

## SUPPLEMENTARY INFORMATION

### **Comprehensive Two-Dimensional Liquid Chromatography of Heavy Oil**

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## Supplementary information

### *S1 – Full chromatograms of HW*

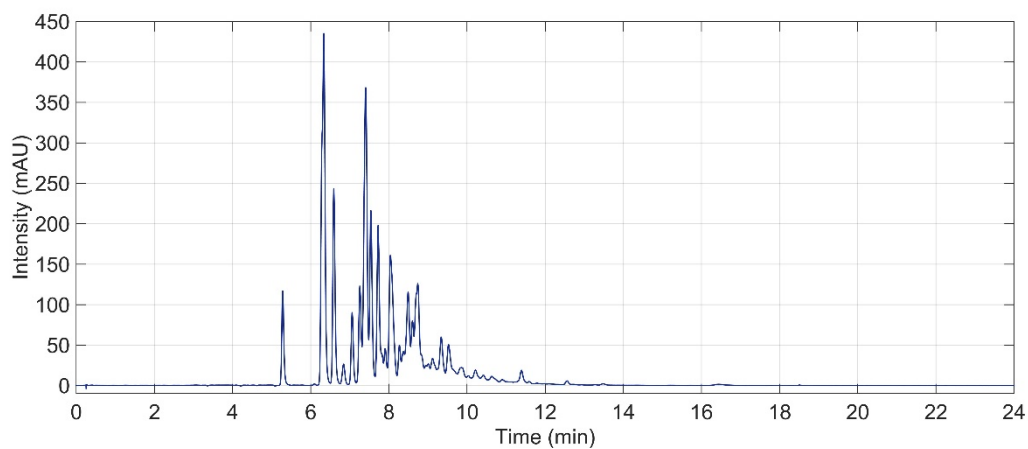


Figure S1.1 – LC -UV chromatograms of the separation of HW, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.1.

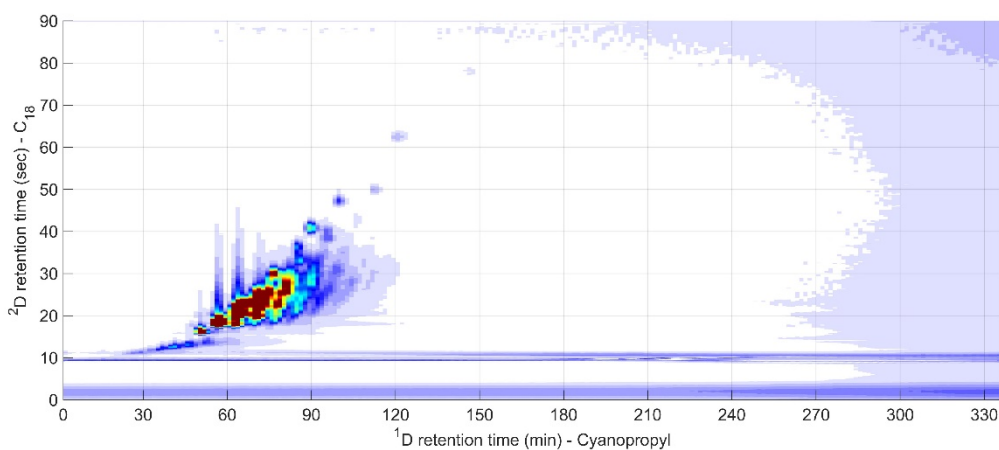


Figure S1.2 – LC×LC-UV chromatograms of the separation of HW, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.2.

