Electronic Supplementary Material (ESI) for Analyst.

Supporting Information for: Quantification of Isomerically Summed Hydrocarbon Contributions to Crude Oil by Carbon Number, Double Bond Equivalent, and Aromaticity using Gas Chromatography with Tunable Vacuum Ultraviolet Ionization

Jeremy A. Nowak[*×], *Robert J. Weber*[ǂ], *Allen H. Goldstein*[ǂ†]

[×]Department of Chemistry, [ǂ]Department of Environmental Science, Policy and Management, and

[†]Department of Civil and Environmental Engineering, University of California, Berkeley,

California 94705, United States

Contents

	Ratio Aromatic: Total EI-MS	Ratio Aromatic: Total Tunable VUV

$C_{16}H_{26}$ (N_{DBE}=4)	0.29 ± 0.04	0.27 ± 0.06
$C_{16}H_{24}$ (N_{DBE}=5)	0.48 ± 0.07	0.46 ± 0.05
$C_{16}H_{22}$ (N_{DBE}=6)	0.50 ± 0.03	0.48 ± 0.02
$C_{20}H_{34}$ (N_{DBE}=4)	0.11 ± 0.08	0.16 ± 0.04
$C_{20}H_{32}$ (N_{DBE}=5)	0.21 ± 0.04	0.31 ± 0.08
$C_{20}H_{30}$ (N_{DBE}=6)	0.23 ± 0.06	0.39 ± 0.03
$C_{24}H_{42}$ (N_{DBE}=4)	0.08 ± 0.02	0.13 ± 0.01
$C_{24}H_{40}$ (N_{DBE}=5)	0.17 ± 0.08	0.25 ± 0.02
$C_{24}H_{38}$ (N_{DBE}=6)	0.11 ± 0.05	0.31 ± 0.02

Table S-1. Ratio of aromatic components to total aromatic plus aliphatic components (± standard deviations) of isomerically summed hydrocarbon molecular formulas in the North Sea oil measured by traditional GCxGC-EI-MS versus by tunable GCxGC-VUV-TOF. Hydrocarbons containing 16, 20, or 24 carbon atoms and double bond equivalents of 4, 5, and 6, which could contain either 1 or 0 aromatic rings, are included to illustrate the increased fraction of isomers which are not measured using EI-MS as the chemical complexity increases.

