

SUPPORTING INFORMATION

Quantitative analysis of hydrocarbons in Gas oils by Two-dimensional Comprehensive Gas Chromatography with Vacuum Ultraviolet Detection

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S1 Prefractionation methodology:

Prefractionation methodology was devised by conducting a study involving a model mixture containing selected saturated and unsaturated species. Test mix composition is given in Table S1. Figure S1B illustrates generated elution profile for the employed mixture which demonstrates efficient separation of the two groups of interest. Method was then transferred to the fractionation of real GOs samples. GC×GC/FID analysis was performed for GOs fractions collected in 15 s intervals to decide on the point of separation and collection of the saturated and unsaturated fractions. GC×GC/FID analysis has demonstrated that the two fractions separation is not completely sharp and that it is rather difficult to decide on the exact start of the collection of the unsaturated fraction for the GO based only on using templates. It can be said that between the two fractions which would contain only the two groups of interest, there would be an intermediate fraction which would contain small amounts of either of the two groups (Figure S3). However, online generated UV spectra during the fractionation demonstrated slight increase of absorbance at 200 nm shortly after the beginning of the elution with the more polar solvent which would indicate presence of unsaturated species (Figure S2). Thus, it was decided to choose the polar solvent introduction time as the point of separation of the two fractions.

Table S1 Model mixture composition.

Compound name	Mass (g)
n-pentane	0.506
n-hexane	0.555
n-heptane	161.224
n-octane	0.546
n-nonane	0.634
n-decane	0.662
n-undecane	0.595
n-dodecane	0.515
n-tridecane	0.519
n-tetradecane	0.485
n-pentadecane	0.683
n-hexadecane	0.667
trans-2-octene	0.564
1-nonene	0.182
1-tetradecene	0.546
1-hexadecene	0.606
3-methyl pentane	0.465
2-methyl heptane	0.557
cycloheptane	0.602
tert-butyl cyclohexane	0.624
1,3 cyclohexadiene	0.560
3-methyl 1,4-pentadiene	0.497
decalin	0.693
tetralin	0.666
m-xylene	0.578
isobutyl benzene	0.756
Toluene	0.696
phenanthrene	0.471
9,10 dimethyl anthracene	0.415
naphthalene	0.517

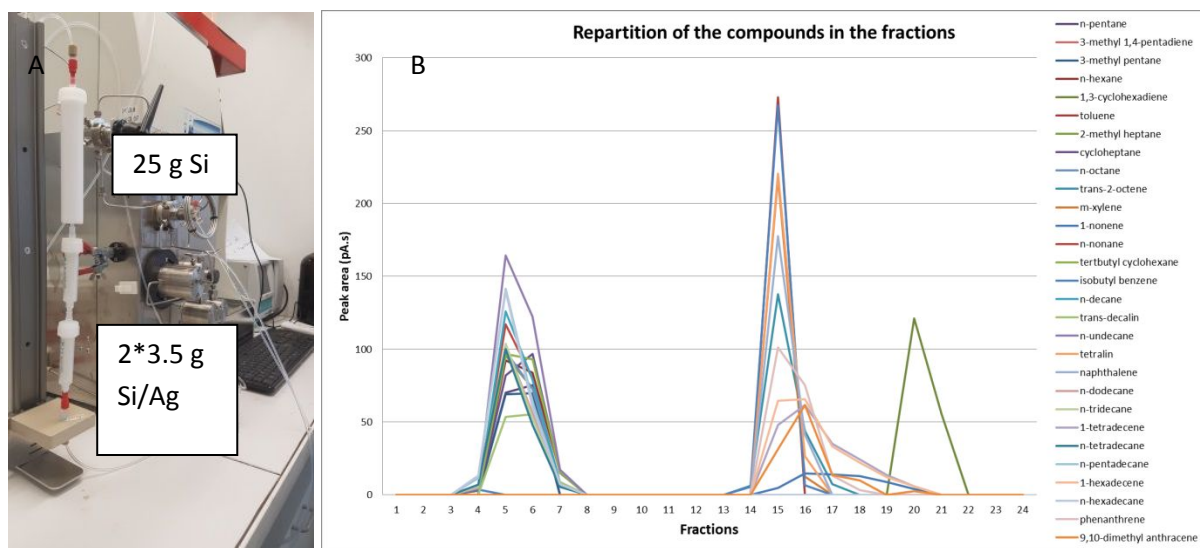


Figure S1 (A) Prefractionation column set; (B) Obtained elution profile for saturates and unsaturates model mixture.

