Supporting Information

Direct inlet probe mass spectrometry with wavelength selective resonance enhanced photo ionisation

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Keywords: atmospheric pressure laser ionisation (APLI), optical parametric oscillator (OPO), high-resolution mass spectrometry, polycyclic aromatic hydrocarbons (PAH), multiphoton ionisation, direct inlet probe (DIP)

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Table S1: Compound list of the standard mixture M1, including their detectability at the four used wavelengths.

Compound	Sum Formula	Exact mass [Da]	concentration [g/L]	213 nm	225 nm	248 nm	266 nm
Indole	C_8H_7N	117.057849	0.05	no	no	no	no
Naphthalene	$C_{10}H_8$	128.062600	0.04	yes	no	no	yes
Cinnamaldehyde	C_9H_8O	132.057515	0.04	no	no	no	no
1-Napthylamine	$C_{10}H_9N$	143.073499	0.04	yes	yes	yes	no
4-Ethylguaiacol	$C_9H_{12}O_2$	152.083730	0.04	yes	yes	no	yes
Biphenyl	$C_{12}H_{10}$	154.078250	0.04	no	no	no	no
2-Phenylthiophene	$C_{10}H_8S$	160.034672	0.04	no	no	no	no
1H-Benzo[g]indole	$C_{12}H_9N$	167.073499	0.04	yes	yes	yes	yes
2,4,5-Trimethylnaphthalene	$C_{13}H_{14}$	170.109550	0.04	yes	yes	yes	yes
Anthracene	$C_{14}H_{10}$	178.078250	0.04	yes	yes	yes	yes
Acridine	$C_{13}H_9N$	179.073499	0.04	no	no	no	no
2-Phenylindene	$C_{15}H_{12}$	192.093900	0.03	yes	yes	yes	yes
Pyrene	$C_{16}H_{10}$	202.078250	0.02	yes	yes	yes	yes
1,1,2-Trimethylbenz[e]indole	$C_{15}H_{15}N$	209.120449	0.02	yes	no	yes	no
4,6-Dimethyldibenzothiophene	$C_{14}H_{12}S$	212.065972	0.02	yes	yes	yes	yes
9-Nitrophenantrene	$C_{14}H_9NO_2$	223.063329	0.02	no	no	no	no
Naphtho[1,2-b:5,6-b]dithiophene	$C_{14}H_8S_2$	240.006744	0.02	yes	yes	yes	yes
Methylpalmitate	$C_{17}H_{34}O_2$	270.255880	0.02	no	no	no	no
6,13-Pentacenequinone	$C_{22}H_{12}O_2$	308.083730	0.02	no	no	no	no

Table S2: Compound list of the standard mixture M2, including their detectability at the four used wavelengths.

Compound	Sum Formula	Exact mass [Da]	concentration [g/L]	213 nm	225 nm	248 nm	266 nm
Benzofuran	C_8H_6O	118.041865	0.05	no	no	no	no
Azulene	$C_{10}H_8$	128.062600	0.04	yes	no	no	no
2-Methylbenzofuran	C_9H_8O	132.057515	0.04	no	no	no	no
2-Methylthianaphthene	C_9H_8S	148.034672	0.04	no	no	no	no
Acenaphthylene	$C_{12}H_8$	152.062600	0.04	no	no	no	no
1,4-Dimethylnaphthalene	$C_{12}H_{12}$	156.093900	0.04	yes	yes	yes	yes
Eugenol	$C_{10}H_{12}O_2$	164.083730	0.04	yes	no	no	yes
Dibenzofuran	$C_{12}H_8O$	168.057515	0.04	yes	yes	yes	yes
Coniferyl aldehyde	$C_{10}H_{10}O_3$	178.062995	0.04	no	no	no	no
9,10-Dihyroanthracene	$C_{14}H_{12}$	180.093900	0.03	no	no	no	yes
2,6-Diethylnaphthalene	$C_{14}H_{16}$	184.125200	0.03	yes	yes	yes	yes
Ferulic acid	$C_{10}H_{10}O_4$	194.057910	0.03	no	no	no	no
Fluoranthene	$C_{16}H_{10}$	202.078250	0.02	yes	yes	yes	yes
Sinapyl alcohol	$C_{11}H_{14}O_4$	210.089210	0.02	no	no	no	no
Dibenzothiophene-S,S-dioxide	$C_{12}H_8O_2S$	216.024502	0.02	no	no	no	no
Chrysene	$C_{18}H_{12}$	228.093900	0.02	yes	yes	yes	yes
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.093900	0.02	yes	yes	yes	yes
5-alpha-Cholestane	$C_{27}H_{48}$	372.375600	0.02	no	no	no	no

Table S3: Compound list of the standard mixture M3, including their detectability at the four used wavelengths.

Compound	Sum Formula	Exact mass [Da]	concentration [g/L]	213 nm	225 nm	248 nm	266 nm
4-Methylbenzolthiol	C_7H_8S	124.034672	0.04	no	no	no	no
2-Methylindene	$C_{10}H_{10}$	130.078250	0.04	no	no	no	no
Benzothiophene	C_8H_6S	134.019022	0.04	no	no	no	no
2-Methoxyl-4-vinylphenol	$C_9H_{10}O_2$	150.068080	0.04	no	no	no	no
Vanillyl alcohol	$C_8H_{10}O_3$	154.062995	0.04	no	no	no	no
2-Ethylnaphthalene	$C_{12}H_{12}$	156.093900	0.04	yes	yes	yes	yes
Fluorene	$C_{13}H_{10}$	166.078250	0.04	yes	yes	yes	yes
3-Hexylthiophene	$C_{10}H_{16}S$	168.097272	0.04	no	no	no	no
Phenanthrene	$C_{14}H_{10}$	178.078250	0.04	yes	yes	yes	yes
Fluorenone	$C_{13}H_8O$	180.057515	0.03	no	no	no	no
3-Methylphenantrene	$C_{15}H_{12}$	192.093900	0.03	yes	yes	yes	yes
Anthrone	$C_{14}H_{10}O$	194.073165	0.03	yes	no	no	no
1-Phenylnaphthalene	$C_{16}H_{12}$	204.093900	0.02	yes	yes	yes	yes
1,3-Diphenylacetone	$C_{15}H_{14}O$	210.104465	0.02	no	no	no	no
1-Methylpyrene	$C_{17}H_{12}$	216.093900	0.02	yes	yes	yes	yes
Triphenylene	$C_{18}H_{12}$	228.093900	0.02	yes	yes	yes	yes
Benzo[a]pyrene	$C_{20}H_{12}$	252.093900	0.02	yes	yes	yes	yes
Dibenzo[a,b]anthracene	$C_{22}H_{14}$	278.109550	0.02	yes	yes	yes	yes

Table S4: Compound list of the standard mixture M4, including their detectability at the four used wavelengths.

