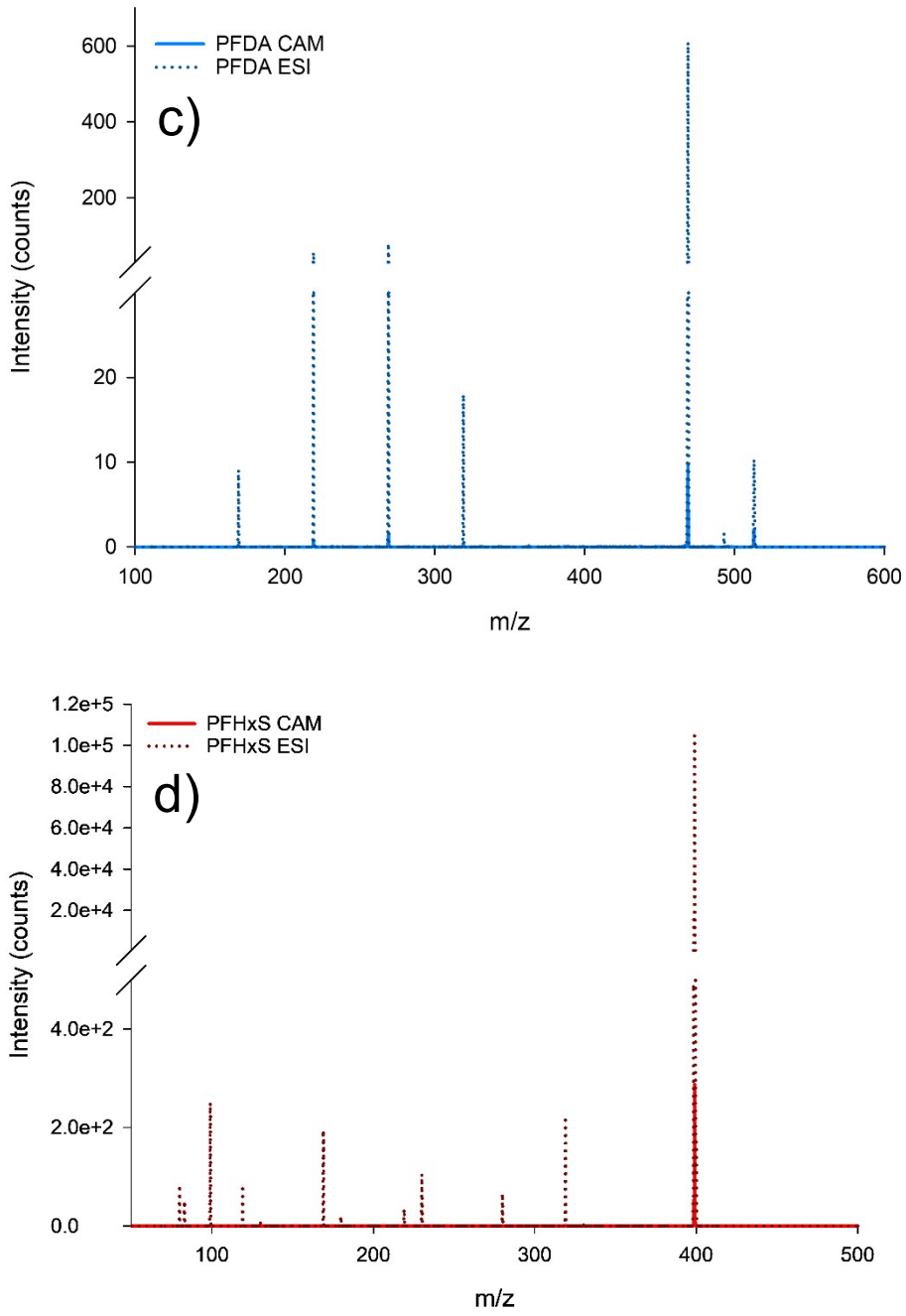


Figure S1 a – d. Comparison between CAM and ESI sources using the same PFAS standards. A table with the numerical values can be found in the main text, table 1.

