Supporting Information

Characterization of the chemical contents of fluorinated and fluorine-free firefighting foams using a novel workflow combining non-target screening and total fluorine analysis

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Table S1: Foam information. Foam IDs finishing by the same last letter were provided by the same manufacturer. Foams in bold are marketed as organofluorine containing foams.

Group	*Foam ID*	*Name*	*Manufacturer or Supplier*	*Year of acquirement*
AFFF	**F1_a**	AFFF 3%	Dafo Brand AB	2014
	F2_a	ARC Miljö	Dafo Brand AB	2014/2016
	F3_b	BSX	Uniteq	2014
	F4_b	EcoDare FluorFree	Uniteq	2016
	F5_c	Fluoex	3FFF Ltd	2016
	F6_c	Freesolv	3FFF Ltd	2016
	F7_d	RF 1-AG	Solberg	2016
	F8_d	RF 3% (UL)	Solberg	2016
	F9_d	RF 3x3 FP-ATC	Solberg	2016
	F10_e	Sthamex AFFF 3%	Dr Sthamer	2014/2016
AR-AFFF	**AR1_d**	Arctic 1x3 ATC	Solberg	2016
	AR2_f	Ecopol AR	BioEx	2016
	AR3_c	Filmex	3FFF Ltd	2016
	AR4_c	Freedol	3FFF Ltd	2016
	AR5_c	Freedol SF	3FFF Ltd	2016
	AR6_g	Moussol FF 3/6	Dr Sthamer	2016
	AR7_h	OneSeven B-AR	Nordic Fire Rescue Service	2016
	AR8_i	Towalex 3% master	Tyco	2014
	AR9_i	Towalex 3% super	Tyco	2014
	AR10_i	Towalex 3x3	Tyco	2014
	AR11_i	Towalex plus	Tyco	2014
AR-AFFFP	**ARP1_j**	Alcoseal 3-6%	Angus/Fire Armour Ltd	2014
AB	AB1_c	Freedex SF	3FFF Ltd	2016
	AB2_c	Genex	3FFF Ltd	2016

LC-MS methanol was purchased from Fisher Scientific (purity 99.99 %, Ottawa, Canada). Glacial acetic acid were purchased from Sigma Aldrich (purity 99.99 %, Steinheim, Germany) for LC analysis and Merck (purity 99.99 %, Darmstadt, Germany) for ISE analysis. Ammonium acetate, sodium carbonate, sodium bicarbonate as well as multi-element chromatography anion standard solution (10 mg/kg) were obtained from Sigma Aldrich (Steinheim, Germany). Sodium chloride, disodium ethylenediaminetetraacetic acid (Na_2EDTA) (dehydrated) and sodium hydroxide were purchased from VWR (Radnor, USA). Sodium fluoride was obtained from Scharlau (Barcelona, Spain). Deionized water (18.2 MΩ) (DI) was prepared using a Milli-Q® water purification system from Millipore (Darmstadt, Germany).

The non-target analysis method was processed using liquid chromatography coupled to a quadrupole time-of-flight mass spectrometer (qToF, Acquity UPLC Xevo Synapt, Waters Corporation, Milford, USA) using an Acquity UPLC BEH C18 column (L 100 mm x ID 2.1 mm, particles of 1.7 µm) with a set temperature of 50 °C and an injection volume of 10 µL. Samples were analyzed with an electrospray ionization in both positive and negative mode with an MS^E method in a full scan mode between m/z 50 and m/z 1200. The mobile phase was:

- In positive mode: 70:30 H_2O:MeOH + 0.1 % acetic acid (A) – MeOH + 0.1 % acetic acid (B)
- In negative mode: 70:30 H_2O:MeOH + 2 mM ammonium acetate (A) – MeOH + 2 mM ammonium acetate (B)

Target analysis mass transitions are summarized below (Table S2):

Table S2: List of target analytes, internal standards (IS) used for the quantification and mass transitions. Quantification traces are indicated with "" in the table.*

Target analyte	Mass transition	IS analyte	IS mass transition
PFBA	212.97 → 169*	$^{13}C_4$ PFBA	216.97 → 172
PFPeA	262.97 → 219*	$^{13}C_2$ PFHxA	314.97 → 270
PFBS	298.9 → 79.96* 298.9 → 98.9	$^{18}O_2$ PFHxS	402.9 → 102.9
PFHxA	312.97 → 118.95* 312.97 → 269	$^{13}C_2$ PFHxA	314.97 → 270
PFHpA	362.97 → 168.97* 362.97 → 319	$^{13}C_2$ PFHxA	314.97 → 270
PFHxS	398.9 → 79.96* 398.9 → 98.9	$^{18}O_2$ PFHxS	402.9 → 102.9
PFOA	412.97 → 168.97* 412.97 → 369	$^{13}C_4$ PFOA	416.97 → 372
6:2 FTSA	427 → 407*	$^{13}C_2$ 6:2 FTSA	429 → 409
PFNA	462.99 → 219* 462.99 → 419	$^{13}C_5$ PFNA	467.99 → 423
PFOSA	497.9 → 78* 497.9 → 168.96	$^{13}C_8$ PFOSA	505.9 → 77.8
PFOS	498.97 → 79.96* 498.97 → 98.96 498.97 → 169.03	$^{13}C_4$ PFOS	502.97 → 98.96
PFDA	512.97 → 219* 512.97 → 469	$^{13}C_2$ PFDA	514.97 → 470
PFUnDA	562.97 → 268.99* 562.97 → 519	$^{13}C_2$ PFUnDA	564.97 → 520
PFDS	598.97 → 79.96* 598.97 → 98.9	$^{13}C_4$ PFOS	502.97 → 98.96
PFDoDA	612.97 → 168.96* 612.97 → 569	$^{13}C_2$ PFDoDA	614.97 → 570
PFTrDA	662.9 → 168.96* 662.9 → 619	$^{13}C_2$ PFDoDA	614.97 → 570
PFTDA	712.9 → 168.97* 712.9 → 669	$^{13}C_2$ PFDoDA	614.97 → 570
PFHxDA	812.9 → 168.96* 812.9 → 769	$^{13}C_2$ PFDoDA	614.97 → 570
PFOcDA	912.9 → 168.96* 912.9 → 869	$^{13}C_2$ PFDoDA	614.97 → 570

The CIC analysis was performed by heating 100 µL of the diluted foam in a combustion module (Analytikjena, Germany) at 1050 °C. At this temperature, bound fluorine is converted to hydrofluoric acid (HF); this HF is then absorbed into Milli-Q® water in a 920 absorbent module (Metrohm, Switzerland). Fluoride anion (F^-) can be quantified in an ion chromatography (IC) flex module (Metrohm, Switzerland) using an exchange column (Metrosep A Supp5 – 150/4) and a carbonate buffer (64 mM sodium carbonate and 20 mM sodium bicarbonate) as eluent in isocratic elution.

The IF analysis was performed mixing 10 µL of the foam, 20 mL of distilled water and 20 mL of a buffer solution homogenized using a stirring bar. The buffer solution was prepared by mixing 58.4 g of sodium chloride, 5 g of Na_2EDTA, 57.5 mL of acetic acid and DI up to 1 L. Sodium hydroxide was used to adjust pH to 5. Since the method is sensitive to ionic strength and pH, buffer solution enables to get a controlled environment for the analysis. Since the method is sensitive to temperature variations, a polystyrene layer was placed between the beaker and the magnetic stirrer to minimize temperature effects. pH value were set up at 5 to get an optimized efficiency for EDTA to bound metal and thus to free fluoride for analysis.

Table S3: Parameters for full scan raw data processing using XCMS.

Parameter		*Description*	*Negative ionization*	*Positive ionization*
General	Polarity	Mode of data acquisition	Negative	Positive
	Retention time format	Time unit (minutes or seconds)	Minutes	Minutes
Feature detection	Method	Feature detection method	centWave	centWave
	ppm	maximal tolerated m/z deviation in consecutive scans, in ppm (parts per million)	30	30
	minimum peak width	minimum chromatographic peak width in seconds	10	10
	maximum peak width	maximum chromatographic peak width in seconds	60	60
	Signal/Noise threshold	Signal to noise ratio cutoff	2	2
	mzdiff	minimum difference in m/z for peaks with overlapping retention times, can be negative to allow overlap	0.01	0.01
	Integration method	Integration method. If =1 peak limits are found through descent on the mexican hat filtered data, if =2 the descent is done on the real data. Method 2 is very accurate but prone to noise, while method 1 is more robust to noise but less exact.	2	2
	prefilter peaks	Prefilter step for the first phase. Mass traces are only retained if they contain at least [prefilter peaks] peaks with intensity >= [prefilter intensity]	3	3
	prefilter intensity	Prefilter step for the first phase. Mass traces are only retained if they contain at least [prefilter peaks] peaks with intensity >= [prefilter intensity]	500	500
	Noise Filter	optional argument which is useful for data that was centroided without any intensity threshold, centroids with intensity < noise are omitted from region of interest detection	0	0

	Parameter	*Description*	*Negative ionization*	*Positive ionization*
Retention time correction	Method	Retention time correction method	Obiwarp	Obiwarp
	ProfStep	Step size (m/z) to use for profile generation from the raw data files	0.5	0.5
Alignment	Grouping method		Density	Density
	Bw	Bandwidth: Tolerated RT deviations (sec)	5	5
	m/z width	Width of overlapping m/z slices to use for creating peak density chromatograms and grouping peaks across samples	0.025	0.025
	Minfrac	Minimum fraction of samples necessary in at least one of the sample groups for it to be a valid group	0	0
	Minsamp	minimum number of samples necessary in at least one of the sample groups for it to be a valid group	1	1
	Max	maximum number of groups to identify in a single m/z slice	100	100
Statistics	Statistical test	Statistical test method. Can be paired/unpaired and parametric/non-parametric	ANOVA parametric	ANOVA parametric
	p-value threshold	Highly significant features have a p-value lower than this	0.01	0.01
	Fold change threshold	Highly significant features have a fold change greater than this	1.5	1.5
	Diffreport value	Into= integrated peak intensities are used for the diffreport Maxo=maximum peak intensities are used	Into	Into
	Normalization	Normalize the intensity values by either probabilistic quotient or cyclic loess normalization.	None	None

Table S4: Various QA/QC tests applied to confirm non-target workflow robustness.

A) ***CIC calibration curve***	Concentration F^- (ng/mL)	Area		Calibration curve equation	R^2
	50	0.192		y = 0.0007x + 0.1469	0.9983
	100	0.222			
	250	0.303			
	500	0.487			
	1000	0.844			
B) CIC test dilution F10	Dilution factor	Concentration calculated after dilution factor multiplication (mg/L)		Average (mg/L)	CV (%)
	10 000	5.43		6.16	9.7
	1 000	6.89			
	100	6.15			
C) CIC test dilution AR7	Dilution factor	Concentration calculated after dilution factor multiplication (mg/L)		Average (mg/L)	CV (%)
	10 000	23.94		24.89	4.4
	1 000	26.42			
	100	24.30			
D) ISE Calibration curve	mV	Log concentration fluoride (mg/L)	Concentration fluoride (mg/L)	Calibration curve equation	R^2
	148	-0.1	0.8	y = -0.019x + 2.75	0.9965
	113	0.6	4		
	80	1.3	20		
	37	2.0	100		
E) ISE test dilution AR7	Added foam volume (µL)	Calculated concentration (mg/L)	Concentration calculated after dilution factor multiplication (mg/L)	Average (mg/L)	CV (%)
	100	42.4	42.4	43.1	1.5
	50	21.0	42.0		
	20	8.8	43.8		
	20	4.3	43.4		
	5	2.2	43.1		

LC parameters are summarized below (Table S5):

Table S5: LC parameters for analysis of the 24 firefighting foams.

	First chromatographic method	*Second chromatographic method*
Run time	13 mins	15 mins
Flow	0.4 mL/min	0.3 mL/min
Gradient Table	From 0 to 10 min: 70 % A : 30 % B	From 0 to 13 min: 70 % A : 30 % B
	From 10 to 12 min: 0 % A : 100 % B	From 13 to 14.20 min: 1 % A : 99 % B
	From 12 to 13 min: 70 % A : 30 % B	From 14.20 to 15 min: 70 % A : 30 % B

Table S6: Results (mg/L) for analysis of 17 PFASs in the 24 foams.