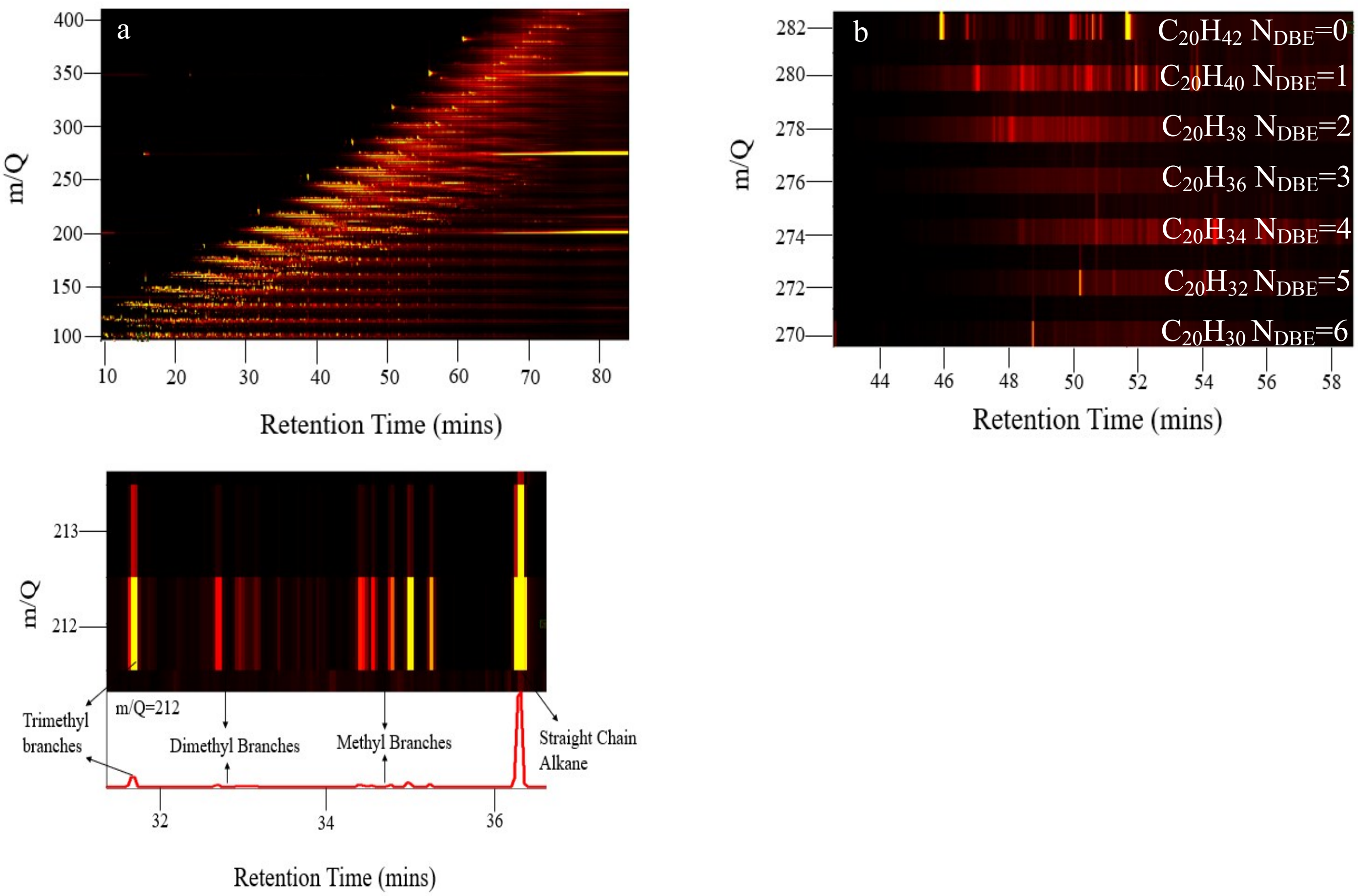


Figure S-1. (a) Complete GCxGC-VUV-TOF chromatogram at 10.5 eV ionization energy of molecular ion mass versus first dimension retention time of the Gulf of Mexico oil. (b) Mass spectrum as a function of chromatographic retention time for the isomers of hydrocarbons with 20 carbon atoms in the Gulf of Mexico oil, showing their classification by mass and N_{DBE} under 10.5 eV VUV ionization. N_{DBE}=0 represents alkanes and N_{DBE}=6 represents a mixture of hexacycloalkanes and aromatic species. (c) Single ion chromatogram (SIC) of pentadecane (m/Q=212, $C_{15}H_{32}$) of the Gulf of Mexico oil, where the straight-chain alkane and its branched isomers are clearly distinguished.

