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VOLATILE CHEMICAL PROFILING OF UNBURNT AND BURNT RON 95 PETROL FROM THREE OIL STATIONS: A PRELIMINARY STUDY

(Pemprofilan Sebatian Kimia Meruap bagi Petrol RON 95 yang Tidak Dibakar dan Dibakar daripada Tiga Stesen Minyak: Satu Kajian Awal)

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Abstract

Commercially available petrol is often used as fire accelerants in arson cases, and the determination of petrol residues are instrumental in fire investigations. When subjected to heat, changes occur to the chemical fingerprint of petrol, resulting in differences between petrol in post-fire and pre-fire. This study aimed to identify the differences in the volatile chemical fingerprints of unburnt and burnt petrol (RON 95) from three different oil stations, X, Y and Z, in Malaysia. Unburnt petrol was prepared by diluting 1 mL of petrol with 1 mL of pentane. Burnt petrol was prepared by burning 30 mL of petrol in an aluminium can for 1 minute. All samples were analysed using the gas chromatography-mass spectrometry (GC-MS). Results revealed that a range of *n*-alkanes, *n*-alkylbenzenes, alcohol, *n*-cycloalkanes and indane were detected from unburnt petrol. In contrast, only *n*-alkylbenzenes were present in the burnt petrol samples across the three oil stations. The majority of the volatile chemical of unburnt petrol were similar across all three oil stations. Some specific volatiles were identified in unburnt petrol, including 3,7-dimethyl-1-octene and 2,2,4-trimethylpentane in X, 2-methyl-1-butene in Y and 2-hexene in Z. Principal Component Analysis (PCA) plot (with 80.1% total variation) supported the discrimination of the three unburnt petrol samples. Conversely, PCA plot (with 91.2% total variation) of burnt petrol samples were indistinguishable due to the loss of lighter volatile compounds, including the specific volatiles. This preliminary profiling study explains the characterisation of specific petrol volatiles, which potentially impart valuable information to the forensic ignitable liquid reference database.

Keywords: petrol, gas chromatography-mass spectrometry, activated carbon tablet, RON 95, principal component analysis

Abstrak

Petrol merupakan bahan api yang biasa digunakan dalam kes-kes arson. Oleh itu, pengenalpastian petrol di tempat kejadian kebakaran amat penting dalam penyiasatan kebakaran. Apabila dibakar, perubahan akan berlaku pada komposisi petrol yang menyebabkan perbezaan antara petrol yang tidak dibakar dan dibakar. Dengan itu, kajian ini bertujuan untuk mengenalpasti perbezaan antara petunjuk utama petrol yang dibakar dengan petrol yang tidak dibakar dari tiga stesen minyak yang berlainan di Malaysia. Sampel petrol yang tidak dibakar disediakan dengan melarutkan 1 mL pentana dengan 1 mL petrol. Sampel petrol terbakar pula disediakan dengan membakar 30 mL petrol dalam tin aluminium selama 1 minit. Semua sampel dianalisis dengan kromatografi gas-spektrometri jisim (GC-MS). Hasil kajian menunjukkan bahawa sebatian *n*-alkana, *n*-alkilbenzena, alkohol, *n*-sikloalkana dan indana dikesan dalam petrol yang tidak terbakar manakala hanya *n*-alkilbenzena dikesan dalam sampel petrol yang terbakar daripada ketiga-tiga stesen minyak. Sebilangan besar sebatian meruap dalam sampel petrol tidak dibakar dari ketiga-tiga stesen minyak adalah sama. Beberapa sebatian meruap spesifik telah dikenalpasti dalam petrol tidak dibakar iaitu 3,7-dimetil-1-oktena dan 2,2,4-trimetilpentana dari X, 2-metil-1-butena dari Y dan 2- heksena dari Z. Plot analisis komponen utama (PCA) (dengan 80.1% total varians) mengukuhkan diskriminasi antara ketiga-tiga sampel petrol tidak dibakar. Sebaliknya, plot PCA (dengan 91.2% total varians) bagi sampel-sampel petrol dibakar tidak dapat dibezakan disebabkan oleh kehilangan sebatian mudah meruap termasuklah sebatian-sebatian meruap spesifik tersebut. Kajian pemprofilan di peringkat permulaan ini menjelaskan bahawa pencirian sebatian meruap yang spesifik dalam petrol berpotensi memberi maklumat tambahan kepada pangkalan data bahan mudah bakar forensik.

Kata kunci: petrol, kromatografi gas-spektrometri jisim, karbon tablet teraktif, RON 95, analisis komponen utama

Introduction

Petrol is a petroleum product that contains a combination of hydrocarbons ranging from 4 to 12 carbon atoms, namely olefinic, naphthenic, paraffinic, and aromatic hydrocarbons with boiling points ranging from 30-225 ºC [1]. The properties of petrol are influenced by the origin of the crude oil, the refining process, and the presence of additives [2], which leads to the generation of a specific formulation of petrol among the different oil stations. Most of the world's largest refineries are situated in the Asia Pacific region, with India hosting the largest refinery complex, followed by Venezuela and South Korea [3]. In Malaysia, refineries are located in Kertih, Port Dickson, Kemaman, and Melaka, to name a few [4].

