Mass-Remainder Analysis (MARA): An Improved Method for Elemental Composition Assignment in Petroleomics.

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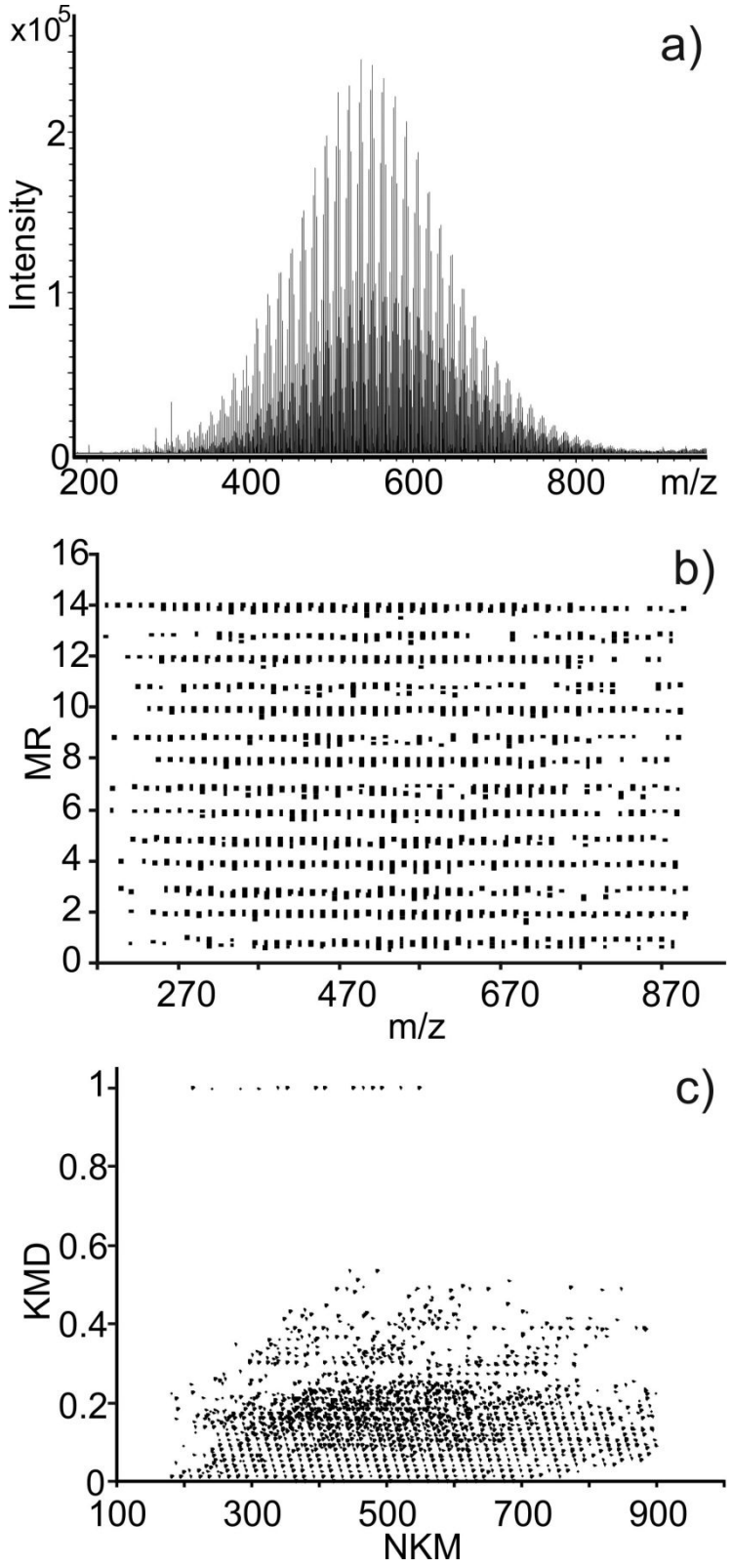

Figure S1. (a) ESI-FT-ICR mass spectrum of the mineral oil based lubricant Leybonol LVO 100, (b) Mass-remainder (MR) versus m/z plot, (c) Kendrick mass defect (KMD) versus nominal Kendrick mass (NKM) plot.