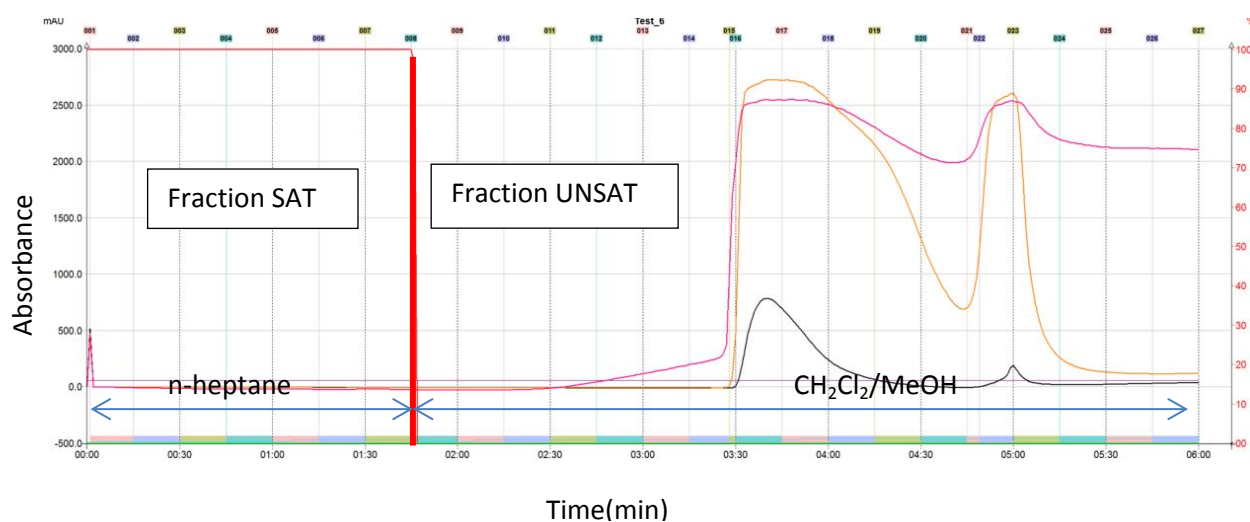


Figure S2 Generated online UV spectra for prefractionated GO with indicates regions of elution and fraction separation. Absorbance at 200 (pink), 254 (orange) and 299 nm (black).

For the sample fractionation, at all times between the elution of the main portions of saturated and unsaturated species, a small mass eluting in the lower region of chromatogram is observed.