The refining process includes the addition of additives to the fuel. Examples of petrol additives include ether oxygenates, such as methyl tert-butyl ether (MTBE), detergent dispersant additives, antiknock agents, and antioxidants compounds [5-7]. In Asia pacific region, MTBE is added as additives to reduce harmful exhaust emissions from motor vehicles by helping petrol burn completely, although several other regions have banned its use due to environmental issues [8]. Detergent dispersant additives function as cleaning agents that polish the engine, which improves engine performance, whereas antiknock agents increase the octane rating of petrol to prevent engine damage, which is indicated by Research Octane Number (RON) [9]. Petrol with a high RON has a lower tendency to cause engine damage when compared to petrol with a lower RON [10]. On the other hand, antioxidants inhibit the radical chain oxidation of petrol; thus, they contribute to the fuel chemical stability. Generally, these additives ensure that the vehicle engine runs smoothly during use, generates clean-burning, and maintains the chemical and thermal stability of the fuel.

Oil and gas (O&G) stations are known to have used several different additives in petrol production. For example, the national O&G station Petronas petrol Primax 97 launched a new additive package that includes the world's first Advanced Dual Friction Modifier in 2020 [11]. Others, such as Shell, provides Shell FuelSave petrol which contains Dynaflex technology to help reduce engine friction [12]. However, the exact additives used has not been disclosed as it serves as their proprietary formulation. Despite each station offering the same type of RON 95 fuel in its entirety, minute composition variations may exist, which can potentially help fire debris analysts for discrimination or classification to the respective stations, which is immensely useful in forensic fire investigations.

Petrol is undoubtedly the most common ignitable liquid used in illegal fire settings or arson cases as it is readily available, reasonably cheap and easy to conceal [13]. Arson cases using petrol was reported to increase from 2016 (4 cases) to 2018 (12 cases) in Malaysia [14]. In fire scenes, it becomes a priority for forensic investigators to collect, detect, and identify the ignitable liquid used, if any, from fire debris samples [15]. The fire debris samples are not only limited to burnt substrates. Seldom, pristine ignitable liquids can also be present [16], likely to have been left behind by the arsonist in its transporting container. Therefore, it is vital to analyse liquid petrol to investigate if the oil stations can be distinguished based on their volatile composition, which can be immensely helpful in scene reconstruction. Petrol that has been burnt on its own (without being doused in other substances) in natural outdoor conditions also needs to be investigated to identify the volatiles present before other compounds mask them. This is especially important in hot climate countries like Malaysia, where daily temperatures can go up to 32ºC [17]. It is postulated that petrol can experience higher evaporation rates at such temperatures, accelerating the loss of volatiles. Therefore, it will be beneficial to observe the volatility of petrol compounds in outdoor tropical climates as the related discussion is limited.

The study on petrol pertaining to fire investigation in Malaysia has been a topic of interest. Few studies have presented petrol residue recovery within a specific period. Pei wen et al. [18] performed controlled burning of petrol on carpet substrate in a metal can and suggested that the maximum recoverable time of petrol in fire residue is preferably within 9 hours and not more than seven days. Samri and Chang [19] discovered that the chromatographic profiles of unburnt petrol were similar to the burnt ones if burnt for 30 seconds or less in a controlled metal container. Discrimination of different types of ignitable liquid with statistical aid was also reported. Kunashegaran utilised principle component analysis (PCA) to classify different unburnt ignitable liquids; petrol, diesel, kerosene and thinner [20]. Similarly, Jais et al. [21] differentiated petrol and diesel in fire debris (burnt cloths) using a similar approach. These works, however, showed less attention or explanation on the discrimination between different oil stations in Malaysia.

Abu Hassan [22] pioneered the analysis of unburnt petrol from three local stations using gas chromatography-flame ionisation detector (GC-FID) using supervised QUEST modelling analysis where they identified that discrimination is possible among the unburnt petrol from three oil stations. However, the limitation is reflected with the use of GC-FID due to its inability to ascertain the exact volatiles responsible for discrimination. The discrimination in Abu Hassan's work was solely based on retention times. Thus the findings only presented limited information in terms of forensic investigation. In this work, GC-MS will be employed to identify the discriminating volatiles based on their *m/z* ratio. This allows for the profiling of the volatile compounds present in RON 95 petrol from three different oil stations in Malaysia for unburnt petrol, particularly performed within Malaysian climate settings. Although forensic fire investigations in Malaysia only require classification of the ignitable liquid classes, knowledge on the volatile organic compound of unburnt and burnt petrol that are produced and distributed in Malaysia may enable brand identification, thus offer additional information during the course of an investigation.

Materials and Methods

Sample

Two litres of unleaded RON 95 petrol were purchased from three different oil stations in Malaysia, X, Y and Z, on the same day. The petrol samples from each station were used for both unburnt and burnt analysis. This was to ensure the continuity of volatile composition from each oil station. The petrol samples were stored in separate tightly sealed aluminium fuel storage containers at room temperature.