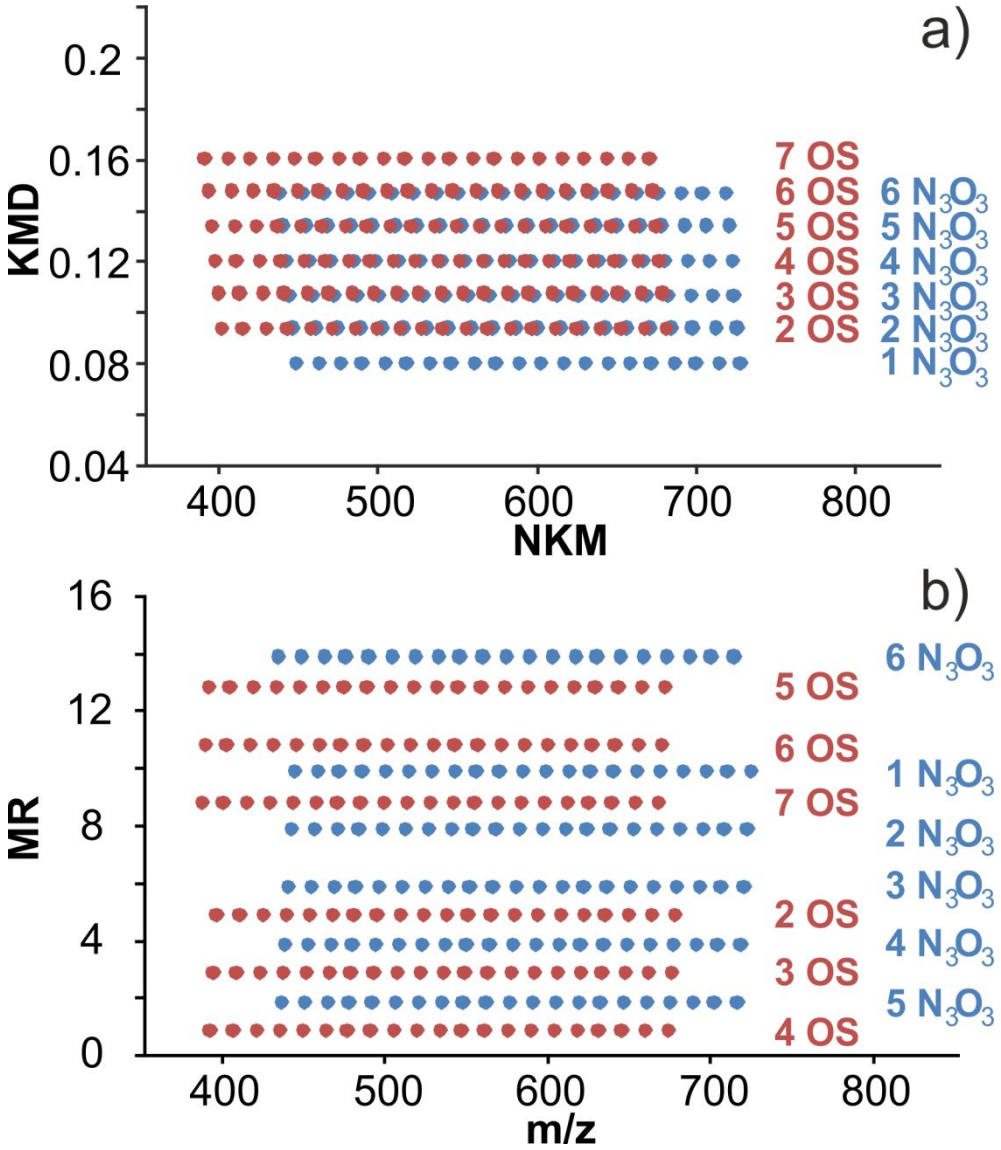

Figure S2 The 2-7 OS and 1-6 N_3O_3 (type class) series depicted in the (a) Kendrick mass defect (KMD) versus nominal Kendrick mass (NKM) plot and (b) Mass-remainder (MR) versus m/z plot (theoretical values).