Foam ID	*PFOSA*	*6:2 FTSA*	*PFBA*	*PFPeA*	*PFHxA*	*PFHpA*	*PFOA*	*PFNA*	*PFDA*	*PFUnDA*	*PFDoDA*	*PFTrDA*	*PFTDA*	*PFBS*	*PFHxS*	*PFOS*	*PFDS*	*∑17 PFASs concentration (mg/L)*	*Sum F^- concentration for the ∑17 PFASs (mg/L)*
molecular mass	499	428	214	264	314	364	414	464	514	564	614	664	714	300	400	500	600		
number of fluorine	17	13	7	9	11	13	15	17	19	21	23	25	27	9	13	17	21		
F1	<0.02	*1.7*	*<0.01*	*0.02*	*0.08*	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.8	1.0
F2	<0.02	4.4	0.55	0.11	1.1	0.02	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	6.1	3.7
F3	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
F4	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
F5	<0.02	33.7	0.31	0.10	0.69	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	34.8	20.2
F6	<0.02	38.9	0.56	0.16	1.5	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	41.2	24.0
F7	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01	0.01
F8	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
F9	<0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01	0.01
F10	<0.02	9.5	0.08	0.02	0.08	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	9.7	5.6
AR1	<0.02	13.3	<0.01	<0.01	0.46	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	13.8	8.0
AR2	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.02	0.01
AR3	<0.02	27.0	0.70	0.23	0.99	0.02	0.10	<0.01	0.04	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29.0	16.9
AR4	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
AR5	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
AR6	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
AR7	<0.02	2.4	1.5	1.1	0.51	0.13	0.003	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	5.6	3.5
AR8	<0.02	4.1	1.1	0.62	10.4	0.15	0.34	0.02	0.08	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	16.8	10.8
AR9	<0.02	0.28	<0.01	<0.01	0.08	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.40	0.20
AR10	<0.02	8.1	1.0	0.55	9.8	0.13	0.24	0.02	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	19.9	12.5
AR11	<0.02	3.4	<0.01	0.08	1.5	0.02	0.07	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	5.1	3.1
ARP1	<0.02	3.8	<0.01	0.03	0.80	0.05	0.12	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	4.8	2.9
AB1	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
AB2	<0.02	25.4	0.80	0.17	1.5	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	27.9	16.3

Table S7: CIC, ISE and mass balance analysis for the 24 foams.

Foam ID	*Total fluorine (TF) concentration (mg/L)*	*Inorganic fluoride (IF) concentration (mg/L)*	*Total organic fluorine concentration (mg/L)*	*Sum F^- concentration for the ∑17 PFASs (mg/L)*	*Unidentified organofluorine (UOF) concentration (mg/L)*	*Mass balance (%)*
F1	3671	2.6	3669	1.0	3668	0.03
F2	2000	4.3	1996	3.7	1992	0.19
F3	8.0	3.8	4.2	0.00	4.2	-
F4	12.6	8.0	4.6	0.00	4.59	-
F5	2000	1.1	1999	20.2	1804	1.0
F6	4457	1.4	4456	24.0	4218	0.54
F7	0.61	0.75	0.00	0.01	0.00	0.20
F8	5.2	1.0	4.2	0.00	4.17	-
F9	0.56	0.58	0.00	0.01	0.00	0.47
F10	8000	6.7	7993	5.6	7988	0.07
AR1	8271	2.8	829	8.0	8188	0.10
AR2	0.59	0.94	0.00	0.01	0.00	0.08
AR3	5114	3.2	5111	16.9	4940	0.33
AR4	0.83	0.82	0.01	0.00	0.01	-
AR5	0.80	0.60	0.20	0.00	0.20	-
AR6	0.39	0.72	0.00	0.00	0.00	-
AR7	24800	42.4	24758	3.5	24739	0.01
AR8	6700	4.5	6695	10.8	6685	0.16
AR9	6600	3.1	6597	0.20	6597	0.003
AR10	4343	4.0	4339	12.5	4326	0.29
AR11	2829	0.90	2828	3.1	2825	0.11
ARP1	2871	1.5	2870	2.9	2867	0.10
AB1	0.74	0.60	0.14	0.00	0.14	-
AB2	3671	2.9	3669	16.3	3652	0.44

Table S8: Instrumental and method detection limits for PFASs target quantification, ISE and CIC analyses.

	Molecule	*Instrumental detection limit (µg/L)*	*Method detection limit (µg/L)**
Target analysis	PFOSA	0.02	2
	6:2 FTSA	0.01	1
	PFBA	0.01	1
	PFPeA	0.01	1
	PFHxA	0.01	1
	PFHpA	0.01	1
	PFOA	0.02	2
	PFNA	0.01	1
	PFDA	0.01	1
	PFUnDA	0.01	1
	PFDoDA	0.01	1
	PFTrDA	0.01	1
	PFTDA	0.01	1
	PFBS	0.01	1
	PFHxS	0.01	1
	PFOS	0.01	1
	PFDS	0.01	1
ISE analysis		800	800
CIC analysis		0.02	170/1.7

*Method detection limit concentrations were calculated by multiplying instrumental detection limit concentrations by the dilution factor (1 for ISE analysis, 100 for target analysis and organofluorine-free foams CIC analysis and 10 000 for organofluorine containing foams CIC analysis).

Table S9: Summary of outliers detected using non-target methodology (hierarchical clustering analysis and mass defect plot analysis).

m/z	*Rt (min)*	*Molecular ion*	*Mass error (ppm)*	*Product ions → Mass error (ppm)*	*Associated samples for the important detected molecules*
			Negative ionization first chromatographic method		
209.0853	4.03	$[C_8H_{18}O_4S\text{-}H]^-$	2.4	96.9603 $[H_2O_4S\text{-}H]^-$ → 7.2 79.9550 $[HO_3S\text{-}H]^-$ → -22.5	**F1**, **F2**, F3, **F10**, **AR8**, **AR10**, **AR11**
237.1170	5.79	$[C_{10}H_{22}O_4S\text{-}H]^-$	3.8	96.9596 $[H_2O_4S\text{-}H]^-$ → -13.4 79.9568 $[HO_3S\text{-}H]^-$ → 0.0	**F1**, **F2**, F3, **F10**, **AR8**, **AR10**, **AR11**
527.0692	6.29	$[C_{13}H_{17}F_{13}N_2O_3S\text{-}H]^-$	3.4	507.0617 $[C_{13}H_{16}F_{12}N_2O_3S\text{-}H]^-$ → 1.0 487.0574 $[C_{13}H_{15}F_{11}N_2O_3S\text{-}H]^-$ → 5.1 181.0632 $[C_5H_{14}N_2O_3S\text{-}H]^-$ → -8.3 120.0113 $[C_3H_7NO_2S\text{-}H]^-$ → -5.0	**F2**, **F10**
569.0798	6.04	$[C_{15}H_{19}F_{13}N_2O_4S\text{-}H]^-$	3.2	549.0739 $[C_{15}H_{18}F_{12}N_2O_4S\text{-}H]^-$ → 4.0 446.0103 $[C_{11}H_9F_{12}NO_2S\text{-}H]$- → 4.3 410.9706 $[C_8F_{13}H_5SO_2\text{-}H]^-$ →-4.4 223.0734 $[C_7H_{16}N_2O_4S\text{-}H]^-$ → -8.5 179.0843 $[C_6H_{16}N_2O_2S\text{-}H]^-$ → -6.1 163.0532 $[C_5H_{12}N_2O_2S\text{-}H]^-$ → -5.5 120.0113 $[C_3H_7NO_2S\text{-}H]^-$ → -5.0	**F10**, **AR8**, **AR10**, **AR11**, **ARP1**
586.0435	6.87	$[C_{15}H_{18}F_{13}NO_4S_2\text{-}H]^-$	7.5	566.0323 $[C_{15}H_{17}F_{12}NO_4S_2\text{-}H]^-$ → -1.1 546.0230 $[C_{15}H_{16}F_{11}NO_4S_2\text{-}H]^-$ → -6.8 206.0475 $[C_7H_{13}NO_4S\text{-}H]^-$ → -5.8	**F1**, **AR8**, **AR9**, **AR10**, **AR11**, **ARP1**

				152.0388 $[C_4H_{11}NO_3S\text{-}H]^-$ → 4.6 135.0117 $[C_4H_8O_3S\text{-}H]^-$ → 0.7 79.9568 $[HO_3S\text{-}H]^-$ → 0.0	
				Negative ionization second chromatographic method	
209.0907	5.27	$[C_8H_{18}O_4S\text{-}H]^-$	28.2	Same as first chromatographic method	**F2**, **F5**, **F6**, F7, F9, **F10**, **AR1**, AR5, AR6, **AR7**, AB2
237.1176	7.57	$[C_{10}H_{22}O_4S\text{-}H]^-$	6.3	Same as first chromatographic method	**F2**, **F5**, **F6**, F8, F9, **F10**, **AR1**, AR5, AR6, **AR7**, AB1, **AB2**
401.2980	9.79	$[C_{21}H_{42}N_2O_5\text{-}H]^-$	-8.7	444,3433 $[C_{23}H_{47}N_3O_5\text{-}H]^-$ → -0.9 387.2851 $[C_{20}H_{40}N_2O_5\text{-}H]^-$ → -2.1 341.2814 $[C_{19}H_{38}N_2O_3\text{-}H]^-$ → 2.9 327.2641 $[C_{18}H_{36}N_2O_3\text{-}H]^-$ → -2.1 102.0540 $[C_4H_9NO_2\text{-}H]^-$ → -14.7	**F5**, **F6**, F7, F8, F9, **F10**, **AR1**, AR2, **AR3**, AR4, AR5, AR6, **AR7**, AB1, **AB2**
527,0691	8.93	$[C_{13}H_{17}F_{13}N_2O_3S\text{-}H]^-$	3.2	Same as first chromatographic method	**F2**, **F10**
569.0798	8.61	$[C_{15}H_{19}F_{13}N_2O_4S\text{-}H]^-$	3.2	Same as first chromatographic method	**F10**, **AR1**, **AR3**
581.0806	9.61	$[C_{15}H_{21}F_{11}N_2O_7S\text{-}H]^-$	-1.7	No product ion on the spectra	**AR7**
586.0547	8.91	$[C_{15}H_{18}F_{13}NO_4S_2\text{-}H]^-$	26.6	Same as first chromatographic method	**F10, AR1**, **AR7**
649.0752	8.46	$[C_{16}H_{23}F_{13}N_2O_6S_2\text{-}H]^-$	6.2	635.0568 $[C_{15}H_{20}F_{13}N_2O_6S_2\text{-}H]^-$ → 2.0 632.0687 $[C_{16}H_{22}F_{12}N_2O_5S_2\text{-}H]^-$ → 0.5 629.0671 $[C_{16}H_{22}F_{12}N_2O_6S_2\text{-}H]^-$ → 3.5 491.0678 $[C_{13}H_{16}F_{12}N_2O_2S\text{-}H]^-$ → 3.1	**F5**, **F6**, **F10**, **AR3**, **AB2**

