High Resolution Mass Spectrometry of Polyfluorinated Polyether – based Formulation

Ian Ken Dimzon, Xenia Trier, Tobias Frömel, Rick Helmus,

Thomas P. Knepper and Pim de Voogt

Supplementary Information

Supplementary Information 1

Higher-order mass defect calculation

SI 1a Higher-order mass transformation of selected accurate masses from the mass spectrum of PFPE formulation.

Accurate Mass, M^0 (1)	Relative Intensity (2)	Relation to m/z 1176.9994			1st Order Transformation			2nd Order Transformation			3rd Order Transformation		
		$-C_2H_4O-$ (3)	$-C_2F_4O-$ (4)	$-CF_2O-$ (5)	M^1 (6)	round(M^1,0) (7)	MD^1 (8)	M^2 (9)	round(M^2,0) (10)	MD^2 (11)	M^3 (12)	round (M^3, 0) (13)	MD^3 (14)
1176.9994	100.0				1176.2990	1176	0.2990	3.7130	4	0.2870	0.7018	1	0.2982
1088.9465	79.5	-2			1088.2985	1088	0.2985	3.7068	4	0.2932	0.7170	1	0.2830
1132.9731	78.4	-1			1132.2989	1132	0.2989	3.7117	4	0.2883	0.7048	1	0.2952
1221.0259	78.0	+1			1220.2993	1220	0.2993	3.7167	4	0.2833	0.6927	1	0.3073
1265.0523	77.9	+2			1264.2995	1264	0.2995	3.7192	4	0.2808	0.6866	1	0.3134
1309.0776	76.8	+3			1308.2986	1308	0.2986	3.7080	4	0.2920	0.7140	1	0.2860
945.0236	95.4		-2		944.4612	944	0.4612	5.7280	6	0.2720	0.6651	1	0.3349
1061.0114	87.0		-1		1060.3800	1060	0.3800	4.7192	5	0.2808	0.6865	1	0.3135
1292.9885	85.8		+1		1292.2190	1292	0.2190	2.7203	3	0.2797	0.6837	1	0.3163
1408.9769	85.2		+2		1408.1384	1408	0.1384	1.7190	2	0.2810	0.6869	1	0.3131
1045.0156	75.6			-2	1044.3937	1044	0.3937	4.8896	5	0.1104	0.2699	0	0.2699
1111.0076	74.8			-1	1110.3464	1110	0.3464	4.3025	4	0.3025	0.7397	1	0.2603
1242.9915	72.6			+1	1242.2518	1242	0.2518	3.1271	3	0.1271	0.3108	0	0.3108
1308.9835	71.2			+2	1308.2045	1308	0.2045	2.5400	2	0.5400	1.3204	1	0.3204
Standard deviation of shaded MD							**0.008**			**0.012**			**0.020**

SI 1b Higher-order mass transformation of the selected exact masses of the repeating unit

Repeating Units	Order	Exact Mass	M^1	round(M^1,0)	MD^1	M^2	round(M^2,0)	MD^2	M^3	round(M^3,0)	MD^3
$-C_2H_4O-$	1	44.0262	44.0000	44	0.00000	0.0000	0	0.0000	0	0	0.0000
$-C_2F_4O-$	2	115.9885	115.9195	116	0.08052	1.0001	1	0.0001	0.0001	0	0.0001
$-CF_2O-$	3	65.9917	65.9524	66	0.04757	0.5910	1	0.4090	1.0001	1	0.0001

Steps in the calculation of higher-order mass defects used in this study and the generation of the different MD graphs.

1. Accurate masses and their corresponding relative intensities were extracted from the mass spectrum of PFPE formulation (Columns 1 and 2 in SI1a).

2. It was decided that the transformations will be in the following order of the bases (repeating units): $-C_2H_4O-$, $-C_2F_4O-$, and $-CF_2O-$.

3. First order transformation (based on the $-C_2H_4O-$ repeating units): M^0 was multiplied by the ratio 44/44.0262 to obtain M^1 (See SI1b). The nominal M^1 was obtained by rounding off M^1 to the nearest ones.

$$MD^1 = M^1 - \text{nominal } M^1$$

4. Second order transformation (based on the $-C_2F_4O-$ repeating units): M^2 was calculated by dividing MD^1 by the MD^1 of $-C_2F_4O-$ (0.08052). The nominal M^2 was obtained by rounding off M^2 to the nearest ones.

$$MD^2 = M^2 - \text{nominal } M^2$$

5. Third order transformation (based on the $-CF_2O-$ repeating units): M^3 was calculated by dividing MD^2 by the MD^2 of $-CF_2O-$ (0.4090). The nominal M^3 was obtained by rounding off M^3 to the nearest ones.