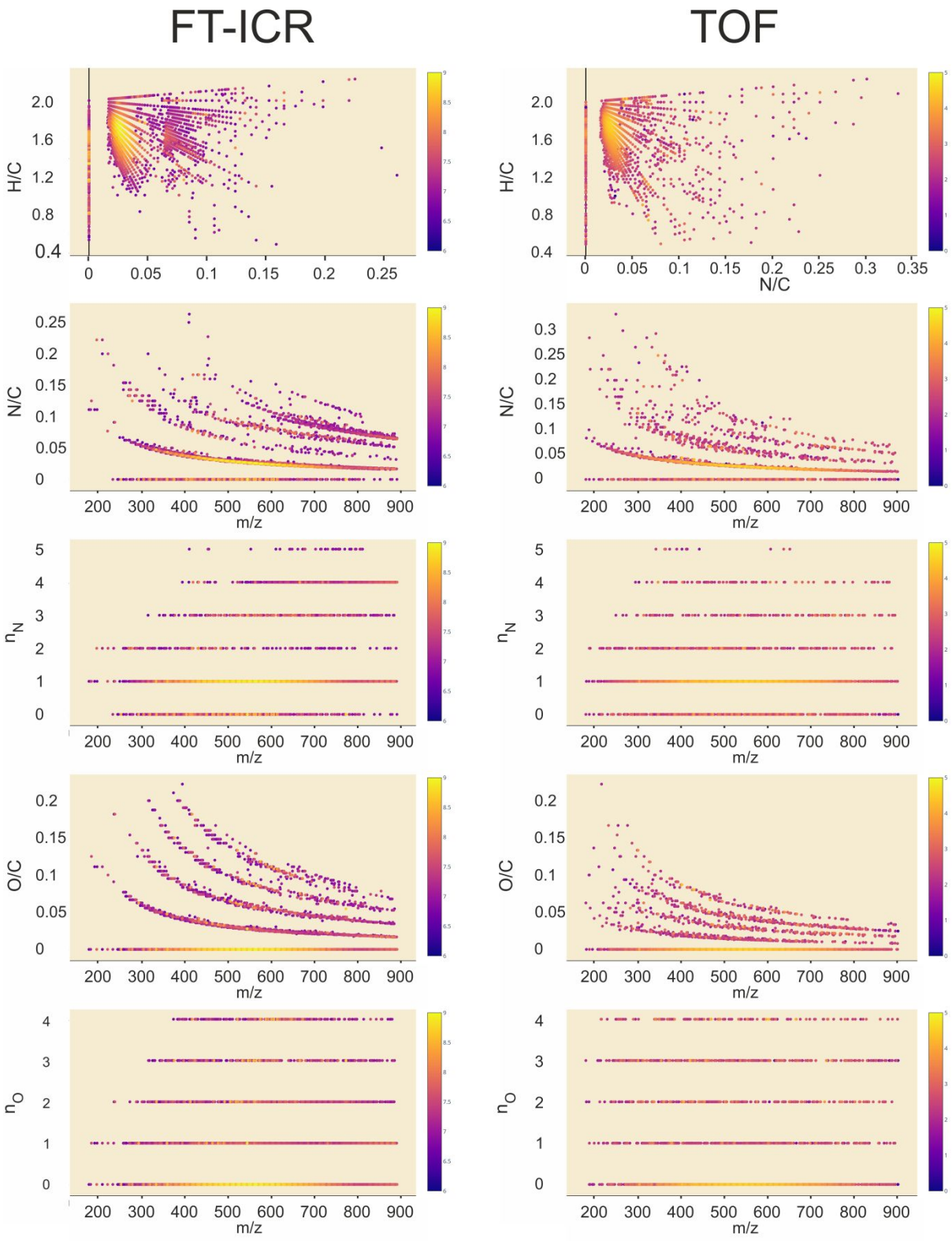

Figure S3. The van Krevelen diagrams and the distributions of N/C, n_N, O/C and n_O values as a function of m/z for the LVO 100 unused lubricant oil measured by ESI-FT-ICR and ESI-TOF instruments. n_O and n_N stand for