Instrumentation

The analysis was carried out with a Shimadzu Series-QP2010 PLUS Gas Chromatography (GC) system coupled with a Mass Selective Detector (MSD) using the ASTM E1618-06 standard method as a guideline. The injector was set at 250 ˚C with 1 µL of the sample being injected into the GC. A split ratio of 5:1 was applied to the instrument with a split flow of 32.7 mL/min. Helium was used as a carrier gas, flowing at a constant rate of 1 mL/min. The column used was a 128-0122 DB-1MS column (25 m × 0.2 mm inner diameter and 0.33 µm film thickness). The initial oven temperature was set to 40 ˚C and held for 5 minutes before ramped at 15 ˚C/min to 280 ˚C and held for 2 minutes. The detector was maintained at 250 ˚C. The MS Quad was set at 150 ˚C and the Ion Source (70 eV) at 230 ˚C. The chromatographic system was controlled using Hewlett Packard Chemstation software to facilitate data acquisition, peak integration and data manipulation.

Sample preparation of unburnt petrol

One millilitre of petrol RON 95 from X was diluted with 1 mL of pentane. Ten microlitres of tetrachloroethylene were used as the internal standard. Tetrachloroethylene (C_2Cl_4) was chosen as the internal standard as it does not interfere with the analysis and elutes approximately in the middle of the chromatogram. Each sample was analysed six times into the GC-MS. The entire process was repeated with petrol RON 95 from Y and Z.

Thermal decomposition

Pilot study

Six replicates containing 30 mL of petrol were completely burned to identify the most suitable burning duration that will prevent the total loss of volatiles. The time taken for 30 mL of petrol to burn off completely ranged from 2 min 15 s to 2 min 40 s. Therefore, several burning durations were tested to identify the duration where all volatiles were not completely consumed. The burning was carried out for 1 min, 1 min 30 s and 2 mins. For both the 1 min 30 s and 2 min burning duration, no volatiles were detected, but volatiles were detected in the 1 min burning duration. Therefore, the burning process was set to 1 min to yield detectable volatiles. The maximum temperatures for all three burning durations were 530 ˚C (X), 582 ˚C (Z) and 562.5 ˚C (X) as depicted in Figure 1, Figure 2 and Figure 3, respectively.

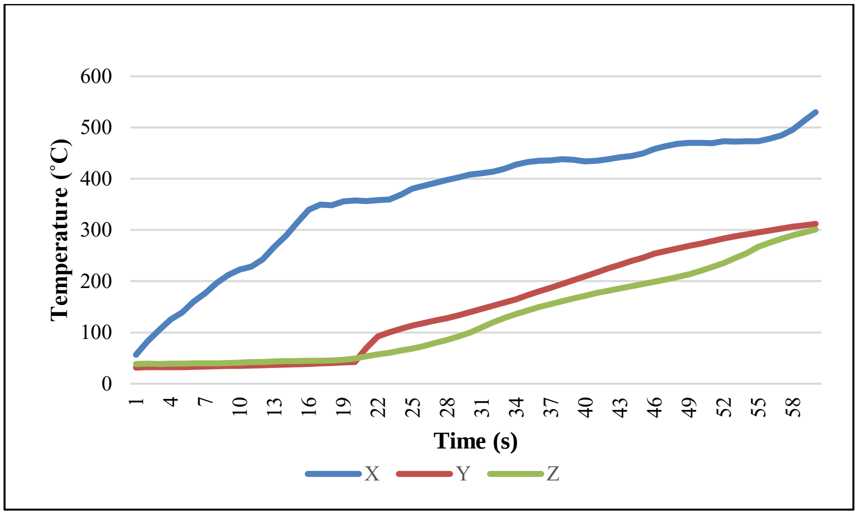

Figure 1. The time-temperature chart for the 1-minute burning of petrol from X, Y and Z

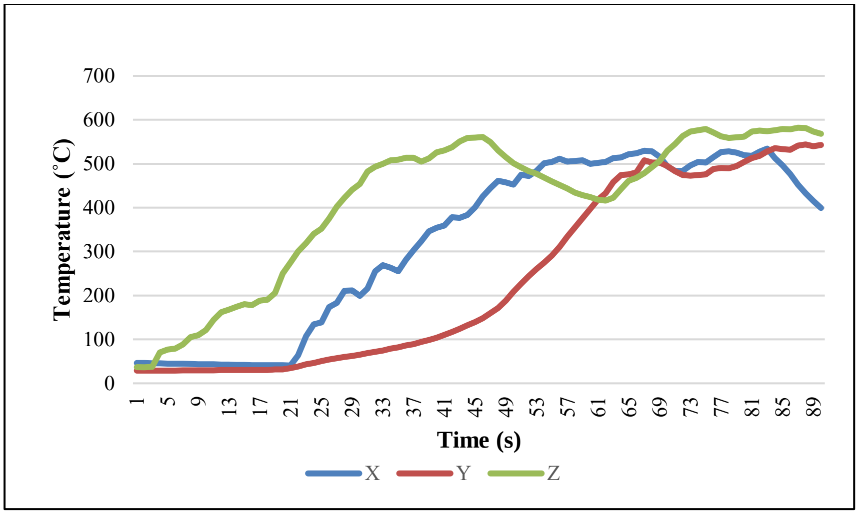

Figure 2. The time-temperature chart for the 1-min 30 sec burning of petrol from X, Y and Z