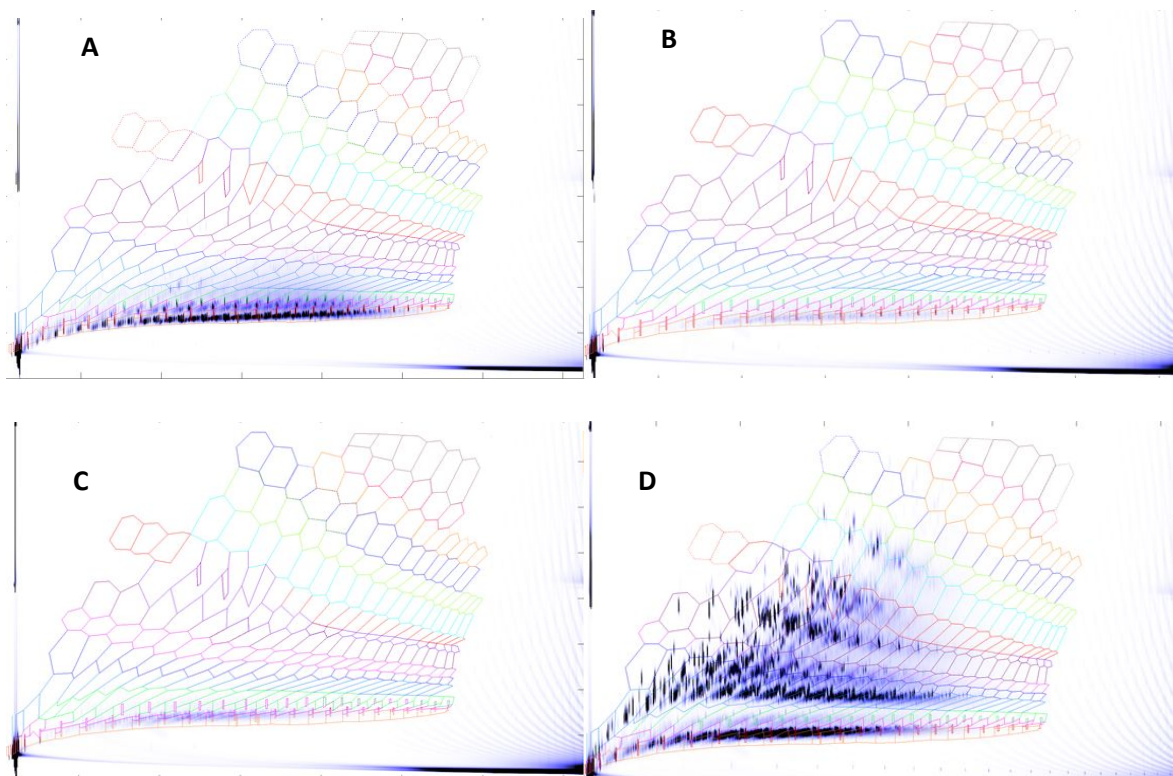


Figure S3 GC×GC/FID chromatograms for fractions collected: (A) 1:15-1:30 min (B) 1:45-2:00 min (C) 2:30-2:45 min (D) 3:15-3:30 min. Cryogenic modulation used for these analyses.

S2 GC×GC template details:

