Atmospheric
Measurement
Techniques

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Supplement of

Mapping and quantifying isomer sets of hydrocarbons ($\geq$ C$_{12}$) in diesel exhaust, lubricating oil and diesel fuel samples using GC $\times$ GC-ToF-MS

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Section S1: Chromatography Methodology

Exposed adsorption tubes were spiked with 1 ng of deuterated internal standard mix for quantification, and desorbed onto the cold trap at 350 °C for 15 min (trap held at 20 °C). The trap was then purged onto the column in a split ratio of 102:1 at 350 °C and held for 4 min. An initial temperature of 90 °C of the primary oven was held for 2 min and then increased at 2 °C min^{-1} to 240 °C, followed by 3 °C min^{-1} to 310 °C and held for 5 min. The initial temperature of the secondary oven of 40 °C was held for 2 min, and then increased to 250 °C by 3 °C min^{-1}, followed by an increase of 1.5 °C min^{-1} to 315 °C and held for 5 min. The modulation period was 10 s. The complete run time was approximately 105 min.

Diluted lubricating oil samples and particulate phase filters were spiked with 50 µL of 1 ng µL^{-1} deuterated internal standard mix for quantification. Filters were immersed in dichloromethane (DCM) and ultrasonicated at 20 °C for 20 min. DCM was chosen as an extraction solvent as this was found to have a greater extraction efficiency over hexane and methanol in extracting the large range of polar and non-polar compounds of interest. The extract was then concentrated to 50 µL under a gentle flow of N$_2$ for analysis on the GC×GC-ToF-MS. 1 µL of the extracted sample was injected in a split ratio 100:1 at 300 °C. An initial temperature of 120 °C of the primary oven was held for 2 min and then increased at 2 °C min^{-1} to 210 °C, followed by 1.5 °C min^{-1} to 325 °C and held for 5 min. The initial temperature of the secondary oven of 120 °C was held for 2 min, and then increased to 200 °C by 3 °C min^{-1}, followed by an increase of 2 °C min^{-1} to 300 °C and a final increase of 1 °C min^{-1} to 330 °C, ensuring all species pass through the column efficiently. The modulation period was 13 s.

24   1 µL of diluted (1:1000) lubricating oil was injected in a split ratio 100:1 at 300 °C. An initial

25   temperature of the primary and secondary ovens were kept the same (175 °C) held for 5 min. The

26   primary oven temperature was increased by 1°C min^{-1} to 325°C, while the secondary oven

27   temperature was increased by 1°C min^{-1} to 330°C. A modulation time of 8 s was used, while a total

28   run time of each sample was 120 min. The transfer line and ion source temperatures were 325 °C

29   and 320 °C, respectively and were kept consistent for all sample analyses. Helium was used as the

30   carrier gas at a constant flow rate of 1 mL min^{-1}.

31

32   **Section S2: Computer Language for Identification of Chemicals (CLIC qualifiers)**

33   Language functions: See Reference 2 (below) for more details on selection language functions.

34

35   *Ordinal* – Returns the ordinal position of the indicated channel (m/z in a mass spectrum) in the

36   intensity-ordered multi-channel array of the current object (blob)

37

38   *Retention* – Returns the retention time of the current object (blob) with respect to the

39   chromatographic column indicated by the dimension parameter. Retention time for dimension 1 is

40   expressed in minutes and dimension 2 is expressed in seconds.

41

42   *Relative* – Returns the intensity value of the indicated channel (m/z in a mass spectrum) in the

43   multi-channel intensity array of the current object (blob) as a relative percentage of the largest

44   intensity value of the array.