				303.0686 $[C_8H_{20}N_2O_6S_2\text{-}H]^-$ → 0.3 182.0492 $[C_5H_{13}NO_4S\text{-}H]^-$ → 2.7 164.0374 $[C_5H_{11}NO_3S\text{-}H]^-$ → -4,3 136.9904 $[C_3H_6O_4S\text{-}H]^-$ → -3.6 119.9889 $[C_3H_5O_3S\text{-}H]^-$ → -6.7 94.9793 $[CH_4O_3S\text{-}H]^-$ → -10.5 79.9568 $[HO_3S\text{-}H]^-$ → 0.0	
			Positive ionization first chromatographic method		
343.1994	6.57	$[C_{20}H_{26}N_2O_3+H]^+$	-8.2	No product ion on the spectra	**F1**, **F2**, F3, **AR10**
423.2717	6.71	$[C_{26}H_{34}N_2O_3+H]^+$	16.3	445.2582 $[C_{26}H_{34}N_2O_3+Na]^+$ → 25.8 240.2298 $[C_{15}H_{29}NO+H]^+$ → -12.1	**F1**, F3
529.1021	5.67	$[C_{13}H_{17}F_{13}N_2O_3S+H]^+$	-35.9	Same as first chromatographic method negative study	**F2**, **F10**
571.1107	5.97	$[C_{15}H_{19}F_{13}N_2O_4S+H]^+$	29.9	Same as first chromatographic method negative study	**F10**, **AR8**, **AR10**, **AR11**, **ARP1**
			Positive ionization second chromatographic method		
285.2897	12.31	$[C_{17}H_{36}N_2O+H]^+$	-3.2	240.2331 $[C_{15}H_{29}NO+H]^+$ → 1.7	**F5**, **F6**, F7, F9, **F10**, **AR1**, AR2, **AR3**, AR4, AR5, AR6, **AR7**, AB1, **AB2**
287.2338	5.24	$[C_{15}H_{30}N_2O_3+H]^+$	1.0	309.2155 $[C_{15}H_{30}N_2O_3+Na]^+$ → 0.3 184.1691 $[C_{11}H_{21}NO+H]^+$ → -5.4	**F5**, **F6**, F7, F8, F9, **F10**, **AR1**, AR2, **AR3**, AR4, AR5, AR6, **AR7**, AB1, **AB2**

315.2666	8.06	$[C_{17}H_{34}N_2O_3+H]^+$	5.7	353.2198 $[C_{17}H_{34}N_2O_3+K]^+$ → 0.9 337.2472 $[C_{17}H_{34}N_2O_3+Na]^+$ → 1.3 212.2024 $[C_{13}H_{25}NO+H]^+$ → 4.7 198.1858 $[C_{12}H_{23}NO+H]^+$ → -4.0	**F5**, **F6**, **F10**, **AR1**, AR2, **AR3**, AR6, **AR7**, **AB2**
343.3038	10.15	$[C_{19}H_{38}N_2O_3+H]^+$	11.7	707.5705 $[C_{38}H_{72}N_4O_6+Na]^+$ → 5.9 685.5880 $[C_{38}H_{72}N_4O_6+H]^+$ → 5.3 365.2787 $[C_{19}H_{38}N_2O_3+Na]^+$ → 1.7 240.2394 $[C_{15}H_{29}NO+H]^+$ → 27.6	**F5**, **F6**, F7, F8, F9, **F10**, **AR1**, AR2, **AR3**, AR4, AR5, AR6, **AR7**, AB1, **AB2**
371.3289	11.83	$[C_{21}H_{42}N_2O_3+H]^+$	-6.7	268.2647 $[C_{17}H_{33}NO+H]^+$ → 2.6 198.1850 $[C_{12}H_{23}NO+H]^+$ → -4.0	**F5**, **F6**, F7, F8, F9, **F10**, **AR1**, AR2, **AR3**, AR4, AR5, AR6, **AR7**, AB1, **AB2**
425.3772	13.93	$[C_{25}H_{48}N_2O_3+H]^+$	6.8	447.3573 $[C_{25}H_{48}N_2O_3+Na]^+$ → 2.2 322.3154 $[C_{21}H_{39}NO+H]^+$ → 13.7	**F5**, **F6**, F7, F8, F9, **F10**, **AR1**, AR2, **AR3**, AR4, AR5, AR6, **AR7**, AB1, **AB2**

	Target	*Semi-quantification*									
Foam ID	6:2 FTSA (mg/L)	DPOSA (mg/L)	6:2 FTAB (mg/L)	6:2 FTSAS (mg/L)	N-HOEAmP-FHxSAPS (mg/L)	Sum tentatively identified compounds concentration (mg/L)	Sum F^- tentatively identified compounds concentration (mg/L)	Sum F^- concentration for the ∑17 PFASs (mg/L)	Sum target and semi-quantification fluorine analysis (mg/L)	Unidentified organofluorine (UOF) concentration (mg/L)	New mass balance (%)
molecular mass	428	528	570	587	650						
number of fluorine	13	13	13	13	13						
F1	1.7	ND	ND	2796	ND	2796	1176	1.8	1178	3668	32.1
F2	4.4	4.7	ND	ND	ND	4.7	2.2	6.1	8.3	1992	0.42
F5	33.7	ND	ND	ND	104	104	39.5	34.8	74.3	1804	4.1
F6	38.9	ND	ND	ND	96.4	96.4	36.6	41.2	77.8	4218	1.9
F10	9.5	6.0	0.1	0.3	39.0	45.3	17.8	9.7	27.5	7988	0.34
AR1	13.3	ND	123	299	ND	423	179	13.8	193	8188	2.4
AR3	27.0	ND	9.2	ND	293	302	115	29.0	144	4940	2.9
AR7	2.4	ND	ND	210	ND	217	91.2	5.6	96.8	24739	0.39
AR8	4.1	ND	18.9	66.6	ND	85.5	36.2	16.8	53.0	6685	0.79
AR9	0.28	ND	ND	5.4	ND	5.4	2.3	0.40	2.7	6597	0.04
AR10	8.1	ND	35.7	91.5	ND	127	54.0	19.9	73.9	4326	1.7
AR11	3.4	ND	21.5	143	ND	164	69.4	5.1	74.5	2825	2.6
ARP1	3.8	ND	23.1	48.1	ND	71.3	30.3	4.8	35.1	2867	1.2
AB2	25.4	ND	ND	ND	295.4	295	112	27.9	140	3652	3.8

Table S10:Semi-quantification of the four tentatively identified organofluorine surfactants and mass balance analysis recalculated according to the sum target and semi-quantification concentrations.

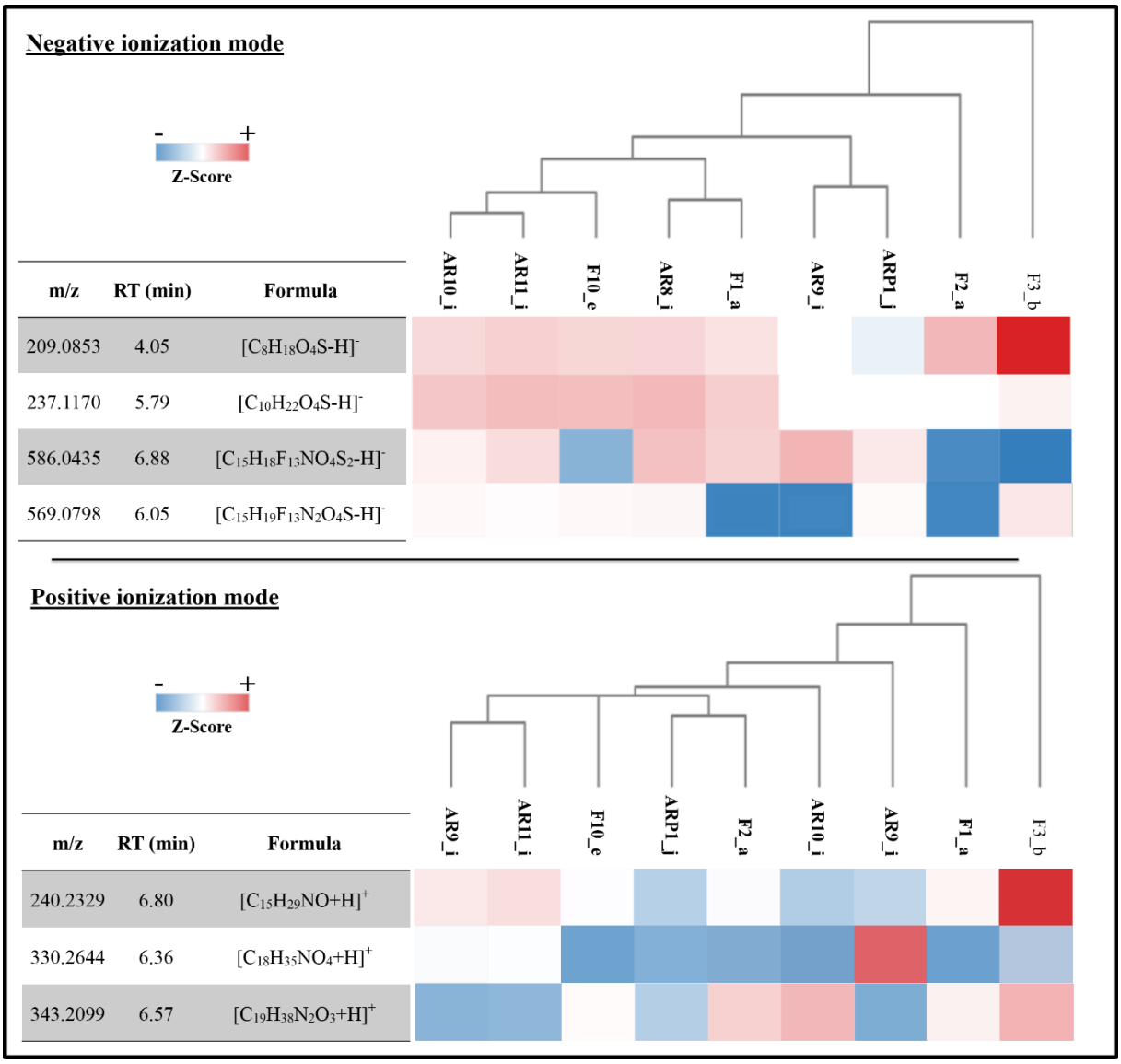
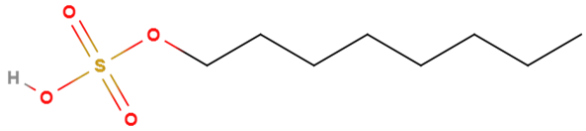


Figure S1: Dendrograms and heatmaps for the first chromatographic method using negative ionization (top) and positive ionization (bottom) ESI mode. The dendrograms show the foam clustering, while the heatmaps show the outliers. Samples marked in bold are marketed as organofluorine containing foams.

