

Comprehensive chemical characterization of lubricating oils used in modern vehicular engines utilizing GCxGC-TOFMS

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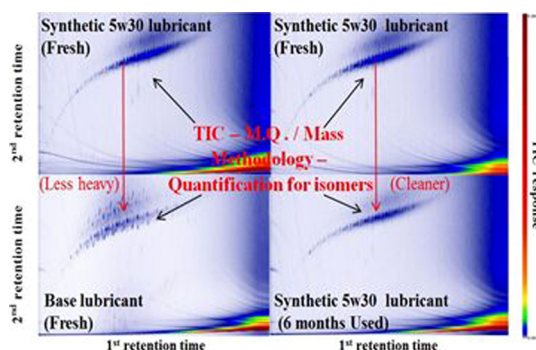
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GRAPHICAL ABSTRACT



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ABSTRACT

A number of major studies have demonstrated that the SVOC (Semi-volatile organic compounds) within engine emissions derive predominantly from unburned fuel and lubricants, and are a major contributor to primary atmospheric aerosol containing thousands of organic compounds. The GC × GC-ToF-MS (2 dimensional Gas Chromatography – Time of Flight – Mass Spectrometry) comprehensive analytical technique was utilized in this study, to resolve the complex mixtures and characterize the SVOC content in eight different commercial lubricants, including 5W30 synthetic and semi-synthetic, mineral and base oil. In order to quantify the aliphatic isomers, which comprise the largest component of the lubricants, a TIC-M.Q./Mass (Total ion current ratio to the molar quantity/mass) method has been developed. The TIC intensity was observed to be proportional to the molar quantity of n-alkanes for carbon number < C₂₅, while being linear to the mass response for these aliphatic compounds with carbon number > C₂₅. Additionally, the TIC intensity of the alkyl-cyclohexanes under the identical retention indices were found to have an equivalent response to those of the n-alkanes, showing that the quantitative calibrations derived for the n-alkane series could be applied to estimate the concentrations of isomeric aliphatic compounds with similar molecular weight. Furthermore, a mesh method was introduced to group the alkane species (n-alkanes, branched alkanes and cyclic alkanes etc.), combining with the use of a soft EI (electron impact) ionization (14 eV) to retain the distinct identity of the isomers with less fragmentation, which allowed the TIC-M.Q./Mass methodology to integrate all the constitutional isomers present in the lubricating oil samples. By utilizing this methodology, compositions from different samples were comprehensively compared, leading to the following conclusions: 1) the synthetic and semi-synthetic oils contained a larger

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abundance of HMW (high molecular weight) aliphatic compounds (carbon number C_{24} – C_{29}), while those in the LMW (low molecular weight range, carbon number C_{18} – C_{25}) were predominant in the mineral and base oil; 2) cycloalkanes were predominant in the synthetic and semi-synthetic oils; whereas the branched alkanes were more prominent in the mineral and base oils; 3) for lubricants used for a short period, a slight increase of LMW compounds was observed, while the HMW compounds underwent a decrease, whereas, there was an overall mass reduction for all the aliphatic compounds detected in the oil samples used for six-months.

1. Introduction

Previous studies have illustrated that vehicle emitted SVOC (semi-volatile organic compounds) are comprised of many thousands of organic compounds that are thought to be derived from unburned fuel, unburned lubricating oil, and as byproducts of incomplete combustion [1–3]. Recent studies have demonstrated a wide range (20–80%) in the contribution of unburned lubricating oil to vehicular emissions [4–6]. Worton and coworkers demonstrated that the POA (primary organic aerosol) emitted from both gasoline and diesel – powered vehicles was dominated by branched cycloalkanes, accounting for more than 80% in mass. The distribution of the aliphatic compounds in POA was inconsistent with those from the unused commercial lubricating oils, especially regarding the high molecular weight constituents [7]. Gordon et al. [8] characterized the POA emissions from several gasoline and diesel off-road engines via smog chamber experiments. They demonstrated that the POA from the 2-stroke diesel engine was 1–2 orders of magnitude higher than from light-duty gasoline vehicles because of the lubricating oil mixed with the fuel in 2-stroke engines [8]. Sonntag et al. [9] measured the PM emissions from 99 vehicles in the Kansas City Light-Duty Vehicle Emissions Study, and estimated that the contribution of lubrication oil to fleet – weighted PM was over 25% by using the survey analysis methods [9]. More recently, Yang and coworkers performed analysis of virgin lube oil, a waste lube oil and regular diesel oil and a biodiesel blend. They demonstrated that the waste lubricating oil was strongly mixed with fuel, such as diesel, biodiesel and gasoline [10]. Though many studies have demonstrated that the lubricating oils make significant contributions to the organic aerosols, little research to date has described and quantified the changes to vehicular lubricants which circulate under harsh conditions adjacent to the high temperature of the engine cylinder which can trigger decomposition and lead to an increase in the emissions, which in turn lead to organic aerosol formation [11]. Comprehensive chemical analysis is necessary to fulfill the diagnostic value of source recognition and interpret the profiles in tracking oil sources, which is particularly significant for evaluation of the source apportionment of hydrocarbons in areas of heavy traffic [12]. Chemical fingerprints of lubricating oils are also key to the identification of contamination or adulteration sources [8].