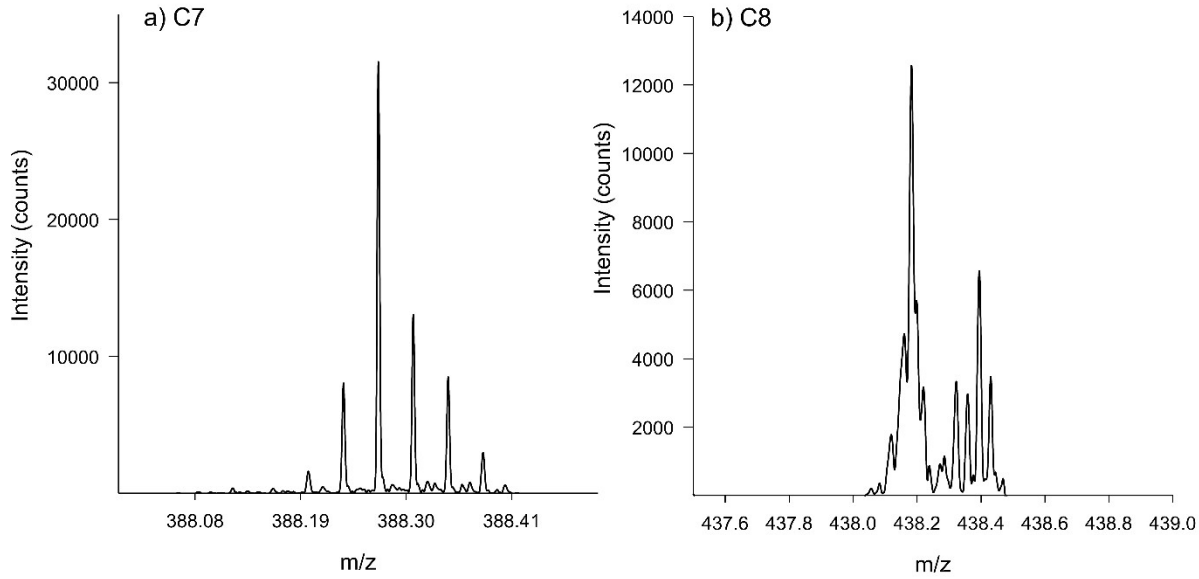


Figure S2 a – b. Mass spectra of C_7 and C_8 perfluoroalkane standads in the positive mode. No peaks appeared at the corresponding m/z.

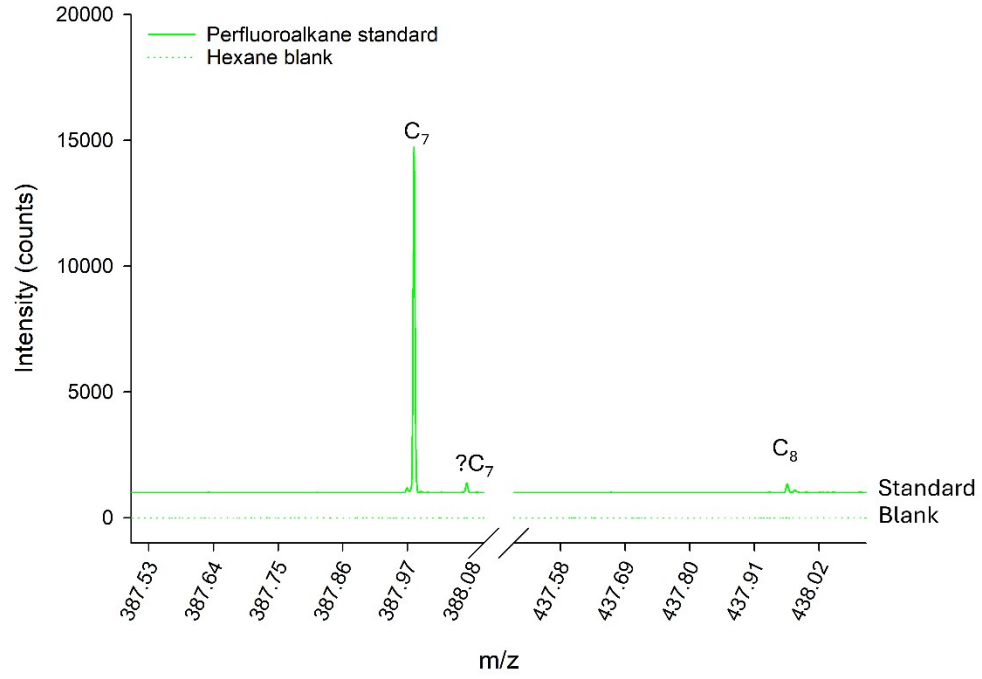


Figure S3. Comparison of mass spectra of perfluoroalkane standard to hexane blank in the negative mode.