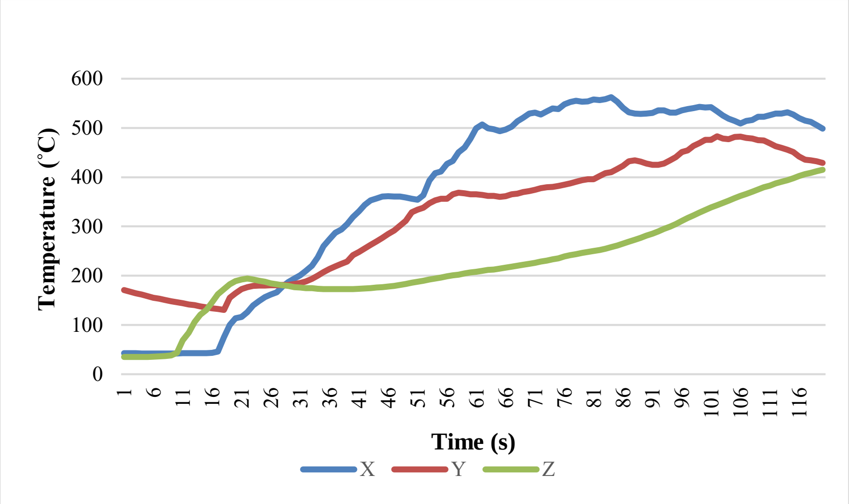

Figure 3. The time-temperature chart for the 2-minute burning of petrol from X, Y and Z

Generation of petrol volatiles

The experiment was set in an outdoor setting. A retort stand was placed on flat ground, and an aluminium can (Scene Safe, United Kingdom) without its lid was placed on a tripod stand for the burning process. Thirty millilitres of petrol were poured into the aluminium can and heated using a Bunsen burner flame underneath the aluminium can for one minute, which was measured from the moment the Bunsen burner was lighted. The temperature of burning was monitored using K-thermocouple (Fluke 80PK-22, United States of America) connected to a digital thermometer model 51 II (Fluke). After one minute, the Bunsen burner was turned off, and the can was closed with a lid to suppress the fire and left to cool before fixing it with an activated carbon tablet (ACT) (250mg, Dyna, Malaysia). Six replicates were carried out for each sample of petrol from X, Y and Z.

Sample extraction

The ACT was fixed using a paperclip and thread in the container headspace. The lid was then secured tightly to the aluminium can. The aluminium can was placed in an oven for 16 hours at 80 ºC for headspace extraction of volatile compounds. After 16 hours, the ACT was removed from the aluminium can and placed in a glass bottle (Fisher Scientific, 50 mL) to be desorbed with 2 mL of pentane (Fisher Scientific, >99%, United Kingdom). The desorbed solution was then filtered using a Polytetrafluorethylene (PTFE) syringe filter, pore size 1.0 µm (Sartorius, Germany) to remove ACT particles and placed into a 2 mL GC vial (Fisher Scientific, United Kingdom). Tetrachloroethylene (EMPLURA, >99%, Germany) was added to the vial as the internal standard (5% v/v).

Sample analysis and detection

Desorbed sample solutions were analysed using the GC-MS method as aforementioned. Identification of the volatile products was conducted on the total ion chromatogram (TIC) of each sample by comparing the mass-to-charge (*m/z*) ratio of the peaks to that of the National Institute of Standards and Technology (NIST) library (acceptable similarity percentage was set at 70% and above), standard test mixture, and database from previous researches identifying key indicators of petrol such as aliphatic hydrocarbons, aromatic hydrocarbons, and alcohols [23-25]. Table 1 shows the functional groups and their respective characteristic *m/z* values that was used as a reference in this study [16].

Data analysis

TIC of the unburnt samples was aligned, and the peak area of identified volatile compounds was acquired. The size of the data matrix for PCA analysis was 18x34, whereby each analysis was theoretically treated as one independent sample due to sampling limitation. Data were normalised to the internal standard and standardised with the power root approach according to the previous work [26-27]. PCA was performed using Minitab Ver. 17.0 (Minitab Inc., USA) with an acceptable total variance of 70% or more. A similar procedure was also performed for chromatographic data of the burnt samples.

Table 1. The functional groups commonly encountered in petrol and their characteristic *m/z* values

Functional Group	*m/z* Value
Alkane	29, 43, 57, 71, 85, 99
Cycloalkane	41, 55, 69, 83
Alkene	41, 55, 69, 83, 97
Alkylbenzene	91, 92, 105, 106, 119, 120
Naphthalene	128, 142, 156, 170
Indane	117, 118, 131, 132
Terpene	93, 136
Alcohol	31, 45, 59

Results and Discussion

Analysis of unburnt petrol samples

Six replicates of petrol samples from each of the three oil stations generated a range of expected volatiles such as *n*-alkanes, *n*-cycloalkanes, benzenes, *n*-alkylbenzenes, and indane. Table 2 displays a summary of the volatiles detected from the three oil stations.