Compound	Sum Formula	Exact mass [Da]	concentration [g/L]	213 nm	225 nm	248 nm	266 nm
Guaiacol	$C_7H_8O_2$	124.052430	0.04	no	no	no	no
2-Methylindole	C_9H_9N	131.073499	0.04	yes	yes	no	no
2-Methylnaphthalene	$C_{11}H_{10}$	142.078250	0.04	yes	yes	no	yes
Vanillin	$C_8H_8O_3$	152.047345	0.04	no	no	no	no
Acenaphthene	$C_{12}H_{10}$	154.078250	0.04	yes	yes	no	yes
2-Naphthalenethiol	$C_{10}H_8S$	160.034672	0.04	no	no	no	no
Carbazole	$C_{12}H_9N$	167.073499	0.04	yes	yes	yes	yes
Diphenylmethane	$C_{13}H_{12}$	168.093900	0.04	no	no	no	no
1,1-Diphenylethylene	$C_{14}H_{12}$	180.093900	0.03	no	no	no	no
Dibenzothiophene	$C_{12}H_8S$	184.034672	0.03	yes	yes	no	no
2-Methylanthracene	$C_{15}H_{12}$	192.093900	0.03	yes	yes	yes	yes
3-Ethylcarbazole	$C_{14}H_{13}N$	195.104799	0.03	yes	yes	yes	yes
Anthraquinone	$C_{14}H_8O_2$	208.052430	0.02	no	no	no	no
2-Nitrofluorene	$C_{13}H_9NO_2$	211.063329	0.02	no	no	no	no
2-Methylanthraquinone	$C_{15}H_{10}O_2$	222.068080	0.02	no	no	no	no
Retene	$C_{18}H_{18}$	234.140850	0.02	yes	yes	yes	yes
5,12-Naphthacenquinone	$C_{18}H_{10}O_2$	258.068080	0.02	no	no	no	no
Coronene	$C_{24}H_{12}$	300.093900	0.02	yes	yes	yes	yes

Table S5: Settings for sum formula annotation with CERES. #N, #O and #S were set to the lowest values that provided broad coverage of the sample while maintaining a low number of falsely annotated peaks.

	Asphaltenes	**CPC/Crude Oil**	**Shale Oil**	**MGO**	**Polystyrene**	**Crumb Rubber**
#C	2-50	2-50	2-50	2-50	2-50	2-50
#H	2-100	2-100	2-100	2-100	2-100	2-100
#N	0-1	0-1	0-1	0-1	0-1	0-3
#O	0-2	0-2	0-2	0-1	0-2	0-3
#S	0-2	0-2	0-3	0-1	0-1	0-3
H/C Ratio	0.4-2.4	0.4-2.4	0.4-2.4	0.4-2.4	0.4-2.4	0.4-2.4
DBE range	0-30	0-30	0-30	0-30	0-30	0-30
mass range	100-1000	100-1000	100-1000	100-1000	100-1000	100-1000

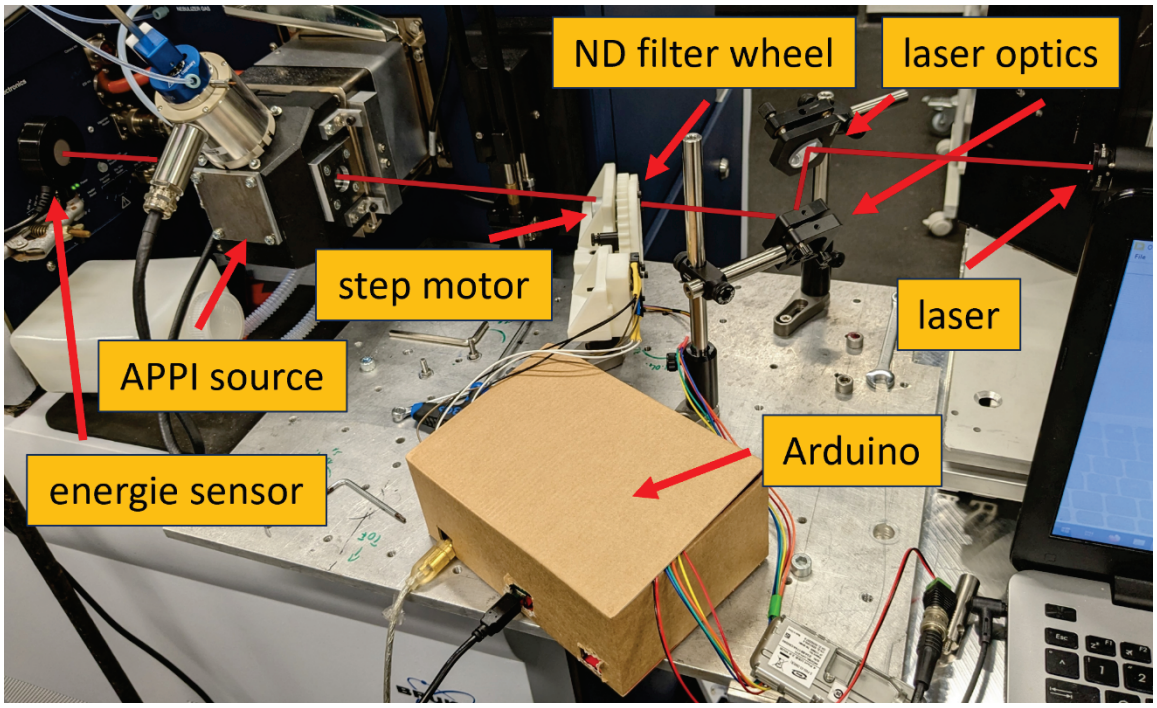

Figure S01: Photographic depiction of the overall laser setup used in this study.