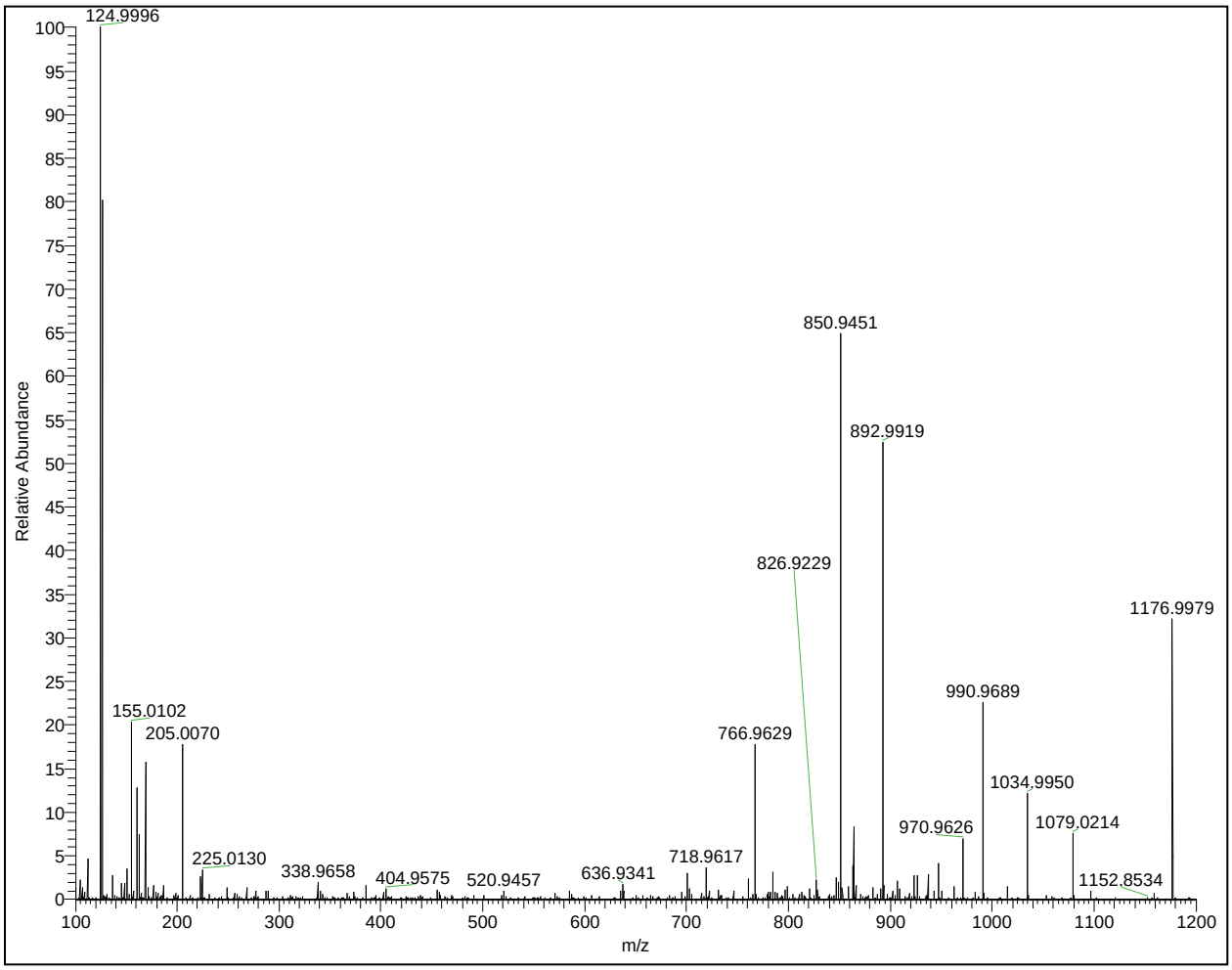
$$MD^3 = M^3 - \text{nominal } M^3$$

6. Different graphs can be generated using SI1a, for example, nominal M^0 vs MD^1; MD^1 vs MD^2; etc. The relative intensities can be added in the graph as a third dimension (e.g. size of the points).