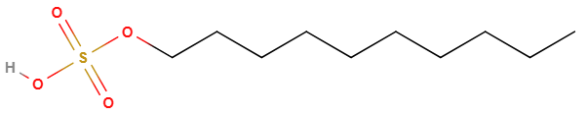


$[C_8H_{18}O_4S\text{-}H]^-$ m/z 209.0848

Octyl hydrogen sulfate

CAS number: 110-11-2

Confidence level: 2

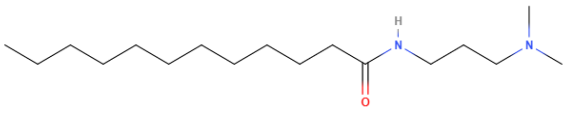


$[C_{10}H_{22}O_4S\text{-}H]^-$ m/z 237.1161

Decyl hydrogen sulfate

CAS number: 142-98-3

Confidence level: 2

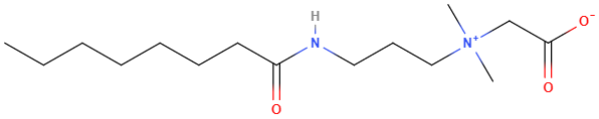


$[C_{17}H_{36}N_2O+H]^+$ m/z 285.2906

Cocamidopropyl dimethylamine

CAS number: 3179-80-4

Confidence level: 2

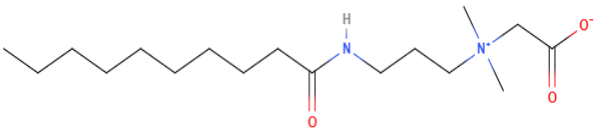


$[C_{15}H_{30}N_2O_3+H]^+$ m/z 287.2335

Caprylamidopropyl betaine

CAS number: 73772-46-0

Confidence level: 2

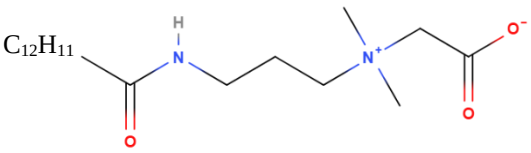


$[C_{17}H_{34}N_2O_3+H]^+$ m/z 315.2648

Capramidopropyl betaine

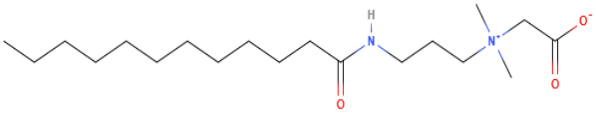
CAS number: 73772-45-9

Confidence level: 2



$[C_{20}H_{26}N_2O_3+H]^+$ m/z 343.2022

Confidence level: 4

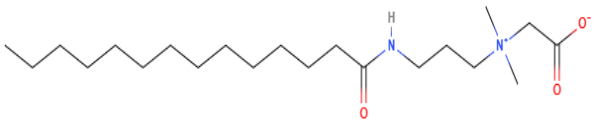


$[C_{19}H_{38}N_2O_3+H]^+$ m/z 343.2961

Cocamidopropyl betaine

CAS number: 4292-10-8

Confidence level: 2

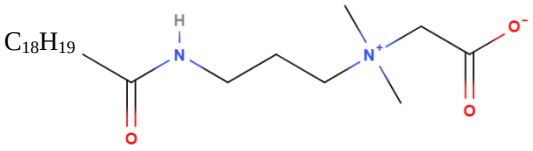


$[C_{21}H_{42}N_2O_3+H]^+$ m/z 371.3274

Myristamidopropyl betaine

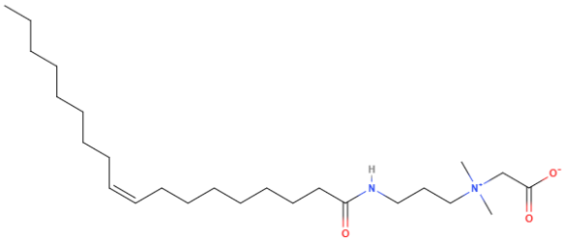
CAS number: 59272-84-3

Confidence level: 2



$[C_{26}H_{34}N_2O_3+H]^+$ m/z 423.2648

Confidence level: 4

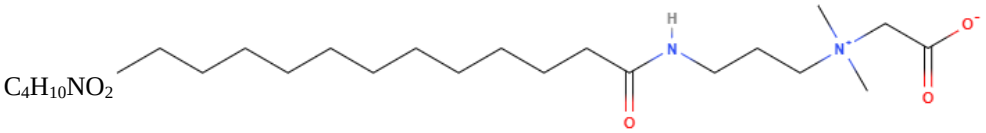


$[C_{25}H_{48}N_2O_3+H]^+$ m/z 425.3743

Oleamidopropyl betaine

CAS number: 25054-76-6

Confidence level: 2



$[C_{23}H_{47}N_3O_5-H]^-$ m/z 444,3437

Confidence level: 4

Figure S2: Formula, structure, CAS number and confidence level for the non-fluorinated outliers found in firefighting foams using positive and negative electrospray ionization.

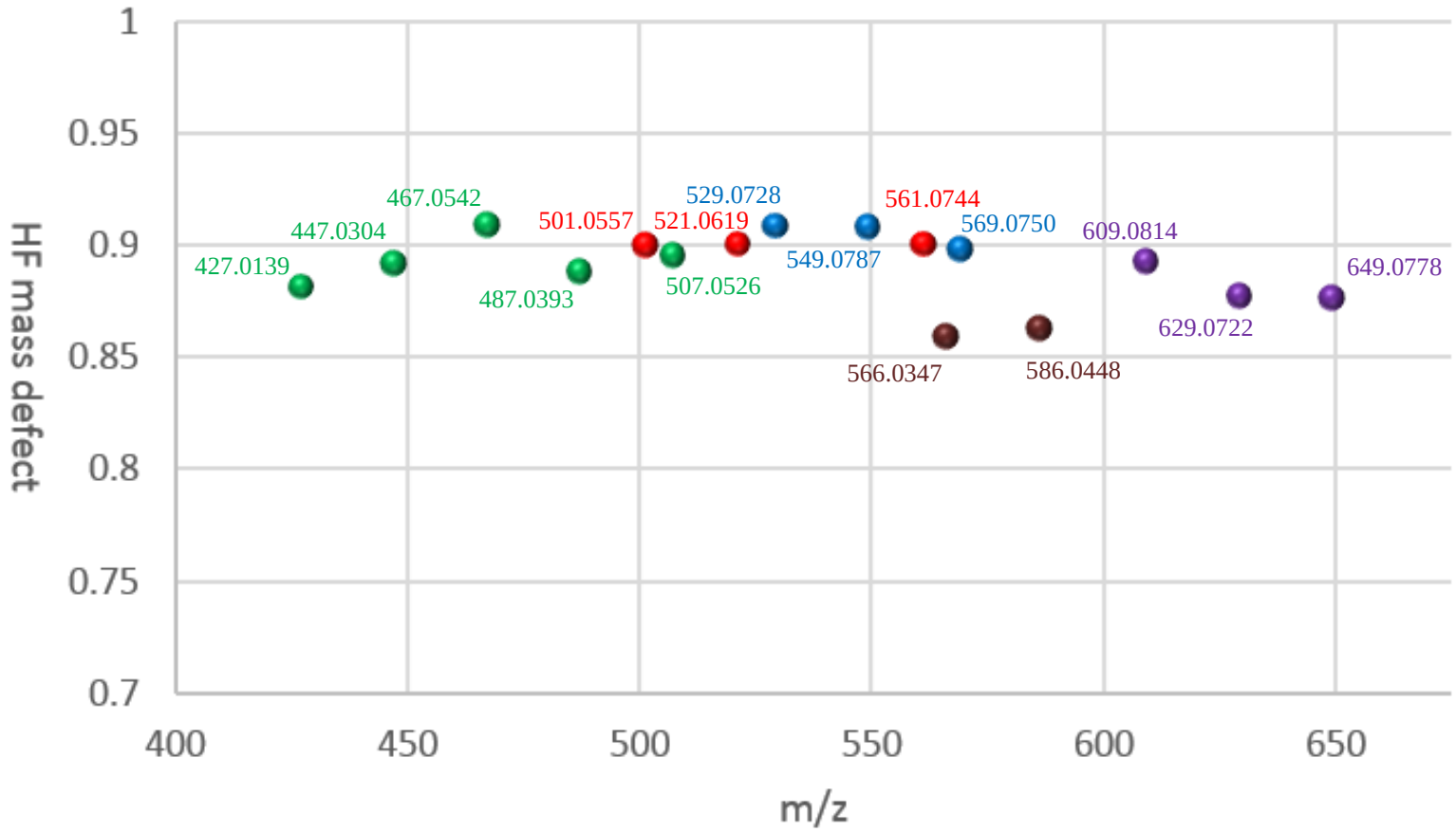


Figure S3: Filtered HF mass defect plot between m/z 400 and m/z 675. Green dots belong to the m/z 527.0674 homologous series, blue dots belong to the m/z 569.0780 homologous series, red dots belong to the m/z 581.0816 homologous series, brown dots belong to the m/z 586.0391 homologous series and purple dots belong to the m/z 649.0712 homologous series.

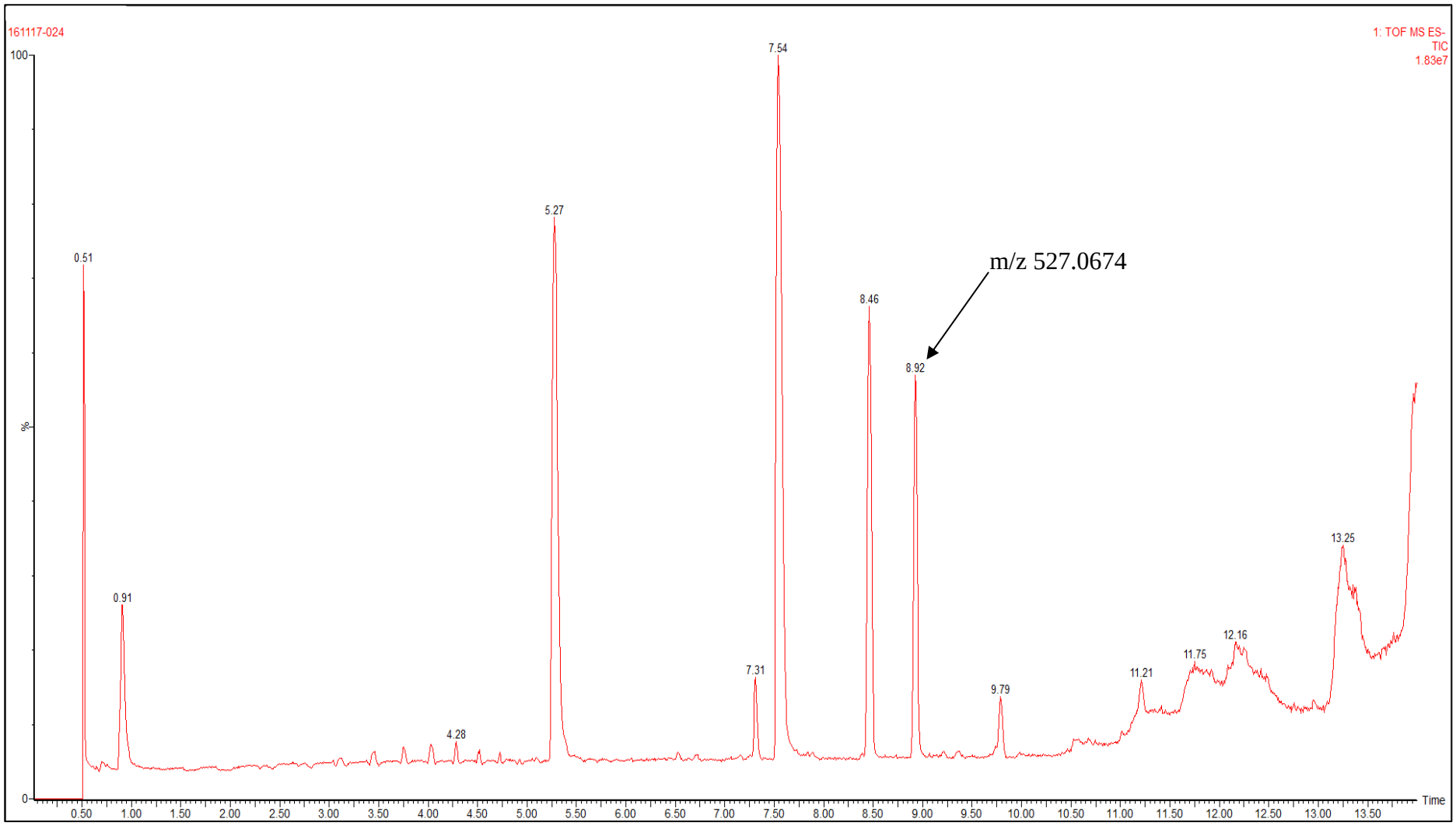


*Figure S4: Chromatogram (total ion current) for **F10** sample using qToF and negative ionization mode.*