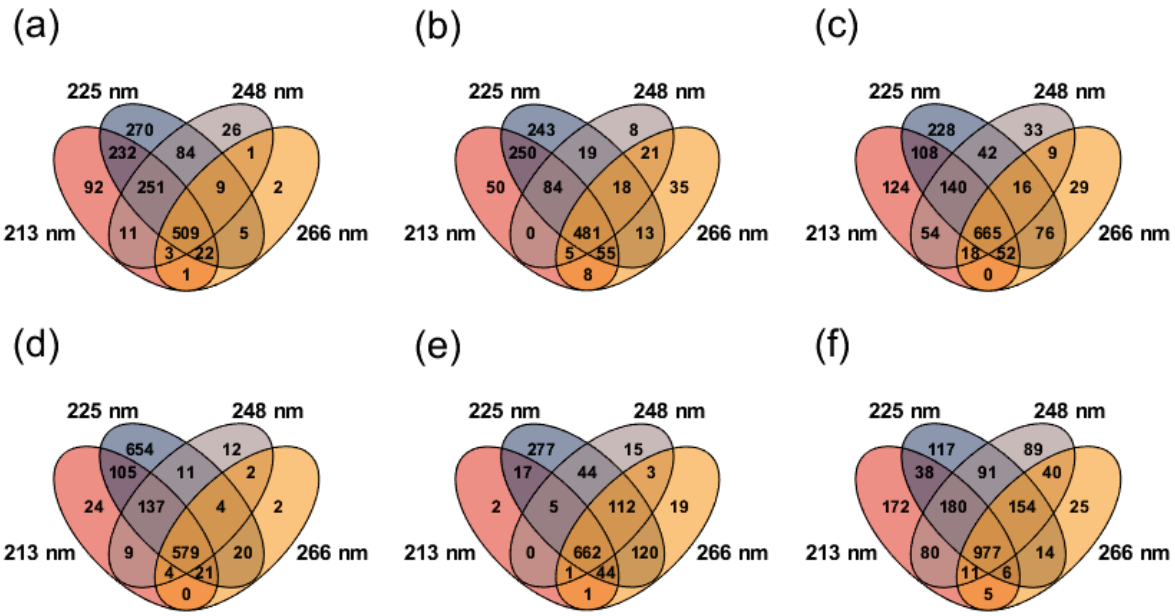

Figure S02: Venn Diagram of assigned compounds for (a) MGO, (b) oil blend, (c) parent crude oil, (d) asphaltene, (e) desulfurized asphaltene, and (f) shale oil at different wavelengths.

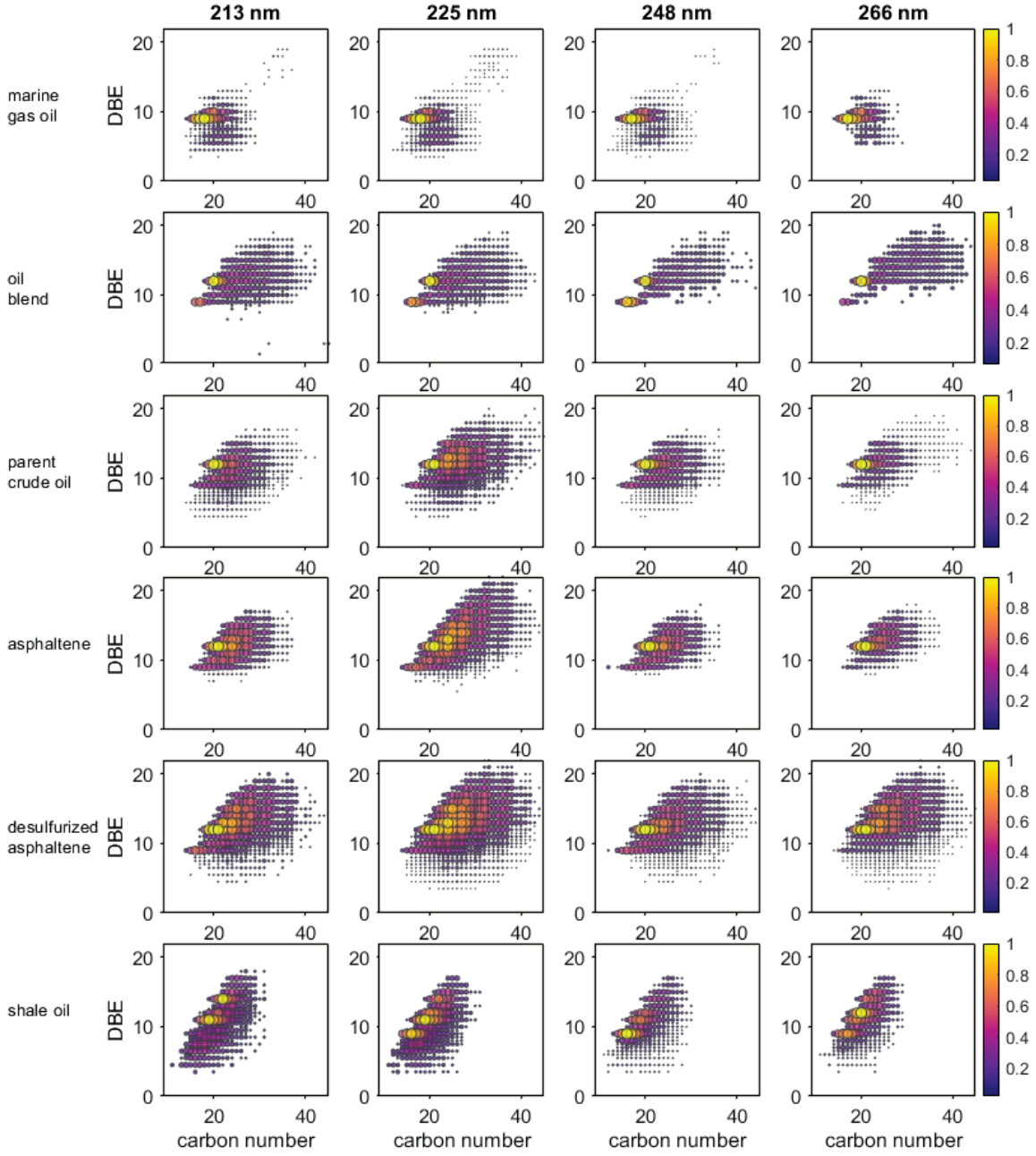

Figure S03: DBE vs carbon number plots for the CHN-class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm, with the relative intensities of each species in a measurement.