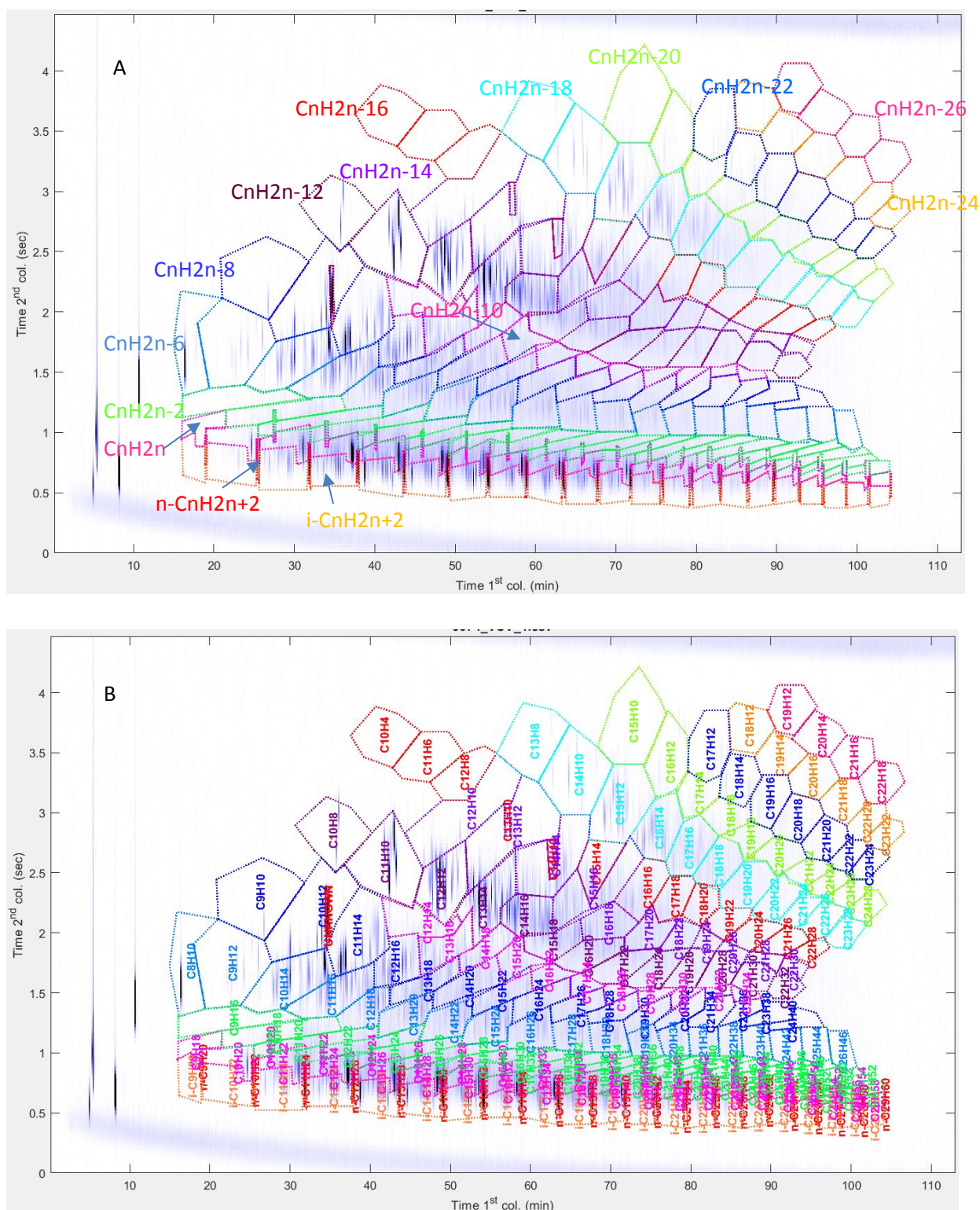


Figure S4 A) Identification template used for analysis of gas oils; B) Template with molecular formulas corresponding to each zone.

S3 VUV RRFs calculated for saturated and unsaturated GO fraction:

Table S2 VUV RRFs per n-C17 as calculated for saturated fraction (125-240 nm Avg. Abs.).

Family name	Compound	No of observ	AVR	RSD	AVR per family	Pooled RSD
n-CnH2n+2	n-C9H20	1	0.95	0%		
n-CnH2n+2	n-C10H22	3	0.98	3%		
n-CnH2n+2	n-C11H24	6	1.02	4%		
n-CnH2n+2	n-C12H26	8	1.02	4%		
n-CnH2n+2	n-C13H28	11	1.00	4%		
n-CnH2n+2	n-C14H30	11	0.99	3%		
n-CnH2n+2	n-C15H32	13	0.99	3%		
n-CnH2n+2	n-C16H34	13	1.00	2%		
n-CnH2n+2	n-C17H36	13	1.00	0%	0.99	3%
n-CnH2n+2	n-C18H38	13	0.99	2%		
n-CnH2n+2	n-C19H40	12	0.99	2%		
n-CnH2n+2	n-C20H42	12	1.00	3%		
n-CnH2n+2	n-C21H44	10	0.99	3%		
n-CnH2n+2	n-C22H46	8	0.99	2%		
n-CnH2n+2	n-C23H48	7	1.02	2%		
n-CnH2n+2	n-C24H50	5	0.99	1%		
n-CnH2n+2	n-C25H52	2	1.00	3%		
i-CnH2n+2	i-C10H22	3	0.88	12%		
i-CnH2n+2	i-C11H24	4	0.83	13%		
i-CnH2n+2	i-C12H26	8	0.84	14%		
i-CnH2n+2	i-C13H28	10	0.89	12%		
i-CnH2n+2	i-C14H30	12	0.91	10%		
i-CnH2n+2	i-C15H32	13	0.94	9%		
i-CnH2n+2	i-C16H34	13	0.96	10%		
i-CnH2n+2	i-C17H36	13	0.99	10%		
i-CnH2n+2	i-C18H38	13	0.98	12%	0.98	10%
i-CnH2n+2	i-C19H40	13	1.01	11%		
i-CnH2n+2	i-C20H42	12	1.02	9%		
i-CnH2n+2	i-C21H44	11	1.05	8%		
i-CnH2n+2	i-C22H46	9	1.02	9%		
i-CnH2n+2	i-C23H48	9	1.02	17%		
i-CnH2n+2	i-C24H50	6	1.15	14%		
i-CnH2n+2	i-C25H52	4	1.17	16%		
i-CnH2n+2	i-C26H54	1	1.03	0%		