the number of oxygen and nitrogen, respectively.

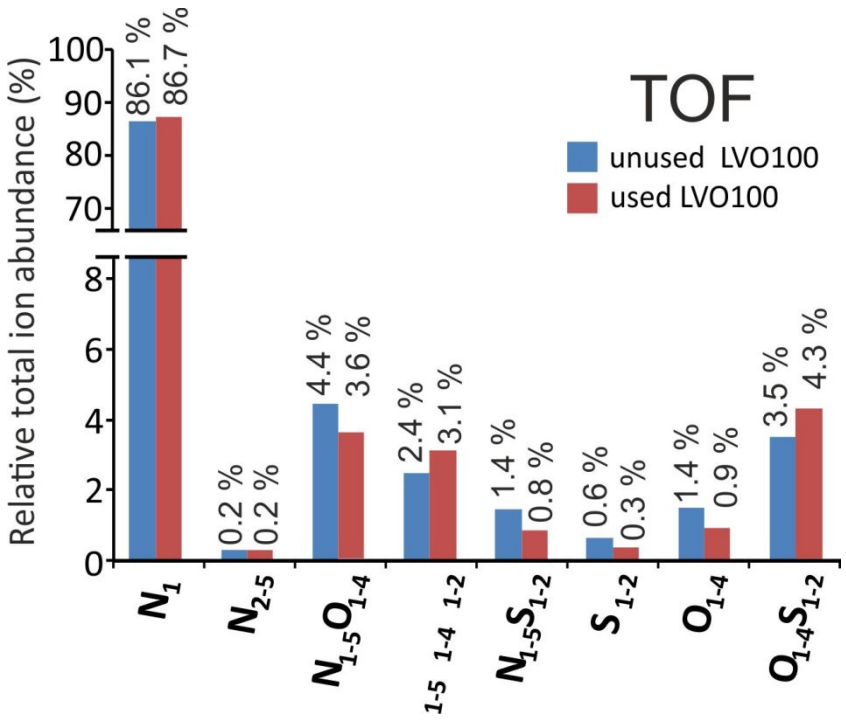

Figure S4 The relative abundances of the major heteroatom classes calculated from the ESI-TOF spectrum of the unused and used mineral oil based lubricant Leybonol LVO 100.