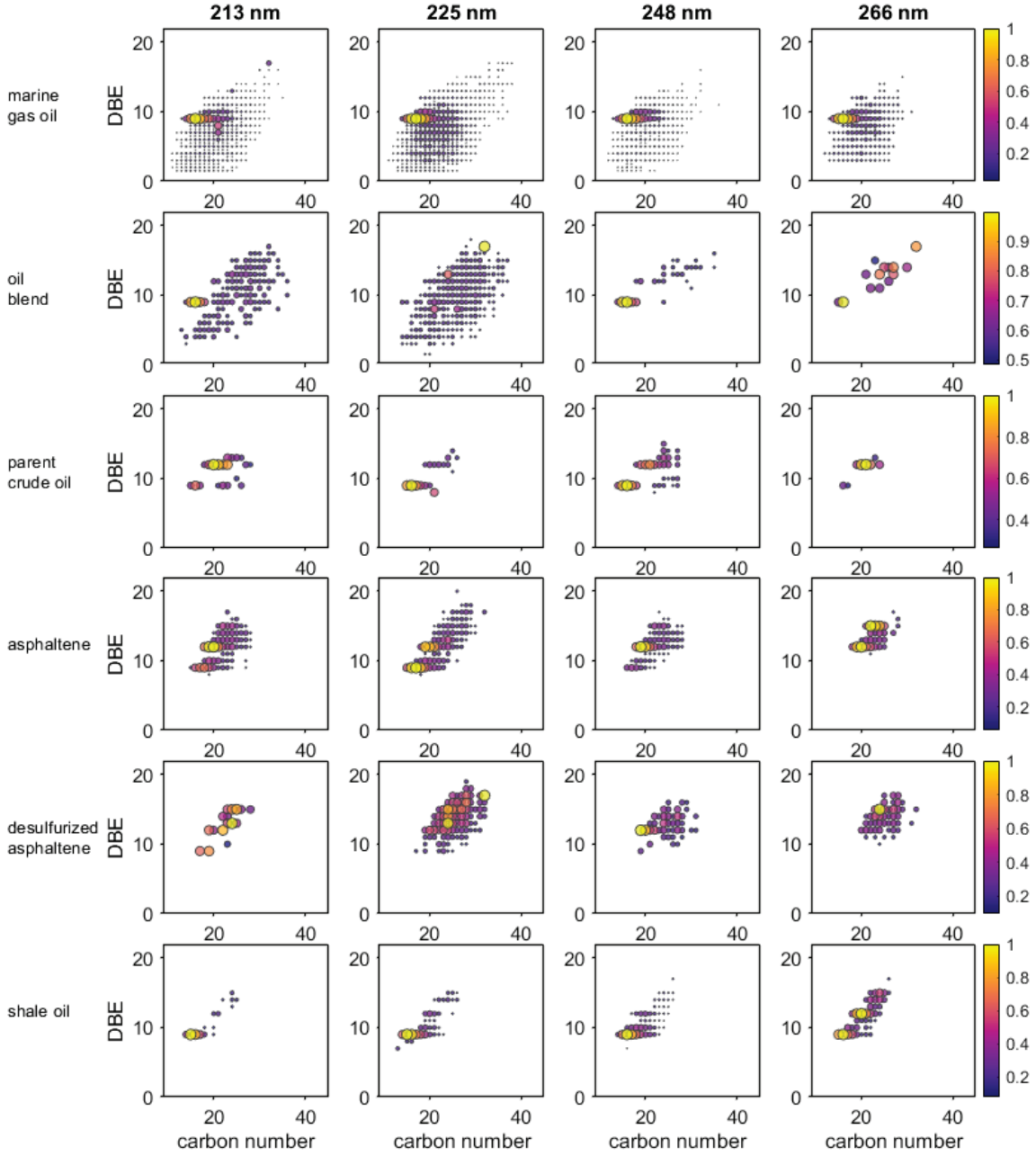

Figure S04: DBE vs carbon number plots for the CHO-class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm, with the relative intensities of each species in a measurement.

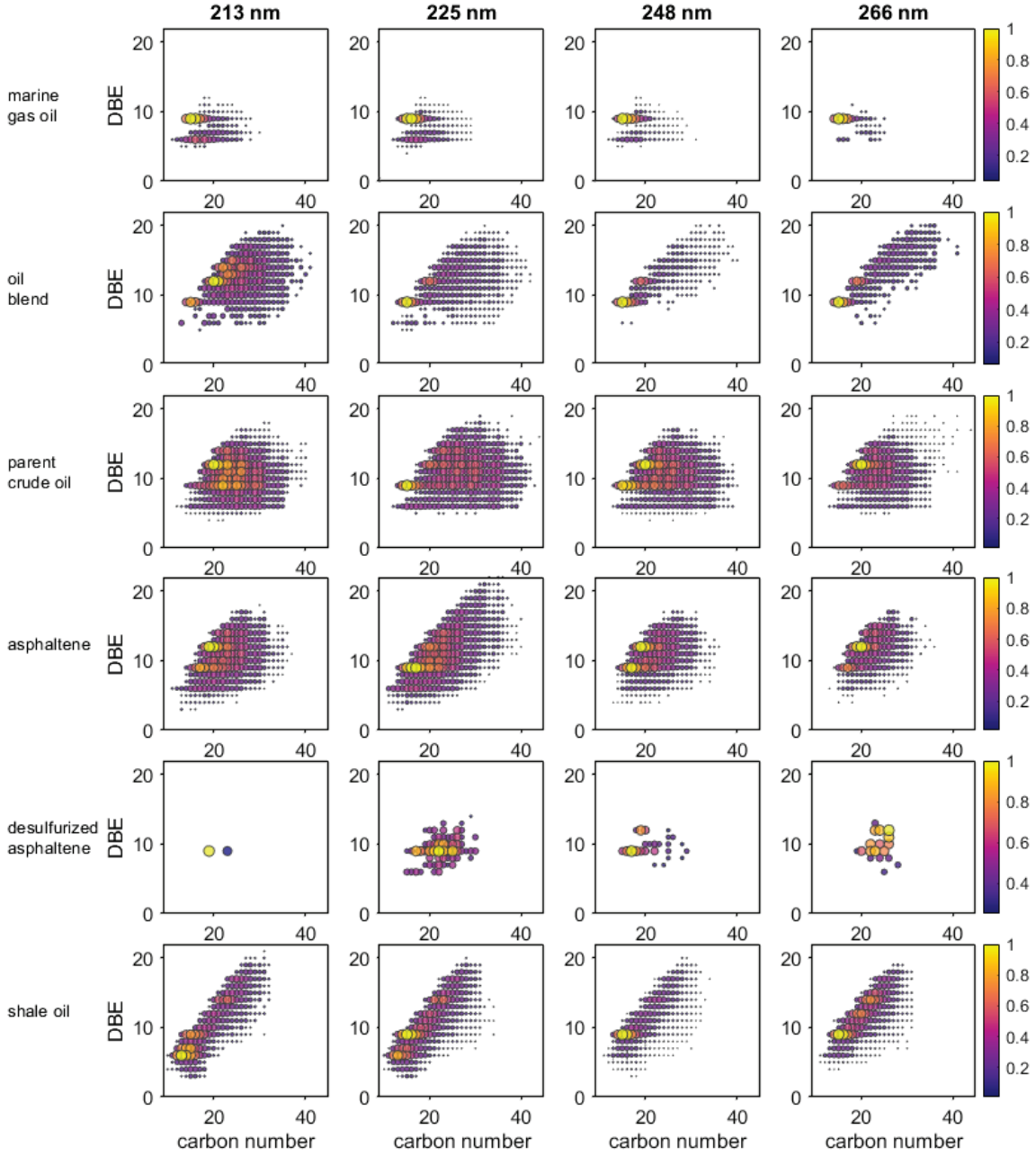

Figure S05: DBE vs carbon number plots for the CHS-class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm, with the relative intensities of each species in a measurement.