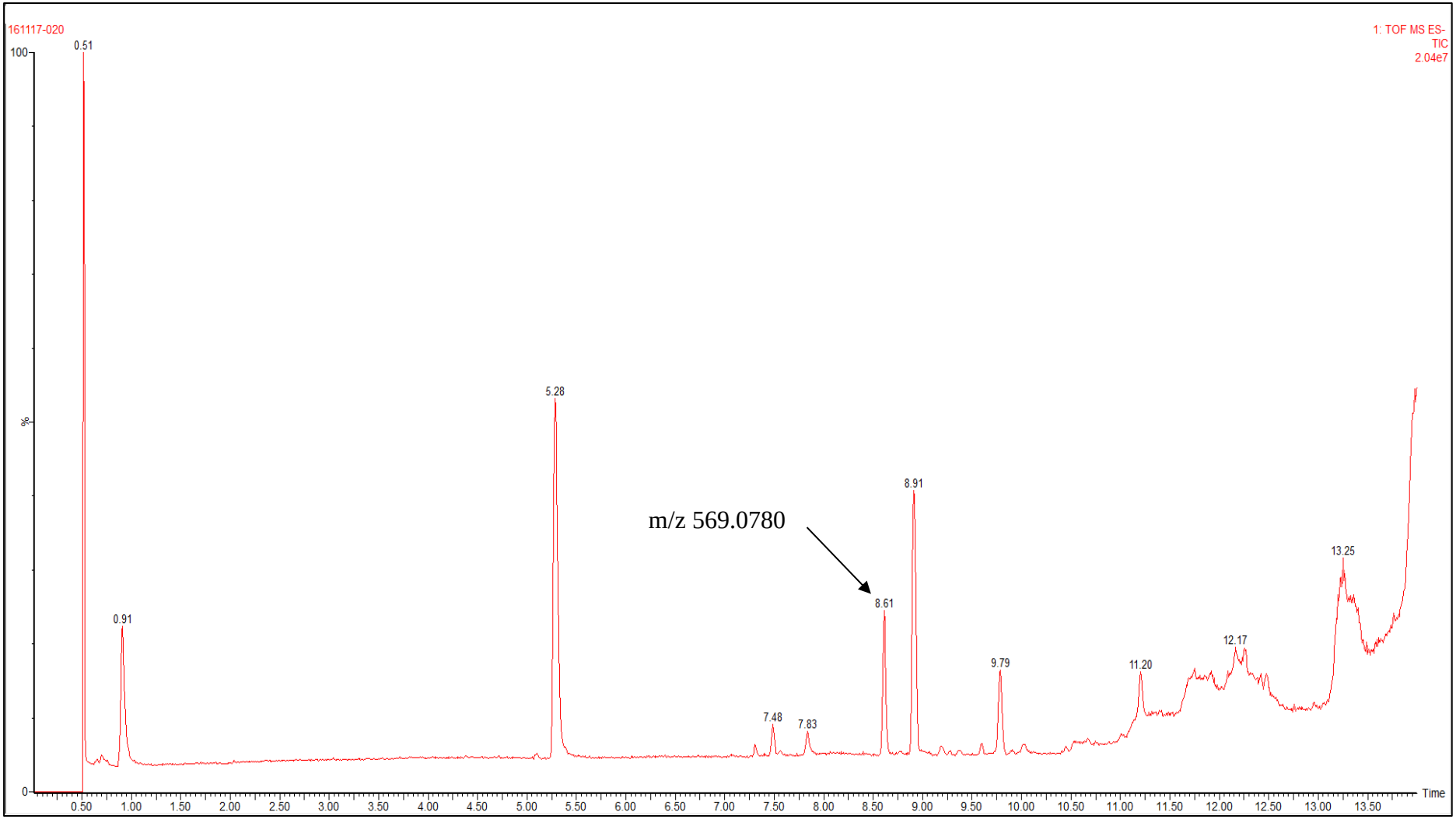


*Figure S5: Chromatogram (total ion current) for **AR1** sample using qToF and negative ionization mode.*

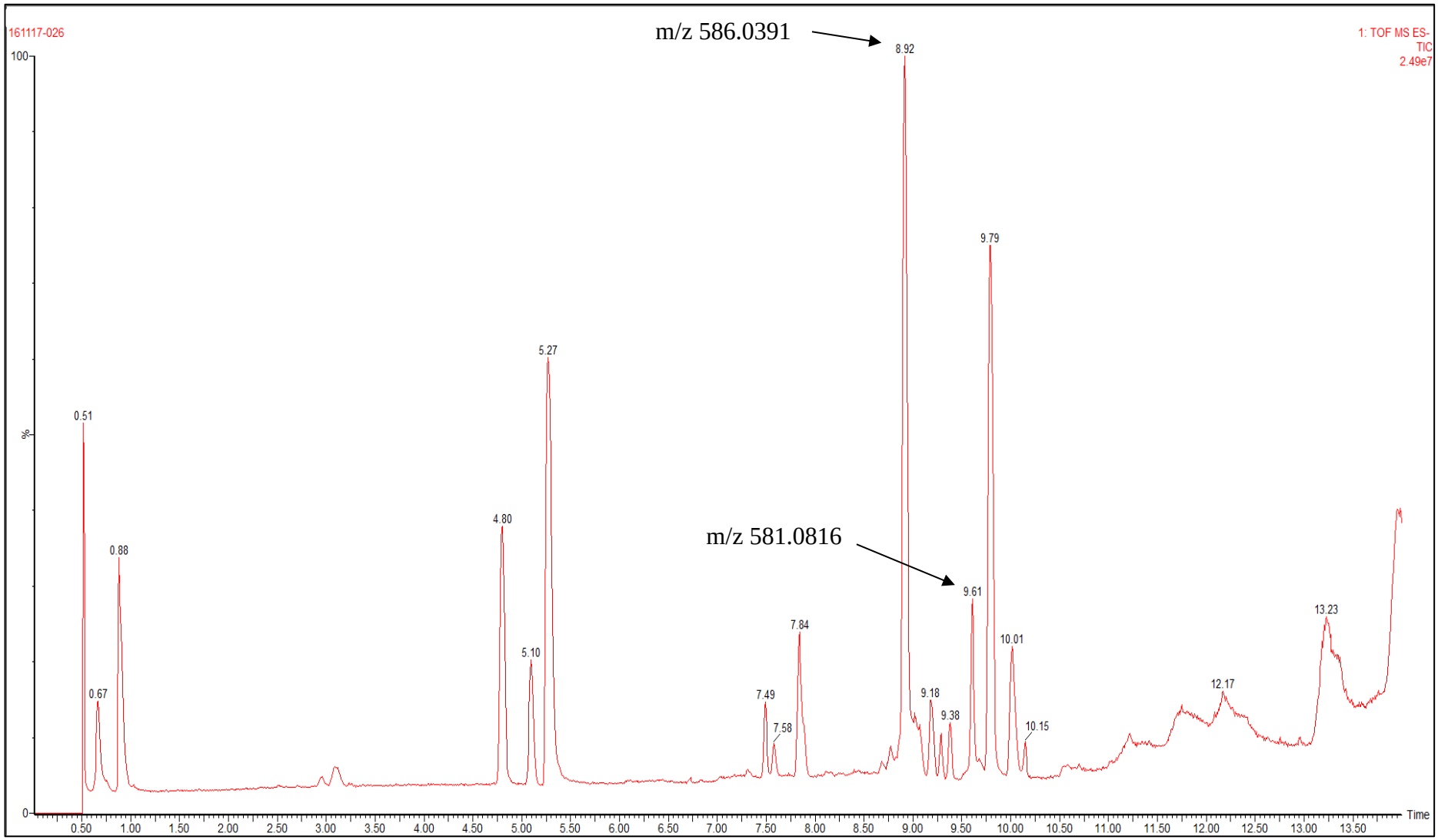


*Figure S6: Chromatogram (total ion current) for **AR7** sample using qToF and negative ionization mode.*

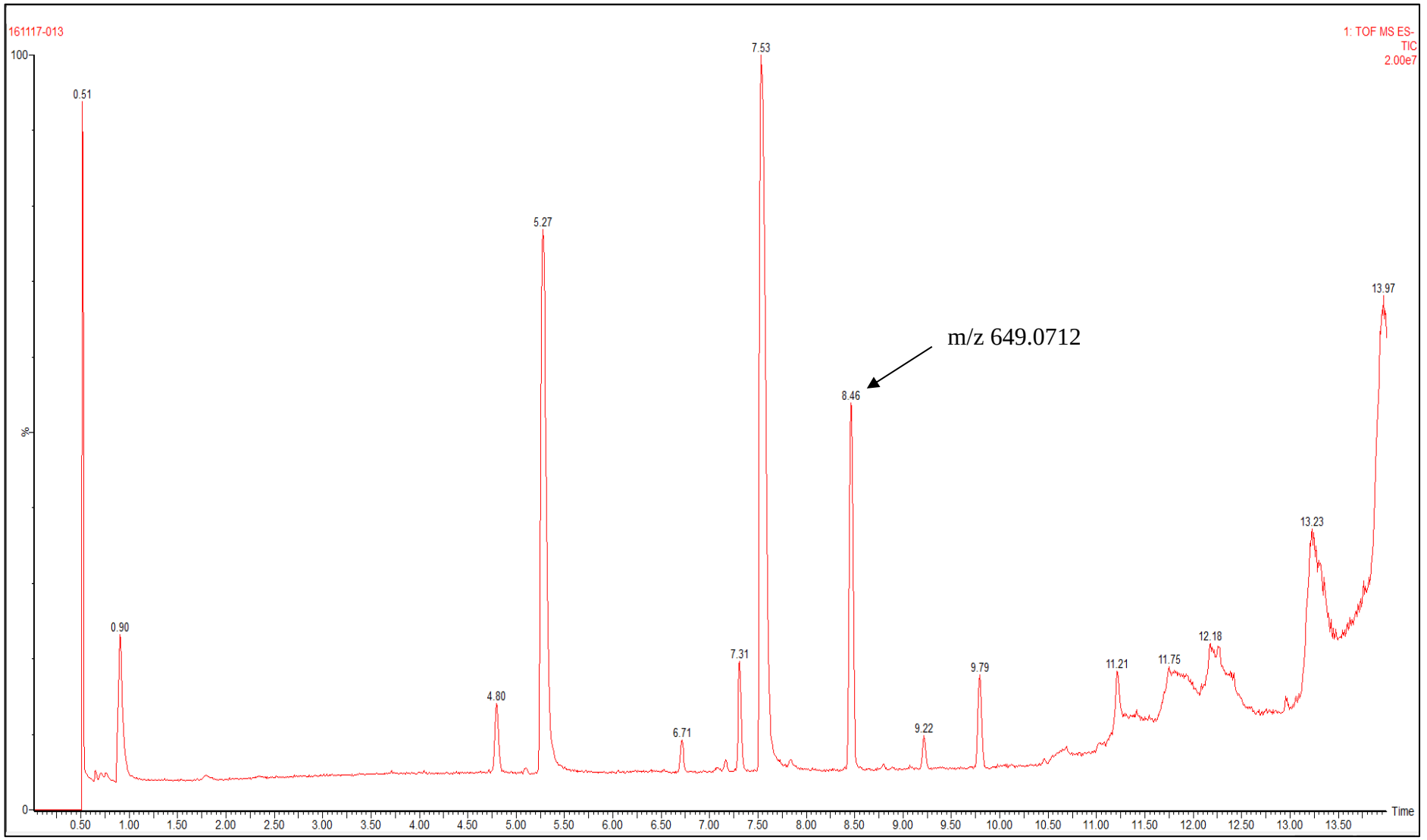


*Figure S7: Chromatogram (total ion current) for **F6** sample using qToF and negative ionization mode.*