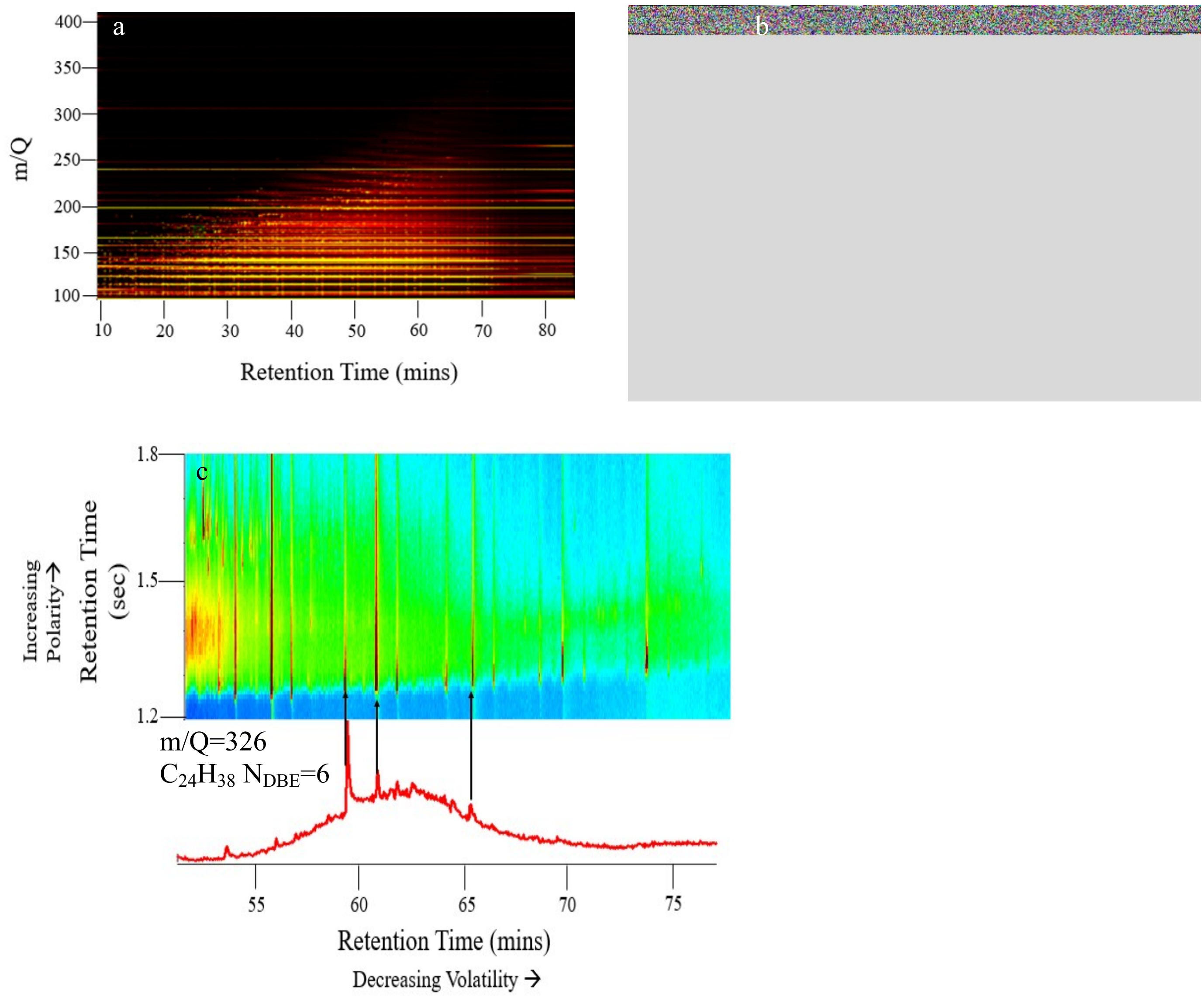


Figure S-2. (a) Complete GCxGC-EI-TOF chromatogram at 70 eV ionization energy of mass versus first dimension retention time of the Gulf of Mexico oil. (b) Complete GCxGC-VUV-TOF chromatogram at 10.5 eV ionization energy of molecular ion mass versus first dimension retention time of the Gulf of Mexico oil. (c) In the GCxGC-EI-MS total ion chromatogram (top), only a few most concentrated isomers are identifiable as individual peaks corresponding to peaks in the single ion GC-VUV-MS chromatogram of m/Q=326 ($C_{24}H_{38}$ N_{DBE}=6) (bottom). Most of the signal for $C_{24}H_{38}$ is from the extremely large number of unresolved isomers eluting between 55 and 70 minutes, which are not separable using GCxGC-EI-MS. GC-VUV-TOF represents these compounds as a single chromatographic trace using the molecular ion, allowing quantification of the sum of all isomers for this carbon number and double bond equivalent by integrating across the signal.

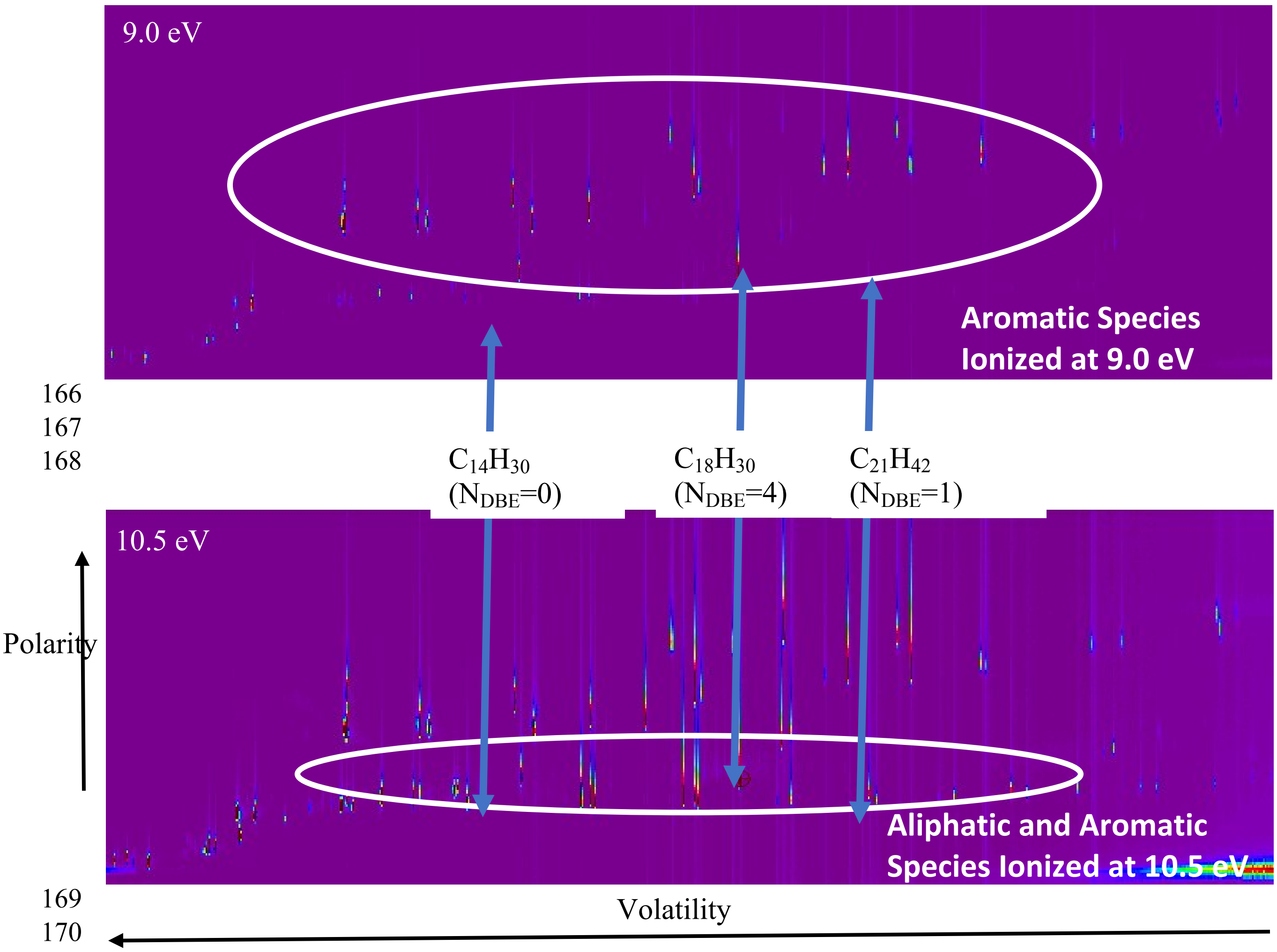
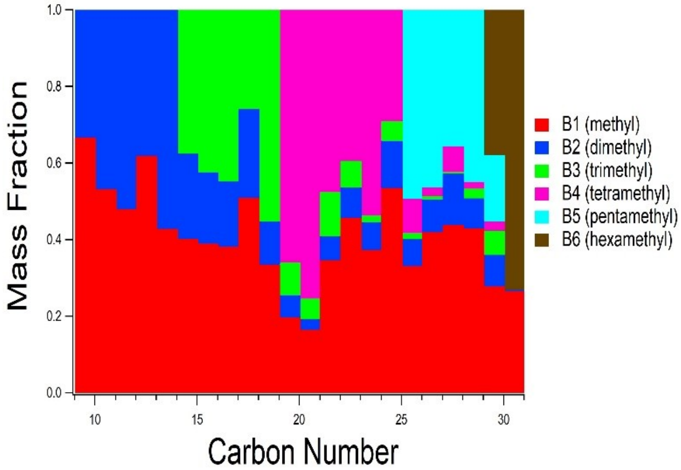