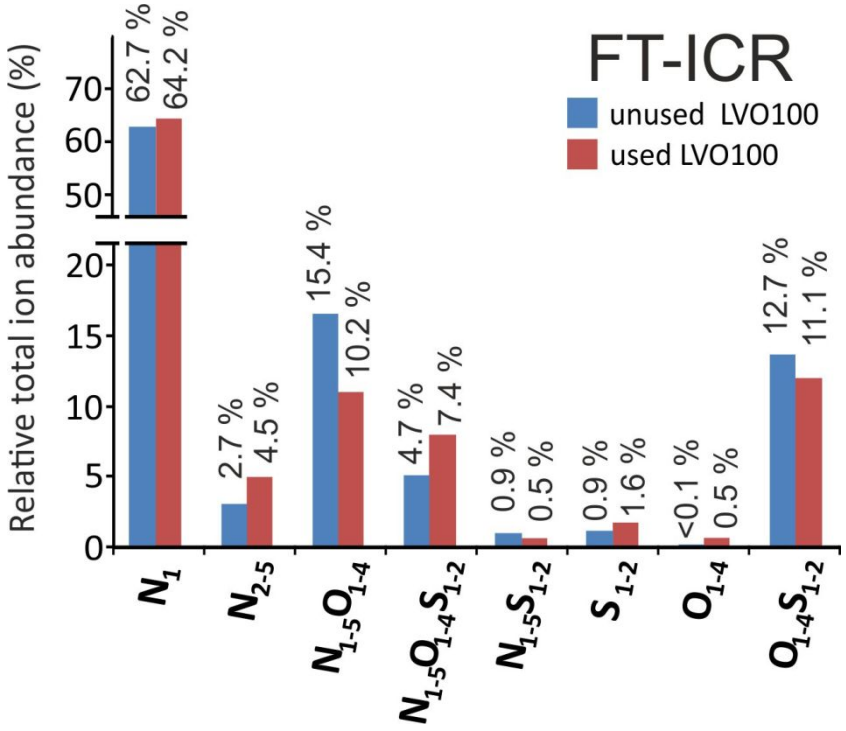

Figure S5 The relative abundances of the major heteroatom classes calculated from the ESI-FT-ICR spectrum of the unused and used mineral oil based lubricant Leybonol LVO 100.

Table S1 Maximum number of heteroatoms selected for crude oil analysis

C_{max}	H_{max}	O_{max}	N_{max}	S_{max}	instrumentation	reference
75	150	10	6	3	FT-ICR	[18]
200	1000	5	4	2	Orbitrap	[19]
150	350	7	3	6	FT-ICR	[3]
unlimited	unlimited	3	2	2	FT-ICR	[20]
unlimited	unlimited	5	5	5	FT-ICR	[4]
unlimited	unlimited	5	5	4	FT-ICR	[5]
100	200	5	5	5	FT-ICR	[1]

Table S2 Possible overlaps within 10 ppm error at m/z 800 and the resolving power requirements for their separation at different m/z. n(O)=0-5, n(N)=0-5, n(S)=0-5, N(heteroatom)=0-10.