45

46   See Reichenbach et al. (2005) for more details on selection language functions.

47   Some examples of CLIC qualifiers are shown below:

48   C2-Alkyl Benzenes
49   =(ordinal(91)=1)&(ordinal(106)=2);

2

50 C3-Alkyl Benzenes
51 =((ordinal(91)=1)&(ordinal(120)<=3)&(retention(1)<30))|((ordinal(105)=1)&(ordinal(120)<=3)&(r
52 etention(1)<30));
53
54 C4-Alkyl
55 Benzenes=((ordinal(91)=1)&(ordinal(134)<=3))|((ordinal(105)=1)&(ordinal(134)<=3)&(retention(
56 1)<80))|((ordinal(119)=1)&(ordinal(134)<=3));
57
58 C5-Alkyl
59 Benzenes=((ordinal(92)=1)&(ordinal(148)<=3))|((ordinal(105)=1)&(ordinal(148)<=4))|((ordinal(11
60 9)=1)&(ordinal(148)<=4))|((ordinal(133)=1)&(ordinal(148)<=3));
61
62 C6-Alkyl
63 Benzenes=((ordinal(92)=1)&(ordinal(162)<=4))|((ordinal(105)=1)&(ordinal(162)<=5))|((ordinal(11
64 9)=1)&(ordinal(162)<=5))|((ordinal(133)=1)&(ordinal(162)<=5))|((ordinal(147)<=2)&(ordinal(162
65)<=5)&(retention(2)<6))|((ordinal(106)=1)&(ordinal(162)<=4))|((ordinal(91)=1)&(ordinal(162)<=4
66));
67
68 C7-Alkyl
69 Benzenes=((ordinal(105)=1)&(ordinal(176)<=4))|((ordinal(133)=1)&(ordinal(176)<=4))|((ordinal(1
70 61)=1)&(ordinal(176)<=4)&(Retention(2)<5.5))|((ordinal(91)=1)&(ordinal(176)<=3))|((ordinal(147
71)=1)&(ordinal(119)<=4)&(ordinal(176)<=4))|((ordinal(106)=1)&(ordinal(176)<=4))|((ordinal(119)
72 =1)&(ordinal(176)<=5));
73
74 C1-Alkyl NAP=(ordinal(141)<=3)&(ordinal(115)<=3)&(ordinal(142)<=3);
75
76 C2-Alkyl
77 NAP=((ordinal(141)=1)&(ordinal(156)=2)&(ordinal(115)=3)&(relative(141)>90)&(relative(156)>5
78 0))|((ordinal(156)=1)&(ordinal(141)=2)&(ordinal(155)=3)&(relative(156)>90)&(relative(141)>50))
79 ;
80
81 C3-Alkyl NAP
82 =((ordinal(155)=1)&(ordinal(170)=2)&(Relative(155)>80)&(Relative(170)>25))|((ordinal(170)=1)
83 &(ordinal(155)=2)&(Relative(170)>80)&(Relative(155)>60))|((ordinal(141)=1)&(ordinal(170)=2)
84 &(ordinal(115)=3)&(Relative(141)>80)&(Relative(170)>25)&(Relative(115)>15));
85
86 C4-Alkyl
87 NAP=((ordinal(155)=1)&(ordinal(184)=2)&(Relative(155)>80)&(Relative(184)>15))|((ordinal(141
88)=1)&(ordinal(184)=2)&(Relative(141)>80)&(Relative(184)>15))|((ordinal(169)=1)&(ordinal(184)
89 =2)&(Relative(169)>80)&(Relative(184)>30))|((ordinal(184)=1)&(ordinal(169)=2)&(Relative(184)
90 >80)&(Relative(169)>50));
91

92

Section S3: Uncertainty of quantification of compounds with no authentic standards

To assess the uncertainty of this method, we estimated known concentrations of compounds for which authentic standards were available. Table S3-1 shows the difference between concentrations estimated with the generic standard and the authentic standard. The overall uncertainty is difficult to estimate. This depends upon both the uncertainty associated with quantifying an individual compound (U), and the number of compounds in a polygon (n). Then

$$U \text{ (polygon)} = (U_1^2 + U_2^2 + U_3^2 \dots\dots U_n^2)^{1/2}$$

where U_1, U_2 …… U_n are the uncertainties associated with individual compounds. There were three polygons for which calibration standards were available for all compounds. These gave collective uncertainties calculated as above of 13.9%, 18.9% and 39.3% (mean = 24%). Although statistically rigorous, we feel that this overestimates the uncertainty as the mass closure figures for the samples as a whole appear realistic and none deviates appreciably from 75-100%, including samples not described in this paper.