*S2 – Full LC×LC-UV chromatograms of PIOTR measurements for PAH610 and HW*

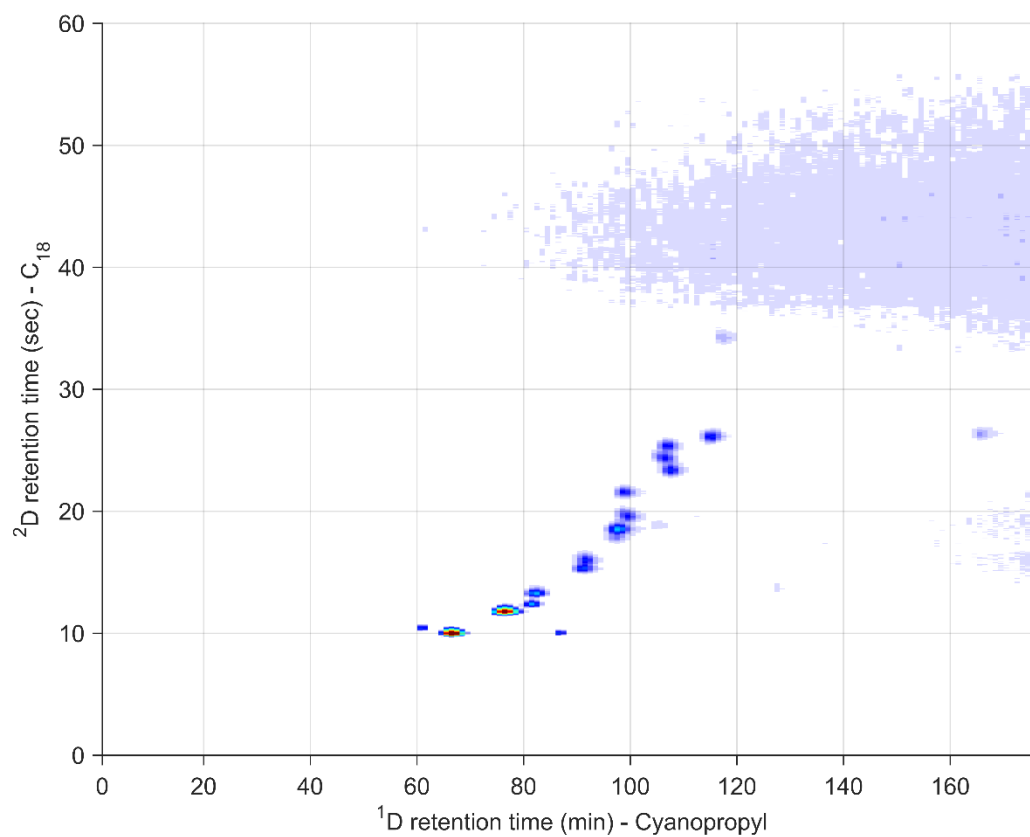


Figure S2.1 – LC×LC-UV chromatogram of the fast separation of PAH610, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.3.