Groupe 1						Groupe 2						n_{hetero} in change	abs difference	Resolving power requirement at m/z			
C	H	O	N	S	mass1	C	H	O	N	S	mass2			200	400	600	800
7	-	3	-	-	131.984745	-	8	-	2	3	131.984961	8	0.000216	925926	1851852	2777778	3703704
7	-	4	2	-	175.985808	-	16	-	-	5	175.985555	11	0.000253	790514	1581028	2371542	3162055
15	-	1	-	-	195.994915	-	12	-	4	4	195.994480	9	0.000435	459770	919540	1379310	1839080
-	-	1	4	-	72.007211	-	8	-	-	2	72.006742	7	0.000469	426439	852879	1279318	1705757
8	-	-	-	-	96	-	4	2	2	1	95.999349	5	0.000651	307220	614439	921659	1228879
-	-	5	-	-	79.974575	1	4	-	-	2	79.975442	7	0.000867	230681	461361	692042	922722
8	-	-	2	-	124.006148	-	12	1	-	3	124.005028	6	0.00112	178571	357143	535714	714286
1	-	-	4	-	68.012296	-	4	4	-	-	68.010960	8	0.001336	149701	299401	449102	598802
16	-	-	-	-	192	-	16	3	-	4	191.998229	7	0.001771	112931	225861	338792	451722
4	-	-	4	-	104.012296	-	8	4	-	1	104.014331	9	0.002035	98280	196560	294840	393120
11	-	-	2	-	160.006148	-	16	1	-	4	160.008399	7	0.002251	88849	177699	266548	355398
4	-	-	-	1	79.972071	-	0	5	-	-	79.974575	6	0.002504	79872	159744	239617	319489
11	-	-	-	-	132	-	8	2	2	2	132.002720	6	0.00272	73529	147059	220588	294118
3	-	1	4	-	108.007211	-	12	-	-	3	108.010113	8	0.002902	68918	137836	206754	275672
18	-	1	-	-	231.994915	-	16	-	4	5	231.997851	10	0.002936	68120	136240	204360	272480
4	-	3	-	-	95.984745	-	4	-	2	2	95.981590	7	0.003155	63391	126783	190174	253566
3	-	-	-	-	36	-	4	-	-	1	36.003371	1	0.003371	59330	118659	177989	237318
10	-	3	-	-	167.984745	-	12	-	2	4	167.988332	9	0.003587	55757	111514	167271	223028
4	-	4	2	-	139.985808	-	12	-	-	4	139.982184	10	0.003624	55188	110375	165563	220751
12	-	1	-	-	159.994915	-	8	-	4	3	159.991109	8	0.003806	52549	105097	157646	210194
0	-	1	4	-	72.007211	3	4	-	-	1	72.003371	6	0.00384	52083	104167	156250	208333
5	-	-	-	-	60	-	-	2	2	-	59.995978	4	0.004022	49727	99453	149180	198906
2	-	5	-	-	103.974575	-	8	-	-	3	103.978813	8	0.004238	47192	94384	141576	188768
12	-	2	-	-	175.989830	-	16	-	-	5	175.985555	7	0.004275	46784	93567	140351	187135
5	-	-	2	-	88.006148	-	8	1	-	2	88.001657	5	0.004491	44534	89067	133601	178134
0	-	-	4	1	87.984367	2	-	4	-	-	87.979660	9	0.004707	42490	84980	127470	169960
13	-	-	-	-	156	-	12	3	-	3	155.994858	6	0.005142	38895	77791	116686	155582
7	-	-	4	-	140.012296	-	12	4	-	2	140.017702	10	0.005406	36996	73992	110988	147984
13	-	-	4	-	212.012296	-	20	2	-	5	212.006685	11	0.005611	35644	71289	106933	142577
14	-	-	2	-	196.006148	-	20	1	-	5	196.011770	8	0.005622	35575	71149	106724	142298
7	-	-	-	-	84	-	4	5	-	-	84.005875	5	0.005875	34043	68085	102128	136170