124 **Table S3-1.** Comparison of true calibrated concentrations and estimated concentrations using this
125 methodology.
126

| Compound	True Calibrated Concentrations in sample (ng/µL)	Concentration using TIC and n-alkane calibration (ng/µL)	% difference
Pristane	9.9	9.3	-6%
Phytane	10.0	10.4	4%
Cyclohexane, pentyl-	3.1	3.3	6%
Cyclohexane, hexyl-	15.2	18.1	19%
Cyclohexane, heptyl-	14.0	16.5	18%
Cyclohexane, octyl-	11.1	12.5	13%
Cyclohexane, nonyl-	8.9	10.0	12%
Cyclohexane, decyl-	10.0	9.5	-5%
Cyclohexane, undecyl-	3.8	4.0	5%
Cyclohexane, dodecyl-	4.1	3.8	-7%
Cyclohexane, tridecyl-	3.7	3.7	0%
Cyclohexane, tetradecyl-	3.1	2.5	-19%
Cyclohexane, pentadecyl-	3.0	2.8	-7%
Compound	True Calibrated Concentrations in sample (ng/µL)	Concentration using TIC and n-alkylcyclohexane calibration (ng/µL)	% difference
naphthalene, 1-methyl-	20.0	24.0	20%
naphthalene, 1-ethyl-	15.0	13.0	-13%
naphthalene, 1-propyl-	12.0	10.0	-17%
naphthalene , 1-hexyl-	32.0	35.0	9%

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128

Section S4: Representative Mass Spectra for diesel and gas phase hydrocarbon identification

Experimentally determined representative mass spectra at 70eV and 12eV ionisation are shown

below. These mass spectra were identical at their respective retention times in different samples.