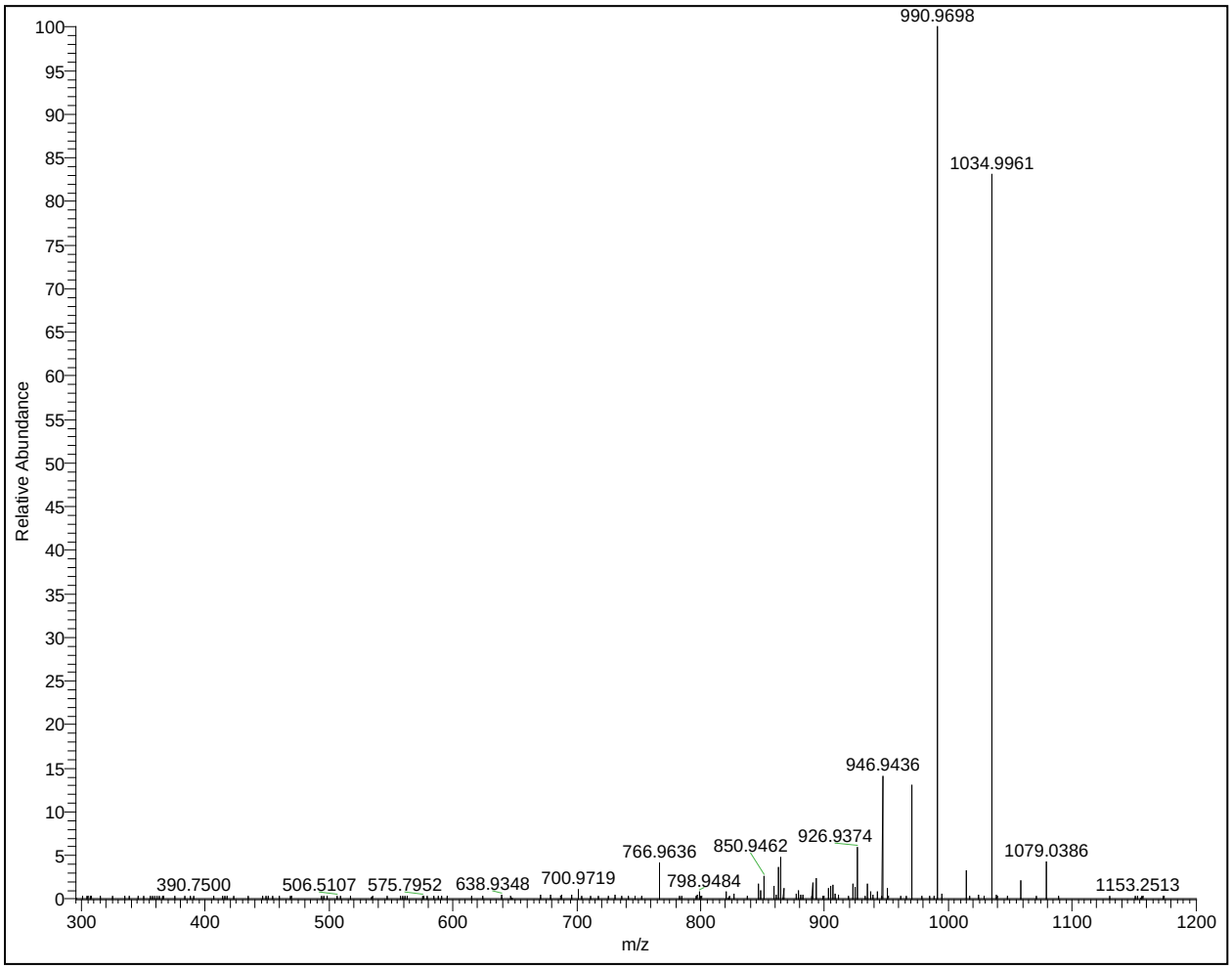
Supplementary Information 2

Sample MS^n mass spectra of *m/z* 1176.999.