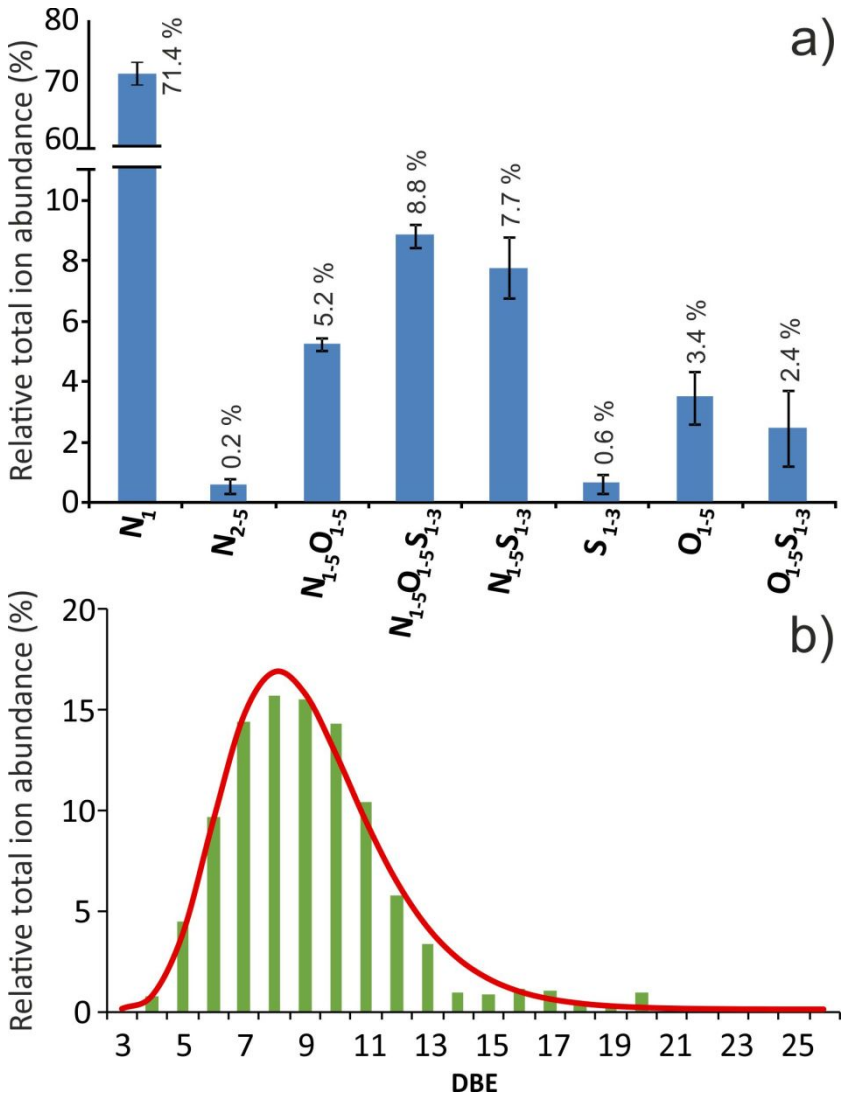

Figure S6. (a) The relative abundances of the heteroatom classes, (b) the DBE distribution for class N_1 calculated from the ESI-TOF spectrum of the Russian crude oil. The red line is the fitted curve of the log-normal probability density function with the parameters: μ=2.2, σ=0.28 and A=100 (A is a scaling factor).