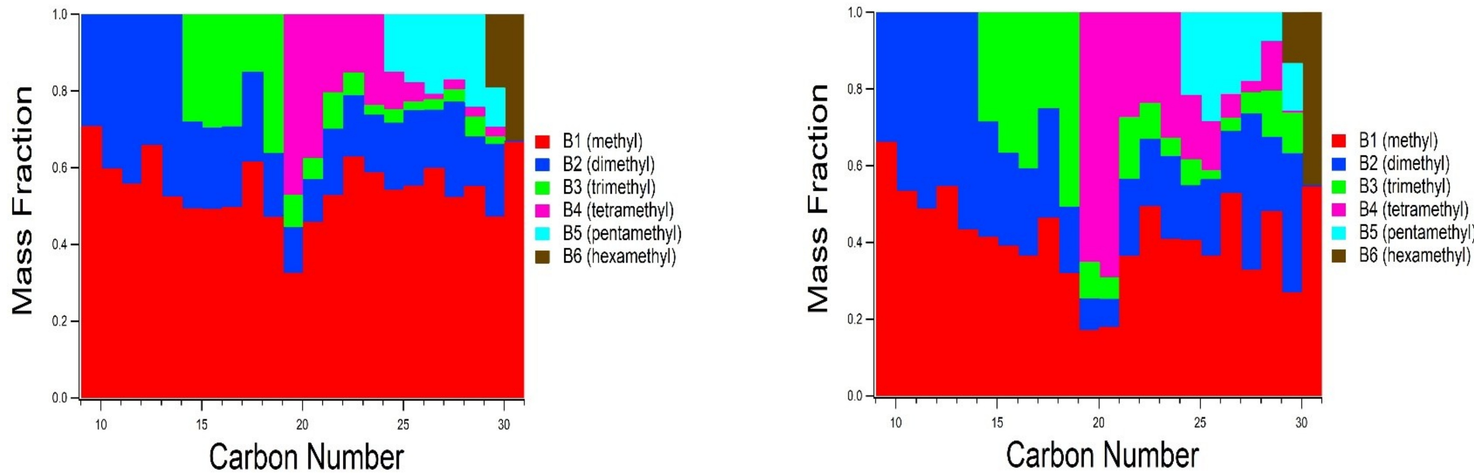
Figure S-3. Two-dimensional chromatograms of a known standard hydrocarbon mixture consisting of both aliphatic (labeled N_{DBE}=0 or 1) and aromatic species (labeled N_{DBE}=4), analyzed at 9.0 eV and 10.5 eV ionization energies. Tunable VUV ionizes hydrocarbons depending on molecular structure, with the aromatic species selectively ionized at 9.0 eV.

a) Azerbaijan b) North Sea



c) Texas

Figure S-4. Isomerically summed mass fractions of the branched alkanes as a function of carbon



number and degree of branching for oils from a) Azerbaijan, b) North Sea, c) Texas, and d) Gulf of Mexico.