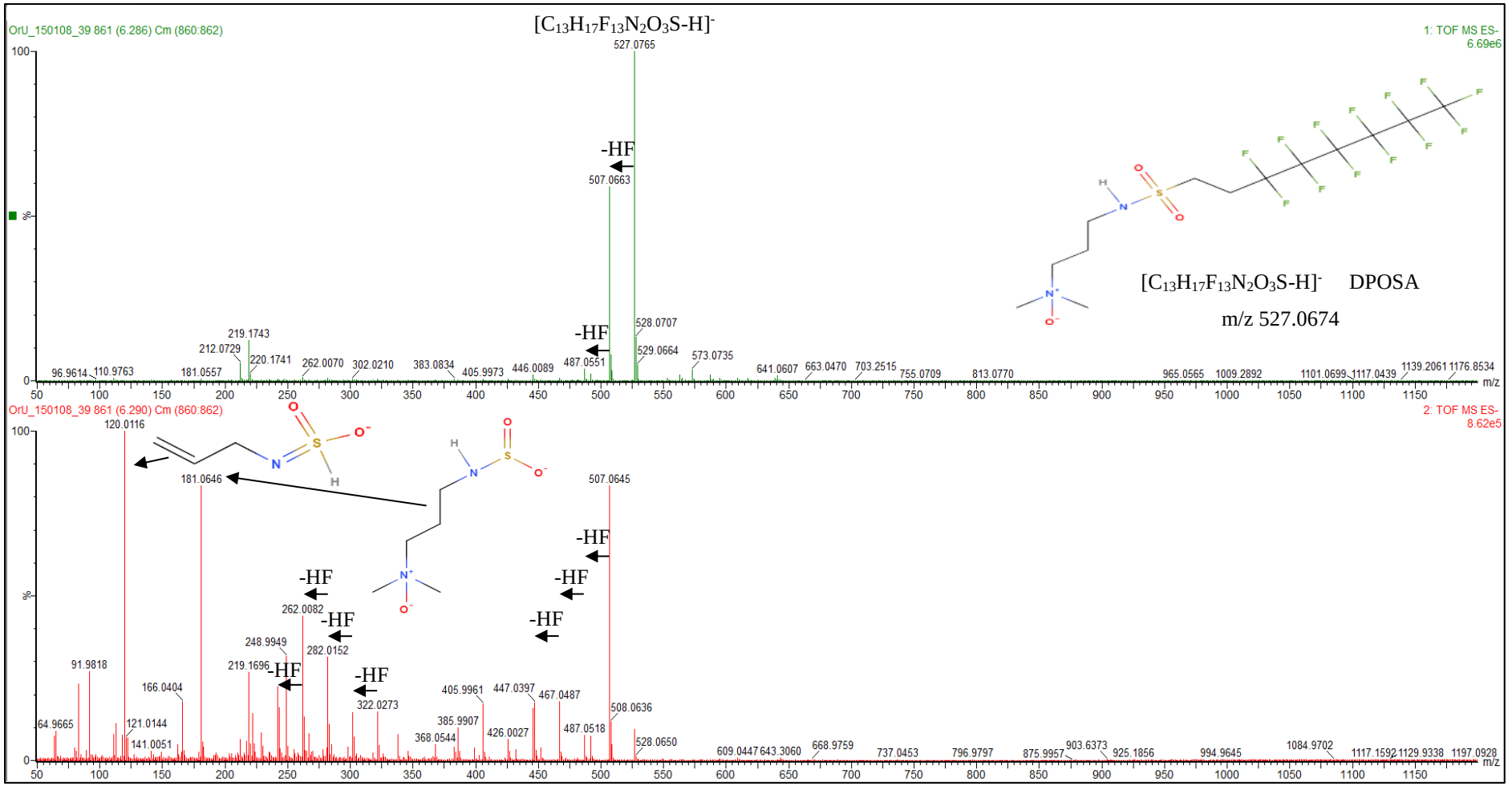


*Figure S8: Full scan mass high resolution spectra for sample **F2** at retention time 6.29 minutes with a low collision energy (top) and a high collision energy (bottom) for the first chromatographic method.*

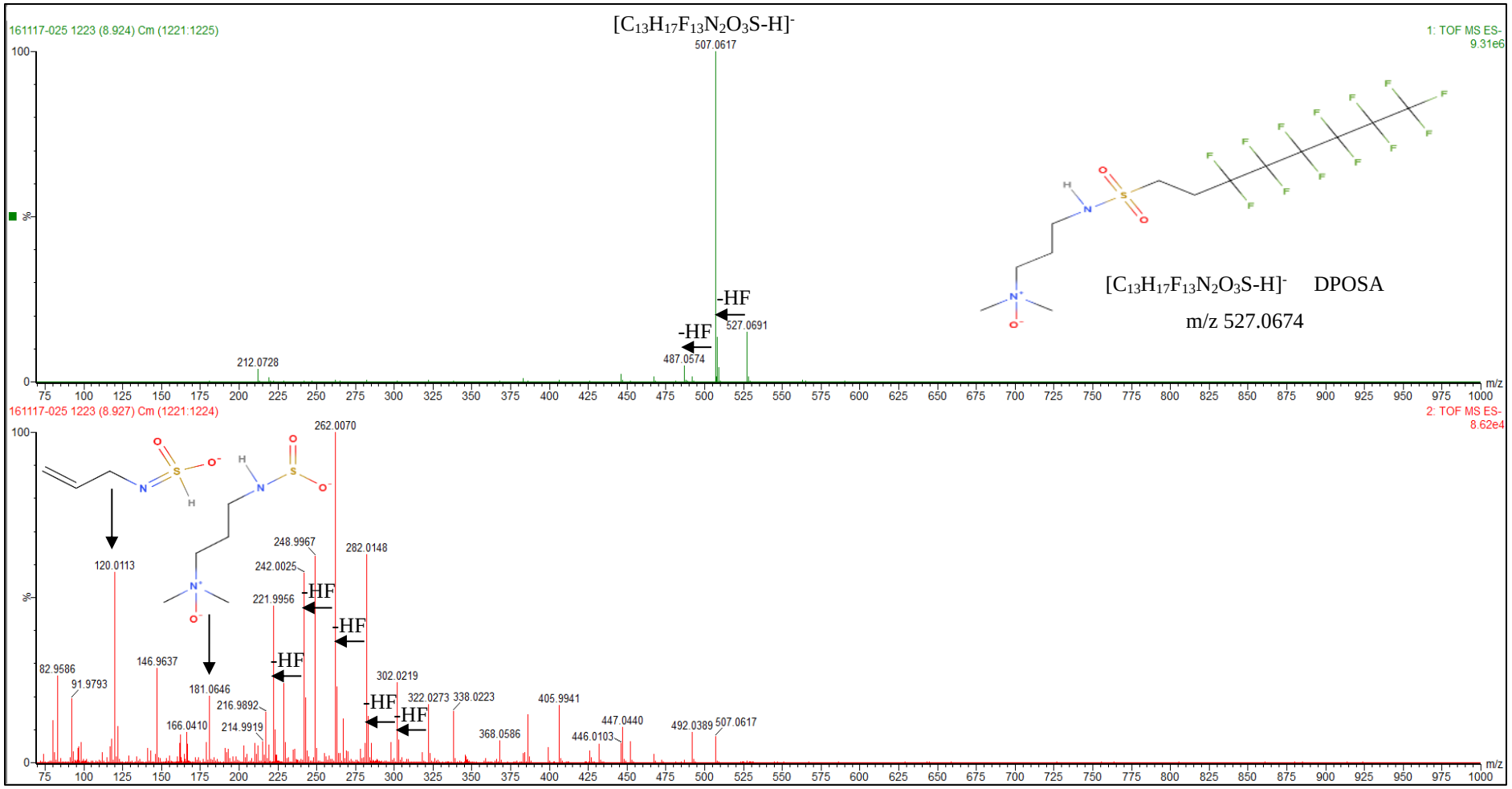


*Figure S9: Full scan high resolution mass spectra for sample **F2** at retention time 8.93 minutes with a low collision energy (top) and a high collision energy (bottom) for the second chromatographic method.*

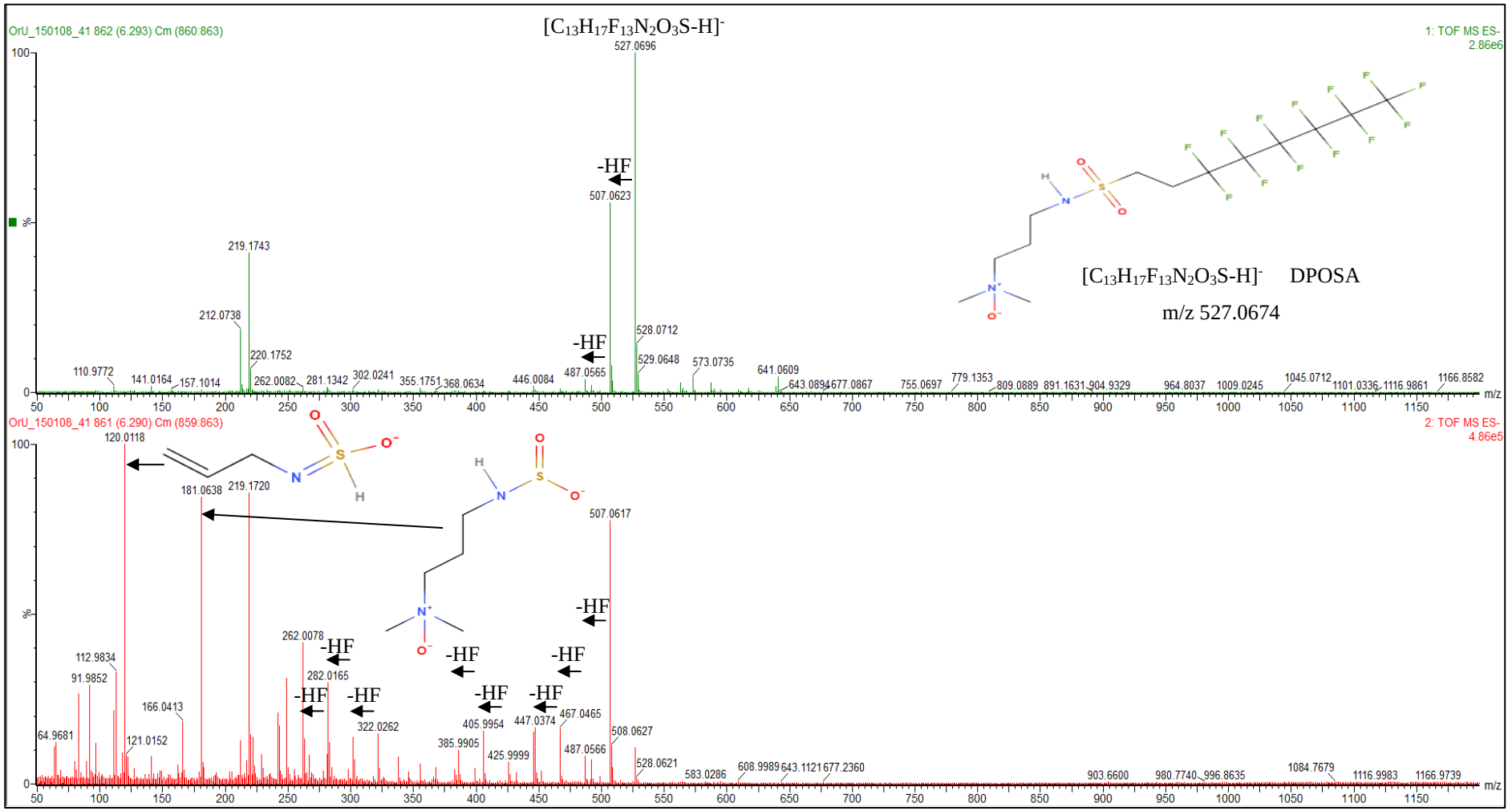


*Figure S10: Full scan high resolution mass spectra for sample **F10** at retention time 6.29 minutes with a low collision energy (top) and a high collision energy (bottom) for the first chromatographic method.*