Current techniques used in the analysis of oil hydrocarbons primarily include GC–MS (gas chromatography - mass spectrometry), GC-MRM-MS (GC coupled to metastable reaction monitoring and MS), GC-FID (GC coupled to flame ionization detection), HPLC (high-performance liquid chromatography), IR (infrared spectroscopy), TLC (thin layer chromatography), UV (ultraviolet), fluorescence spectroscopy and the combined usage of these techniques [13–16]. Conventional GC-FID and GC–MS have been utilized to characterize crude oils and have achieved impressive results in the past, but show many limitations due to the large contribution of the unresolved complex mixture (UCM), which is composed of many thousands of constitutional isomers of aliphatic hydrocarbons [14,17–19]. Recently, comprehensive 2D gas chromatography (GC × GC), based on the combination of two GC columns with different orthogonal stationary phases, has vastly enhanced peak resolving capacity, thus being able to identify and quantify thousands of individual compounds and classes of compounds [20] in fresh and weathered crude oils [17,20–22]. Eiserbeck and co-workers have successfully combined the techniques of GC-MRM-MS, GC × GC-

FID, and GC × GC-ToFMS (Time of flight mass spectrometry) to characterize the biomarkers in tertiary oils and rock extracts, and have evaluated the differences and advantages in instrumental performance [23]. While the GC × GC-FID results displayed improved peak shape, clear quantitative peak areas and high reproducibility; GC × GC-ToFMS analysis provided higher resolution separation, retaining full mass spectra throughout the whole chromatogram. However, the significant fragmentation observed due to electron impact (EI) ionization (70 eV) yields many smaller fragments, which makes it difficult to differentiate structurally similar compounds. More recently, Worton and co-workers used GC/VUV-MS (GC coupled to vacuum ultraviolet ionization mass spectrometry), which substantially reduced fragmentation of the molecular ion and facilitated the classification of hydrocarbon compounds, hence improving isomer resolution, to analyze Gulf of Mexico crude oil. By adopting this technique, linear alkanes and branched alkanes and cycloalkanes were quantitatively distinguished with 8%, 11% and 37% respectively, indicating that cycloalkanes dominated the mass of the crude oil [3,7]. By using the HPLC system coupled to a UV detector and a high resolution quadrupole TOF-MS, Kreisberge and coworkers explored the methods capable of performed phase extraction effectively, which was successfully adopted to observe the degradation processes of the products in used engine oils [24].

In this study, GC × GC-ToF-MS combined with both hard (70 eV) and soft ionization (14 eV), was utilized for characterization of eight different motor lubricating oils. This methodology adopted lower ionization energies, leading to less fragmentation, thus retaining the molecular ion and maximizing its signal/noise ratio [25], and provided an alternative to GC/VUV-MS. A large number of isomeric organic compounds between C_{13} – C_{32} , in the previous UCM of all the motor oil samples have been separated and identified. Furthermore, a quantification methodology based on the relationship of TIC (Total ion current) to M.Q. (Molar quantity)/Mass, has been examined and successfully adopted to quantify and compare fresh and used lubricants, giving insights into the extent of compositional differences.

2. Experimental setup

2.1. Analytical instrumentation

Samples were analysed by using a gas chromatograph (GC, 7890B, Agilent Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2 cryogenic modulator (Houston, TX, USA). The primary dimension was equipped with a SGE DBX5, non-polar capillary column (30 m, 0.25 mm ID, 0.25 μ m – 5% phenyl polysilphenylene-siloxane). The second dimension used a polar column, SGE DBX50 (4.0 m, 0.1 mm ID, 0.1 μ m – 50% phenyl polysilphenylene-siloxane), situated in a secondary oven. The GC × GC was interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (ToF-MS, Markes International, Llantrisant, UK), with a scan speed of 50 Hz, covering the mass range of up to 525 m/z . Electron impact ionization energies can be tuned between 10 eV and 70 eV, the former retaining the molecular ion, while the latter causes extensive fragmentation, but allows comparison with standard library spectra [25]. Data were processed by using GC Image v2.5 (Zoex Corporation, Houston, US).

2.2. Calibration of the GC × GC-ToFMS

Prior to analysis of samples, relative response factors were determined by injection of authentic standards (24 n-alkanes (C₁₁–C₃₄), 22 n-alkyl cyclohexanes (C₁₁–C₃₁) along with deuterated n-alkanes C₁₂, C₁₃, C₂₀, C₂₅, C₃₀), and *p*-terphenyl. The ion currents were related to the molar quantities and mass of the compounds analysed. The instrument detection limits, defined as the amount of a compound that gives a signal to noise ratio of 3:1 are presented in Table S1.

2.3. Chromatographic analysis

2.3.1. Lubricating oils

The oil samples included 5W30 synthetic (fresh and used, a & b-type), 5W30 semi-synthetic (fresh and used), Heavy Duty (HD) mineral (fresh) and Base oil (fresh). The a-type and b-type of 5W30 synthetic oil were offered by different manufacturers. The properties of these lubricants are detailed in the Supporting Information, Table S2 and S3. 1 μL of the diluted oil (1:1000) was injected (split ratio 100:1) into the first column of the instrument at an injector temperature of 300 °C. The oven temperature programming was performed from an initial temperature of 175 °C of the primary oven (held for 5 min), then increased at 1 °C/min to 325 °C (held for 10 min). The temperature of the secondary oven was initially the same as the primary oven, but was increased at a rate of 1 °C/min to 330 °C. The transfer line temperature was 325 °C and the ion source temperature was 280 °C. The modulator was operated at 275 °C and held for 5 min, following by an increase of 1 °C/min to 400 °C. The modulation period was 8 s. Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min.