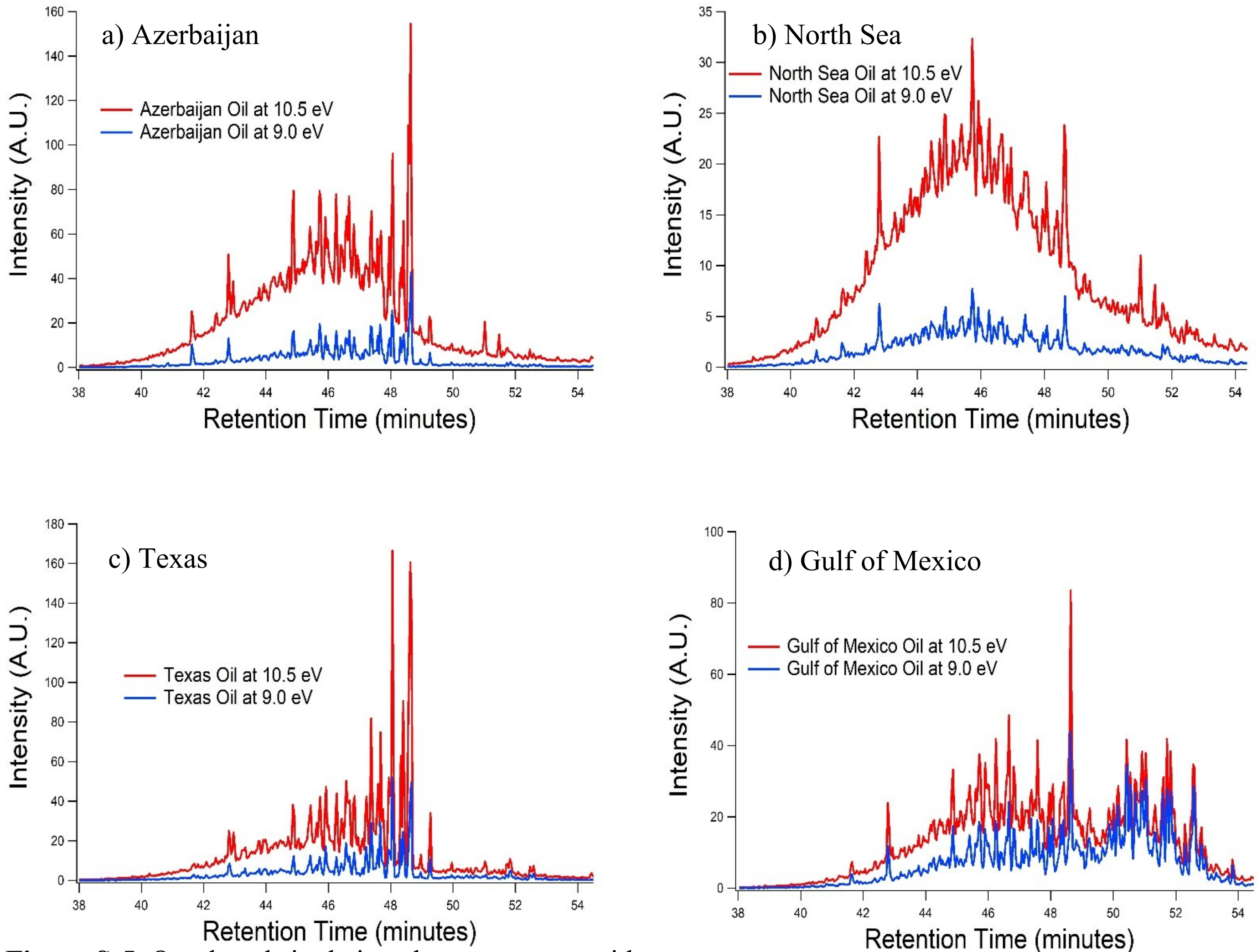


Figure S-5. Overlayed single ion chromatograms with arbitrary units of intensity (A.U.) at 9.0 eV and 10.5 eV ionization energies for $C_{18}H_{30}$ (N_{DBE}=4, m/Q=246) for oils from a) Azerbaijan, b) North Sea, c) Texas, and d) Gulf of Mexico.