The number of petrol volatiles detected from stations X, Y, and Z differed. Unburnt petrol X had 27 volatiles whereas petrol Y and Z had 32 volatiles and 31 volatiles respectively. Although the number of volatiles detected varied, the majority of functional groups detected were similar to each other, namely *n*-alkanes, *n*-cycloalkanes, alcohol, *n*-alkylbenzenes, and indane. While similar volatiles were detected across the three oil stations, a few of them were specific to each oil station. The compounds were highlighted in bold text in Table 2. The volatile 3,7-dimethyl-1-octene, an alkyl-α-olefin, was detected in the petrol sample from X and was not detected in both Y and Z. Another specific volatile detected from petrol samples from X was 2,2,4-trimethylpentane, an isomer of octane. For samples from Y, 2-methyl-1-butene was a specific volatile, whereas 2-hexene, a linear alkene, was detected exclusively in Z. Figures 4 illustrates the total ion chromatograms (TIC) for petrol samples from X, Y and Z, respectively.

The alkyl-α-olefin. 3,7-dimethyl-1-octene, detected in the petrol sample from X, was not detected in both Y and Z. This specific volatile was also found in a fuel called NSR (Natural State Research Inc) that was created from waste plastics to replace petrol. The NSR fuel burns more efficiently in comparison to commercial petrol as well as being environmentally friendly [29-31]. The presence of 3,7-dimethyl-1-octene in petrol obtained from X could indicate that oil station X utilised additives or refining techniques similar to those used in NSR fuel to make the petrol more energy-efficient and environmentally friendly.

Another specific volatile detected from oil station X was 2,2,4-trimethylpentane, an isomer of octane. This volatile is an additive that is usually added to petrol to increase resistance to auto-ignition or also known as an antiknock index [32]. An antiknock index is indicated by the research octane number (RON), which is measured relative to a reference mixture of 2,2,4-trimethylpentane and *n*-heptane [33]. Petrol with a higher-octane number can withstand high temperatures without auto-igniting, thus enabling more power to be discharged by a higher compression ratio [34]. Therefore, 2,2,4-trimethylpentane could have been added to increase the antiknock index of petrol. The presence of 3,7-dimethyl-1-octene and 2,2,4-trimethylpentane in X's petrol indicates the use of these compounds in X's petrol formulation.

The compound 2-methyl-1-butene was a volatile specific to fuel Y. It is a reactive isoamylene compound which is an olefin of the C_5 fraction of oil [35], with an undesirably high Reid vapour pressure (RVP) reading. Based on ASTM D323-56, the RVP test is a test used to evaluate petroleum fractions for their evaporation rate [36]. Petrol with lower RVP reduces evaporation loss, and this is especially important in hot regions like Malaysia [37], where temperatures can go up to 32ºC [17]. Therefore, the presence of 2-methyl-1-butene can cause petrol to evaporate at a faster rate. This compound also has high atmospheric reactivity and a high potential for tropospheric ozone formation, which is known to have detrimental effects on the environment [38]. Thus, it is usually treated with primary alcohols to produce oxygenates such as *tert*-amyl methyl ether (TAME), which in turn produces a more suitable fuel for the environment [39]. TAME is catalytically produced in the liquid phase by the reaction of isoamylenes; 2-methyl-1-butene, 2-methyl-2-butene, and methanol [40]. TAME works as an octane enhancing additive in petrol which reduces pollution [41]. The presence of 2-methyl-1-butene in the petrol from Y could indicate that the petrol was not treated with primary alcohols, possibly explaining its detection in this study.

A specific compound in Z, 2-hexene, is a linear alkene that has a RON of 92.7. RON is often related to antiknock properties where higher octane numbers are known to have a higher antiknock index, as discussed earlier. Octane numbers are influenced by the position of the double bond on linear alkenes [42]. For example, 1-hexene (double bond on the first carbon-carbon bond) has a lower RON compared to 2-hexene (double bond on the second carbon-carbon bond). Therefore, it is pivotal to convert 1-hexene (RON 76.4) in petrol into 2-hexene (RON 92.7). The conversion of 2-hexene can be done using CoMo/ γ-Al_2O_3, which is a catalyst used in the hydrotreatment of different oil distillates during the refining process [42]. The presence of 2-hexene in the petrol sample from Z gives an insight into the possible refining techniques that were used as well as the catalyst that may have been used.

The chromatographic data of the volatiles are further explored statistically. PCA method simplifies the differentiation among the unburnt samples, which are demonstrated in a three-dimensional (3D) score plot in Figure 5. Petrol from each station is grouped according to their chemical compositions which accounts for 80.1% total variation (PC1 = 58.3%, PC2 = 12.2%, PC3 = 9.6%). It is important to note that the sample was obtained once from each oil station. Therefore, intra and inter-location variation may occur. More rigorous sampling is planned to determine if the specific compounds detected in this study are found only in their respective oil stations or if they are specific to the location of the oil station.