3. Methodology

3.1. TIC-M.Q./mass methodology

Previous work shows that total ion current (TIC) signal can be scaled to molar quantity (depending on saturation and effective vapor pressure) [25]. The TIC intensity of the individual authentic n-alkane standards (C₁₂–C₃₄), with seven injected concentrations covering 0.5 ng/μL, 1 ng/μL, 1.5 ng/μL, 2 ng/μL, 2.5 ng/μL, 4 ng/μL and 5 ng/μL was investigated. Below C₂₅, the TIC intensity of alkanes increased linearly with the molar quantity (1/MW_{individual n-alkanes}) indicating that

the TIC signal is proportional to the molar quantity (MQ) (Fig. 1, red curves). The TIC-M.Q. of alkyl-cyclohexanes (C₁₂–C₃₄) are also plotted here to compare with the curves of n-alkanes (Fig. 1, black curves). The curves of the n-alkyl-cyclohexanes overlap with those of the n-alkanes in the same injection, illustrating that n-alkyl-cyclohexane and n-alkanes have a very similar response when they have the same carbon number. This is also found to be the same for other species with increasing alkyl chain length (e.g. alkyl benzenes and alkyl naphthalenes). However, as the carbon number increases > C₂₅, the TIC response becomes linear with the compound mass, which is plotted in Fig. S1 as an illustration. The perfect overlap of the curves also demonstrates that the TIC intensity was almost unaffected by the individual chemical structure for the same injection mass. For the HMW alkyl-cyclohexanes, only C₂₅ and C₃₃ were investigated due to the limitation of the available authentic standards.

The TIC-M.Q. behaviour of deuterated standards is also provided in Fig. S2 (Supporting Information) to further support the above view. Additionally, the TIC versus molar quantity graphs for each alkane and alkyl-cyclohexane series are presented in Figs. S3 and S4 (Supporting Information).

3.2. Mesh method

GC × GC provides enhanced separating capability due to the orthogonal separation by two capillary columns of different stationary phases. The two columns are connected in series by a modulator which is employed to provide focusing of the primary column eluent [26,27]. Compounds of similar chemical structure are classified into distinct groups in ordered chromatograms based on their volatility and polarity, providing information that aids identification.

Conventional electron impact ionization at 70 eV imparts a large amount of excess energy causing extensive fragmentation, with a tendency to generate similar mass spectra, thus for example the isomeric alkanes all exhibit the same *m/z* 43, 57, 71, 85, 99 patterns, thus obscuring the match with the NIST library and making identification from the mass spectrum very difficult. To address this issue, a lower ionization energy (14 eV) was employed in our study so that the organic compounds are ionized with minimal excess internal energy and thus less fragmentation, hence retaining the distinct identity of the molecule with a much larger fraction of the molecular ion [28].

By utilizing the soft ionization technique (14 eV), a large number of

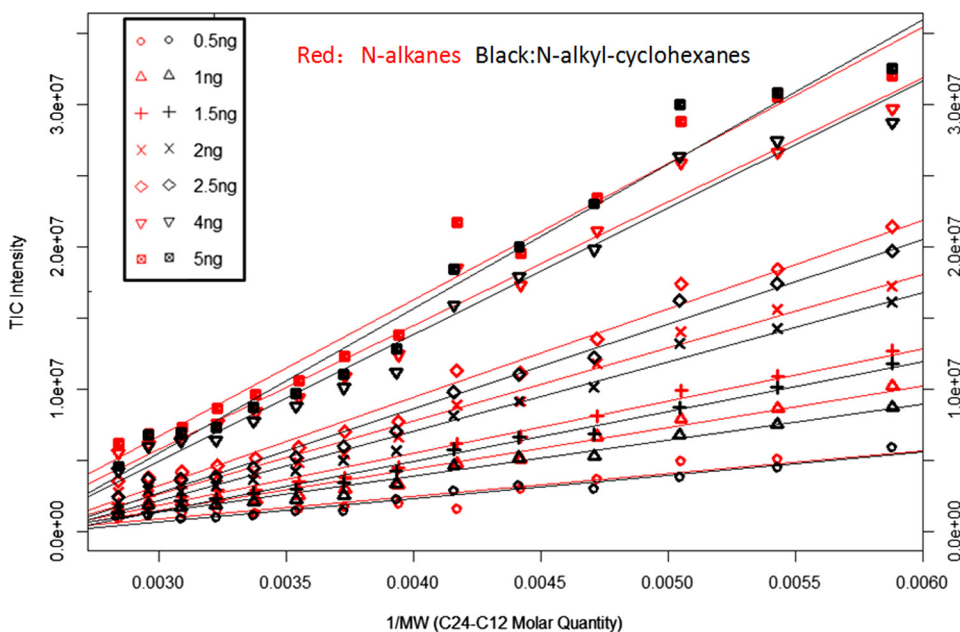


Fig. 1. TIC intensity response to the molar quantity of individual n-alkanes and n-alkyl-cyclohexanes (C₁₂–C₂₄). Each line joins the TIC values for the same mass injected for compounds from C₂₄ (left) to C₁₂ (right of x-axis).

isomers were identified in our recent study (as exemplified in Fig. 2) [28]. The n-alkanes, the branched alkanes and cycloalkanes appear as clear and largely separate groupings based on their volatility and polarity. The n-alkanes and branched alkanes are enclosed in red grids while the cycloalkanes are classified in green grids based on the polarity difference. Since it is possible to quantify individual n-alkanes by calibration with authentic standards and internal standards, the amount of branched alkanes can be estimated by subtracting the concentrations of n-alkanes from the total concentration in the red grid, which can be achieved using the TIC-M.Q./Mass relationships. The polarity of the alkene series is greater than the n-alkanes but lower than the n-alkyl-cyclohexanes. Consequently, a proportion of the alkene species are included in the green mesh, causing an overestimation of the alkane compounds. However, since the commercial lubricants are produced from high-boiling distilled fractions of crude oil, they are not expected to contain significant amounts of alkene species, which has been confirmed by previous work [29].