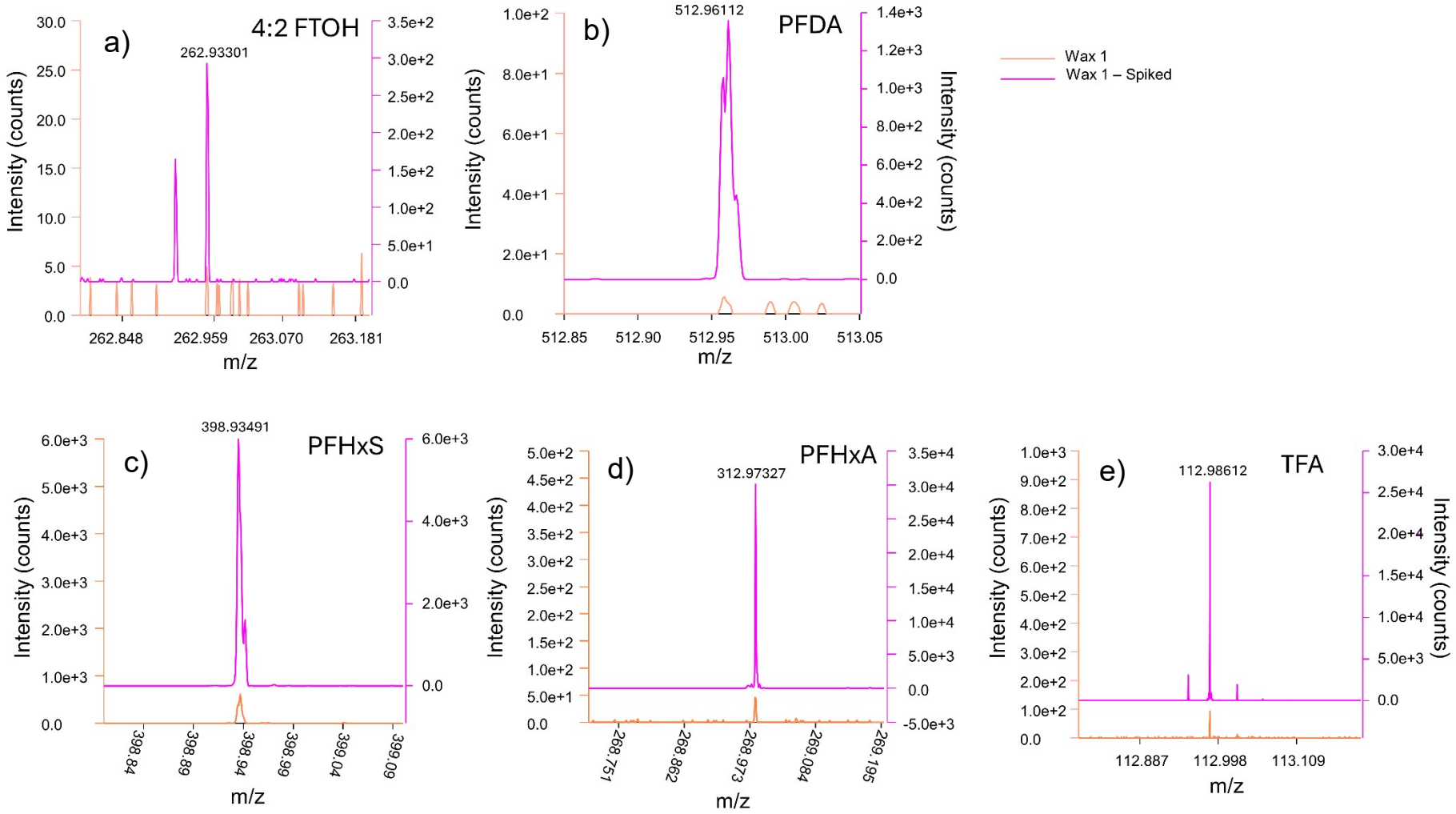


Figure S5 a – e. Comparison of mass spectra of selected neutral and ionic PFAS in spiked and non-spiked wax, extracted with 70 : 30 methanol : water, using CAM – LS-APGD in the negative mode.