Nonetheless, the identification of specific volatiles has facilitated the discrimination of these samples. Another study corroborated the importance of characterising additives for petrol discrimination [43]. Additives identified using DART-MS coupled with PCA and varified using partial least squares discriminant analysis (PLS-DA) proved that petrol from different brands can be differentiated using proprietary additives blended in each petrol sample as markers. The ability to discriminate between oil stations will prove to be fruitful in cases where pristine petrol samples are collected from the fire scenes.

Table 2. Summary of volatiles detected in unburnt petrol samples from X, Y and Z

No	Retention Time (min)	Volatiles	X	Y	Z
1	1.15	isobutane	/	/	/
2	1.19	butane	/	/	/
3	1.29	**2-methyl-1-butene**		/	
4	1.58	2,2-dimethylbutane	/	/	/
5	1.66	cyclopentene		/	/
6	1.75	2,4-dimethyl-3-pentanol	/	/	/
7	1.90	3-methylpentane	/	/	/
8	2.06	hexane	/	/	/
9	2.12	2-methyl-2-pentene		/	/
10	2.19	**2-hexene**			/
11	2.27	3-methyl-2-pentene	/	/	/
12	2.35	methylcyclopentane	/	/	/
13	2.41	2,4-dimethylpentane	/	/	/
14	2.68	benzene	/	/	/
15	2.78	3,3-dimethylpentane	/	/	/
16	2.83	cyclohexane	/	/	/
17	3.05	2-methylhexane	/	/	/
18	3.21	3-methylhexane	/	/	/
19	3.33	cis-1,3-dimethylcyclopentane	/	/	/
20	3.40	**3,7-dimethyl-1-octene**	/		
21	3.45	**2,2,4-trimethylpentane**	/		
22	3.80	heptane	/	/	/
23	4.28	methylcyclohexane	/	/	/
24	5.48	toluene	/	/	/
25	5.79	2,3-dimethylhexane	/	/	/
26	6.0	2-methylheptane	/	/	/

Table 3 (cont'd). Summary of volatiles detected in unburnt petrol samples from X, Y and Z

No	Retention Time (min)	Volatiles	X	Y	Z
27	6.20	3-methylheptane	/	/	/
28	7.82	ethylbenzene	/	/	/
29	8.00	p-xylene	/	/	/
30	8.37	o-xylene	/	/	/
31	9.52	ethyltoluene	/	/	/
32	9.97	1,2,3-trimethylbenzene	/	/	/
33	9.98	1,2,4-trimethylbenzene	/	/	/
34	10.47	indane		/	/

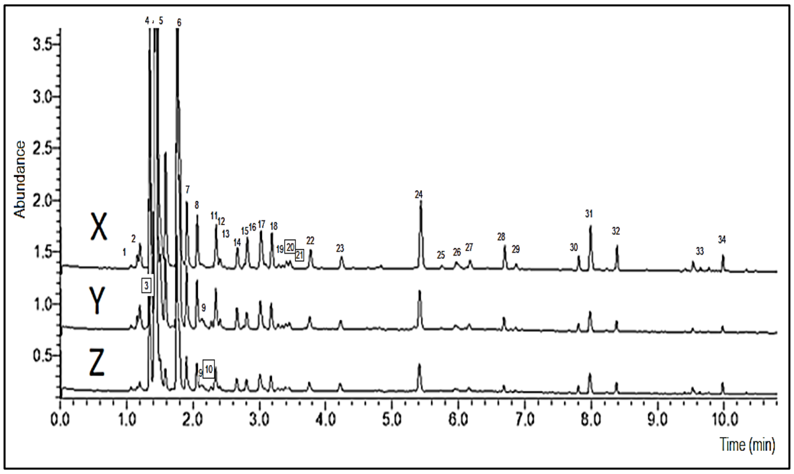

Figure 4. TIC for unburnt petrol samples from X, Y and Z. Peak number corresponds to compound listed in Table 2

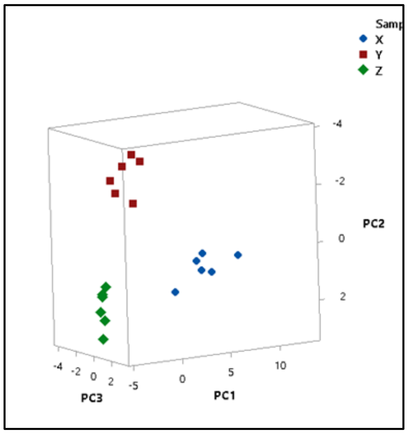

Figure 5. 3D score plot of unburnt petrol from X, Y and Z

Analysis of burnt petrol samples

A small range of *n*-alkylbenzene volatiles were detected in burnt petrol, as listed in Table 3. Figures 6 illustrates the TIC for burnt petrol from X, Y and Z, respectively.