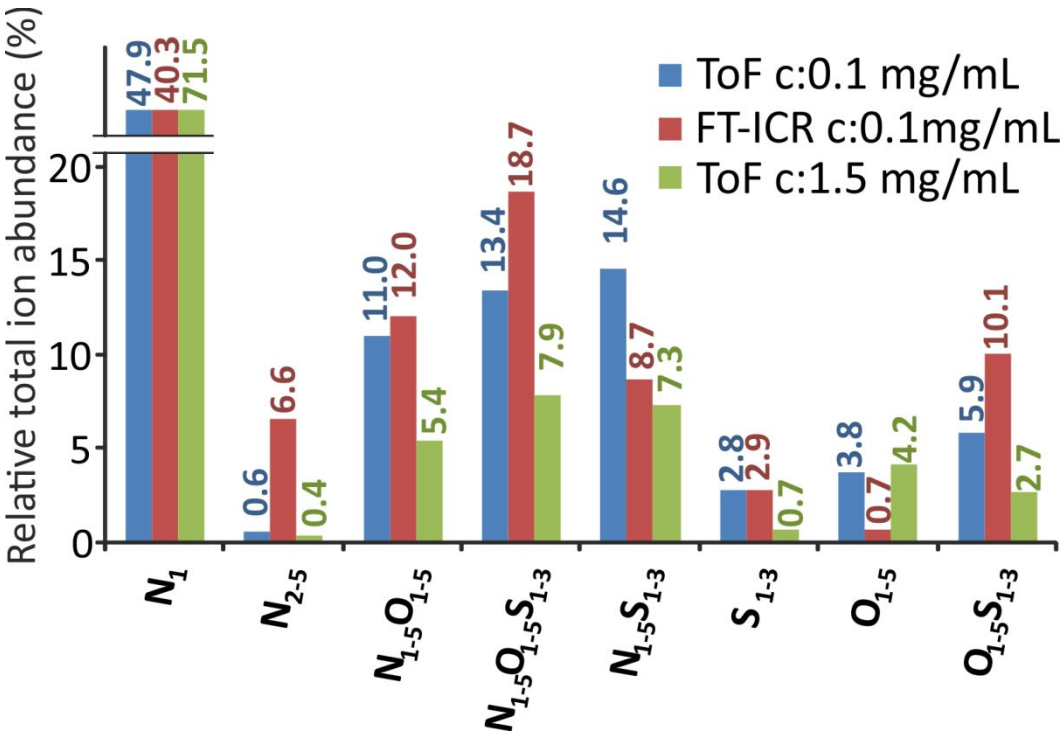

Figure S7. Class distributions for the Russian crude oil measured by ESI-TOF (lower concentration) (blue), ESI-FT-ICR (red), and ESI-TOF (higher concentration) (green)

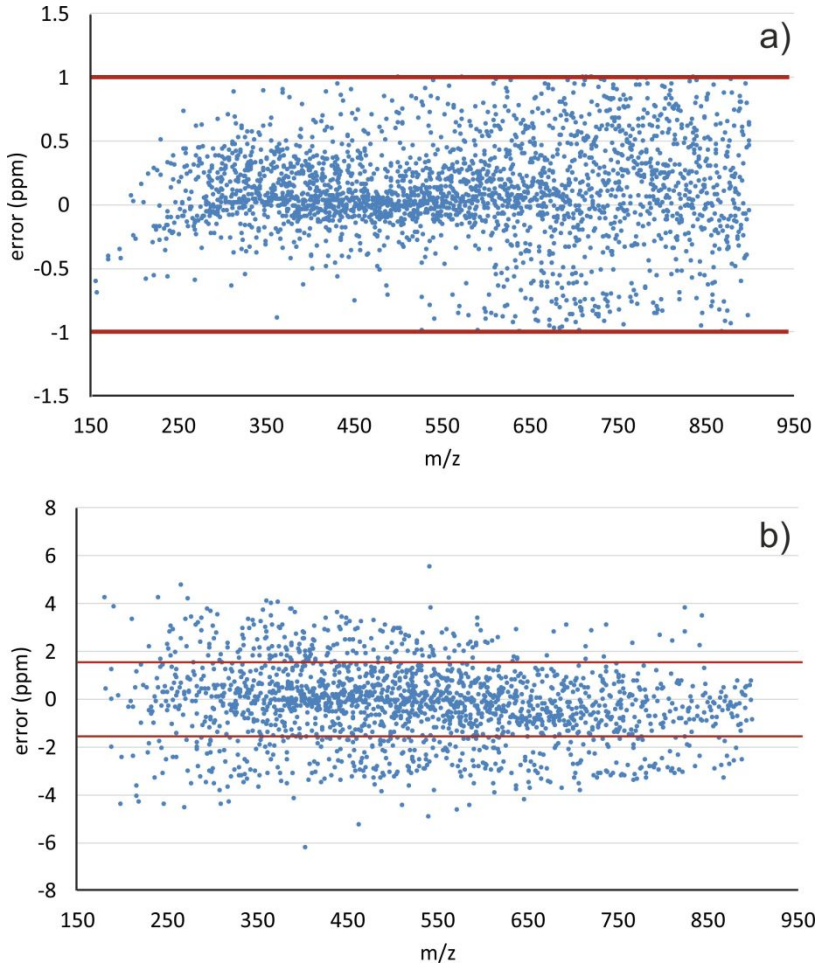

Figure S8. The error distribution of the assignation as function of m/z applying FT-ICR (a) and TOF (b) instruments.

Conversion from the $^{12}C = 12$ scale to the Kendrick mass scale to $CH_2 = 14$.

$$\text{Kendrick mass} = m/z \times 14/14.01565 \quad \text{(S1)}$$

where *m/z* is the IUPAC mass measured by MS. The homologous series will have identical Kendrick mass defect values defined in Eq. 2.

$$\text{KMD} = \text{Nominal Kendrick Mass} - \text{Kendrick Mass} \quad \text{(S2)}$$