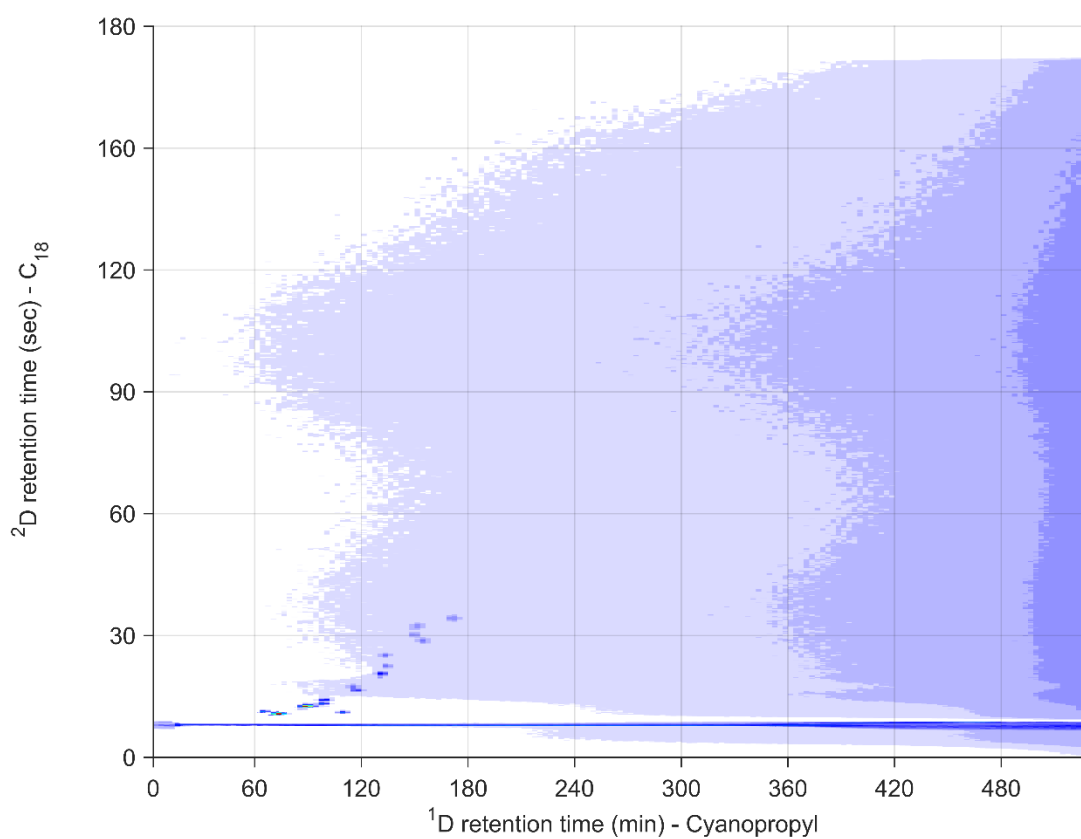


Figure S2.2 – LC×LC-UV chromatograms of the slow separation of PAH610, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.3.

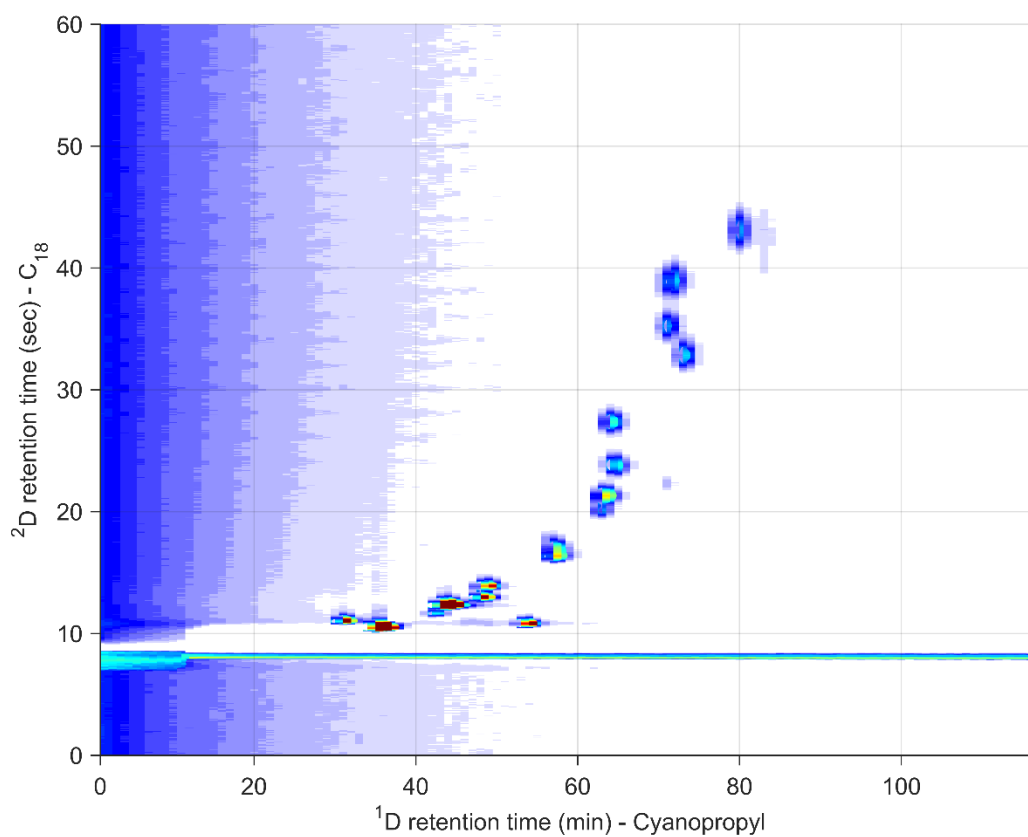


Figure S2.3 – LC×LC-UV chromatograms of the optimized separation of PAH610, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.5.