Mass spectra at the bottom panel (blue peaks) are from 12 eV ionisation, while the top panels (red
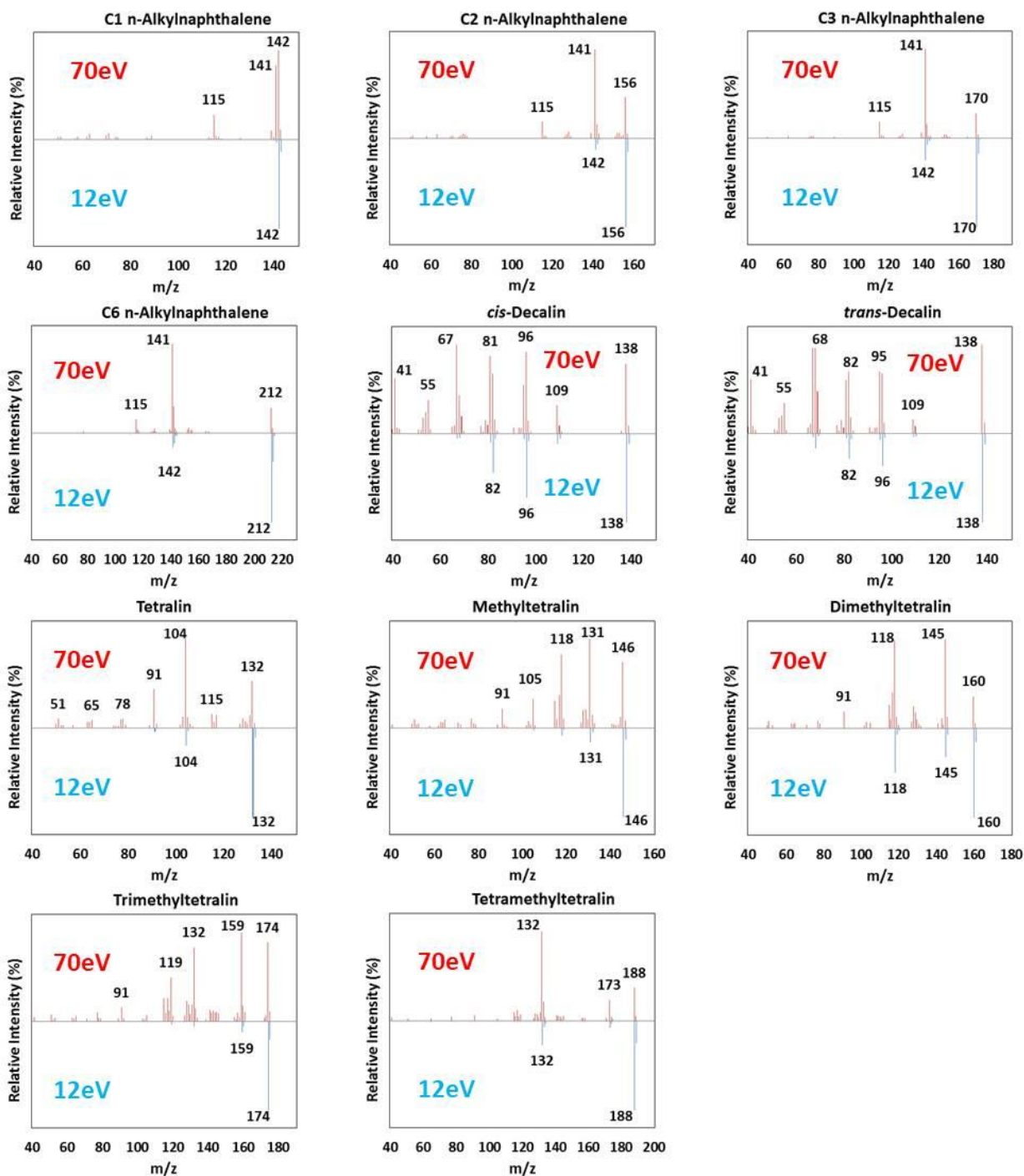
peaks) are from 70eV ionisation.
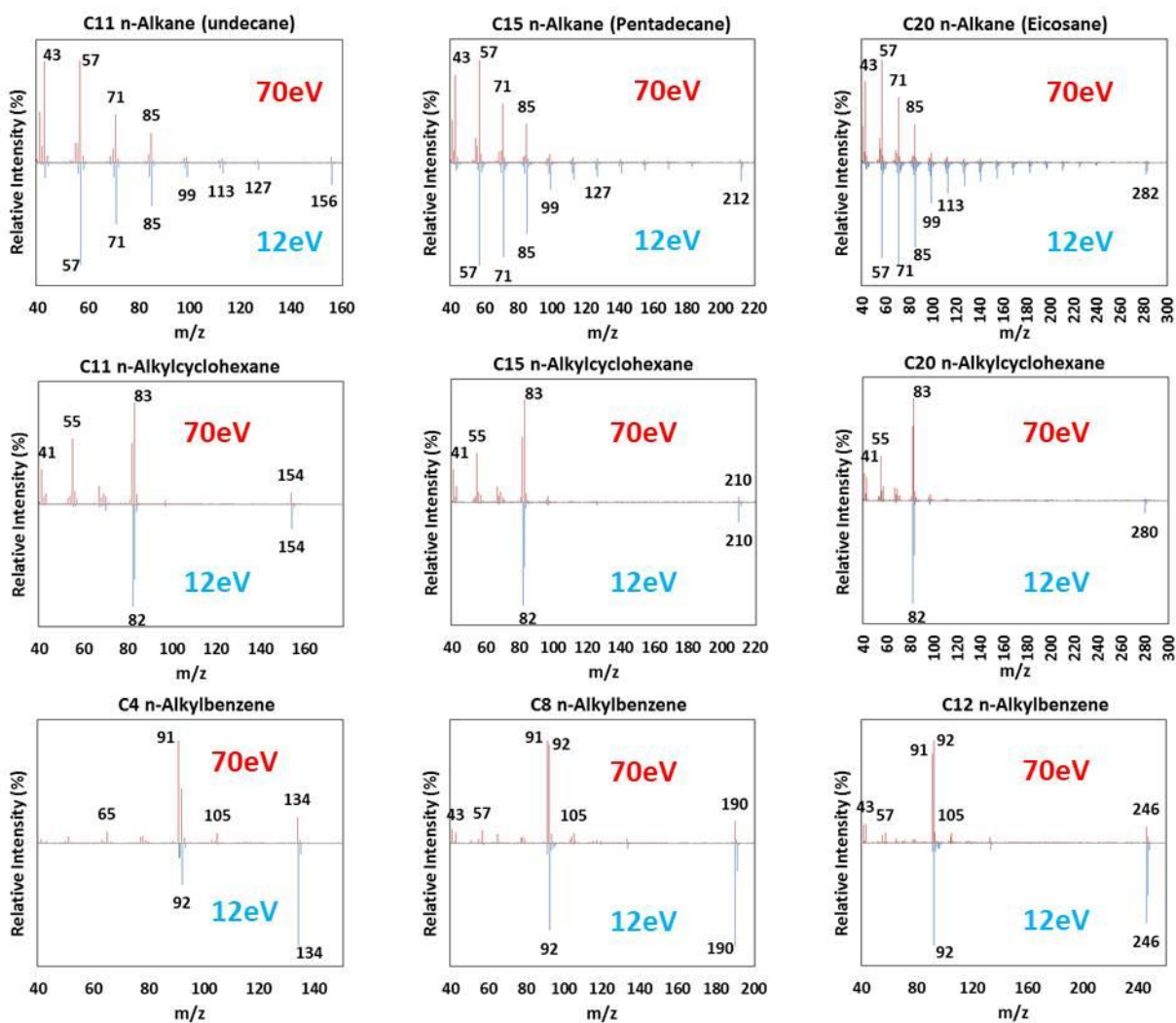
Figure S4-1. Representative mass spectra of n-alkanes, n-alkylcyclohexanes and n-alkylbenzenes.
Top graphs with red peaks are 70eV ionisation mass spectra, while bottom graphs with blue peaks
are 12eV spectra.