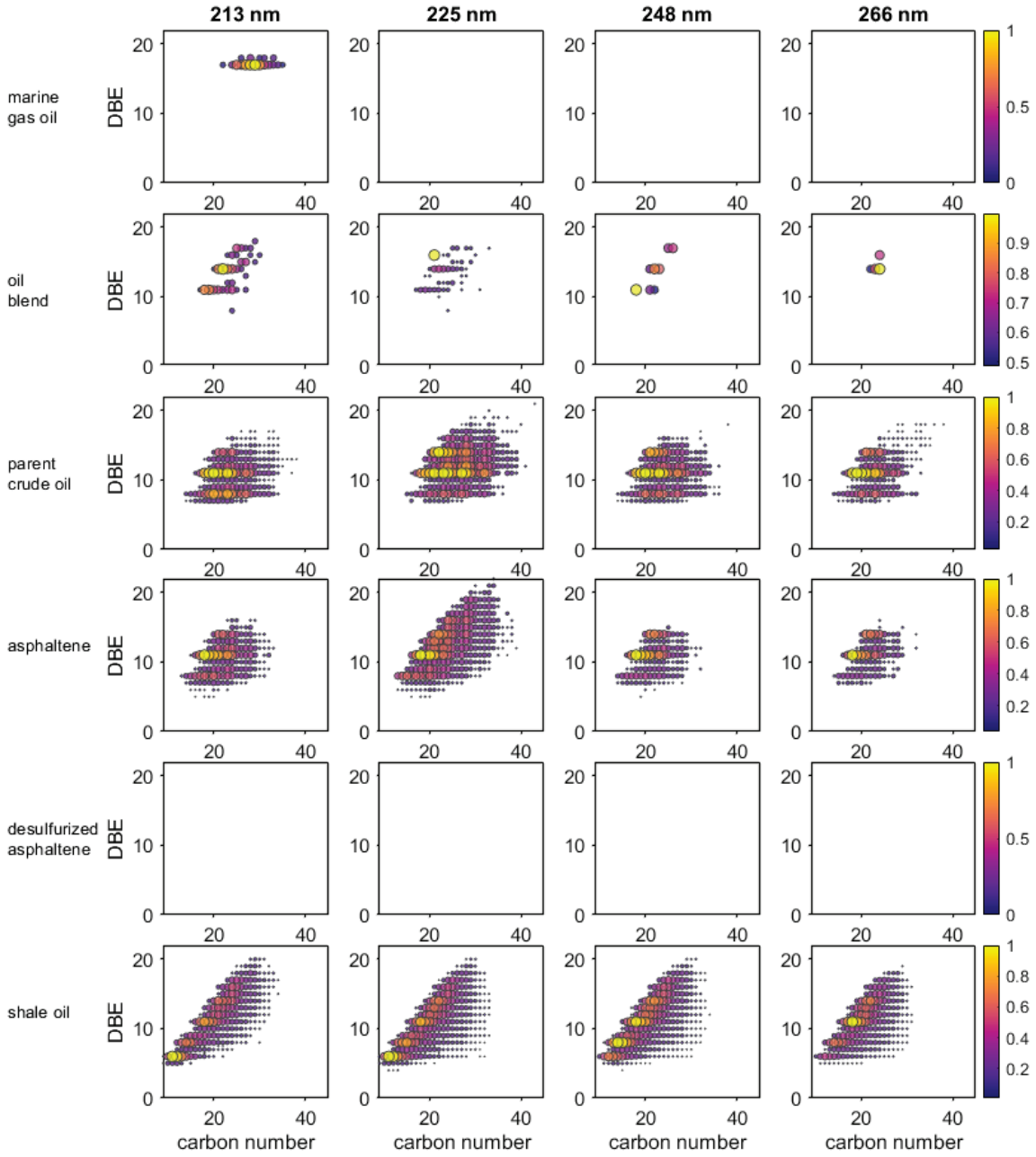

Figure S06: DBE vs carbon number plots for the CHS2-class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm, with the relative intensities of each species in a measurement.