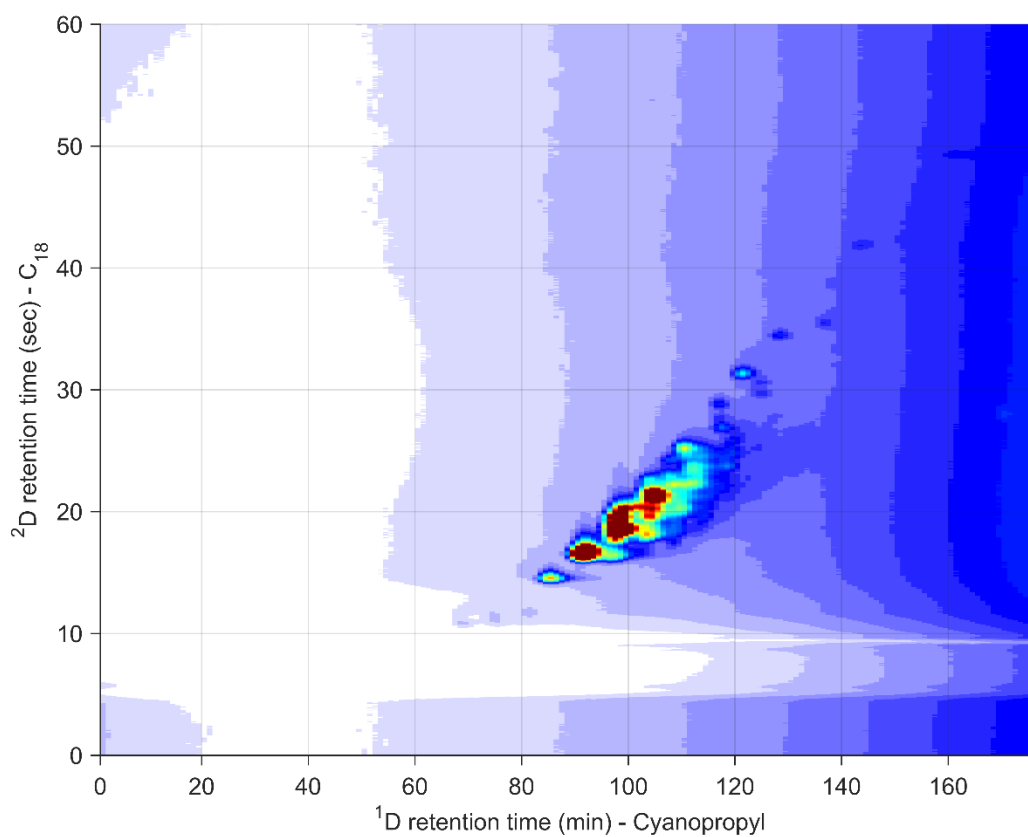


Figure S2.4 – LC×LC-UV chromatograms of the fast separation of HW, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.3.