CnH2n	C10H20	2	1.23	5%		
CnH2n	C11H22	2	1.25	10%		
CnH2n	C12H24	7	1.04	13%		
CnH2n	C13H26	8	1.07	11%		
CnH2n	C14H28	9	1.01	9%		
CnH2n	C15H30	11	1.03	10%		
CnH2n	C16H32	11	1.01	11%		
CnH2n	C17H34	13	0.99	10%	1.00	10%
CnH2n	C18H36	13	0.98	13%		
CnH2n	C19H38	11	0.98	6%		
CnH2n	C20H40	10	0.99	6%		
CnH2n	C21H42	5	0.95	7%		
CnH2n	C22H44	5	0.97	7%		
CnH2n	C23H46	4	0.93	6%		
CnH2n	C24H48	3	0.89	9%		
CnH2n-2	C11H20	2	0.99	6%		
CnH2n-2	C12H22	7	0.90	22%		
CnH2n-2	C13H24	9	0.95	18%		
CnH2n-2	C14H26	10	1.01	14%		
CnH2n-2	C15H28	11	1.02	15%		
CnH2n-2	C16H30	13	1.00	15%		
CnH2n-2	C17H32	13	0.96	15%	0.97	15%
CnH2n-2	C18H34	11	0.96	14%		
CnH2n-2	C19H36	11	0.94	14%		
CnH2n-2	C20H38	11	0.94	15%		
CnH2n-2	C21H40	8	0.95	16%		
CnH2n-2	C22H42	4	0.97	13%		
CnH2n-2	C23H44	1	0.96	0%		

Table S3 VUV RRFs per n-C17 as calculated for unsaturated fraction (125-240 nm Avg. Abs.).

Family name	Compound	No of observ	AVR	RSD	AVR per family	Pooled RSD
CnH2n	C9H18	1	0.65	0%		
CnH2n	C10H20	3	0.66	4%		
CnH2n	C11H22	4	0.70	7%		
CnH2n	C12H24	6	0.71	6%	0.73	7%
CnH2n	C13H26	6	0.72	6%		
CnH2n	C14H28	6	0.72	7%		
CnH2n	C15H30	6	0.73	5%		

CnH2n	C16H32	6	0.74	7%		
CnH2n	C17H34	5	0.74	10%		
CnH2n	C18H36	4	0.74	5%		
CnH2n	C19H38	3	0.77	9%		
CnH2n	C20H40	1	0.85	0%		
CnH2n-2	C9H16	2	0.61	1%		
CnH2n-2	C10H18	3	0.61	5%		
CnH2n-2	C11H20	7	0.57	12%		
CnH2n-2	C12H22	5	0.63	7%		
CnH2n-2	C13H24	7	0.61	10%		
CnH2n-2	C14H26	4	0.65	6%		
CnH2n-2	C15H28	6	0.64	12%	0.64	11%
CnH2n-2	C16H30	9	0.69	16%		
CnH2n-2	C17H32	7	0.69	11%		
CnH2n-2	C18H34	5	0.66	7%		
CnH2n-2	C19H36	4	0.64	4%		
CnH2n-2	C20H38	1	0.68	0%		
CnH2n-2	C21H40	1	0.74	0%		
CnH2n-6	C9H12	9	0.39	4%		
CnH2n-6	C10H14	12	0.41	4%		
CnH2n-6	C11H16	12	0.44	5%		
CnH2n-6	C12H18	12	0.47	7%		
CnH2n-6	C13H20	12	0.48	5%		
CnH2n-6	C14H22	13	0.51	7%		
CnH2n-6	C15H24	13	0.54	9%		
CnH2n-6	C16H26	13	0.55	8%	0.53	7%
CnH2n-6	C17H28	12	0.56	7%		
CnH2n-6	C18H30	12	0.59	7%		
CnH2n-6	C19H32	12	0.60	9%		
CnH2n-6	C20H34	8	0.62	7%		
CnH2n-6	C21H36	7	0.62	6%		
CnH2n-6	C22H38	5	0.64	5%		
CnH2n-6	C23H40	5	0.66	6%		
CnH2n-8	C10H12	10	0.40	6%		
CnH2n-8	C11H14	12	0.42	6%		
CnH2n-8	C12H16	13	0.44	5%	0.48	6%
CnH2n-8	C13H18	12	0.46	8%		
CnH2n-8	C14H20	13	0.47	4%		