Six *n*-alkylbenzene volatiles, namely toluene, ethylbenzene, *p*-xylene, *o*-xylene, ethyltoluene and 1,2,3-trimethylbenzene were detected across petrol samples from X, Y and Z, showing that outdoor burning of petrol in a hot climate would still leave characteristic compounds consistent with petrol residue. These *n*-alkylbenzenes which are subsets of aromatic hydrocarbons, are common volatiles found in burnt petrol [55] and can be used to distinguish petrol from other petroleum distillates [25] as *n*-alkylbenzenes are one of the dominant components to classify petrol in addition to indanes [15]. However, in this study, indane was not detected in the burnt samples. Several other studies also shared similar outcomes in terms of the absence of indanes [23-24]. The possible reason for this being that some petrol samples tend to have a very low abundance of indane, causing it to be nearly imperceptible during analysis [44]. Indane is also a heavier molecular compound in comparison to the other *n*-alkylbenzenes detected in this study. The evaporation of petrol begins with the lightest volatile and proceeds to the heavier volatiles, and since the burning duration in this study was only 1 minute, it was probably not sufficient to release indane, accounting for its absence. Thus, the use of these ranges of *n*-alkylbenzenes; toluene, ethylbenzene, *p*-xylene, *o*-xylene, ethyltoluene, and 1,2,3-trimethylbenzene, to identify petrol at fire scenes is more robust, and the absence of indane does not necessarily conclude the absence of petrol.

The specific compounds detected in unburnt petrol from each oil station, namely 3,7-dimethyl-1-octene, 2,2,4-trimethylpentane, 2-methyl-1-butene, and 2-hexene, were not detected after the burning process. This entails that these specific compounds can no longer be used to differentiate oil stations in burnt petrol. This was supported by PCA (Figure 7), where no apparent grouping was displayed among the three stations for burnt petrol. The presence of the volatile compounds from burnt petrol sufficiently classified the sample as petrol. However, discrimination based on its respective station could not be done as shown in the 3D score plot of burnt petrol compounds (accounts for 91.2% total variation, PC1 = 59.2%, PC2 = 20.9% and PC3 = 10.6%) in Figure 7. No apparent grouping is displayed among the three stations. Petrol X is largely scattered around a large group which is predominantly comprised of petrol Y and Z, while petrol X and Y were inseparable, as seen at the upper and lower region of the PC2 axis.

Table 4. Summary of volatiles detected in burnt petrol samples from X, Y and Z

No	Retention Time (min)	Volatiles	X	Y	Z
1	5.49	toluene	/	/	/
2	7.83	ethylbenzene	/	/	/
3	8.01	*p*-xylene	/	/	/
4	8.40	*o*-xylene	/	/	/
5	9.54	ethyltoluene	/	/	/
6	9.99	1,2,3-trimethylbenzene	/	/	/