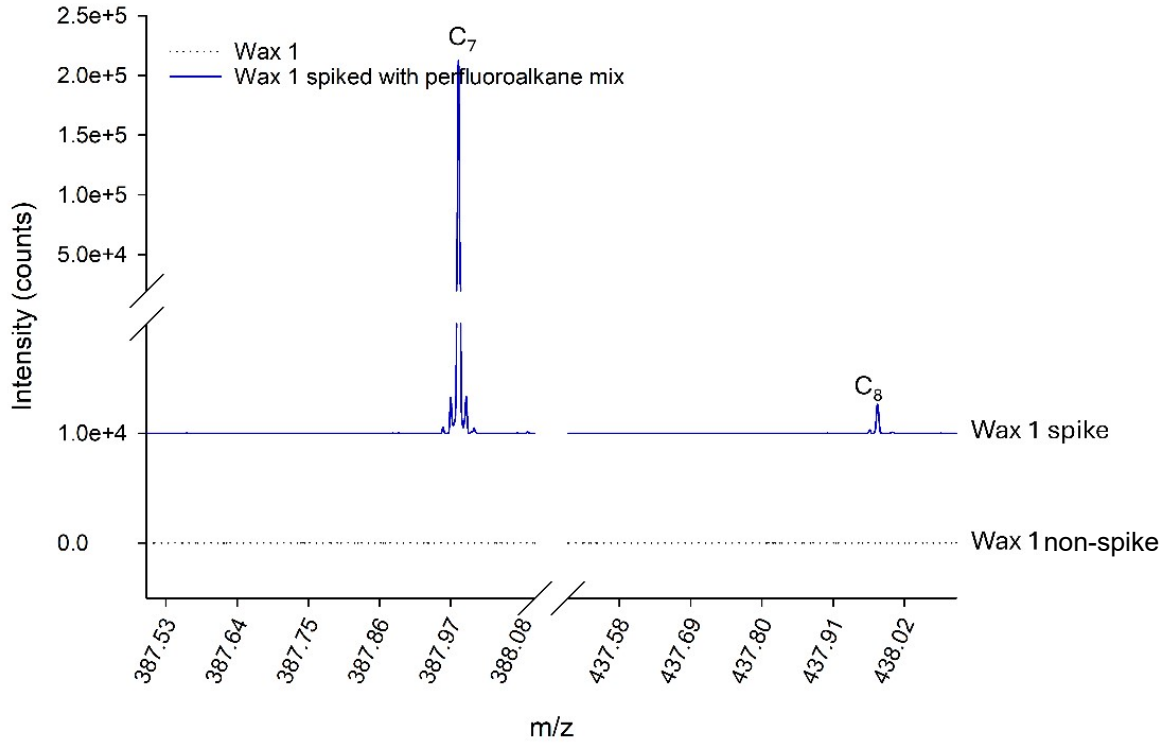


Figure S6. Comparison of mass spectra of perfluoroalkanes in spiked and non-spiked wax, extracted with hexane, using CAM – LS-APGD in the negative mode.