Figure S4-2. Representative mass spectra of n- alkylnaphthalenes, cis and trans-decalin, tetralin,
147 methyl-, dimethyl-, trimethyl-, and tetramethyl tetralins. Top graphs with red peaks are 70eV
148 ionisation mass spectra, while bottom graphs with blue peaks are 12eV spectra.
149
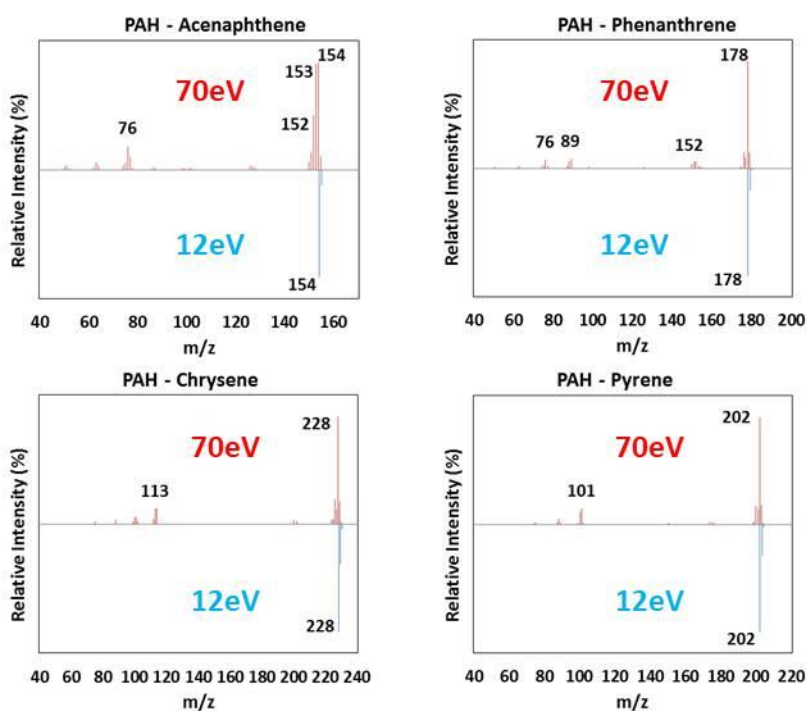
Figure S4-3. Representative mass spectra of four PAH. Top graphs with red peaks are 70eV
ionisation mass spectra, while bottom graphs with blue peaks are 12eV spectra.

When two compounds co-elute, it is often possible to quantify each by using the low ionisation

energy mass spectrum.   The molecular ion of the higher molecular weight component is used to

provide an ion current which is scaled upward to include the other peaks in the mass spectrum to

give a total ion current due to the component.   The second component can be determined by

difference. The molecular ions for a C_{11} and a C_{12} cycloalkane are at m/z 154 and 168, respectively.

These peaks would be present in the mass spectrum of co-eluting compounds, but can be separated

by isolating the ion current attributed to a peak by assessing the mass spectrum that contains only