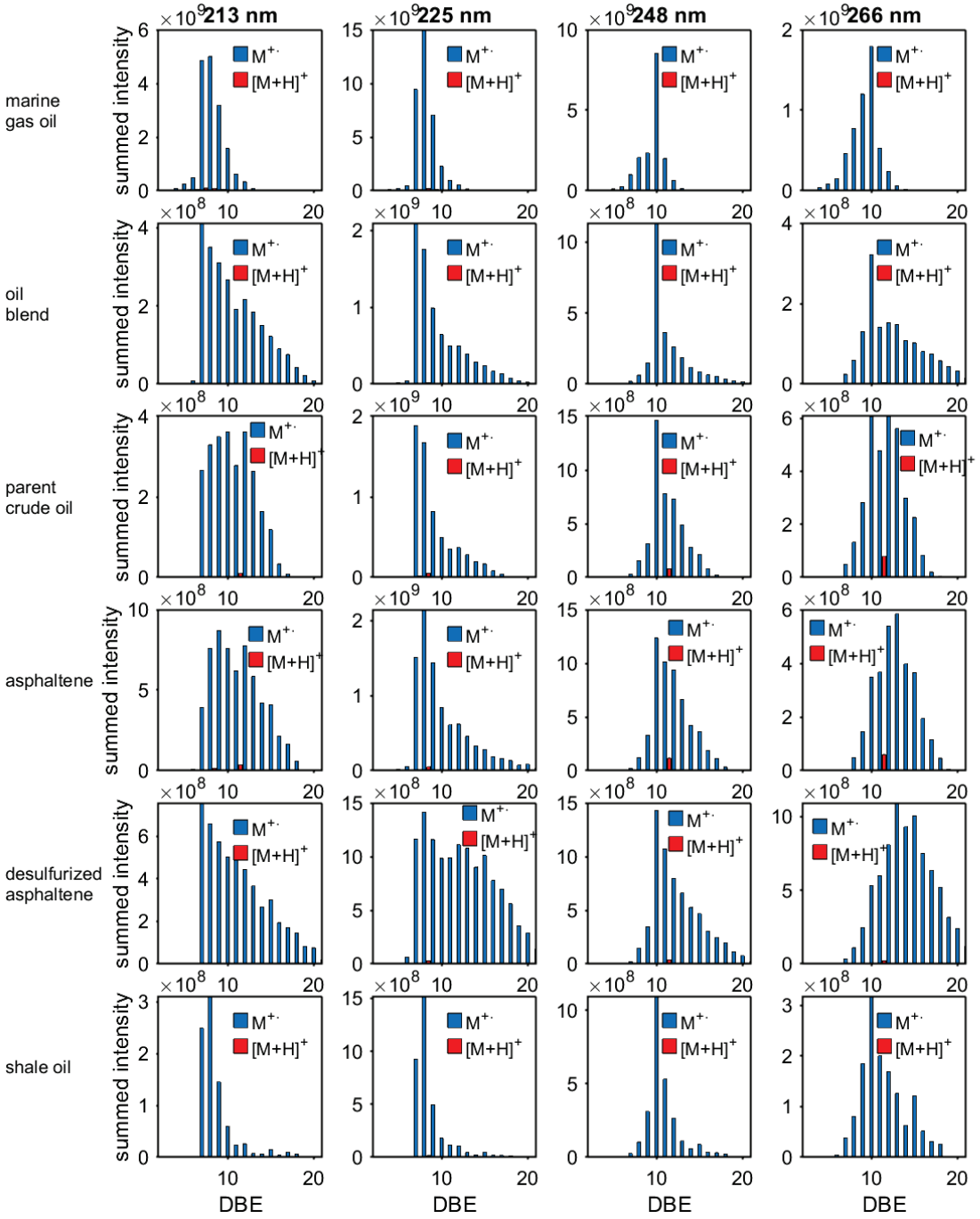

Figure S07: DBE Distribution of the CH class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm. The red bars represent even electron species, while the blue ones represent odd electron species as visual guidance.

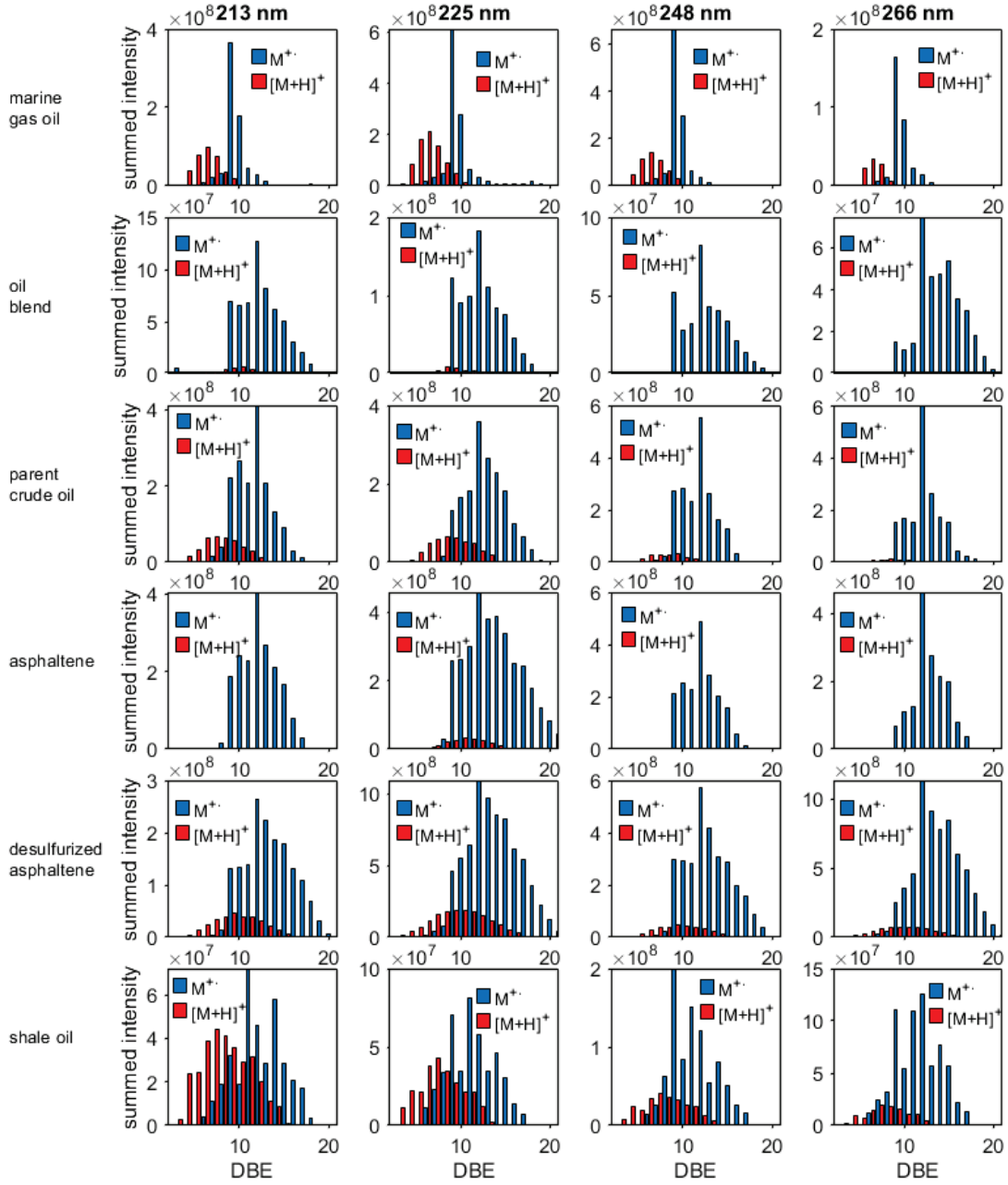

Figure S08: DBE Distribution of the CHN class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm. The red bars represent even electron species, while the blue ones represent odd electron species as visual guidance.