CnH2n-8	C15H22	13	0.48	6%		
CnH2n-8	C16H24	12	0.48	7%		
CnH2n-8	C17H26	12	0.51	3%		
CnH2n-8	C18H28	10	0.51	5%		
CnH2n-8	C19H30	8	0.52	5%		
CnH2n-8	C20H32	8	0.55	4%		
CnH2n-8	C21H34	5	0.58	6%		
CnH2n-8	C24H40	1	0.55	0%		
CnH2n-10	C12H14	5	0.38	5%		
CnH2n-10	C13H16	13	0.41	7%		
CnH2n-10	C14H18	13	0.43	8%		
CnH2n-10	C15H20	12	0.44	5%	0.44	7%
CnH2n-10	C16H22	9	0.45	9%		
CnH2n-10	C17H24	6	0.48	6%		
CnH2n-10	C18H26	3	0.47	4%		
CnH2n-10	C19H28	1	0.50	0%		
CnH2n-12	C10H8	1	0.27	0%		
CnH2n-12	C11H10	9	0.30	9%		
CnH2n-12	C12H12	13	0.31	6%		
CnH2n-12	C13H14	13	0.33	7%		
CnH2n-12	C14H16	13	0.35	8%		
CnH2n-12	C15H18	13	0.38	8%	0.40	7%
CnH2n-12	C16H20	13	0.42	7%		
CnH2n-12	C17H22	12	0.45	7%		
CnH2n-12	C18H24	12	0.47	5%		
CnH2n-12	C19H26	8	0.51	8%		
CnH2n-12	C20H28	5	0.54	9%		
CnH2n-12	C21H30	5	0.56	10%		
CnH2n-14	C12H10	4	0.27	4%		
CnH2n-14	C13H12	13	0.30	9%		
CnH2n-14	C14H14	13	0.32	6%		
CnH2n-14	C15H16	13	0.34	6%	0.35	7%
CnH2n-14	C16H18	12	0.37	8%		
CnH2n-14	C17H20	12	0.40	8%		
CnH2n-14	C18H22	6	0.43	7%		
CnH2n-16	C14H12	5	0.34	3%		
CnH2n-16	C15H14	12	0.32	6%		
CnH2n-16	C16H16	12	0.35	4%	0.36	5%
CnH2n-16	C17H18	12	0.36	4%		
CnH2n-16	C18H20	6	0.41	4%		

CnH2n-16	C19H22	5	0.46	6%		
CnH2n-18	C14H10	3	0.29	4%		
CnH2n-18	C15H12	8	0.31	5%		
CnH2n-18	C16H14	11	0.32	5%		
CnH2n-18	C17H16	11	0.35	5%	0.35	5%
CnH2n-18	C18H18	8	0.38	5%		
CnH2n-18	C19H20	6	0.43	7%		
CnH2n-20	C16H12	1	0.29	0%		
CnH2n-20	C17H14	1	0.28	0%	0.30	0%
CnH2n-20	C18H16	1	0.31	0%		
CnH2n-22	C17H12	1	0.32	0%		
CnH2n-22	C18H14	1	0.34	0%	0.34	0%
CnH2n-22	C19H16	1	0.38	0%		

S4 Calculation of linear combination of the spectra:

When two averaged spectra corresponding to the same mass of olefins and naphthenes are available, their linear combination can be estimated.

According to the condition that the linear combination of vector a and b is an orthogonal projection of vector x, it can be written:

$$x - (\alpha \cdot a + \beta \cdot b) \perp a \text{ and } b \quad (1)$$

Where a and b are starting vectors whose linear combination is to be estimated and x is a target vector.

Thus:

$$\langle x - (\alpha \cdot a + \beta \cdot b), a \rangle = 0 \quad (2)$$

And

$$\langle x - (\alpha \cdot a + \beta \cdot b), b \rangle = 0 \quad (3)$$

Hence scaling factors α and β can be calculated:

$$\alpha = \frac{\langle b, b \rangle \cdot \langle a, x \rangle - \langle a, b \rangle \cdot \langle b, x \rangle}{\langle a, a \rangle \langle b, b \rangle - \langle a, b \rangle^2} \quad (4)$$

$$\beta = \frac{\langle a, a \rangle \cdot \langle b, x \rangle - \langle a, b \rangle \cdot \langle a, x \rangle}{\langle a, a \rangle \langle b, b \rangle - \langle a, b \rangle^2} \quad (5)$$

Obtained scaling factors allow to calculate contribution of each species in the mixture spectra.