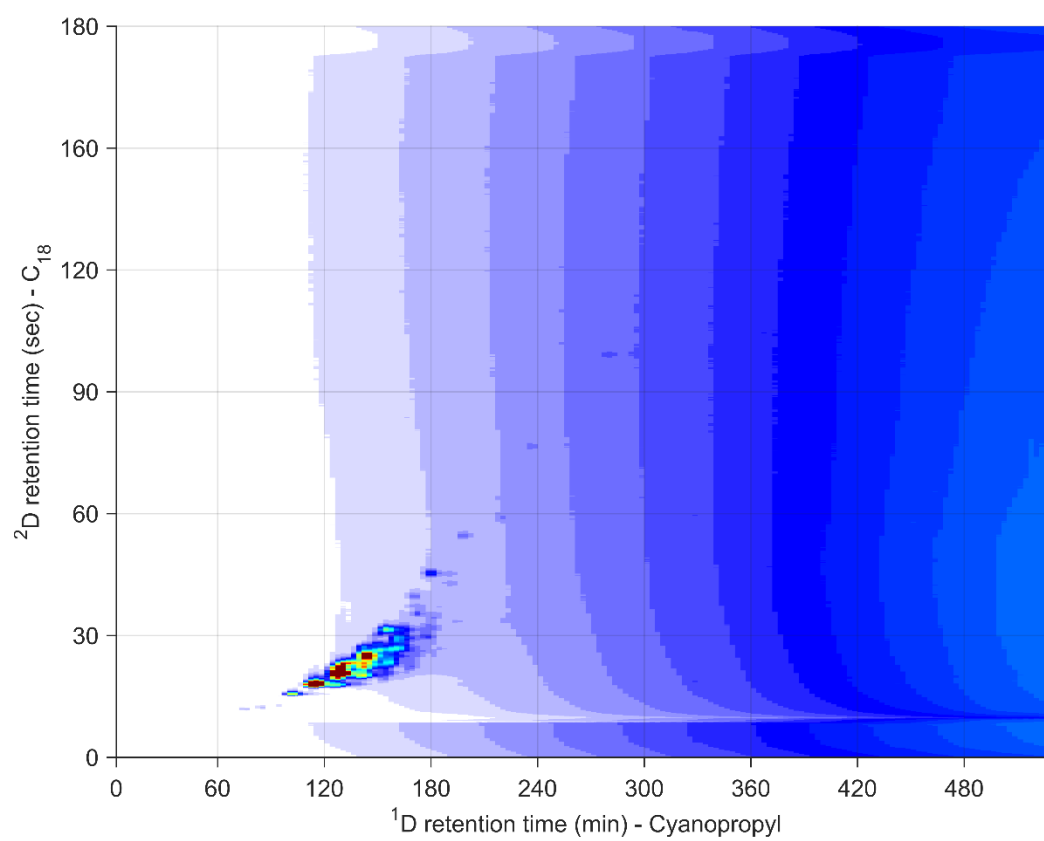


Figure S2.5 – LCxLC-UV chromatograms of the slow separation of HW, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.3.