the molecular ion of one of the compounds. This avoids the issue of co-elution of some compounds.
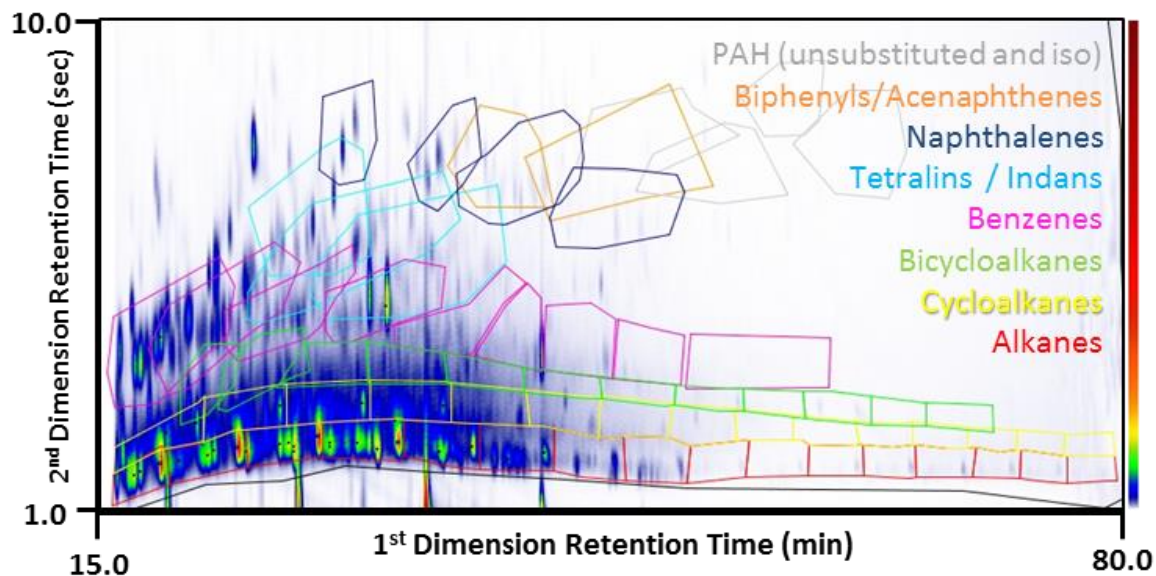
166

Figure S5. A chromatogram of diesel exhaust emissions in the gas phase collected on an adsorption tube and analysed via thermal desorption with 70eV ionization mass spectrometry.

167

Section S6 – Representative mass spectra for compound classes identified in the lubricating oil

n + i-Alkanes were identified by the SIC of m/z 57 and selecting the corresponding molecular ion of

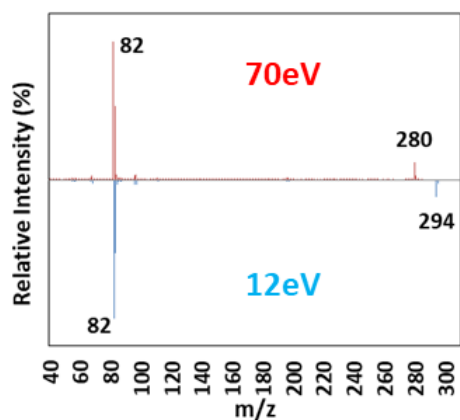the alkane. Figure S8-1 shows two representative alkanes with the molecular ions 282 (C20) and

296 (C21).
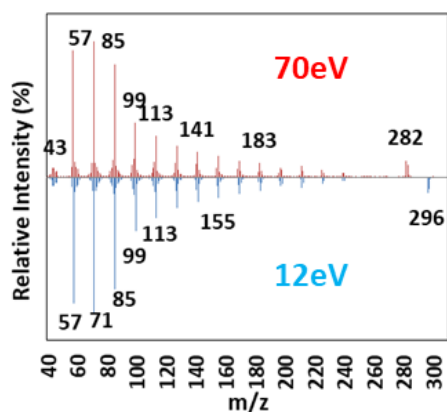
172
Figure S6-1. n-Alkane mass spectra at 12eV for m/z 57 and the molecular ion 282 and 296 for C20 n-alkane (top mass spectum, red) and C21 n-alkane (bottom mass spectrum, blue), respectively.
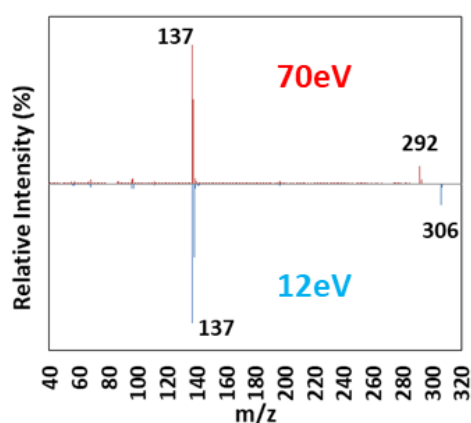
175

9

176   Monocyclic alkanes were identified by the SIC of m/z 82 and selecting the corresponding molecular

177   ion of the specific monocyclic alkane. For example, Figure S8-2 shows two representative

178   monocyclic alkanes with the molecular ions 280 (C20) and 294 (C21).