4. Results and discussion

4.1. SVOC compounds in different types of lubricating oils

The aliphatic compounds accounted for the largest proportion of the lubricants. The mass spectra of these five oils exhibited strong C_nH_{2n+1} , C_nH_{2n-1} and C_nH_{2n-3} sequences. m/z 57 ($C_4H_9^+$), m/z 82,83 ($C_6H_{10}^+$, $C_6H_{11}^+$) and m/z 69 ($C_5H_9^+$) were the most abundant mass fragments, characteristic of electron ionization of aliphatic compounds, indicating that the majority of the SVOC in the lubricants is likely to be straight chain, branched or cycloalkanes (including monocyclic, bicyclic and tricyclic compounds) (Fig. 3(A)) [25]. As illustrated in Fig. 3(B), the HMW alkane compounds with carbon numbers from C_{24} – C_{29} are pronounced for the synthetic and part-synthetic oil, while those in LMW range, with carbon numbers of C_{18} – C_{25} , are predominant in the base

and HD mineral oil.

Application of the GC/VUV-MS technique allowed Worton et al. [3,23] to separate compounds and classes according to different N_{DBE} (number of double bond equivalents) at high resolution. According to their findings, the straight chain, branched and cyclo-alkanes (mono-, bi- and tricyclic ones) were typically making up more than 50% of the mass of the oils. On average, methyl alkanes comprised more than half of the branched alkane mass. With regard to the cycloalkanes, the vast majority of mass was dominated by those with one or more alkyl side chains on the ring or rings. Here, we offer an alternative way (GC \times GC-ToFMS) to quantify the aliphatic compounds in three groups – straight chain, branched and cyclic alkanes, due to their large proportions in the oil samples, and more intensively focus on their distribution in different types of lubricants. The aliphatic compounds comprised more than 60% of overall mass, with the cycloalkanes being the largest proportion, followed by branched alkanes, which is consistent with Worton's analysis and also other previous findings [3,7,30]. The detailed composition with respect to n-alkanes, branched alkanes and cycloalkanes for different types of oils is listed in Table 1. The cycloalkane content of the 5 W30 synthetic(a), 5 W30 part-synthetic and 5 W30 synthetic(b) lubricants accounts for the majority of mass, with 30%, 38%, 41% of total mass, followed by the branched alkanes with 27%, 35% and 24% of mass, respectively. The most likely cycloalkane ring structures are cyclopentane and cyclohexane because of the minimal ring strain required for these configurations, which can be readily detected and are shown in Fig. 2 (the two abundant spots located in the upper-right corner of the green grids) [31]. The branched alkane content of HD mineral oil and mineral base oil are 24% and 41% respectively, accounting for a larger percentage than the cycloalkanes, which are 22% and 20%, probably due to the lesser refining of these oils [3,31].

The final row in Table 1 is the percentage contribution of total alkanes of the three groups. The total hydrocarbon (the sum of three groups) quantified in these five oils of 5 W30 synthetic(a), 5 W30 part-