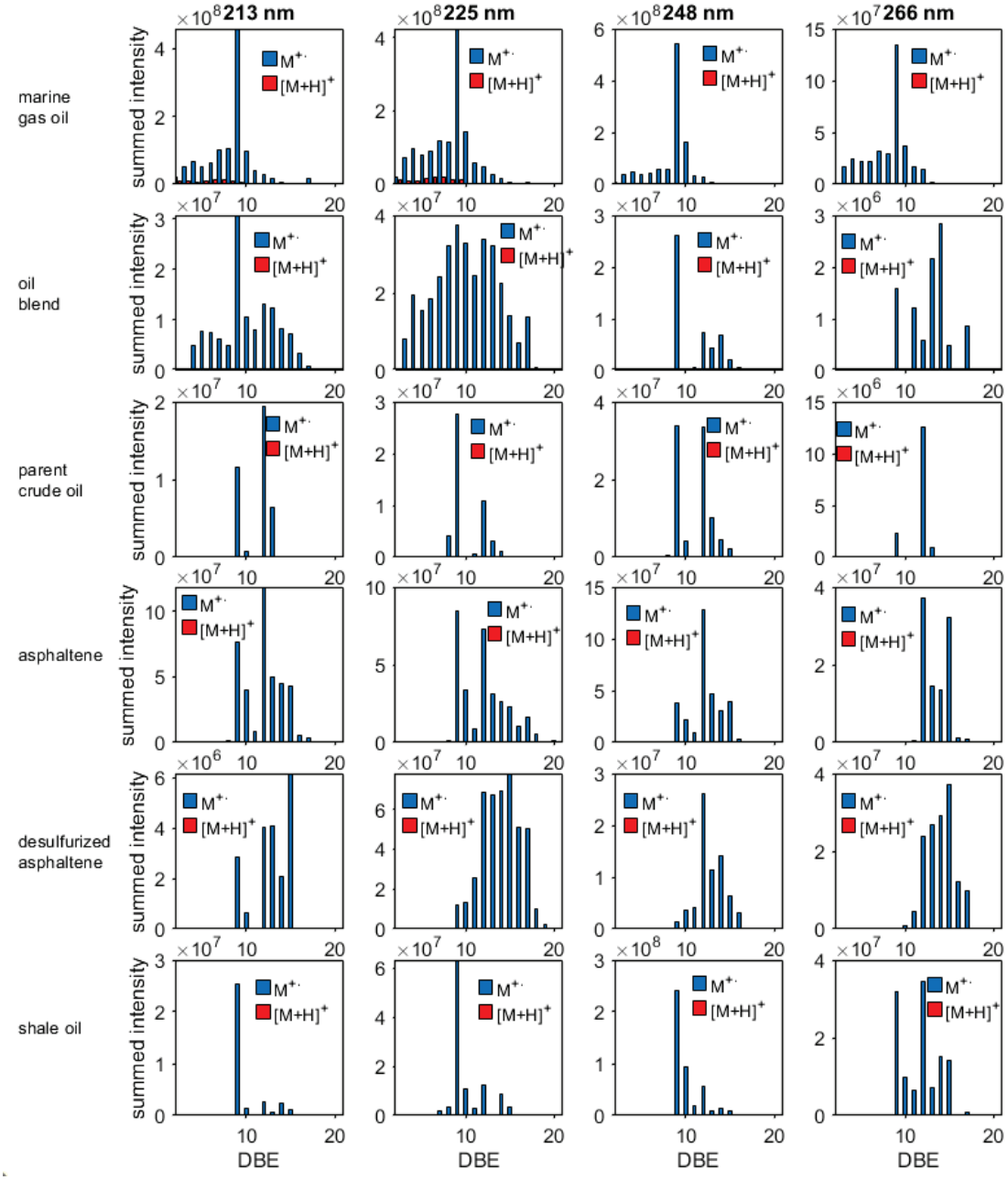

Figure S09: DBE Distribution of the CHO class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm. The red bars represent even electron species, while the blue ones represent odd electron species as visual guidance.

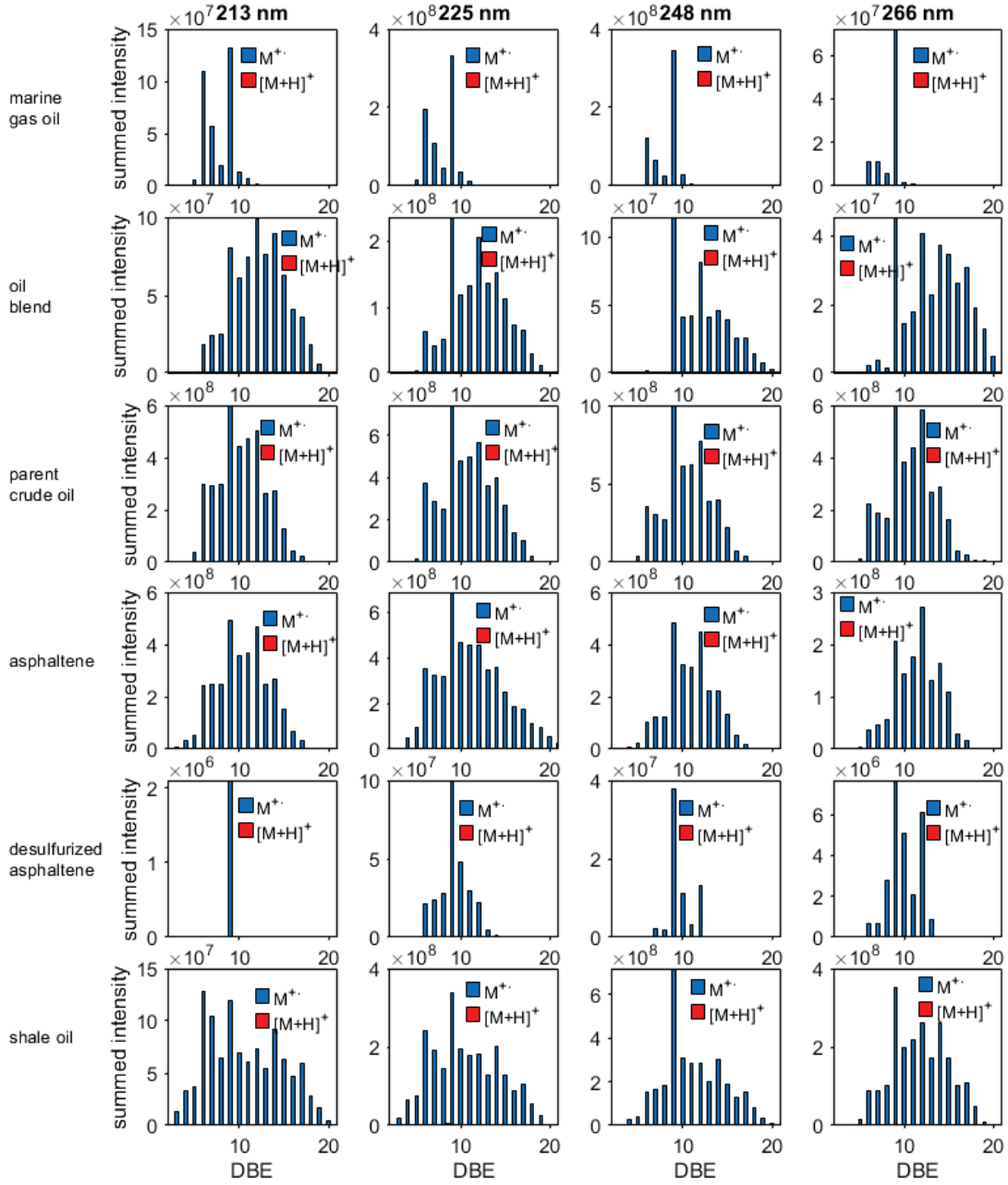

Figure S10: DBE Distribution of the CHS class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm. The red bars represent even electron species, while the blue ones represent odd electron species as visual guidance.