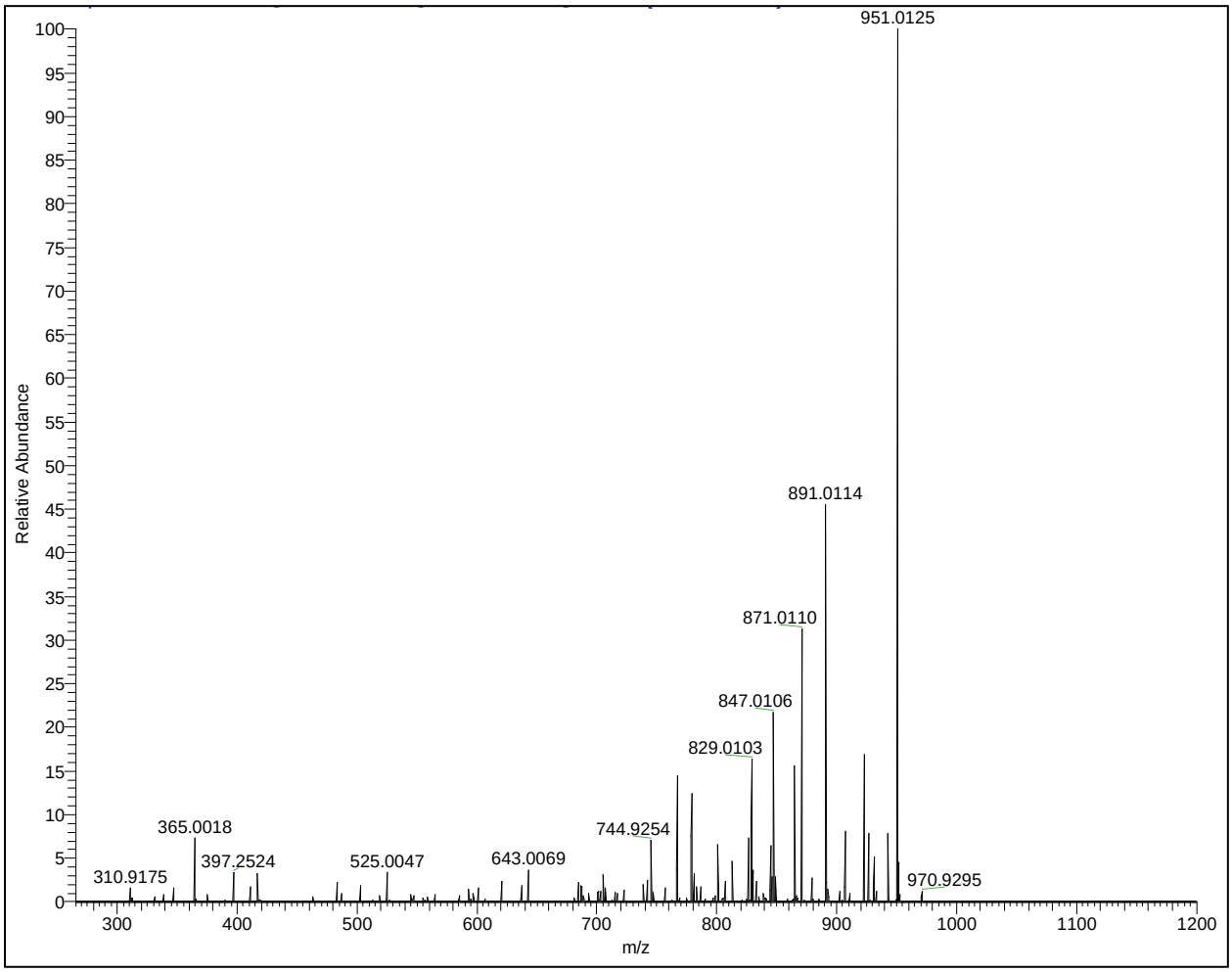
SI 2a Fragmentation of *m/z* 1176.9 as precursor ion in the HCD at a normalized collision energy of 25%; recorded in the FTMS mode



SI 2b MS^3 with the following precursor ions: 1176.9 → 1079.0 *m/z* in the CID at a normalized collision energies of 23% and 20% respectively; recorded in the FTMS mode



SI 2c MS^4 with the following precursor ions: 1176.9 → 990.9 → 970.9 *m/z* in the CID at a normalized collision energies of 23%, 20% and 20% respectively; recorded in the ITMS mode



Supplementary Information 3

Summary of fragmentation of some major ions selected by data-dependent acquisition

Precursor Ion (*m/z*) (1)	Relation to *m/z* 1177				Observed Fragment Ions (*m/z*)		
	$-C_2H_4O-$ (2)	$-C_2F_4O-$ (3)	$-CF_2-$ (4)	difference from *m/z* 1177 (5)	Neutral Loss of 18 *m/z* (6)	Neutral Loss of 98 *m/z* (7)	Series of 44 *m/z* losses starting from the *m/z* in column (7) (8)
945		-2		-232	927	847	803; 759; 715
1017	-1	-1		-160	999	919	875; 831; 787
1061		-1		-116	1043	963	919; 875; 831;
1105	+1	-1		-72	1087	1007	963; 919; 875; 831
1111		-1	+1	-66	1093	1013	969; 925; 881
1127			-1	-50	1109	1029	-
1133	-1			-44	1115	1035	991; 947
1155	+1	-1	+1	-22	-	1057	1013; 969; 925
1177				**0**	**1159**	**1079**	**1035; 991; 947**
1227			+1	50	-	1129	-