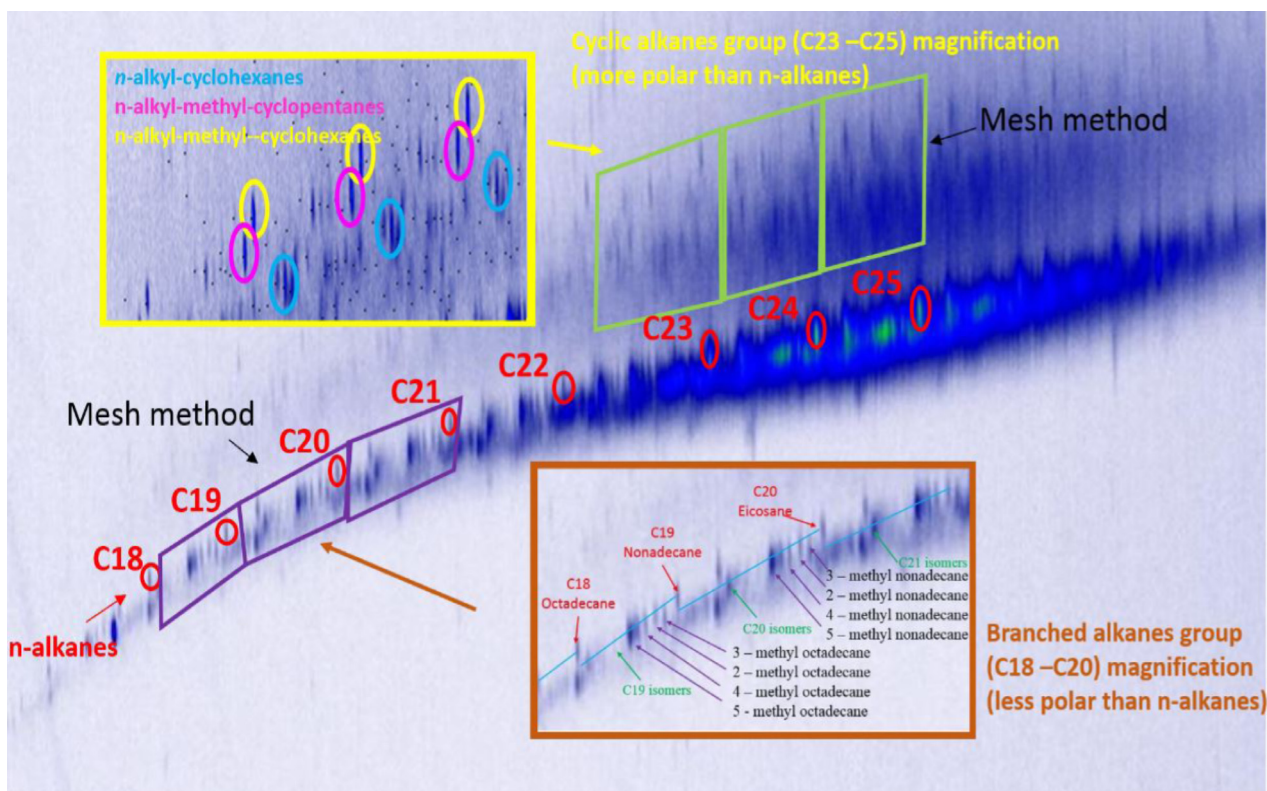
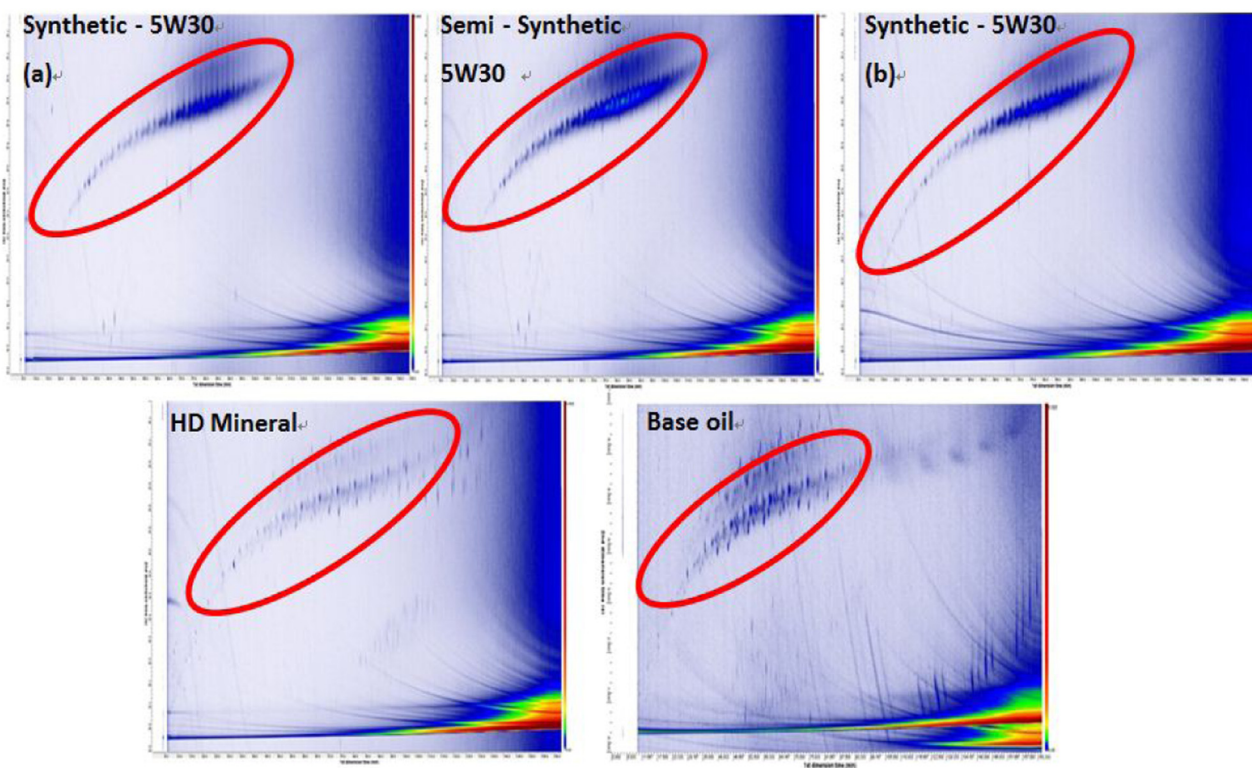
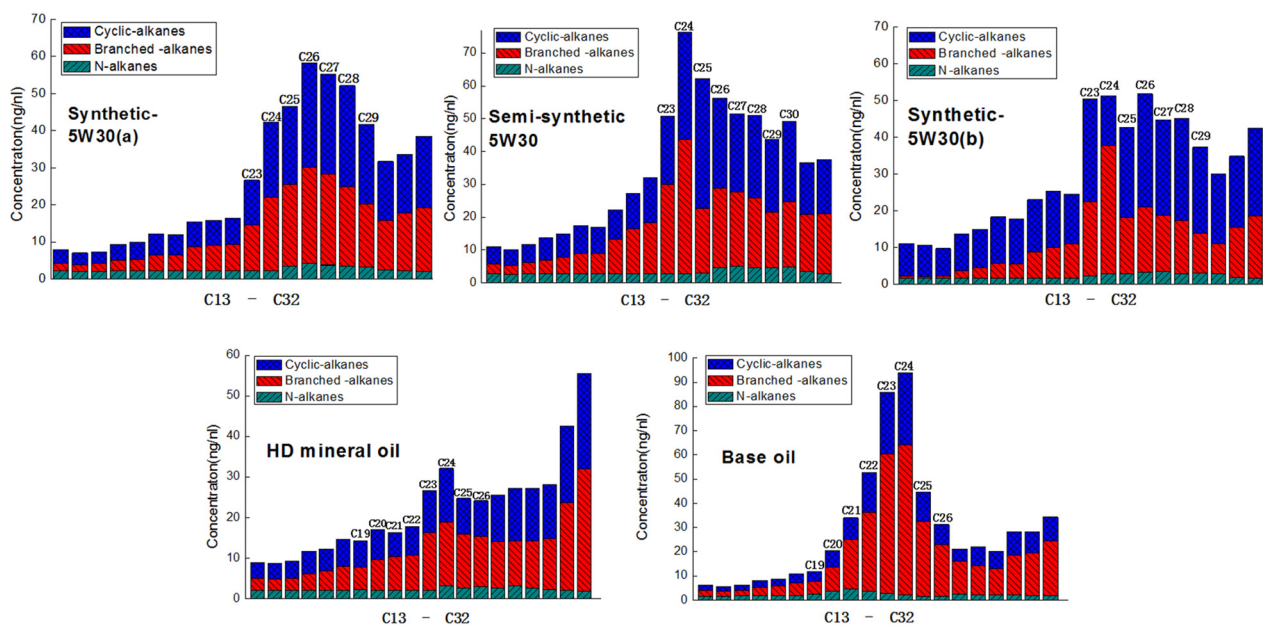