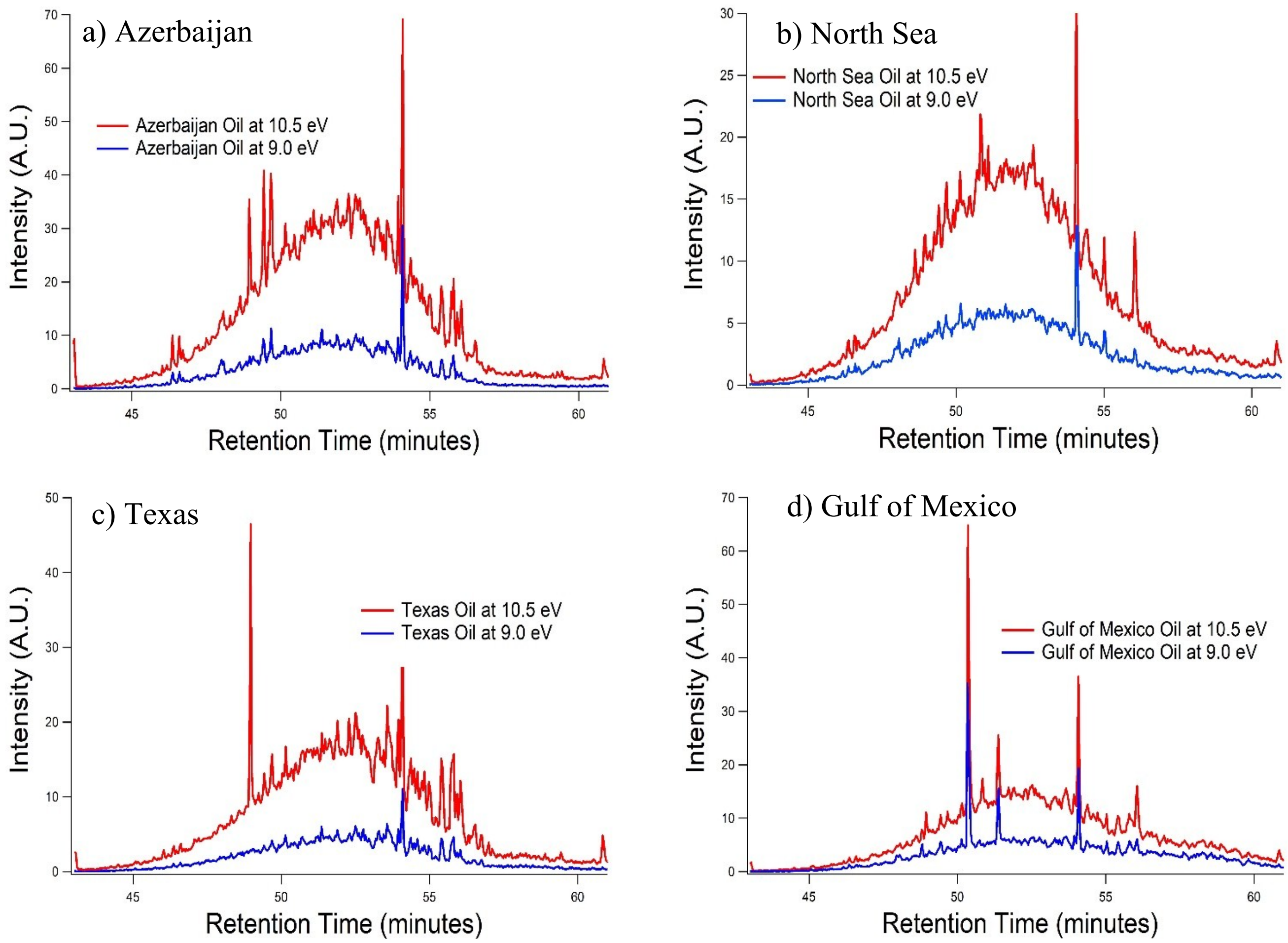


Figure S-6. Overlayed single ion chromatograms with arbitrary units of intensity (A.U.) at 9.0 and 10.5 eV ionization energies for $C_{20}H_{32}$ (N_{DBE}=5, m/Q=272) for oils from a) Azerbaijan, b) North Sea, c) Texas, and d) Gulf of Mexico.