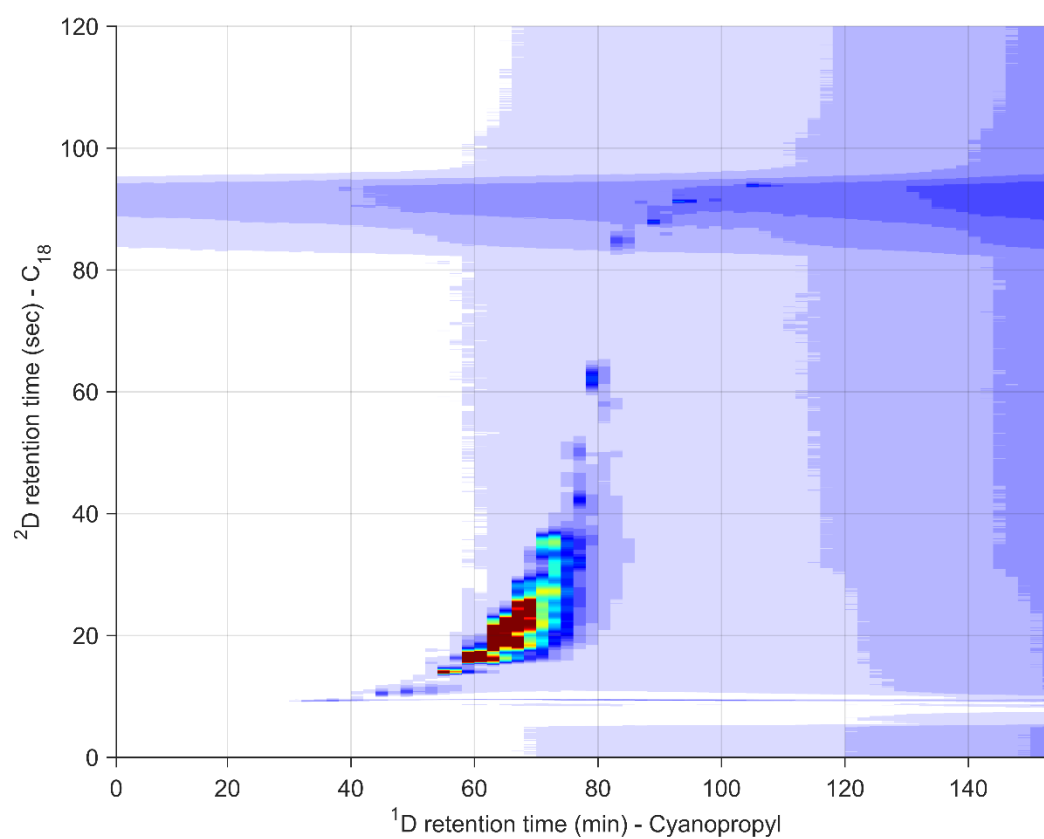


Figure S2.6 – LC×LC-UV chromatograms of the optimized separation of HW, shown at a detection wavelength of 340 nm. The chromatogram was recorded according to method section 2.4.4.

*S3 – Validation results for the optimum method applied to PAH610*

**Table S3.1 – Validation table for the optimum method applied to PAH610. Red coloured rows indicate the peaks for which the verification showed a significant difference between the predicted and experimental data.**

<b>Experimental <sup>1D</sup>t<sub>R</sub> (min)</b>	<b>Predicted <sup>1D</sup>t<sub>R</sub> (min)</b>	<b>Difference (%)</b>	<b>Experimental <sup>2D</sup>t<sub>R</sub> (min)</b>	<b>Predicted <sup>2D</sup>t<sub>R</sub> (min)</b>	<b>Difference (%)</b>
31.20949	32.91626	5.468743	0.183574	0.180096	1.894467
32.08371	34.0448	6.112395	0.16958	0.168921	0.388714
35.52342	37.85154	6.553777	0.174141	0.171703	1.399855
39.80124	41.24555	3.628821	0.190806	0.185737	2.656909
42.72835	44.626	4.441195	0.193948	0.191108	1.464367
44.02376	45.81758	4.074663	0.205036	0.202401	1.285406
53.63123	55.64878	3.76191	0.180017	0.175251	2.647405
48.22152	50.08869	3.872077	0.216489	0.430626	98.91386
48.59181	50.32474	3.566309	0.231473	0.340488	47.09606
49.38012	51.53323	4.360277	0.239663	0.300248	25.27948
57.25835	59.01377	3.0658	0.272235	0.297894	9.425485
56.29424	57.9023	2.856519	0.298323	0.322958	8.257741
62.91351	64.49346	2.511313	0.334585	0.356563	6.568843
63.35919	64.79985	2.273804	0.354908	0.377344	6.321762
64.51378	66.29393	2.759331	0.397589	0.424602	6.794226
64.21263	65.79645	2.466512	0.455769	0.481334	5.609071
71	72.63488	2.302643	0.587183	0.617945	5.238929
71.72433	73.38392	2.313845	0.648974	0.693341	6.836547
80	81.16446	1.45558	0.718433	0.770467	7.242607

*S4 – Performance-test results of <sup>1</sup>D and <sup>2</sup>D columns*

**Table S4.1 – Performance test results of <sup>1</sup>D Biphenyl (BiPh), Cyanopropyl (CN) and Pentafluorophenyl (F5) columns and <sup>2</sup>D Octadecyl-silica (C<sub>18</sub>) and Polymeric Octadecyl-silica (PAH) columns**