Fig. 2. Contour plot of the 5 W30 synthetic oil (b) analysed using the 14 eV ionization source. Red circles indicate n-alkanes, orange frame indicates co-eluting species belonging to the isomers of the branched alkanes + n-alkanes (C_{18} – C_{20}), yellow frame indicates the resolved cycloalkane isomers (C_{23} – C_{25}). The mesh method is illustrated by introducing the green grids for the cycloalkane group and purple grids for n-alkanes + branched alkanes group.



(A)



(B)

Fig. 3. (A) Two dimensional chromatograms of various lubricating oils; (B) comparison of specific alkane series (straight, branched and cyclic alkanes) distributions between the fresh lubricating oils. The x-axis shows individual carbon numbers between C_{13} (left) and C_{32} (right).

synthetic, 5 W30 synthetic(b), HD mineral and base oil, are 63%, 81%, 70%, 52%, 66% for carbon number C_{13} – C_{32} , respectively. However, the HMW compounds ($> C_{33}$) were not considered. As Fig. 3(B) shows, it seems there is a declining trend for hydrocarbons over C_{31} for these five oils. It has, however, been estimated that these species will count for not less than 10% of the total weight [7,30], which means the more

complete mass closure can be achieved if they and the aromatic compounds are included.

4.2. SVOC compounds comparison between the fresh and used lubricants

A quantitative comparison of fresh and used synthetic(a) and (b),

Table 1
The detailed composition of alkane series (straight, branched and cyclic alkanes) for five different tested lubricants, including 5W30 synthetic(a), 5W30 semi-synthetic, 5W30 synthetic(b), HD mineral and Base oils.

Carbon Number (Specific groups)	5w30-synthetic (a)			5w30-semi-synthetic			5w30-synthetic (b)			HD Mineral			Base Oil		
	n-Alkanes (ng/nL)	Branched-Alkanes (ng/nL)	Cyclic-Alkanes (ng/nL)	n-Alkanes (ng/nL)	Branched-Alkanes (ng/nL)	Cyclic-Alkanes (ng/nL)	n-Alkanes (ng/nL)	Branched-Alkanes (ng/nL)	Cyclic-Alkanes (ng/nL)	n-Alkanes (ng/nL)	Branched-Alkanes (ng/nL)	Cyclic-Alkanes (ng/nL)	n-Alkanes (ng/nL)	Branched-Alkanes (ng/nL)	Cyclic-Alkanes (ng/nL)
C ₁₃	2.13	2.21	3.53	2.65	3.06	5.3	1.64	0.75	8.76	2.11	2.91	3.97	1.65	2.41	2.04
C ₁₄	2.10	1.78	3.10	2.63	2.65	4.79	1.65	0.37	8.68	2.14	2.65	3.97	1.64	2.16	1.90
C ₁₅	2.12	2.14	3.05	2.67	3.42	5.54	1.70	0.56	7.52	2.01	3.01	4.27	1.69	2.45	2.10
C ₁₆	2.13	2.85	4.35	2.67	4.20	6.80	1.70	2.04	10.1	2.16	4.07	5.53	1.74	3.52	2.85
C ₁₇	2.13	3.20	4.61	2.69	5.05	7.02	1.70	2.78	10.4	2.17	4.67	5.47	1.75	4.17	2.74
C ₁₈	2.15	4.31	5.72	2.69	6.24	8.48	1.70	4.15	12.5	2.19	5.78	6.71	1.85	5.24	3.65
C ₁₉	2.20	4.23	5.52	2.70	6.21	8.07	1.69	3.97	12.1	2.21	5.61	6.48	2.34	5.40	3.91
C ₂₀	2.19	6.48	6.71	2.71	10.5	9.06	1.68	7.06	14.4	2.18	7.54	7.39	3.55	10.2	6.64
C ₂₁	2.18	6.84	6.84	2.72	13.8	10.6	1.69	8.37	15.3	2.18	8.31	5.87	4.53	20.5	8.94
C ₂₂	2.18	7.12	7.14	2.72	15.5	13.7	1.71	9.35	13.5	2.16	8.71	7.02	3.82	32.5	16.3
C ₂₃	2.21	12.3	12.1	2.78	27.1	20.9	2.21	20.4	27.9	2.15	14.2	10.3	2.64	57.8	25.5
C ₂₄	2.18	19.8	20.4	2.71	40.9	32.7	2.94	34.8	13.5	3.19	15.7	13.2	2.12	62.0	29.8
C ₂₅	3.47	22.0	21.1	3.07	19.6	39.5	2.91	15.2	24.5	2.66	13.3	8.83	1.65	31.0	11.8
C ₂₆	4.21	26.0	29.1	4.62	24.3	27.3	3.41	17.7	30.8	3.02	12.3	8.90	1.63	21.2	8.40
C ₂₇	3.74	24.5	26.9	4.95	22.7	23.9	3.52	15.3	26.0	2.65	11.4	11.5	2.55	13.4	5.06
C ₂₈	3.46	21.4	27.2	4.48	21.3	25.3	3.00	14.5	27.8	3.18	11.1	13.0	2.21	12.2	7.73
C ₂₉	3.21	17.0	21.4	4.53	17.0	22.2	3.06	10.8	23.5	2.71	11.5	13.0	1.98	11.2	7.03
C ₃₀	2.44	13.3	15.9	4.82	19.8	24.6	2.88	8.09	19.1	2.22	12.6	13.2	2.09	16.4	9.65
C ₃₁	2.27	15.5	15.9	3.39	17.3	15.9	1.88	13.7	19.2	2.12	21.6	18.8	1.95	17.4	8.68
C ₃₂	2.06	17.1	19.3	2.74	18.3	16.5	1.58	17.1	23.8	2.00	30.1	23.4	1.71	22.7	10.0
Total	50.8	230	259	64.9	299	328	44.2	207	349	47.4	207	191	45.1	354	175
%	6%	27%	30%	8%	35%	38%	5%	24%	41%	6%	24%	22%	5%	41%	20%