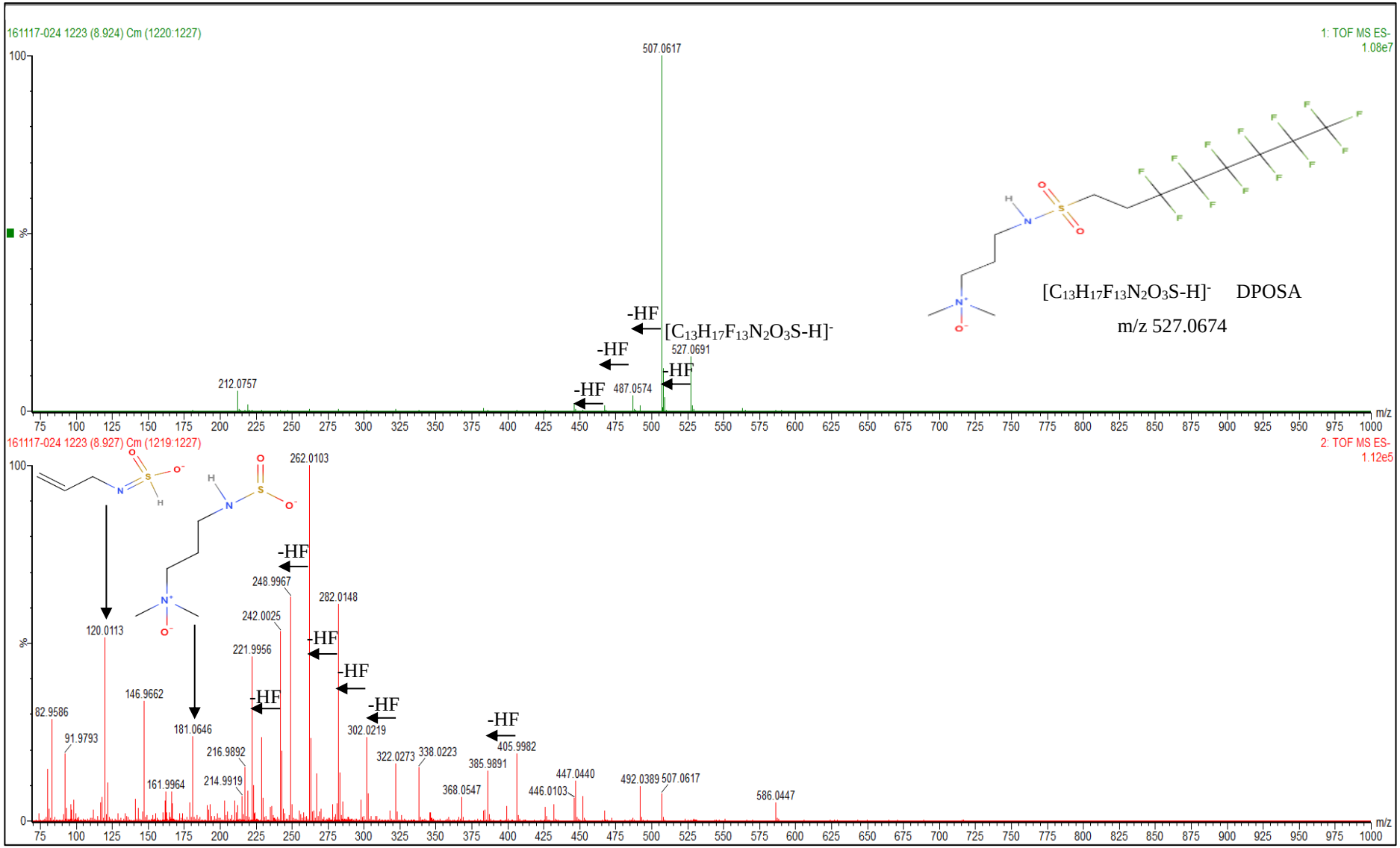


*Figure S11: Full scan high resolution mass spectra for sample **F2** at retention time 8.93 minutes with a low collision energy (top) and a high collision energy (bottom) for the second chromatographic method.*

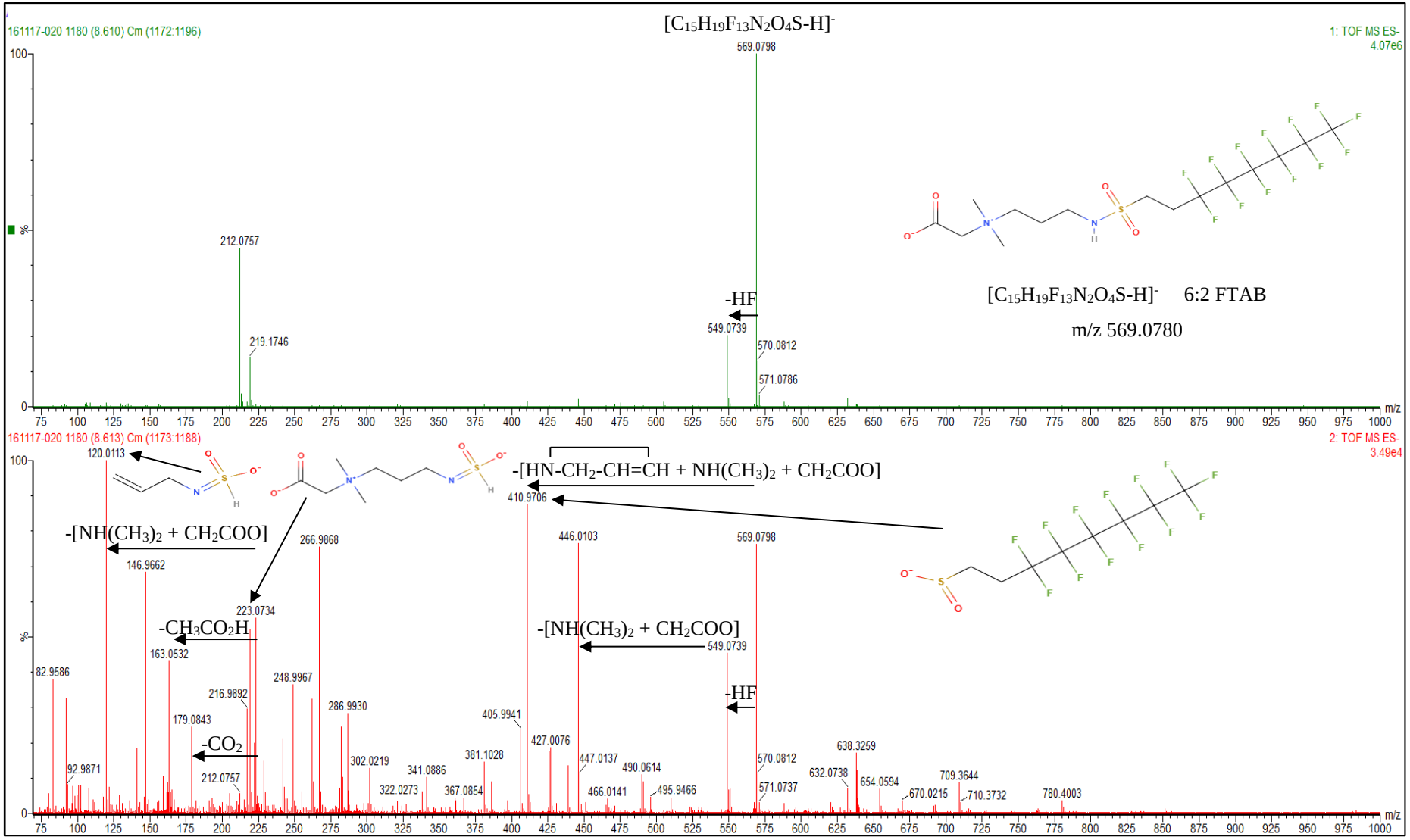


*Figure S12: Full scan high resolution mass spectra for sample **AR1** at retention time 8.61 minutes with a low collision energy (top) and a high collision energy (bottom) for the second chromatographic method.*

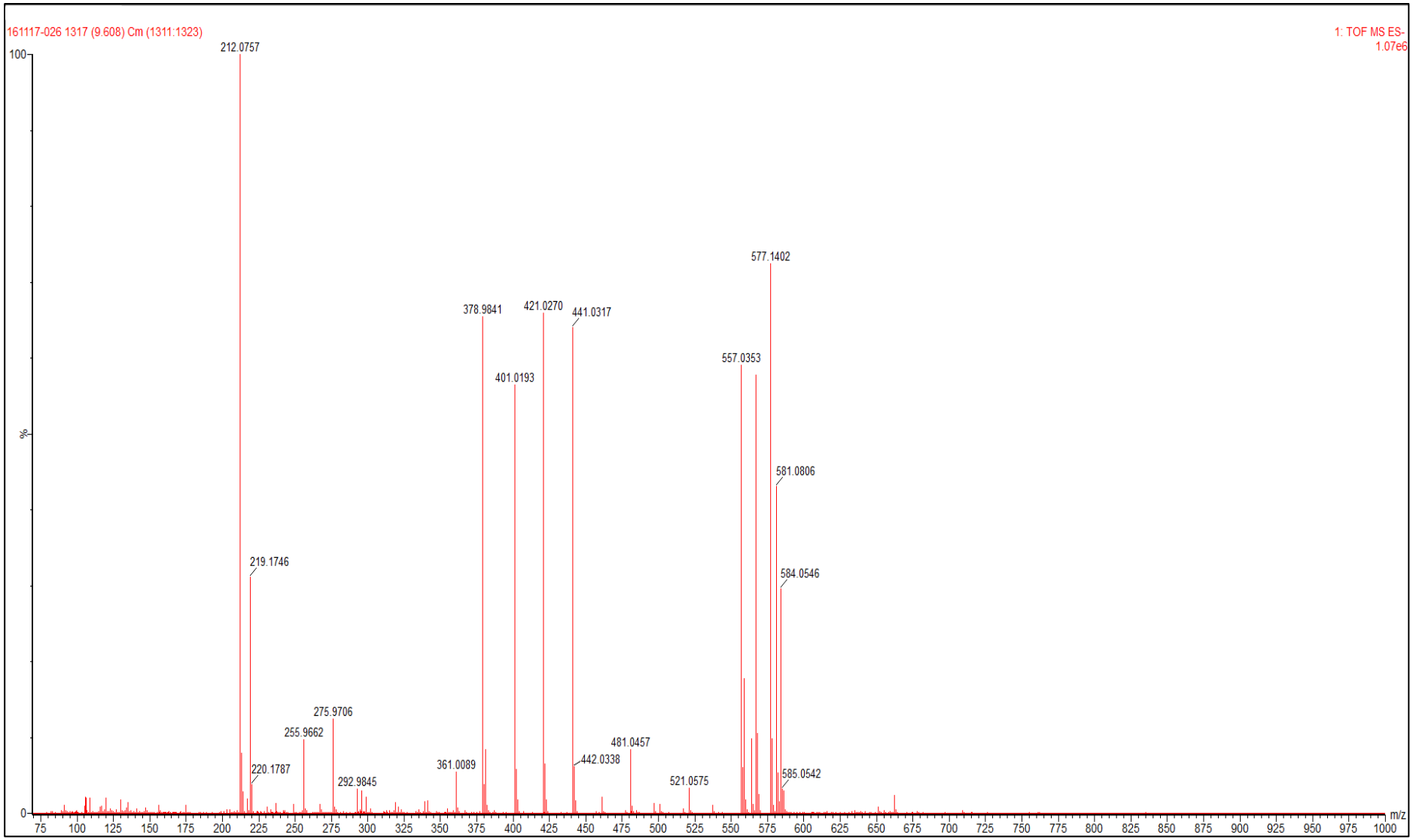


*Figure S13: Full scan high resolution mass spectra for sample **AR7** at retention time 9.61 minutes with a low collision energy for the second chromatographic method.*