179

180   **Figure S6-2.** Monocyclic alkane mass spectra at 12eV for m/z 82 and the molecular ions 280 and
181   294 for C20 monocyclic alkane (top mass spectum, red) and C21 monocyclic alkane (bottom mass
182   spectrum, blue), respectively.

183

184   Bicyclic alkanes were identified by the SIC of m/z 137 and selecting the corresponding molecular

185   ion of the specific bicyclic alkane. For example, Figure S8-3 shows two representative bicyclic

186   alkanes with the molecular ions 292 (C21) and 306 (C22).

187
188

189   **Figure S6-3.** Bicyclic alkane mass spectra at 12eV for m/z 137 and the molecular ions 292 and 306
190   for C21 bicyclic alkane (top mass spectum, red) and C22 bicyclic alkane (bottom mass spectrum,
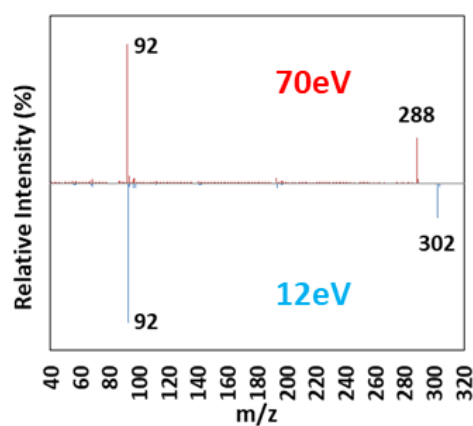191   blue), respectively.

192

193 Tricyclic terpanes were identified by the SIC of m/z 191 and selecting the corresponding molecular

194 ion of the specific tricyclic terpane carbon number. For example, Figure S8-4 shows two

195 representative tricyclic terpanes with the molecular ions 276 (C20) and 290 (C22).
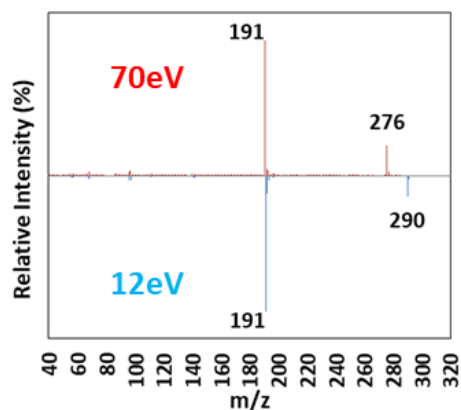
196
197 **Figure S6-4.** Tricyclic terpanes mass spectra at 12eV for m/z 191 and the molecular ions 276 and
198 290 for C20 tricyclic terpane (top mass spectum, red) and C21 tricyclic terpane (bottom mass
199 spectrum, blue), respectively.

200

201 This analysis was repeated for all the compounds shown in Table 1 and representative mass spectra

202 are shown in Figures S8-5 to S8-7 below.

203
204 **Figure S6-5.** Monocyclic aromatics mass spectra at 12eV for m/z 92 and the molecular ions 288
205 and 302 for C21 (top mass spectum, red) and C22 (bottom mass spectrum, blue), respectively.

206
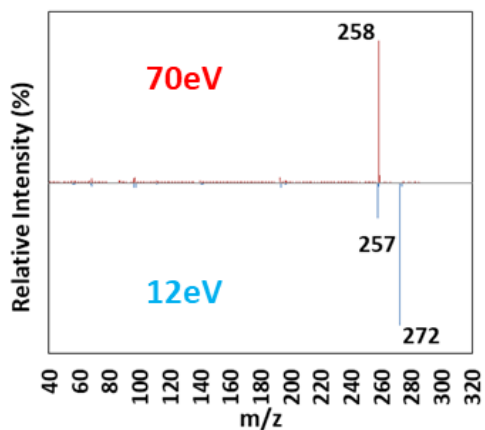
Figure S6-6. Pentacyclic alkanes mass spectra at 12eV for the molecular ions 258 (top mass
spectum, red) and methyl pentacyclic alkane with molecular ion 272 and m/z 257 mass fragment
(bottom mass spectrum, blue).