<b>Column type</b>	<b>Column ID (mm)</b>	<b>Column Length (mm)</b>	<b>Particle size (µm)</b>	<b>Plate no. of naphthalene 1<sup>st</sup> injection</b>	<b>Plate no. of naphthalene 2<sup>nd</sup> injection</b>	<b>Plate no. of naphthalene 3<sup>rd</sup> injection</b>
CN	2.1	100	3.5	7969	7883	7930
BiPh	3	100	2.6	20268	20470	20564
F5	3	100	2.6	19057	18985	18788
C <sub>18</sub>	3	50	1.8	9748	9850	9803
PAH	3	50	1.8	9575	9474	9576

*S5 – Modifier comparisons for the CN and F5 columns*

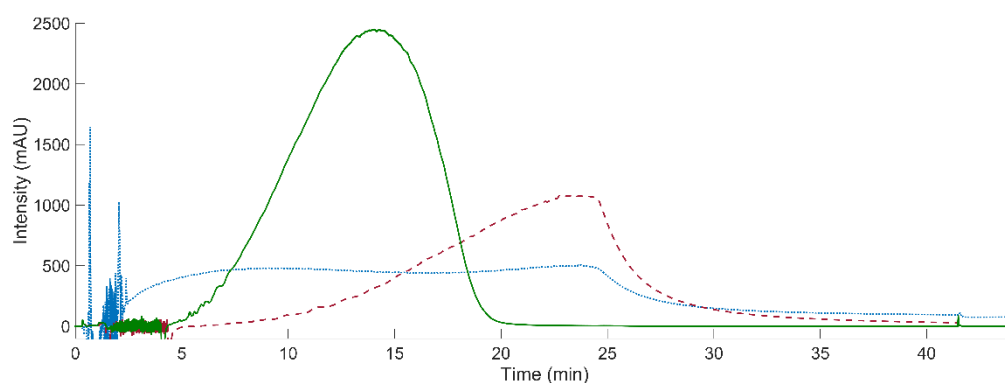


Figure S5.1 – LC-UV chromatogram of an aromatic fraction of maltenes, shown at a detection wavelength of 254 nm, run over a MeOH gradient (red, dashed line); an ACN gradient (blue, dotted line); and a THF gradient (green, solid line) over a CN column. Recorded according to method section 2.4.1.

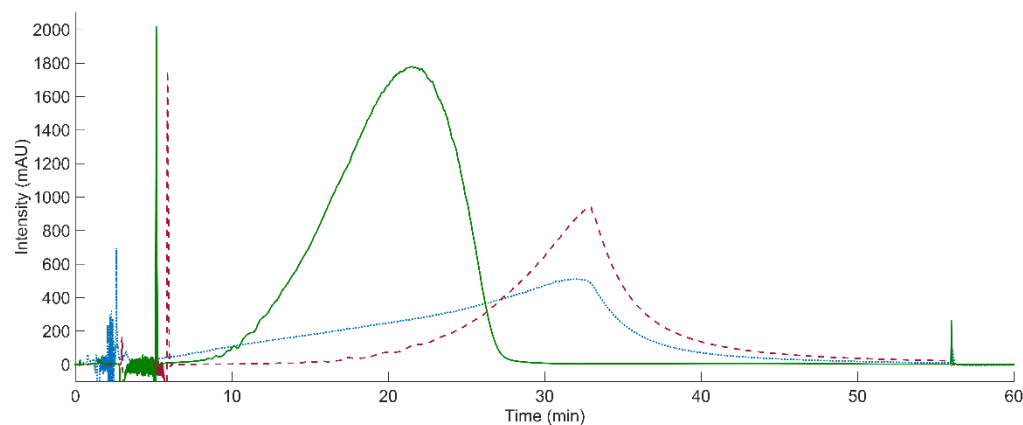


Figure S5.2 – LC-UV chromatogram of an aromatic fraction of maltenes, shown at a detection wavelength of 254 nm, run over a MeOH gradient (red, dashed line); an ACN gradient (blue, dotted line); and a THF gradient (green, solid line) over a F5 column. Recorded according to method section 2.4.1.