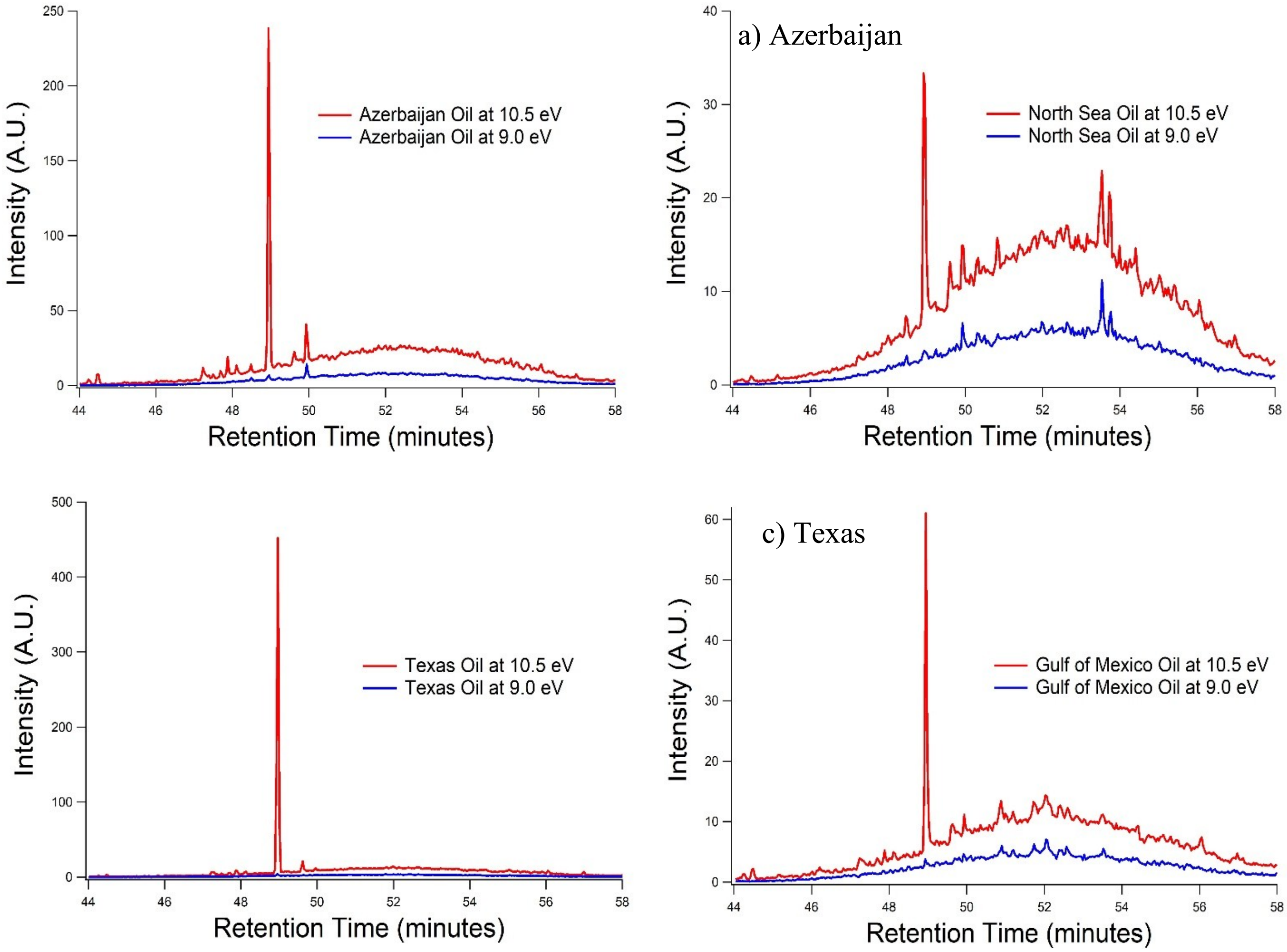


Figure S-7. Overlayed single ion chromatograms with arbitrary units of intensity (A.U.) at 9.0 and 10.5 eV ionization energies for $C_{20}H_{30}$ (N_{DBE}=6, m/Q=270) for oils from a) Azerbaijan, b) North Sea, c) Texas, and d) Gulf of Mexico. The signal present at ~49 minutes in all four oils is that of the ^{13}C isotope of the C_{19} alkane, which is ionized in the 10.5 eV runs, but not in the 9.0 eV runs.

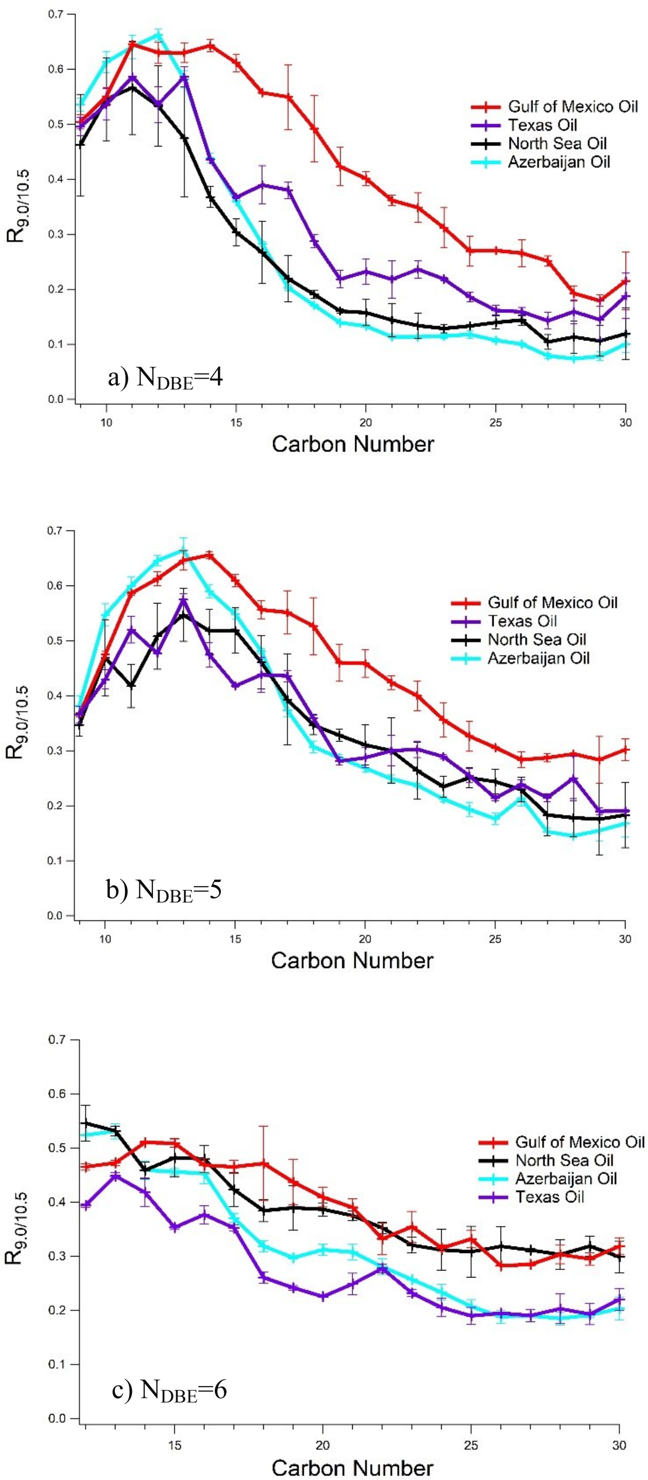


Figure S-8. Ratio of signal responses at 9.0 and 10.5 eV ionization energies ($R_{9.0/10.5}$) as a function of carbon number for oils from Azerbaijan, North Sea, Texas, and Gulf of Mexico, indicated by color, in three classes of double bond equivalents: N_{DBE}=4, 5, and 6 (a, b, and c, respectively).