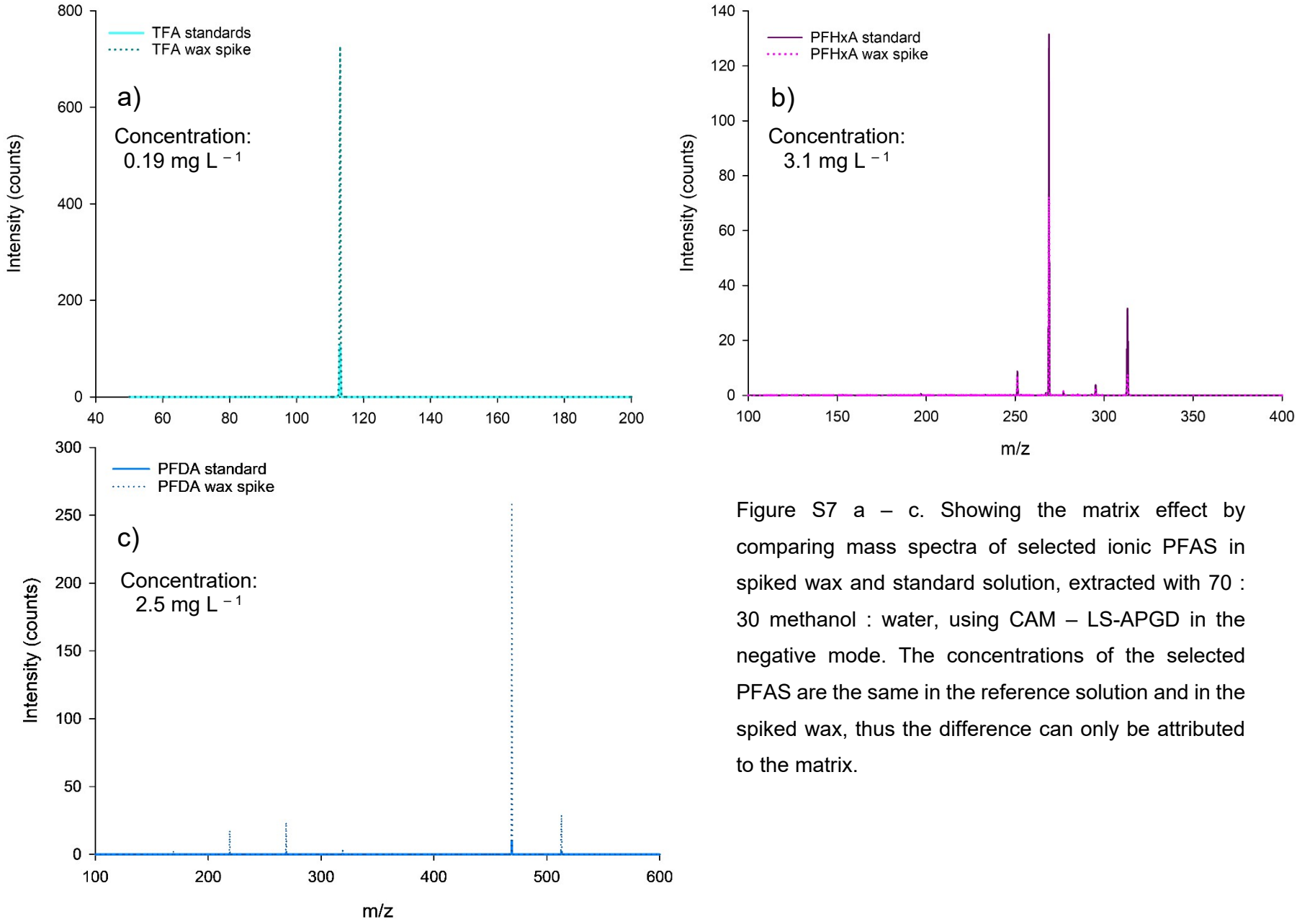


Figure S7 a – c. Showing the matrix effect by comparing mass spectra of selected ionic PFAS in spiked wax and standard solution, extracted with 70 : 30 methanol : water, using CAM – LS-APGD in the negative mode. The concentrations of the selected PFAS are the same in the reference solution and in the spiked wax, thus the difference can only be attributed to the matrix.

Table S1. Table 1. Intensities of perfluorocarboxylic acids in the standard solution and in the spiked wax measured with the CAM source.

PFAS	Concentration (mg/L)	Intensity standard	Intensity wax spike	Standard to wax spike (%)
TFA	0.19	150	750	20
PFHxA	3.1	140	75	187
PFDA	2.5	10	275	4