and part-synthetic oils is illustrated in Fig. 4. There is a small decrease in the concentration of the HMW alkanes in the used synthetic(a) and part-synthetic lubricants which have circulated in engine A (see Table S4) for ten days (5–7 h engine tests per day). The total alkanes between C_{25} – C_{35} of synthetic (a) type oil demonstrated a decrease by nearly 5–7 ng/nl on average in the used oil as compared with the fresh oil, while those between C_{21} – C_{25} of part – synthetic oil exhibited a decline by 3–4 ng/nl in the used type. The HMW alkanes decrease drastically by nearly 20 ng/nl for the carbon number between C_{25} – C_{29} for the used synthetic(b) type, the utilization period of which in the engine (B; see Table S4) exceeded more than six months (3–4 h engine tests during each working day), much longer than that of the other two lubricants (The quantitative detail of the alkane series is shown in Table 2). The abundance of the LMW alkane compounds showed a small increase for both the short-term used oils (less than 2 ng/nl increase for the carbon between C_{15} – C_{20} for both oils), which has three possible explanations: firstly, diesel fuel may possibly penetrate past the piston rings and dilute the lubricant especially under low-load/low-speed engine operation conditions, which can increase the concentration of the LMW compounds; secondly, HMW compounds may decompose via C–C bond scission under the thermal cracking or hydro-cracking process, resulting in the generation of the LMW compounds [31]; thirdly a hot engine can partially burn oil when the valve guides or piston rings are worn [32].

As illustrated in Table 2, there is a mass loss of hydrocarbons amounting to 2% and 6% for the used synthetic(a) and part-synthetic used oils when compared with the fresh ones, respectively. The slight change in mass accounted for may be due to the alkane compounds being oxidized to more polar species, which were not analysed in our study. However, for the synthetic(b) oil, there is an overall reduction (21%) in the alkane compounds accounted for after the oil has been used in the engine for half a year. While exposed to temperatures above 500 K, the lubricating oil may undergo decomposition: larger alkyl paraffin radicals are isomerised and subsequently branched to form a radical chain [33]. After a six-month period, the HMW compounds in the synthetic oil(b) may possibly have decomposed, partitioning into LMW components as they were in the synthetic(a) and semi-synthetic used oil types, and continued to evaporate after long-term usage [32]. The mass balance in the used oils is also affected by the formation of constituents such as elemental carbon which are not G.C.-volatile, and the presence of metallic additives.

5. Conclusion

The SVOC content in five different commercial lubricants, including 5 W30 synthetic and semi-synthetic, mineral and base oil were characterized by using the advanced GC × GC-ToF-MS analytical technique. A TIC-M.Q./Mass methodology has been developed and examined in order to quantify the aliphatic isomers, which comprise the largest component in the lubricants. The TIC intensity was observed to be proportional to the molar quantity of n-alkanes for carbon number < C_{25} , and linearly related to the mass quantity for carbon number > C_{25} . More importantly, the TIC intensity of the alkyl-cyclohexanes were found to have an equivalent response to those of the n-alkanes, illustrating that quantitative calibrations derived from the n-alkane series could be applied to estimate the concentrations of isomeric aliphatic compounds with identical first retention indices. Furthermore, a mesh method was introduced to aggregate the alkane species (n-alkanes, branched alkanes and cyclic alkanes, etc.) combined with use of a lower ionization energy (14 eV), allowing the TIC-M.Q./Mass methodology to successfully integrate the constitutional isomers present in the chromatography. By utilizing this method, eight different types of commercial-vehicular lubricants have been analysed, and the following findings were obtained: 1) HMW aliphatic compounds were abundant in the synthetic and semi-synthetic oils, while the LMW compounds were predominant in the mineral and base oil; 2) cycloalkanes were pronounced in the synthetic and semi-synthetic oils; whereas the branched alkanes were more abundant in the mineral and base oils; 3) The amount of LMW aliphatic compounds increased and the HMW components showed a slight decrease in the oil used for a short time, while there was overall fall in mass accounted for in the lubricants used over a longer period.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the