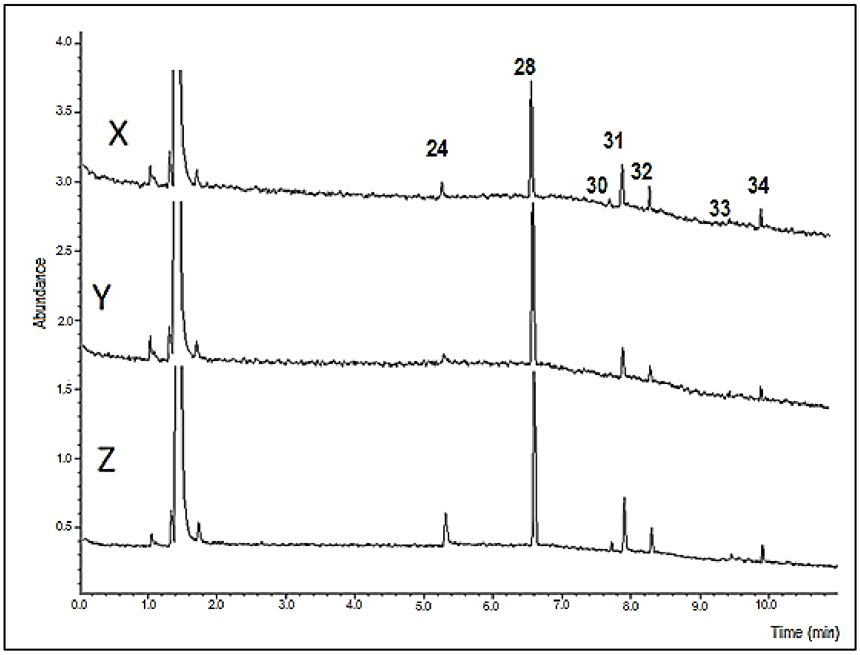

Figure 6. TIC for burnt petrol from X, Y and Z

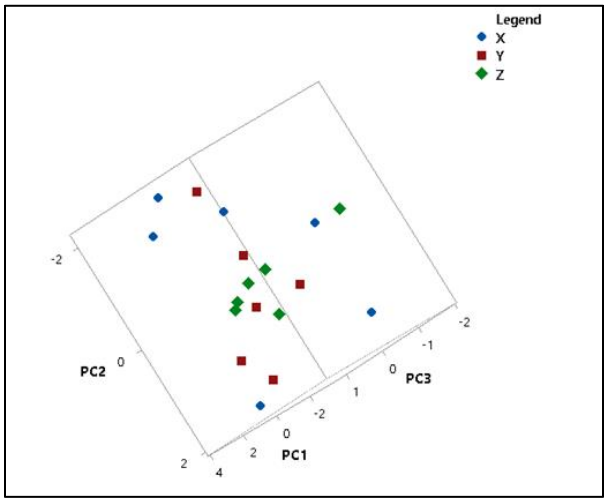

Figure 7. 3D score plot of residual petrol compounds for X, Y and Z

Comparison between unburnt and burnt petrol

In comparison to unburnt petrol, the number of compounds detected from burnt petrol was very small. In each unburnt sample that was analysed from the three oil stations, at least 27 to 32 compounds (*n*-alkanes, *n*-cycloalkanes, alcohol, benzenes, *n*-alkylbenzenes, and indane) were detected, whereas, in burnt samples, only six remaining compounds (*n*-alkylbenzenes) were detected.

This is mainly because compounds in petrol are known to undergo rapid loss during burning [23-24]. Due to the burning that occurred at high temperatures up to 580 ºC, some hydrocarbons have potentially evaporated and were no longer detected after the one-minute burning. Compounds with high vapour pressures tend to evaporate faster at high temperatures compared to compounds with low vapour pressures. The vapour pressure of a compound can be related to its molecular weight; the lower the molecular weight of a compound, the higher its vapour pressure [45]. Hence, *n*-alkanes, *n*-cycloalkanes, and alcohols that have lower molecular weight compared to *n*-alkylbenzenes will evaporate faster due to their higher vapour pressure which explains why they were no longer detected in the burnt petrol samples.

This can also be related to the strength of the bonds in the molecule. The bond that is most easily broken will be favoured [46]. An alkane or cycloalkane is known to have weaker bonds compared to *n*-alkylbenzenes. *n*-Alkylbenzenes also have higher stability due to the presence of the benzene ring in its backbone and, therefore, is not easily broken [47]. At high temperatures, the volatiles with the weaker bond will break and evaporate first, leaving behind volatiles like *n*-alkylbenzenes, which has stronger bonds. *n*-Alkylbenzenes are known to be persistent, particularly at high temperatures and readily detectable at fire scenes [48].

Although undetected in burnt petrol, the lighter hydrocarbons (*n*-alkanes and *n*-cycloalkanes) were detected in the unburnt petrol sample. Comparable differences were observed between unburnt and burnt petrol samples because during the burning process, the temperature of petrol increases which causes the residues of burnt petrol to have different chemical properties compared to unburnt petrol [49]. This is because when the temperature increases, the complex mixture of volatile hydrocarbons in petrol do not burn at the same rate. It is a blended product that covers the boiling point of 40ºC to 190ºC. The evaporation starts with the lightest and most volatile compound and progresses to the heavier, lesser volatile compounds as the temperature increases [49]. Therefore, after a burning process, heavier compounds like *n*-alkylbenzenes have a higher tendency to remain in the burnt petrol compared to lighter *n*-alkanes, *n*-cycloalkanes, and alcohols.

Due to their high volatility, the specific volatiles (3,7-dimethyl-1-octene and 2,2,4-trimethylpentane in X, 2-methyl-1-butene in Y and 2-hexene in Z) detected in unburnt petrol did not manifest in burnt petrol, possibly affecting the discrimination of burnt petrol (Figure 7). For the unburnt petrol where specific volatiles were detected, PCA score plots (Figure 5) have shown the ability to group unburnt petrol samples accurately. Therefore, these initial findings suggest that even though the majority of the volatiles were the same across the oil stations, distinguishment between oil stations can still be made due to the specific volatiles that were detected in the unburnt samples. However, when more than 70% of the volatiles were lost after burning, discrimination between different oil stations was difficult. Identification of specific volatiles and additive compounds is advantageous as supplemental data for pristine petrol samples comparison if collected in fire investigation.

Conclusion

The analysis of unburnt petrol samples from three different oil stations detected a range of similar volatiles: *n*-alkanes, cycloalkanes, alcohol, benzenes, *n*-alkylbenzenes, and indane. Additionally, specific volatiles were also detected, namely 3,7-dimethyl-1-octene and 2,2,4-trimethylpentane in X, 2-methyl-1-butene in Y and 2-hexene in Z, which potentially contributed to meaningful differentiation of petrol from these three oil stations. Petrol samples that were burnt generated only *n*-alkylbenzenes namely toluene, 1,2,3-trimethylbenzene, *p*-xylene, *o*-xylene, ethyltoluene, and ethylbenzene. The other functional groups were not detected. The chromatographic output of unburnt and burnt petrol samples also differed vastly. Data subjected to PCA revealed that unburnt petrol could be distinguished to each oil station. However, burnt petrol could not be distinguished. This is largely attributed to temperature and burning duration. As this preliminary study involved limited sampling, variation studies to ascertain intra and inter variation of more oil stations are planned. Besides that, a percentage degradation study in outdoor settings under the influence of the two factors to study the volatiles of petrol is planned. Perhaps, investigators could consider the identification of specific volatiles in liquid petrol examination to serve as intelligent information that may aid the investigation.

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