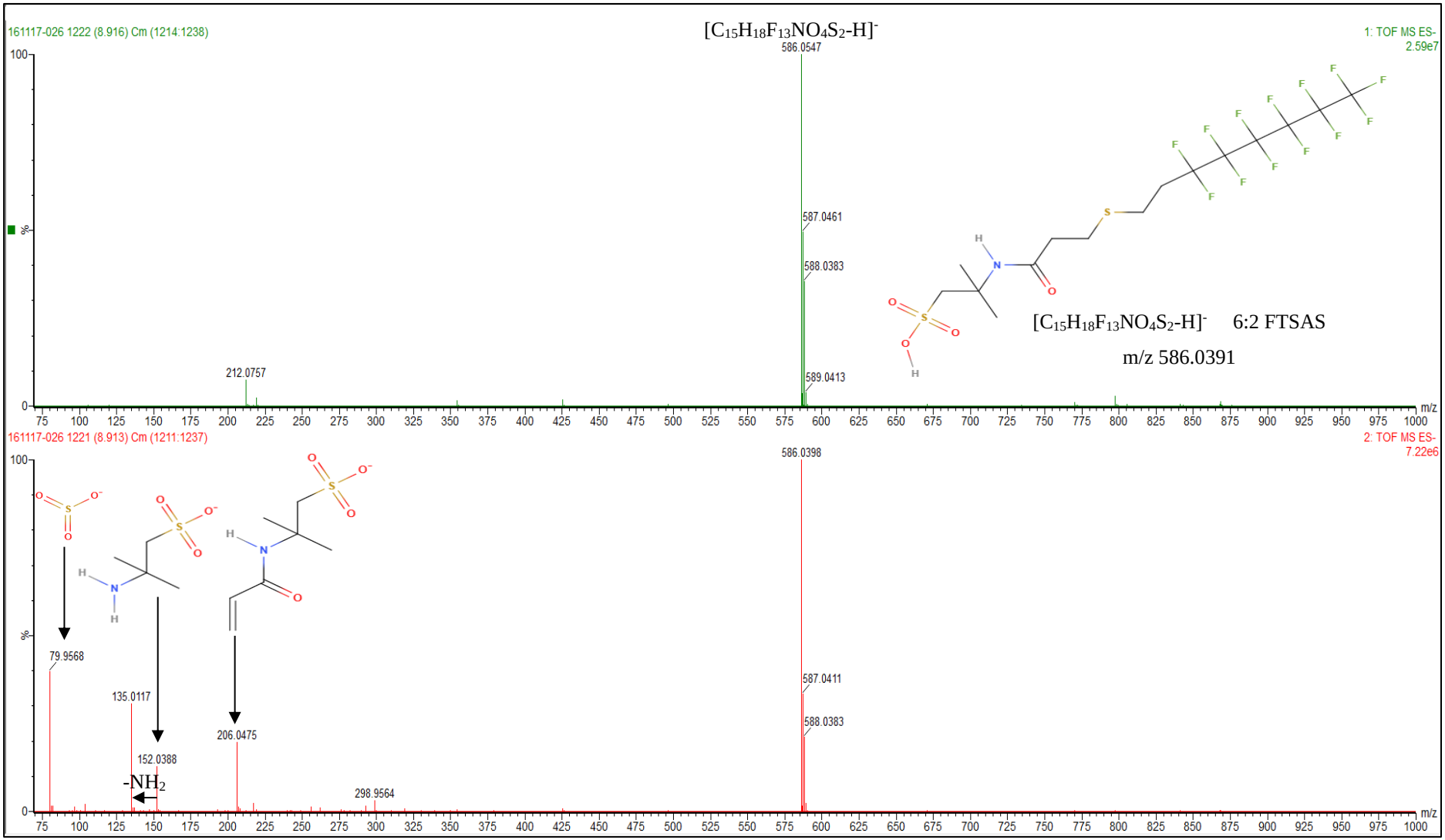


*Figure S14: Full scan high resolution mass spectra for sample **AR7** at retention time 8.91 minutes with a low collision energy (top) and a high collision energy (bottom) for the second chromatographic method.*

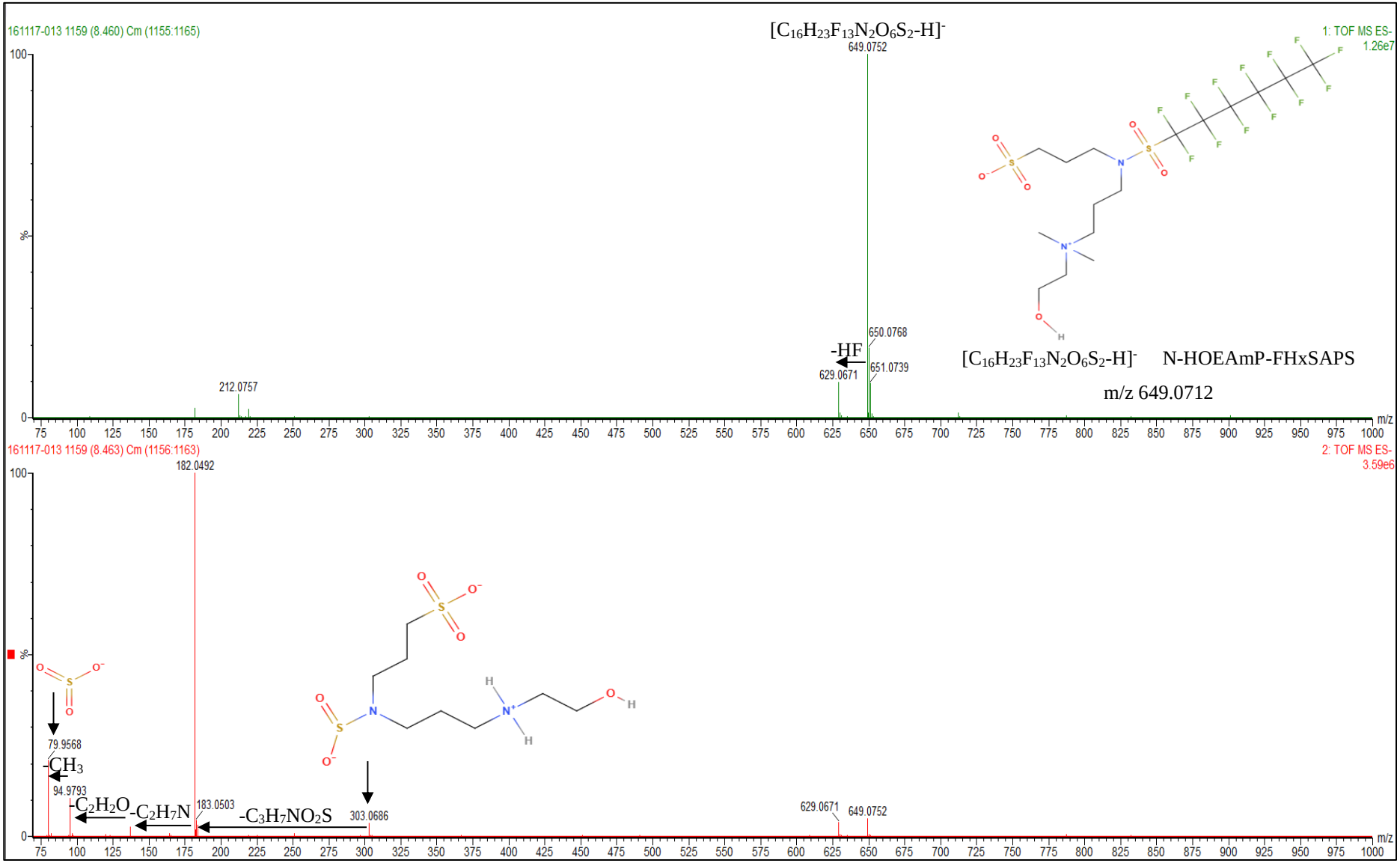


*Figure S15: Full scan high resolution mass spectra for sample **F6** at retention time 8.46 minutes with a low collision energy (top) and a high collision energy (bottom) for the second chromatographic method.*

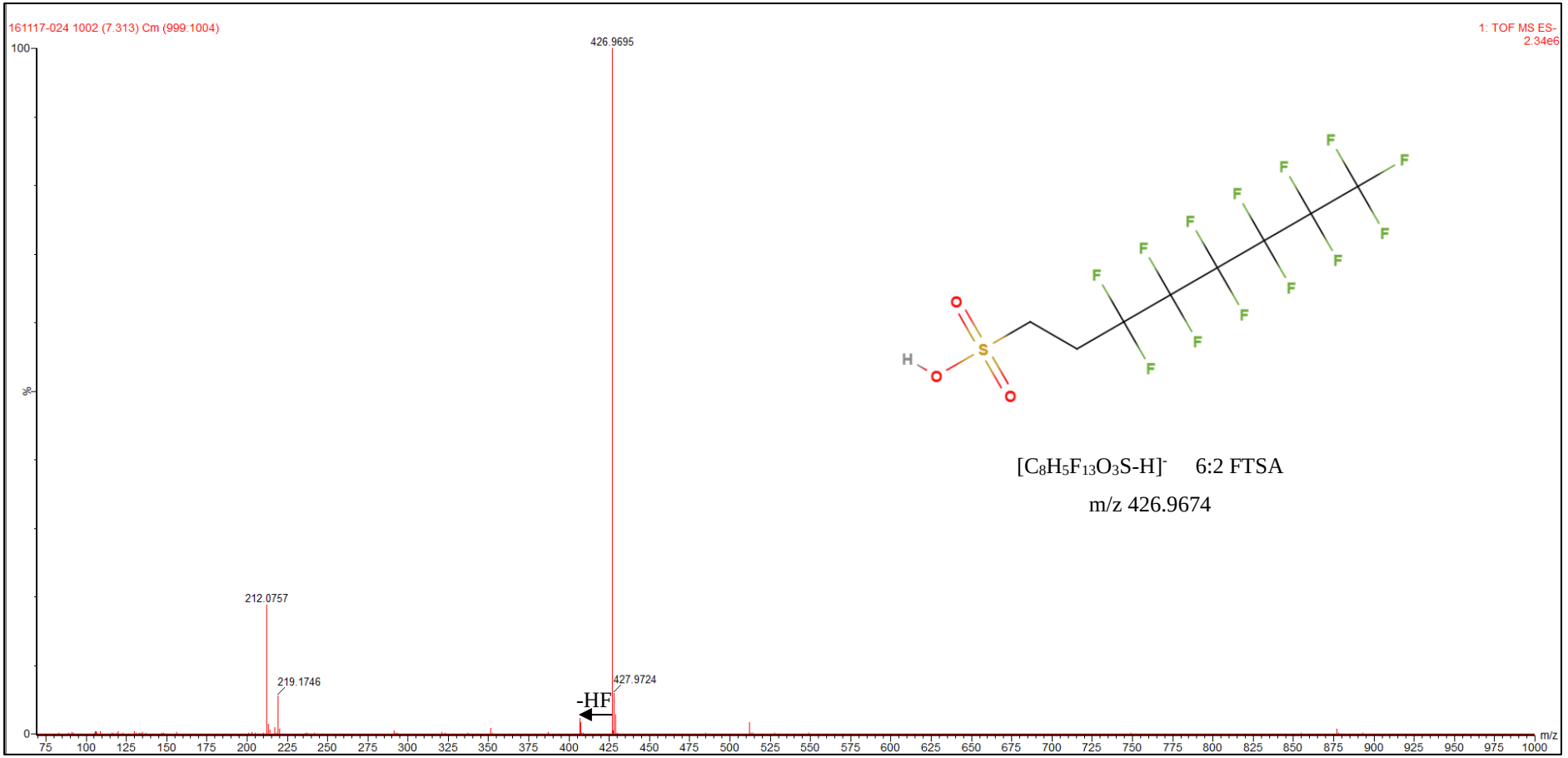


*Figure S16: Full scan high resolution mass spectra for sample **F10** at retention time 7.31 minutes with a low collision energy for the second chromatographic method.*

Equation S1: Equations A-C show the different calculations performed for fluorine mass balance and mass defect analysis.

A: Conversion target compound concentration to total fluorine concentration	$[F^-] = \sum [i] \frac{M_F * nF_i}{M_i}$	[F-]: total targeted PFASs fluorine concentration [i]: concentration of the target molecule i M_F: Atomic mass of fluorine atom nF_i: number of fluorine atoms in the target molecule i M_i: Molecular mass of the target molecule i
B: Mass balance analysis	TOF = TF - IF UOF = TOF - $\sum_{17}$ PFASs Mass balance (%) = $\frac{\sum_{17} \text{PFASs}}{\text{TOF}} * 100$	TOF : Total organic fluorine TF: Total fluorine IF: Inorganic fluoride UOF: Unknown Organic Fluorine $\sum_{17}$ PFASs: Sum of the 17 targeted PFASs concentrations
C: Mass defect plot analysis	$\text{KM(X)} = \text{IUPAC mass} \times \frac{\text{nominal mass(X)}}{\text{exact mass(X)}}$ If scale ratio higher than one: $\text{MD(X)} = \text{exact KM(X)} - \text{nominal KM(X)}[\text{round down}]$ If scale ratio below one: $\text{MD(X)} = \text{nominal KM(X)}[\text{round up}] - \text{exact KM(X)}$	KM (X): Kendrick mass for the scale (X) Scale ratio : $\frac{\text{nominal mass(X)}}{\text{exact mass(X)}}$ MD (X): Mass defect for the scale (X)