211
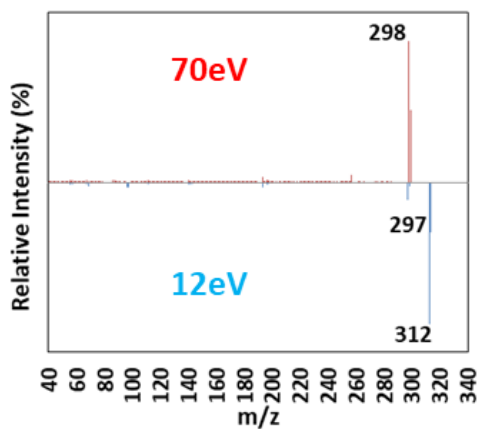
Figure S6-7. Hexacyclic alkanes mass spectra at 12eV for the molecular ions 298 (top mass
spectum, red) and methyl hexacyclic alkane with molecular ion 312 and m/z 297 mass fragment
(bottom mass spectrum, blue).

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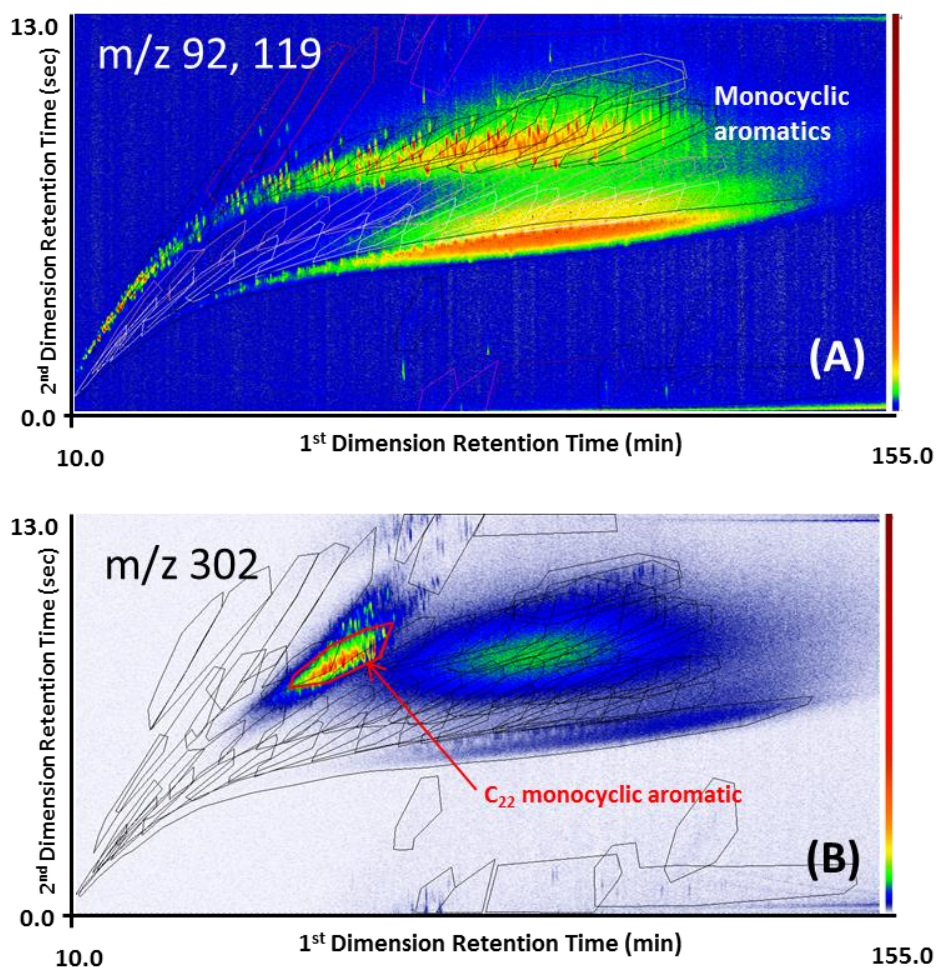**Figure S7**

Figure S7. A selected ion chromatogram of lubricating oil (5W30) with mass fragments **(A)** m/z 92 and 119 signifying monocyclic and methyl-monocyclic aromatics (at 70eV ionization mass spectrometry) and **(B)** m/z 302 signifying the M^+ for C_{22} monocyclic aromatic isomers (at 12eV ionization mass spectrometry).

220

221

REFERENCE

Reichenbach, S. E. Kottapalli, V., Ni, M., Visvanathan, A.: Computer language for identifying chemicals with comprehensive two-dimensional gas chromatography and mass spectrometry. Journal of Chromatography A, 1071, 1, 263-269, 2005.

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