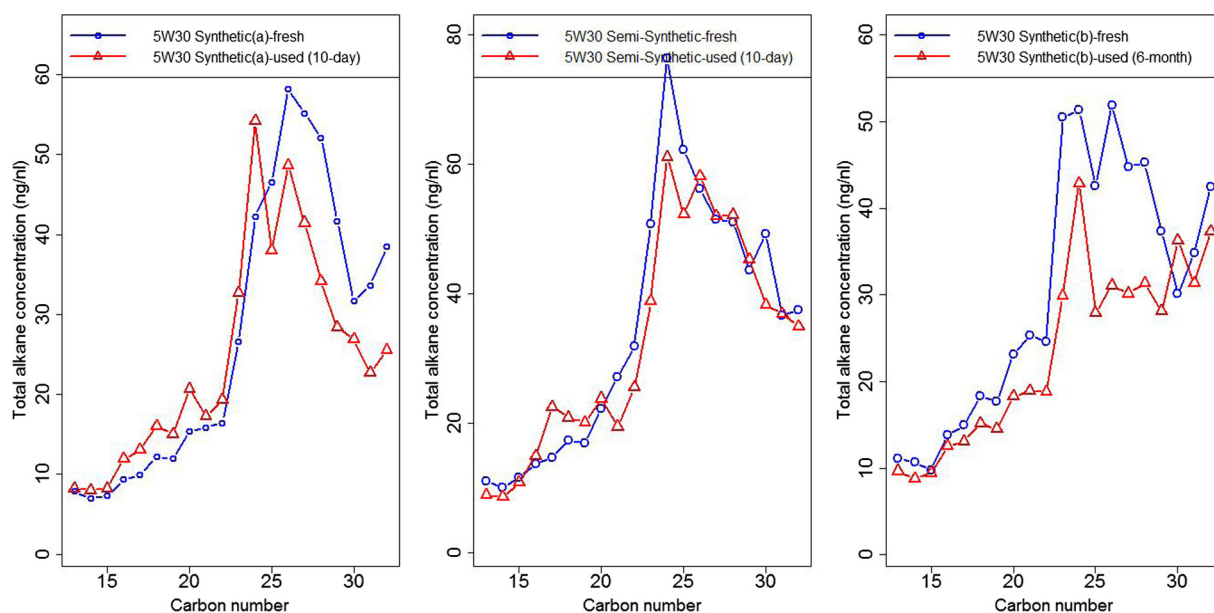


Fig. 4. The comparison of total alkane series (straight, branched and cyclic) distributions between the fresh and used lubricants, including the 5 W30 synthetic(a), 5 W30 part-synthetic, 5 W30 synthetic(b) types.

Table 2

The quantitative comparison of alkane series (straight, branched and cyclic alkanes) between the fresh and used lubricants, including the 5W30 synthetic(a), 5W30 semi-synthetic, 5W30 synthetic(b) types.

Carbon Number (All alkanes)	5w30-Synthetic (a)			5w30-Semi-Synthetic			5w30-Synthetic (b)		
	Fresh (ng/nL)	Used (ng/nL)	Reduction (ng/nL)	Fresh (ng/nL)	Used (ng/nL)	Reduction (ng/nL)	Fresh (ng/nL)	Used (ng/nL)	Reduction (ng/nL)
C ₁₃	7.88	10.2	-30%	11.0	8.85	20%	11.2	9.67	13%
C ₁₄	6.98	10.0	-43%	10.1	8.57	15%	10.7	8.77	18%
C ₁₅	7.30	10.2	-40%	11.6	18.9	7%	9.8	9.42	4%
C ₁₆	9.32	13.9	-49%	13.7	15.0	-9%	13.8	12.5	9%
C ₁₇	9.94	15.1	-51%	14.8	22.5	-53%	14.9	13.1	12%
C ₁₈	12.2	18.1	-48%	17.4	20.9	-20%	18.3	15.2	17%
C ₁₉	12.0	17.0	-43%	17.0	20.1	-19%	17.7	14.5	18%
C ₂₀	15.4	22.7	-48%	22.2	23.8	-7%	23.1	18.3	21%
C ₂₁	15.9	19.2	-21%	27.1	19.5	28%	25.3	18.9	25%
C ₂₂	16.4	21.3	-29%	31.9	25.5	20%	24.6	18.8	23%
C ₂₃	26.6	34.7	-30%	50.7	38.8	23%	50.5	29.9	41%
C ₂₄	42.3	56.2	-33%	76.3	61.1	20%	51.3	42.9	16%
C ₂₅	46.6	40.1	14%	62.2	52.3	16%	42.6	27.9	34%
C ₂₆	58.3	50.7	13%	56.2	58.2	-3%	51.9	31.1	40%
C ₂₇	55.1	43.4	21%	51.5	52.0	-1%	44.8	30.2	33%
C ₂₈	52.1	36.1	31%	51.1	52.2	-2%	45.2	31.4	31%
C ₂₉	41.7	30.4	27%	43.7	45.2	-4%	31.3	28.1	25%
C ₃₀	31.7	28.9	9%	49.3	38.3	22%	30.1	36.3	-20%
C ₃₁	33.7	24.7	27%	36.6	36.9	-1%	34.9	31.3	10%
C ₃₂	38.4	27.5	28%	37.6	35.0	7%	42.5	37.3	12%
Total	540	530	2%	692	648	6%	600	473	21%

online version, at <http://dx.doi.org/10.1016/j.fuel.2017.11.142>.

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