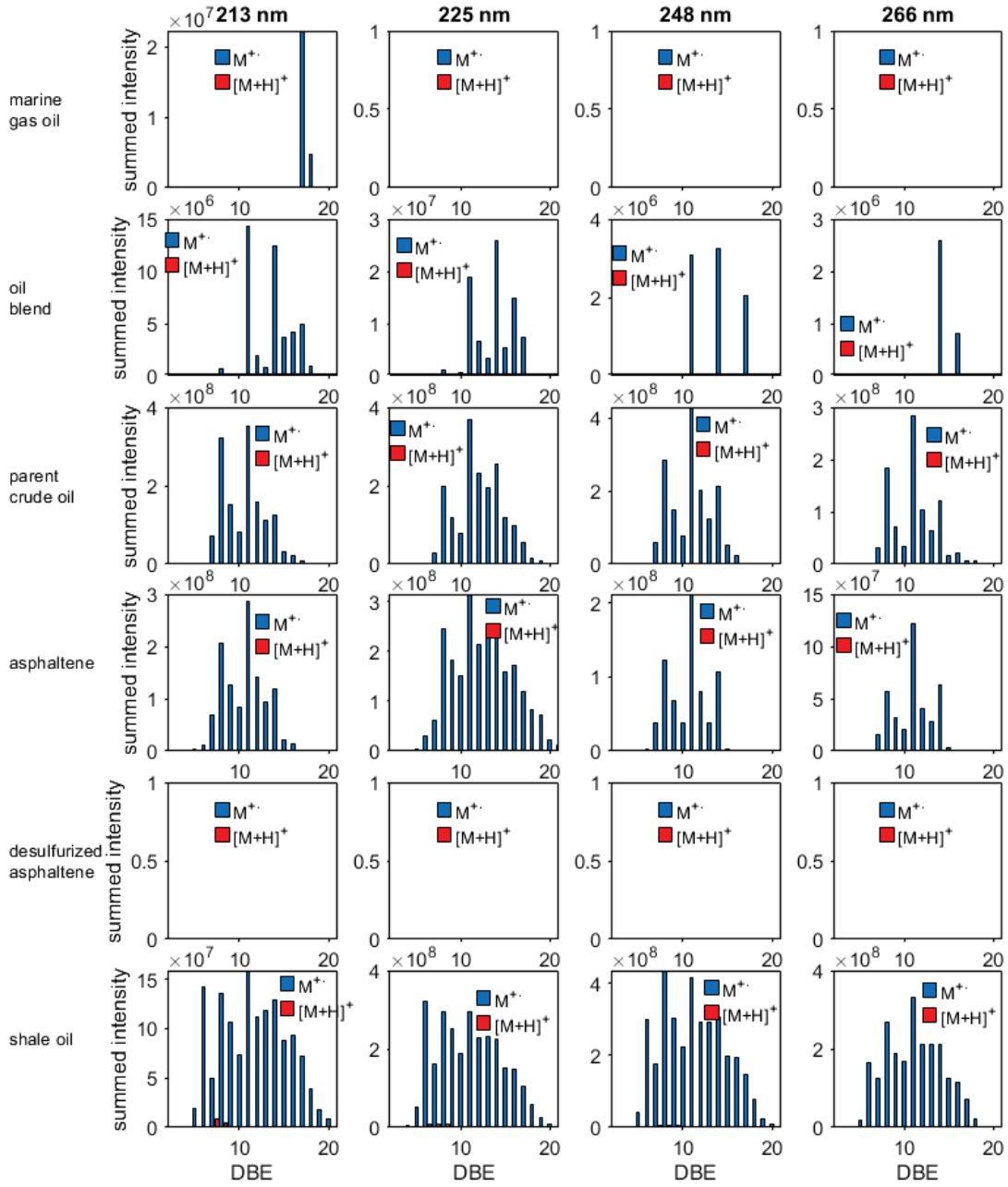

Figure S11: DBE Distribution of the CHS_2 class of the fossil oil samples measured at, going from left to right, 213 nm, 225 nm, 248 nm, and 266 nm. The red bars represent even electron species, while the blue ones represent odd electron species as visual guidance.

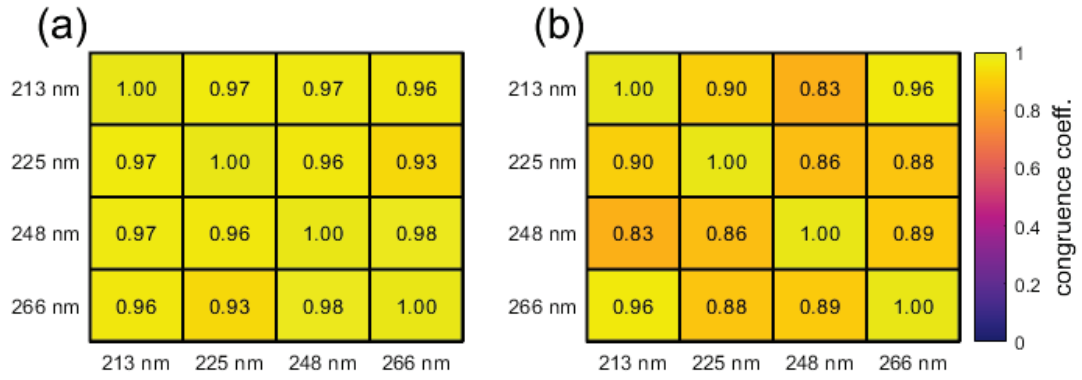

Figure S12: Congruence coefficients between polymer samples measured at different wavelengths for (a) polystyrene and (b) rubber.

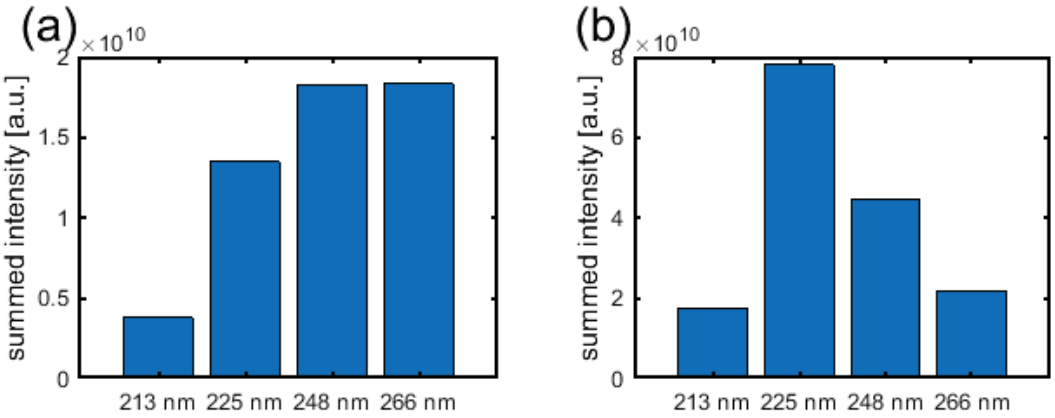

Figure S13: Total ion intensities of polymer samples measured at different wavelengths for (a) polystyrene and (b) rubber.