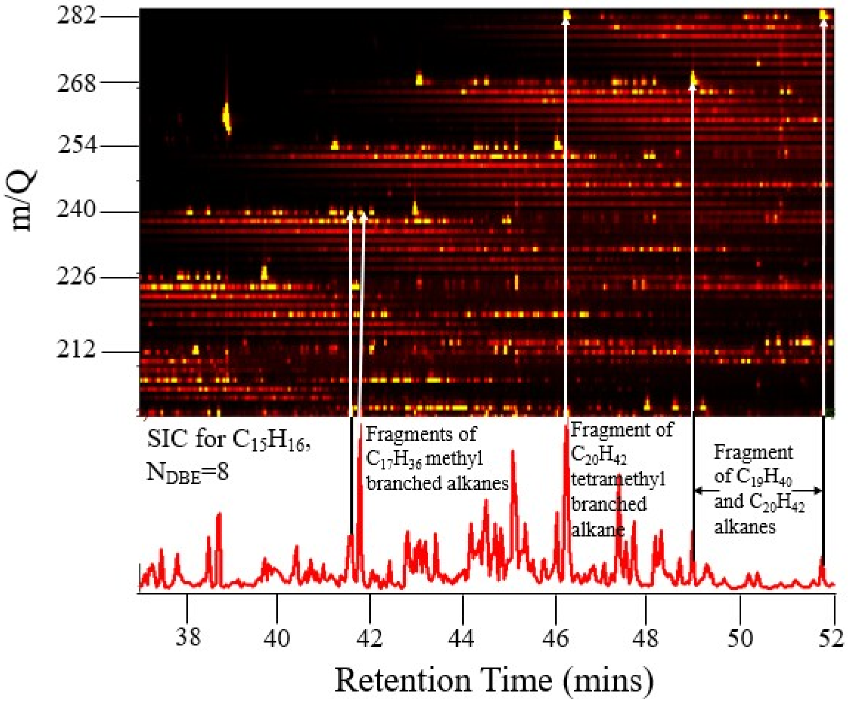


Figure S-9. Single ion chromatogram (SIC) of m/Q=196 (equivalent to $C_{15}H_{16}$, N_{DBE}=8) and mass spectrum versus retention time chromatogram at 10.5 eV. The SIC includes signal from $C_{15}H_{16}$ isomers and aliphatic fragments of higher molecular weight species (e.g. $C_{17}H_{36}$, $C_{19}H_{40}$, $C_{20}H_{42}$).

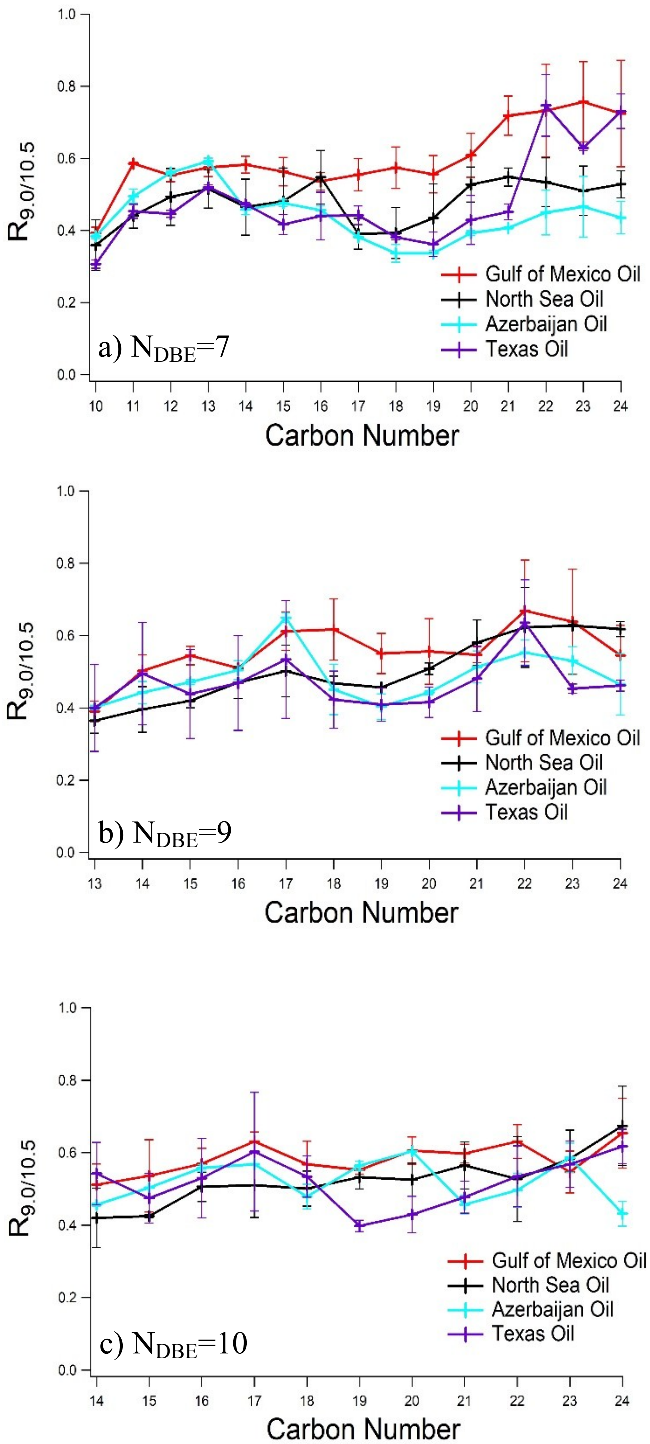


Figure S-10. Ratio of signal responses at 9.0 and 10.5 eV ionization energies ($R_{9.0/10.5}$) as a function of carbon number for oils from Azerbaijan, North Sea, Texas, and Gulf of Mexico, indicated by color, in three classes of double bond equivalents: N_{DBE}=7, 9, and 10 (a, b, and c, respectively).